

¹This is the first mention of "the platinum tube," which must have been placed in the flow train between the cotton-wool plug *D* and the brass cylinder.

²*Pioneer Research on the Atom: The Life Story of Frederick Soddy*, by Muriel Howarth (New World Publications, London, 1958), pp. 82-84.

³A student, and subsequently a colleague, of Rutherford's a few years after the time of this work.

⁴*Nic*; compare the later quotation from the last paper of the series.

⁵That is, deprived of the ability to produce emanation.

⁶The "normal" kind, that was not carried away by the air stream.

⁷This, as they noted, was generally accepted by all workers in the field.

⁸The other two were K. Fajans and A. S. Russell.

BIBLIOGRAPHY

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4 The Existence of Atoms

Classical physics had no particular need for the concept of atoms. The development of the concept was, of course, followed and understood by physicists; in some areas of physics it provided at least a convenient terminology, and there were those who accepted it wholeheartedly and used it. But at the end of the nineteenth century there was no apparent compelling need to believe in atoms; and, as mentioned in Chapter 1, there were a number of scientists who did not—including some of the foremost chemists of the time, despite the fact that much of the evidence in favor of the atomic hypothesis was chemical.

The skeptics had their doubts cleared away in 1908 and 1909 by a single piece of research, carried out by Jean Perrin. His work, reported in barest outline in a series of papers in the journal *Comptes Rendus des Séances Hebdomadaires de l'Académie des Sciences* (Proceedings of the Weekly Meetings of the Academy of Sciences), and in detail in the *Annales de Chimie et de Physique*,¹ showed conclusively that Brownian motion implied the existence of molecules; and it included two distinct methods of determining Avogadro's number, the number of molecules in one gram mole, from the properties and behavior of emulsions. In recognition of this work, which is described in the present chapter, Perrin received the Nobel prize for physics in 1926.

Brownian motion is the name applied to a phenomenon discovered in 1827 by a botanist named Brown: that very small bits of solid matter (such as pollen grains), when suspended in a fluid, are in continual random motion. Perrin describes it this way: ". . . every particle situated in the liquid, instead of taking on,

according to its density, a regular movement of falling or rising, is rather found animated by a completely irregular movement. It comes and goes, it stops, it starts again, it rises, it sinks, it rises again, without at all tending toward immobility." However, according to Perrin, "The odd phenomenon discovered by Brown did not attract much attention. Rather it was ignored for a long time by most physicists, and it can be supposed that those who had heard about it believed that it was analogous to the motion of dust motes that we see dancing in a sunbeam under the action of weak air currents caused by slight differences of temperature or pressure."

It is significant that those who did study the phenomenon, almost without exception, were drawn to the conclusion that it was molecular in origin. Perrin quotes the explanation given by one Father Carbone in the late 1870's:

In the case of a surface of some extent, the collisions of the liquid molecules, the cause of pressure, do not produce an agitation of the suspended body, because their aggregate effect acts equally on the body in all directions. But if the surface is smaller than the extent that can provide compensation of the irregularities, there is no longer reason to consider the mean pressure, one must take account of pressures that are unequal and varying continually from point to point, which the law of large numbers no longer reduces to uniformity, and whose resultant is not zero, but changes constantly in magnitude and direction.

It is this changing force that gives rise to the erratic motion of the particle. "Moreover," Father Carbone continued, "the inequalities become more and more apparent in proportion as the body is imagined to be smaller, and consequently the oscillations at the same time become more and more lively. . . ." This aspect of the phenomenon will be discussed in more detail later in the chapter.

As has already been mentioned, the atomic hypothesis was well known in 1908, and had been for several decades. The quotation in the preceding paragraph shows how earlier workers on the phenomenon of Brownian motion had utilized the concept of molecular motion to account for the phenomenon. Perrin felt that the argument could be made equally well, and perhaps even

more convincingly, the other way around: that the existence of Brownian motion could be used to deduce the existence of molecules. His line of reasoning was as follows:

What is really strange and new in Brownian motion is just that it never stops. At first this seems in contradiction to our daily experience with friction. If, for example, we pour a bucket of water into a tub, it will seem proper to us that after a little while the motion first possessed by the liquid mass has disappeared. However, let us analyze how this apparent equilibrium is reached: All the particles of the water at first had their velocities approximately equal and parallel; this arrangement is broken up as soon as some of the particles, striking the sides of the tub, bounce off in different directions with changed velocities, to be immediately deflected anew by their collisions against other parts of the liquid. Thus, some instants after the fall, all the parts of the water are still in motion, but it is already necessary to consider a rather small part in order for the velocities of its different points to have approximately the same direction and the same magnitude. This is easily seen by mixing into the liquid some grains of colored powder that take on more and more irregular motions relative to each other.

