Einstein, Perrin, and the reality of atoms: 1905 revisited

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We have repeated Perrin's 1908 experiment for the determination of Avogadro's number by determining the mean square displacement of small particles undergoing Brownian motion. Our apparatus differs from Perrin's by the use of a CCD camera and is much less tedious to perform. We review Einstein's 1905 analysis of Brownian motion and Langevin's alternative derivation of the Einstein equation for the mean square displacement. We also show how Einstein's thinking was a reflection of his belief in the validity of molecular-kinetic theory, a validity not universally recognized 100 years ago.
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I. INTRODUCTION

As is well known, Einstein published three great papers in 1905. As Pais[1] has emphasized, his doctoral dissertation,[2] also submitted in 1905, is equally important. The first two papers on relativity[3] and on light quanta[4] have overshadowed the third paper[5] in which he treated the fluctuations of the motion of a suspension of particles rather than true solutions, which he had considered in his dissertation. As we shall see, the connection between the dissertation and third paper is not trivial.

In 1905 many scientists such as Mach and Ostwald, who believed in philosophical positivism, considered energy the fundamental physical reality and regarded atoms and molecules as mathematical fictions. Einstein did a statistical analysis of molecular motion and its effect on particles suspended in a liquid. From this analysis he calculated the mean square displacement of these particles. In Ref. 5 he argued that observation of this displacement would allow an exact determination of atomic dimensions. He also recognized that failure to observe this motion would be a strong argument against the molecular-kinetic theory of heat.

The experimental confirmation of this prediction of the relation between the mean square displacement and Avogadro's number as well as a physical explanation of the phenomenon of Brownian motion led to acceptance of the atomic or molecular-kinetic theory. As Sommerfeld remarked[6] in his contribution to Einstein's 70th birthday, "The old fighter against atomistics, Wilhelm Ostwald, told me once that he had been converted to atomistics by the complete explanation of Brownian motion."

Perrin, a brilliant experimentalist, believed strongly in molecular reality. He did a series of experiments[7] in the first decade of the twentieth century, one of which depended on Einstein's calculation of the mean square displacement of suspended particles. His results confirmed Einstein's relation and thus the molecular-kinetic theory.

In this paper we shall review the Einstein relation for mean square displacement concentrating especially on his assumptions in formulating it. We then describe a modern version of Perrin's displacement experiment. Although the apparatus is essentially the same as Perrin's, the use of a modern camera coupled to a computer makes the measurement far easier.

II. EINSTEIN'S EQUATION FOR THE MEAN SQUARE DISPLACEMENT

In his autobiographical notes[8] Einstein described his goal of proving the existence of atoms. He accepted Maxwell-Boltzmann statistics and its relation to the molecular-kinetic theory of heat. In his dissertation "On a new determination of molecular dimensions," Einstein based his analysis on van't Hoff's laws of dilute solutions and osmotic pressure and calculated the molecular dimensions of the dissolved molecules. The Brownian motion paper became possible with his recognition that particles suspended in a liquid behave much like solute molecules dissolved in a liquid. His great insight was the recognition that these suspended particles also exhibit osmotic pressure.

He based this insight on the argument that a suspended particle differs from a dissolved molecule solely by its dimensions. He verified this conjecture by calculating the entropy and free energy of the entire system of particles and liquid. The calculation required integrating over all configuration space. This analysis showed that just as the molecular-kinetic theory leads directly to the ideal gas law, so does it explain the osmotic pressure of a suspension of particles. We concur with Hinshelwood[9] who wrote, "Osmosis is sometimes dismissed as an obscure and secondary effect. It is, on the contrary, the most direct expression of the molecular and kinetic nature of solutions." We believe that Einstein would have agreed strongly with this statement.

Let us outline Einstein's arguments in going from solution to suspension that led to his equation for the mean square displacement of suspended particles, the basis of Perrin's experiment. There is an excellent summary and discussion of the arguments in his dissertation and the Brownian motion paper in Ref. 1, pp. 86–101. In his dissertation Einstein balanced the Stokes dissipative force depending on Navier-Stokes motion of a viscous liquid with the fluctuating force arising from thermal molecular motions caused by the solvent. The diffusion current balances that created by the Stokes law.