What we observe, therefore, as long as we can distinguish anything, is not that the movement stops, but that it becomes more and more disorderly, that it is distributed in a more and more irregular manner among smaller and smaller parts.

Does this disordering proceed indefinitely?

To have some information for judging this, in any event to follow this disordering as far as possible, we must give up observing with the naked eye and make use of a microscope, and for indicator grains, make use of microscopic granules. Now, these are precisely the conditions under which we perceive Brownian motion; we are, then, assured that the coherence of movement, so evident on the ordinary scale of our observations, does not proceed indefinitely, and, on the microscopic scale, we prove an equilibrium between coherence and decoherence. . . . And there appears to be no way to avoid the following conclusion:

Since the dispersal of motion in a fluid does not proceed indefinitely and is limited by a spontaneous reordering, the fact is that fluids are themselves composed of grains, of molecules, which can indeed take on, relative to one another, all possible motions, but to the interior of which no transfer of motion is possible. If such molecules did not exist, there would appear to be no way to have a limit on the disordering of motion.

These arguments seem impressive; but as always in physics, they were of no value unless they could be supported by evidence

of a quantitative sort. Perrin now addressed himself to the problem of providing such evidence.

One of the consequences of the molecular theory is the law relating the average kinetic energy W of a gas molecule to the pressure p and volume V of its container:

$$W = \frac{3}{2} pV/n, \quad (4.1)$$

where n is the number of molecules present in the container. Now imagine a dilute solution separated from a body of pure solvent by a semipermeable membrane, one which offers no impedance to the passage of solvent molecules but which completely stops molecules of the solute. In such an arrangement, there is a pressure exerted on the membrane, known as osmotic pressure. Exactly the same line of reasoning that led to Eq. (4.1) can be applied to the molecules of the solute, with the result that an equation of exactly the same form is found to relate the mean kinetic energy of the solute molecules to the osmotic pressure. Moreover, the Dutch chemist van't Hoff had found that experimental values of osmotic pressure were just the same as the pressures that would have been exerted by the respective solutes if they had been gases of unchanged densities.²

In the case of gases, there is another relation between pressure and volume: the gas law,

$$pV = NRT,$$

where T is the absolute temperature, N is the number of moles of gas, and R is a universal constant. This equation together with Eq. (4.1) imply

$$W = \frac{3}{2} (NR/n) T. \quad (4.2)$$

The ratio of the number n of molecules to the number N of moles is also a constant, Avogadro's number, denoted by N_0 . Equation (4.2) is thus a statement that the mean kinetic energy of a gas molecule depends only on the absolute temperature of the gas. According to the preceding paragraph, an exactly parallel statement is true for the molecules of solvent in a dilute solution.

This last statement is completely free of all reference to the nature of either the solvent or the solute. If one considers a solute which is itself a liquid, ethyl alcohol for example, then,

according to Perrin, "... this indifference to the nature of the molecules of the liquid in which it is moving makes it almost impossible to believe that it will not have the same energy if it is in ethyl alcohol, that is, if it is one of the molecules of pure ethyl alcohol." A much more significant to the present discussion is that there is no upper limit placed on the size of the solute molecules, and there seems to be no obstacle to extending the law to "a particle yet a little larger, itself formed of several molecules, in one word a grain of powder." Apparently, then, Eq. (4.2), or more properly its equivalent form

$$W = \frac{3}{2} (R/N_0) T, \quad (4.3)$$

applies also to particles observed in Brownian motion.

Let us return to Perrin's own description:

Suppose that it were possible to realize an emulsion of completely identical grains, an emulsion of which I will say, for brevity, that it is uniform. . . .