In the Brownian motion paper[5] Einstein used essentially the same argument, applying the van't Hoff law to suspensions, assuming Stokes's law, and describing the Brownian motion as a diffusion process. From these assumptions he derived an expression for the mean square displacement $\langle x^2 \rangle$

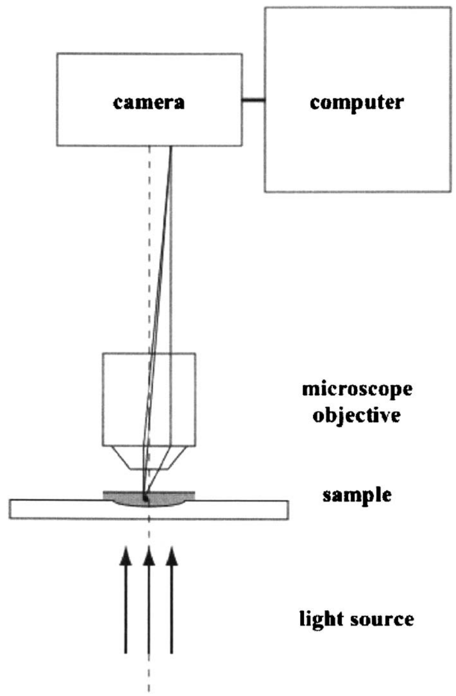

Fig. 1. Apparatus for viewing Brownian motion. It is essentially the same as Perrin's except that a CCD camera and software replace his *camera lucida*.

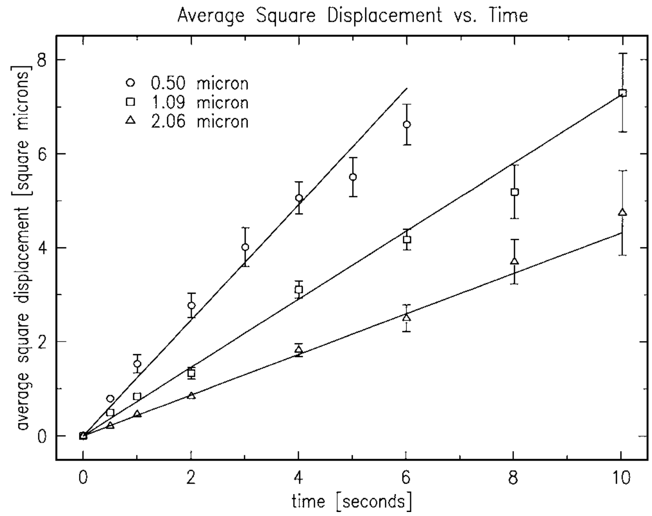

Fig. 2. Mean square displacements as a function of time.

of a suspended particle. The derivation led to an expression for Avogadro's number N_A in terms of the mean square displacement

$$N_A = (1/\langle x^2 \rangle)(RT/3\pi\eta r)\tau, \tag{1}$$

where R is the gas constant, T is the absolute temperature, η is the viscosity, r is the particle radius, and τ is the time interval between measurements of the particle position. Einstein mentioned that Eq. (1) does not hold for time intervals τ that are too small, because the root mean square displacement divided by τ would blow up as τ approaches zero.

Appendix A gives the details of the derivation. For a complete exegesis of his thought consult the collection of his papers on Brownian motion published between 1905 and 1911.[10]

Three years after Einstein's first paper Langevin[11,12] obtained the same equation for Avogadro's number by a different and simpler derivation. His derivation is based on a Newtonian approach and is given in Appendix B.

III. PERRIN'S DETERMINATION OF AVOGADRO'S NUMBER

Perrin used several approaches in determining Avogadro's number,[7] including direct measurements of the mean square displacement and application of Einstein's equation. He prepared suspensions of particles of gamboge and of mastic of uniform size and observed the particles with a *camera lucida*, a device that projects an image on a plane surface suitable for tracing. He made measurements of the displacements for as many as 200 distinct granules and obtained $N_A = 7.15 \times 10^{23}$.

We essentially replicated Perrin's experiment, although with a few modern touches. The apparatus, shown schematically in Fig. 1, consists of a microscope objective, a sample of uniform spherical particles dispersed in a saline solution, a CCD camera with a computer interface, and software to determine the positions of the particles. The main difference between Perrin's arrangement and ours is the replacement of the *camera lucida* by a CCD camera.

Our experiment was performed using an American Optical Microstar trinocular microscope. The $100\times$ objective was chosen to maximize displacement of the microsphere image at the camera's CCD array. In principle, the experiment can be performed using less magnification, especially if long time intervals are chosen. The microscope body is optional. Given appropriate mounts, the objective, camera, and light source are the only mandatory components. The computer communicates with the camera via a FireWire interface.

Preparing a suitable sample is important. A dimpled slide was chosen to minimize convection within the sample. A simple alternative is to use a standard slide with a parafilm gasket between the slide and cover slip. Polystyrene microspheres were obtained from Polysciences, Inc.[13] The size of the spheres was chosen for convenience. One micron diameter spheres are ideal. The samples were mixed in concentrations of a few microliters of microsphere solution per milliliter of solute. An ionic solute is desired to minimize electrostatic interactions between the microspheres. A buffered saline solution can be mixed from scratch;[14] we used saline solution intended for use with contact lenses. The viscosity of the saline solution (1.02×10^{-3} Pa s) was obtained by interpolation from a table in Ref. 15.

Sequential images were recorded at fixed time intervals. The focus control of the microscope was used to keep the microsphere in focus, effectively projecting a three-dimensional random walk onto a plane. The microsphere was located in each image using Image/J, an open source Java application for image analysis and processing. The mean-square incremental displacement in units of pixels was calculated for both x- and y-coordinates and averaged. The CCD pixel size was calibrated by imaging a replica diffraction grating with known line spacing.

Each data point in Fig. 2 represents approximately 200 incremental displacements. The mean-square displacement for time intervals ranging from 0.50 to 10.0 s, for 0.50, 1.09, and 2.06 micron diameter spheres, is shown. The lines are

Table I. Particle diameter, $2r$, slope of $\langle x^2 \rangle$ versus time, and estimate of N_A using Eq. (1).

Particle diameter (microns)	Slope ($10^{-13} m^2/s$)	N_A (10^{23})
0.50±0.02	12.3±0.4	8.2±0.4
1.09±0.04	7.3±0.2	6.4±0.3
2.06±0.02	4.3±0.2	5.7±0.2

fits to the data, forced to go through the origin. Avogadro's number is deduced from the slope using Eq. (1). The results are given in Table I. Note that the values for N_A decrease for increasing particle size. We are not certain of the reason for this dependence. However, Brownian motion is sensitive to the size of the particles in suspension and begins to disappear as a size of 2 microns is reached.

IV. SUMMARY

We believe that several reasons justify the effort of repeating an experiment 100 years after it was first done. As stated in Sec. I, Einstein's statistics paper has been in the shadow of the relativity and light quantum papers of 1905. It is a beautiful piece of scientific exposition, presented in a modest fashion. Einstein did not claim that his results explained Brownian motion or proved the validity of the molecular kinetic theory. Rather he said that the predictions, if observed, would be consistent with the theory, adding that failure to observe them would weigh strongly against the theory. It is significant that a theoretician as great as Einstein recognized that theory must stand or fall with experiment.

The experiment has important pedagogic value as well. Statistical concepts are, by their very nature, abstract. To grasp the ideas in a physical context is easier. We were struck by our own reactions to measuring the successive positions of a particle. Consider 100 frames taken at 1 s intervals. We selected a particle and record its position. This procedure is not difficult because the software makes the measurement. The next frame is selected and the measurement repeated. The process is repeated for all 100 frames. Each time the particle moves but a short distance. In this way we obtained a truly hands-on feeling for Brownian motion and its statistical nature. The result is that the statistical analysis loses its arcane nature and leads to a fuller conceptual understanding for students.