Imagine a uniform emulsion in equilibrium, which fills a vertical cylinder of cross section s . The state of the horizontal slab bounded by the heights h and $h + dh$ would not be changed if it were entrapped between two pistons permeable to the molecules of water, but impermeable to the grains. . . . Each of these semipermeable pistons is subjected, by the impacts of the grains that it stops, to an osmotic pressure. If the emulsion is dilute, this pressure can be calculated by the same reasoning as for a gas or an extended solution, with the result that, if at height h there are n grains per unit volume, the osmotic pressure P will be equal to $\frac{3}{2}nW$, if W denotes the mean energy of the grains; it will be $\frac{3}{2}(n + dn)W$ at height $h + dh$. Now, the slab of grains under consideration does not sink, for this it is requisite that there be equilibrium between the difference of osmotic pressures, which acts upwards, and the total weight of the grains, diminished by the buoyant force that they experience, which acts downwards. Thus, denoting by φ the volume of each grain, Δ its density, and δ that of the suspending liquid, we see that²

$$-\frac{3}{2} W dn = ns dh \varphi (\Delta - \delta) g$$

or

$$-\frac{3}{2} W \frac{dn}{n} = \varphi (\Delta - \delta) g dh,$$

which, by an obvious integration, gives rise⁶ to the following relation

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between the concentrations n_1 and n_2 at two points whose difference in heights is h :

$$3W \ln \frac{n_2}{n_1} = \varphi(\Delta - \delta)gh, \quad (4.4)$$

a relation that can be called the *equation of distribution of the emulsion*.

The point of the foregoing derivation is this: Equation (4.3) expresses the mean energy of a suspended grain in terms of the absolute temperature and a quantity characteristic of the atomic-molecular hypothesis, Avogadro's number. But the mean energy cannot be measured directly; the motion of the particles is too fast and too short-ranged to be followed. It is necessary to relate the mean energy to quantities that could be measured. Equation (4.4) expresses such a relation, obtained *without* reference to the atomic hypothesis. Perrin has this to say:

In short, by whatever path it be, we find ourselves led to think that the mean energy of translation of a molecule is equal to that possessed by the grains of an emulsion. If then we find a method of calculating this granular energy in terms of measurable quantities, we shall have in the same stroke a method of judging our theory. Once the experiments are done, two cases can in fact present themselves: Either the numbers obtained will be substantially different from those that are given by the kinetic arguments summarized above, and, in this case, especially if the numbers change with the grains studied, the credibility of the kinetic theories will be reduced, and the origin of the Brownian motion will remain to be found; or the numbers will be of the order of magnitude predicted, and, in this case, not only do we have the right to regard the molecular theory of this motion as established, but also we can seek in our experiments a method, perhaps precise this time, of knowing molecular magnitudes.

The stage was thus set for the experiment. The concept, once again, was simple: to determine the concentrations at two levels in an emulsion of particles of known size and density and at known temperature. The execution, however, was extremely tedious, as will be evident.

The first step was to select a suitable material to form the emulsion. Apparently there had been some earlier studies; all that had been learned from them was that "a large number of

colloidal solutions become clear in their upper portions when they are left alone for several weeks or several months." Perrin himself had made "some attempts without result on these colloidal solutions." Finally, "after some gropings," he had found it possible to make emulsions on emulsions of gamboge, a yellow resin used in water colors,⁷ or of mastic, a resin used in making varnish. Perrin does not specify the properties that he sought in his emulsions, but one feature that he is careful to mention about both gamboge and mastic is that the suspended particles are spherical. This meant that once a uniform suspension had been obtained, that is, one in which all the particles were the same size, the volume φ could be expressed in terms of the radius a , as $\varphi = \frac{4}{3}\pi a^3$ —provided, of course, that the radius could be measured.

The suspensions as originally formed,⁸ however, consisted of particles of a variety of sizes, and it was necessary to "sort them out" by size. This was done by a process that Perrin calls "fractional centrifuging." Here is his description of the technique:

The centrifuge tube is filled to a given depth, 10 cm for example, with a pure emulsion; the machine is set in motion at a fixed angular speed, for example 30 revolutions per second (which gives, at 15 cm from the axis, a centrifugal force about 500 times greater than the weight); the drive of the machine is stopped after a fixed time, 60 minutes for example, and it is allowed to stop by itself, which must take a few minutes; the tube is carefully withdrawn.

A fairly firm sediment, with a clearly defined surface, occupies the bottom of this tube to a depth usually negligible relative to the depth of the liquid; it contains all the grains that have reached the bottom during the centrifuging, pressed together much as the grains of sand filling a sack might be.

Let us denote by e_1 the radius that a grain located at the surface of the liquid at the start of the centrifuging would have to have in order to arrive at the bottom of the tube just at the moment when the centrifuging stopped; every larger grain will a *fortiori* have arrived in the deposited sediment, but this sediment contains in addition many smaller grains, that had time to reach the bottom because they were found, at the beginning, at lower levels in the emulsion.

By means of a siphon, the liquid which is above the sediment is carefully decanted; the tube is refilled with distilled water up to the original depth; it is shaken with the sediment, the grains of which all separate, and the preceding operation is carried out again with the

same angular speed and the same duration of centrifuging. All the grains of radius greater than a_1 will again have time to reach the bottom, but a small grain which previously was able to do so because it was already close will not be able to this time if chance makes it start near the surface. In short, the second sediment contains, like the first, all the grains whose radii exceed a_1 , and contains many fewer smaller grains.

The supernatant emulsion is decanted, already paler than the fraction decanted first, and the same operations are repeated until the liquid that is found above the sediment at the end of each centrifuging becomes nearly clear water. Now this sediment contains all the grains of the original emulsion whose radius exceeds a_1 and no others; all the smaller grains have been eliminated.

Let us repeat the same operations on the final sediment, but with a little shorter duration of centrifuging. Let us designate by a_2 the radius that a grain at the surface must have to reach the bottom of the tube just at the end of this centrifuging. The liquid that is found above the sediment can only contain grains of a radius less than a_2 ; according to its origin, it can only contain grains of radius greater than a_1 ; thus if a_1 is near a_2 , this liquid is practically a uniform emulsion which needs only to be decanted.

I think it is needless to explain how one can in an analogous fashion, if it is so desired, extract from the overlying fractions a uniform emulsion of still smaller grains, or from the residual sediment a uniform emulsion of still larger grains.

As is so often the case, the procedure appears simple and straightforward in retrospect. It was clearly ingenious, however, and must have been very time-consuming—note that Perrin gives no hint of how many repetitions were required for a complete separation.

The density of the grains was determined by two methods. One was simply to heat the emulsion so as to evaporate the water; the resin then melts, but on cooling solidifies again to a glassy substance whose density can be determined by standard methods. This procedure, however, implies the assumption that the resin has the same density in bulk form as it has in the form of suspended grains. Perrin therefore used a second method as a check. He determined the masses m of water and m' of emulsion needed to fill the same container at the same temperature. He then dried the emulsion and measured the mass μ of resin that it contained. If d is the density of water, the volume of the container is m/d ;

the volume of the liquid originally in the emulsion is $(m' - \mu)/d$; the difference between these two numbers is then the volume occupied by the resin in the emulsion, which divided into its mass μ is its density. The two methods gave values in excellent agreement.

A flat cylindrical vessel was now formed by placing on a microscope slide a thin sheet of glass, usually 0.1 mm thick, with a hole through it. A drop of uniform emulsion was placed in this vessel, and a microscope cover-glass sealed over it with paraffin or varnish. With evaporation thus prevented, a single preparation could be observed during a period of as much as several weeks. The whole was then placed on the stage of a microscope; it was necessary to take pains to see that the stage was level, so that motion of the body tube, and hence of the objective, would be accurately vertical. The whole arrangement is shown schematically in Fig. 4.1.