We quote Pais (Ref. 1, p. 97), "…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."

As a community, we are sometimes forgetful of the history of physics. Students often believe that progress in physics is a smooth road without controversy. New theories are not accepted without a fight. We should remember that the molecular kinetic theory was accepted only after many bitter fights. As Ostwald said (see Ref. 6), it was the work of Einstein and Perrin that convinced him of its validity. We hope that this paper will serve as a reminder of this history.

ACKNOWLEDGMENTS

We thank the two anonymous referees who went beyond their requisite duties. One pointed out the significance of Einstein's dissertation and its relation to his first paper on Brownian motion. Their suggestions and comments have improved the paper. It now presents a better picture of Einstein's thinking in 1905. The section on the Einstein equation is also clearer, thanks to them.

A shortened version of this paper was presented at the meeting at the University of Paris (Orsay) on 21 October 2005 for the retirement of Jean-Pierre Delaboudiniere from the Institut d'Astrophysique Spatiale.

APPENDIX A: EINSTEIN'S DERIVATION

In his dissertation Einstein combined van't Hoff's laws for osmotic pressure with Stokes law for particles moving in a viscous medium and applied them to the diffusion process. Because there are both thermal and dynamic equilibria, these two laws led to a relation between the diffusion constant D and the viscosity η for molecules dissolved in a liquid.

$$D = (RT/N_A)(1/6\pi\eta r). \tag{A1}$$

In his 1905 Brownian motion paper[5] Einstein extrapolated van't Hoff's law for the osmotic pressure of a solute to a suspension of undissolved particles. As he did in his dissertation, he also assumed Stokes law

$$K = 6\pi\eta r v, \tag{A2}$$

where K is the resistive force (Einstein used K because the German word for force is *Kraft*), and v is the velocity of the particle.

He combined the osmotic pressure, which gives rise to a compensating diffusion, and Stokes law and then treated Brownian motion as subject to a diffusion equation for the concentration n of the suspension:

$$D(\partial^2 n/\partial x^2) = \partial n/\partial t. \tag{A3}$$

If we integrate Eq. (A3), we obtain the concentration as a function of position and time:

$$n(x,t) = [n/(4\pi D\tau)^{1/2}]\exp(-x^2/4D\tau). \tag{A4}$$

The mean square displacement $\langle x^2 \rangle$ from the origin is then

$$\langle x^2 \rangle = (1/n)\int x^2 n(x,t)\, dx = 2D\tau. \tag{A5}$$

The final result is the Einstein equation,

$$\langle x^2 \rangle = (RT/3\pi\eta N_A r)\tau. \tag{A6}$$

APPENDIX B: LANGEVIN'S DERIVATION

Langevin's derivation of the Einstein relation goes as follows. Each colloidal particle is subject to two forces. One is a random molecular bombardment F that causes Brownian motion. The other is a resistive force, δv, proportional to the velocity v of the particle where δ is the damping coefficient related to viscosity. We write the equation of motion of a particle in one dimension as

$$m(d^2x/dt^2) + \delta(dx/dt) - F = 0. \tag{B1}$$

We multiply Eq. (B1) by x and remember that

$$x(d^2x/dt^2) = (1/2)d^2(x^2)/dt^2 - (dx/dt)^2, \tag{B2}$$

and obtain

$$(m/2)d^2(x^2)/dt^2 - m(dx/dt)^2 + (\delta/2)d(x^2)/dt + Fx = 0. \tag{B3}$$

For a large number of particles, the average value of Fx is zero, because F will, on the average, have equal positive and negative values. From the equipartition theorem the average value of the kinetic energy of a single particle for one degree of freedom is

$$(m/2)(dx/dt)^2 = RT/2N_A. \tag{B4}$$

Let α equal the mean value of $d(x^2)/dt$. We can write Eq. (B3) as

$$(m/2)(d\alpha/dt) - RT/N_A + \delta\alpha/2 = 0. \tag{B5}$$

We integrate Eq. (B5) and obtain

$$\alpha = 2RT/N_A\delta + Ae^{-t\delta/m}, \tag{B6}$$

where A is an integration constant. If we take the specific gravity of the colloid particles as unity, set δ equal to $6\pi r\eta$ from Stokes's law, and take r as 1μ and η as the viscosity of water at room temperature, we find that m/δ equals 10^{-5} s^{-1}. Hence for any reasonable observation time τ, the term $Ae^{-t\delta/m}$ is close to zero. Therefore Eq. (6) becomes