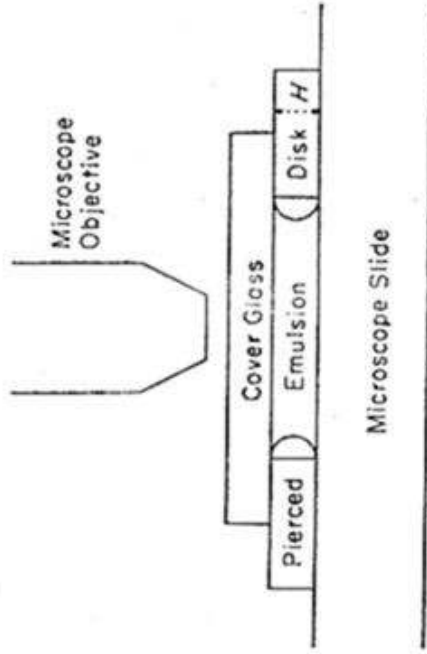


FIG. 4.1 Experimental arrangement for measuring the distribution of grains in an emulsion. The drawing proper is from Perrin's work; the legend has been translated. [Perrin, *Oeuvres Scientifiques*, p. 193, Fig. 21.]

The objective was chosen to give high magnification but to have only a small depth of field, of the order of a micron (the 0.1-mm depth of the container is equal to 100 microns). It was pos-

sible, then, to see clearly at one time only those grains in a very thin horizontal slab of the emulsion. If the body tube were raised or lowered, the grains in another slab would be seen, and the vertical distance between the slices, which would correspond to the difference in height h of Eq. (4.4), could be determined from the scale on the micrometer movement of the microscope.¹⁰

The next step was to determine the number of grains in a given area—the field of view, say—at each of two levels. This was by no means easy: "... it is not a matter of counting fixed objects, and when, on putting one's eye to the microscope, one discerns in the field some hundreds of grains that jiggle in every direction, and moreover continually disappearing at the same time as other grains appear, one is quickly convinced of the uselessness of any efforts that could be made to know even roughly the average number of grains present in the slice observed." This, of course, is an exaggeration. One means immediately suggests itself, that of photographing the layer and counting the clear images of grains. Even if the emulsion were so dilute that the number were small and thus subject to relatively large fluctuations,¹¹ the same layer could be photographed again and again so as to obtain an accurate average value. This method proved useful, but only when the grains were more than about $\frac{1}{2}$ micron in diameter; for smaller grains, the photographic images were not good. In such cases another scheme was used. In the focal plane of the microscope ocular was placed a disk of opaque foil, pierced with a small round hole by means of a dissecting needle. This cut down the field of view to the point where the number of particles could be taken in at a glance, say during the illumination admitted by a camera shutter. "Working in this way at regular intervals, every 15 seconds for example, one observes a series of numbers whose mean value approaches more and more closely a limit which defines the mean frequency of the grains, at the level studied, in the little cylindrical layer on which the microscope is focused." The same process repeated at a different level would give the mean frequency in an equal volume, and "the ratio of the two numbers gives the desired ratio of concentrations." It was necessary, however, to take several thousand readings to achieve any degree of precision.

The remaining quantity was the radius of the grains. Here again Perrin found more than one means of measurement, to provide a check. The first made use of Stokes's law, governing the fall of a sphere of radius a , of density Δ , through a fluid of density δ and viscosity η : The sphere acquires a limiting velocity called the terminal velocity, when the viscous drag of the fluid just counterbalances the net downward force, weight minus buoyancy; the terminal velocity satisfies the equation

$$6\pi\eta a v = \frac{4}{3}\pi a^3(\Delta - \delta)g.$$

If an extremely tall vertical column of a uniform emulsion is produced, then, as Perrin puts it, "One will be far enough from the equilibrium distribution that the grains at the upper levels will sink like the droplets of a cloud, practically without one's needing to take into consideration the counter motion due to the accumulation of grains at lower levels. The upper part of the liquid thus becomes clear, and the extent of the clarified zone, divided by the time elapsed since the emulsion was left to itself, gives the velocity of fall to which Stokes's law is applied." The procedure, accordingly, was to seal a quantity of emulsion into a capillary tube (the narrow tube eliminated motion due to convection currents), install it vertically in a temperature bath, and observe the daily descent of the top of the cloud of grains; for such small grains, the terminal velocity would be reached in a matter of seconds, but would be measured in millimeters per day.

Perrin recognized that the application of Stokes's law to such small grains might be questionable,¹² so he used two more direct methods. One was to count the number of grains in a known volume of standardized emulsion—that is, emulsion in which the concentration of emulsion by mass was known. It was not practical, of course, to count the granules actually in suspension; but Perrin had "had occasion to notice that in a weakly acid medium (for example 0.01 gram mole per liter) the grains of gamboge or mastic collect on the glass walls that hold in the preparation." It was not a matter of destroying the suspension, but only that the grains stick to the glass when they happen to strike it, so that after several hours, all the grains originally present in one of his cells

would be fixed to the surfaces of the container. Moreover, a "protective colloid" present in the natural latex of gamboge and added to the emulsion kept the grains separate rather than in partially coagulated globs. Finally, there was no significant lateral migration of the grains during the deposition process, so that those originally in a given vertical column ended up, apart from fluctuations, on the portions of the top and bottom plates that marked the ends of the column. Simple counting¹³ then gave the number of grains in a known volume of emulsion, from which together with the mass per unit volume the size of each grain could be calculated.

A third method, still more direct, was usable for grains more than half a micron in diameter. In this case, it was found that the grains tended to arrange themselves in fairly regular arrays, within which could be distinguished straight rows of three to five grains. An example is shown in Fig. 4.2. While the image of a single grain was too much enlarged by diffraction to permit more than a rough estimate of its diameter, the length of such a row could be reasonably easily measured, either in direct view or on a photograph, thus permitting a determination of the diameter of a single grain.

The three methods gave closely comparable results. Six emulsions ultimately served as the source of Perrin's results; the values obtained for the radii of five of the six, and one extra, are given in Table 4-1. Perrin notes that to achieve the one case of three-

TABLE 4-1. Radii of Grains in Six Emulsions, in Microns

Material	Counting	Method		Rows
		Counting	Stokes's law	
Gamboge	0.14	0.15
Gamboge	0.212	0.213
Gamboge	0.30	0.29	0.30	0.30
Gamboge	0.46	0.45	0.455	0.455
Gamboge	...	0.49	0.50	0.50
Mastic	...	0.52	0.54	0.54

figure accuracy, he had to count 11 000 grains.

The emulsion of 0.14-micron particles gave poor results, for reasons which Perrin does not specify. The resulting value of