$$\alpha = 2RT/N_A\delta. \tag{B7}$$

Integrating over the observation time τ gives the mean squared displacement (for one degree of freedom) as

$$\langle x^2 \rangle = RT\tau/3\pi N_A r\eta, \tag{B8}$$

which is the Einstein equation. A measurement of the mean square displacement combined with the observation time, the absolute temperature, the radius of the particles, and the viscosity allows us to determine Avogadro's number.

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[1] A. Pais, *Subtle Is the Lord* (Oxford U. P., New York, 1982), pp. 88–92.
[2] A. Einstein, "On a new determination of molecular dimensions," doctoral dissertation, University of Zürich, 1905.
[3] A. Einstein, "Zur Elektrodynamik Bewegter Körper," Ann. Phys. **17**, 891–921 (1905).
[4] A. Einstein, "Ueber einen die Erzeugung und Verwandlung des Lichtes Betreffenden Heuristischen Gesichtspunkt," Ann. Phys. **17**, 132–148 (1905).
[5] A. Einstein, "Die von der Molekularkinetischen Theorie der Wärme Gefordete Bewegung von in ruhenden Flüssigkeiten Suspendierten Teilchen," Ann. Phys. **17**, 549–560 (1905).
[6] A. Sommerfeld, "To Albert Einstein's seventieth birthday," in *Albert Einstein, Philosopher-Scientist*, edited by Paul Schilpp (Library of Living Philosophers, Evanston, IL, 1949), p. 105.
[7] J. Perrin, "Brownian movement and molecular reality," translated by F. Soddy (Taylor and Francis, London, 1910). The original paper, "Le Mouvement Brownien et la Réalité Moleculaire" appeared in the Ann. Chimi. Phys. **18** (8^{me} Serie), 5–114 (1909).
[8] A. Einstein, "Autobiographical notes" in *Albert Einstein, Philosopher-Scientist*, edited by Paul Schilpp (Library of Living Philosophers, Evanston, IL, 1949), pp. 47, 49.
[9] C. N. Hinshelwood, *The Structure of Physical Chemistry* (Oxford, 1951), p. 91.
[10] A. Einstein, *Investigations on the Theory of Brownian Movement*, translated by A. D. Cowper (Dover, New York, 1956).
[11] P. Langevin, "Sur la Theorie du Mouvement Brownien," C. R. Acad. Sci. (Paris) **146**, 530–533 (1908).
[12] D. Lemons and A. Gythiel, "Paul Langevin's 1908 paper on 'On the theory of Brownian motion'," Am. J. Phys. **65**, 1079–1081 (1997), a translation of Ref. 11.
[13] Polysciences, 400 Valley Road, Warrington, PA 18976 [www.Polysciences.com].
[14] See S. P. Smith, S. R. Bhalotra, A. L. Brody, B. L. Brown, E. K. Boyda, and M. Prentiss, "Inexpensive optical tweezers for undergraduate laboratories," Am. J. Phys. **67**(1), 26–35 (1999).
[15] *CRC Handbook of Chemistry and Physics*, 77th ed., edited by David R. Lide (CRC, Boca Raton, FL, 1996), pp. 6–213. The table title is "Viscosity of aqueous solutions."

EINSTEIN'S PASSIONS

Albert Einstein was a man of many passions. Foremost among them was his desire to understand nature and to get at underlying truths. He was devoted to his research. ''I wouldn't want to live if I didn't have my work,'' Einstein wrote to his friend Michele Besso. He admitted that he ''sold himself body and soul to science,'' but he didn't regret it. Research was his life, and he devoted himself to it wholeheartedly.

Barry Parker, *Einstein: The Passions of a Scientist* (Prometheus Books, 2003), p. 13.