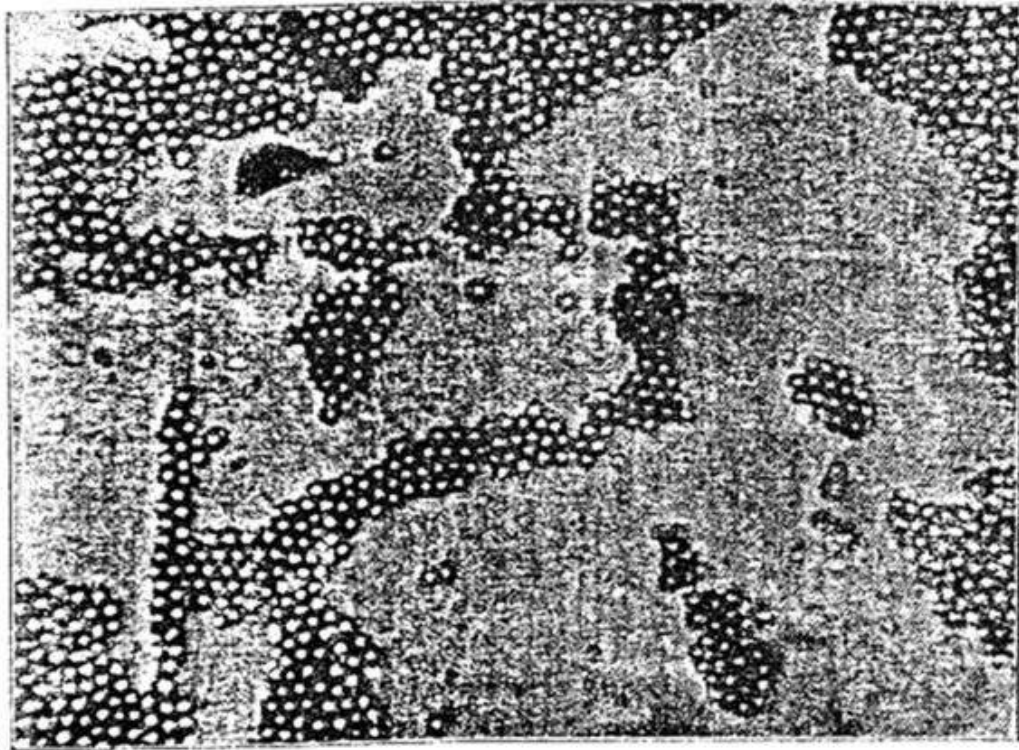


FIG. 4.2 A photograph of emulsion grains deposited on one surface of a container, showing the approximately regular array which permitted measurement of diameters. [Perrin, *Oeuvres Scientifiques*, facing p. 199, plate I.]

N_0 is given merely as "between" 5.0×10^{23} and 8.0×10^{23} per gram mole. Two series of measurements were made on emulsions of radius about 0.30 micron; one, probably the one whose radius measurements are tabulated, gave $N_0 = 7.5 \times 10^{23}$ per gram mole, while the other, for which the radius is reported as 0.29 micron, gave $N_0 = 6.6 \times 10^{23}$ per gram mole. The 0.45-micron emulsion gave $N_0 = 7.2 \times 10^{23}$ per gram mole, while the 0.52-micron one of mastic gave $N_0 = 7.0 \times 10^{23}$ per gram mole. The total numbers of grains counted in determining the concentration ratios for these five were between 3000 and 7500. The series of which Perrin was evidently proudest, however, was that on the 0.212-micron emulsion. He counted at four levels for a total of 13 000 grains, and obtained the result $N_0 = 7.05 \times 10^{23}$ per gram mole.

Considering the nature of the experiment and the difficulties involved, the agreement among these various values is quite satisfactory. Perrin notes that they cover a fortyfold range of masses, a nearly fivefold range of difference in density between grains and liquid,¹⁴ and a thirtyfold range in rate of decrease of concentration with increase in height. He concludes, already at this point, that "it is quite difficult to deny the objective reality of molecules."

But he carried the matter still another step. It must not be thought that a given particle in Brownian motion merely undergoes an irregular motion around an equilibrium position. Rather, it traces out an irregular, wildly wandering path. Figure 4.3 shows three examples. On each of the paths, the points are plotted at intervals of 30 seconds; the size of the divisions is not given, but is of the order of one or a few microns. "One of these patterns contains 50 consecutive positions of a single grain. It gives only a very faint idea of the stupendous entanglement of the real trajectory. If, in fact, one were to make the mark second by second, each of the straight line segments would be replaced by a polygonal path of 80 sides, relatively as complex as the pattern here reproduced, and so on."

Einstein had analyzed this motion in a series of articles published in 1905 and 1906.¹⁵ His analysis centered on the net displacement of a particle during an interval τ , that is, the distance from its position at the start of the interval to its position

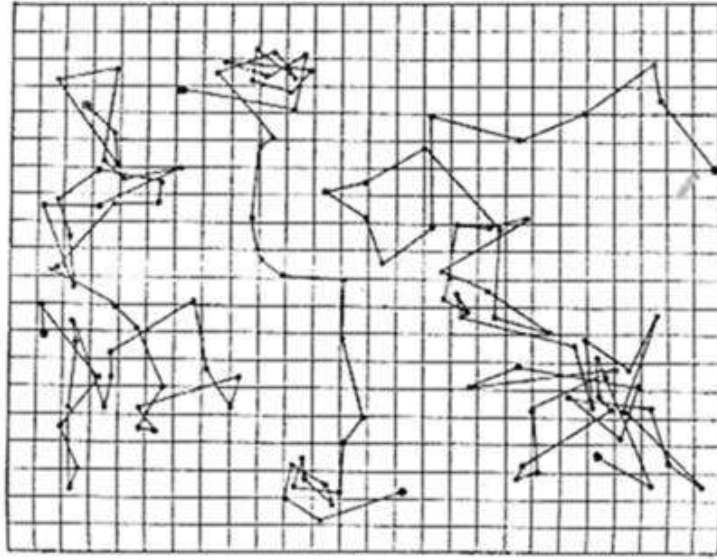


FIG. 4.3 Three examples of the paths of particles in Brownian motion. [Perrin, *Oeuvres Scientifiques*, p. 219, Fig. 25.]

at the end. As is evident from Fig. 4.3, this quantity does not have a single value, but many values. Each value is, of course, a vector quantity, for which the component along some specified direction can be found. What Einstein calculated was the average of the squares of the values of such a component. If this quantity is denoted by $\langle x^2 \rangle$, then for a spherical particle of radius a suspended in a liquid of viscosity η , the value is

$$\langle x^2 \rangle = \frac{Rf\tau}{N_0 3\pi a\eta} \quad (4.5)$$

where, as before, R is the gas constant, T is the absolute temperature, and N_0 is Avogadro's number.

In fact, at least three earlier studies had dealt with this aspect of Brownian motion; and all three, two of which were carried out after Einstein's work, appeared to be in contradiction with those results. Nevertheless, there were sufficient grounds for doubting the validity of the earlier works that Perrin and a student of his, named Chaudesaigues, were thoroughly willing to try again. Working with "grains of exactly known diameter which I knew how to prepare," Chaudesaigues "registered the position of a grain with the camera lucida,¹⁰ from half-minute to half-minute, he began again with another grain, and so on. . . . There was then nothing more but to see whether the value given . . . by Einstein's equation . . . agrees, within the limits of error of the experiment, with the value already determined."

As a preliminary check, Chaudesaigues studied some grains of gamboge only indifferently identical. The results were encouraging, so a more careful effort was made. The 0.212-micron emulsion already discussed was used. Each of 100 grains was followed for four 30-second intervals, 50 grains at each of two values for the viscosity of the liquid. The first group of 50 gave $N_0 = 7.3 \times 10^{23}$ per gram mole, the second gave $N_0 = 6.8 \times 10^{23}$ per gram mole. For a third group of 50 grains the viscosity was increased about fivefold by adding sugar; the mean displacement was reduced in the theoretically predicted ratio, and the resulting value for N_0 was 5.5×10^{23} per gram mole.

Finally, three series of measurements were made, in collaboration with one M. Dabrowski, on emulsions of mastic. The values for N_0 , in units of 10^{23} per gram mole, were 6.45, 7.15, and 7.7. The overall value obtained by this method was taken to be 7.15×10^{23} per gram mole, in quite reasonable agreement with the value determined from the distribution law.

Perrin devotes the last portion of his paper to a review of other methods of estimating N_0 (including a rather surprising one, due to Lord Rayleigh, involving the intensity of the blue light from the sky), and notes that all of them lead to results comparable with his own. He then gives this summary:

I believe it is impossible for an intellect free of prejudice to reflect on the extreme variety of phenomena that converge in this way toward

the same result, without feeling a very strong effect; and I think that from now on it will be difficult to defend by rational arguments an attitude hostile to the molecular hypothesis, which breaks through all convictions one after another, and to which one must grant at least as much credence as to the principles of energetics.¹⁷ There is certainly no question of contrasting these two great disciplines with one another, and the union of Atomistics and Energetics will glorify their double triumph.

FOOTNOTES

¹All quotations in the present chapter are from this paper. The paper was of such significance that translations into English and German were published in 1910, the former being made by Frederick Soddy (see bibliography).

²All of the foregoing analysis may have been due to van't Hoff also; Perrin is, at times, careless about making clear how much of the background was drawn from the work of others. Similarly, the succeeding arguments may have been generally known.

³This is a far more drastic extension than it may appear at a casual glance. It ignores the fact that the original deduction depended on a distinction between solvent and solute.

⁴A single French word, *pousière*, is translated "grain of powder."

⁵The left-hand side is the difference between the two osmotic pressures, multiplied by the area on which each acts, the right-hand side is the difference of two terms each of which is a number of particles per unit volume times the volume $s dh$ of the slab, giving the total number of particles, times the volume of each particle, times a density, times the acceleration due to gravity, and is therefore the difference between the total weight of the particles and the total buoyant force on them.

⁶This step must be taken on faith by readers who have not studied calculus. The notation "ln" in Eq. (4.5) represents the logarithm to the base $e = 2.7182 \dots$, called "natural logarithm." Note that for any x , there holds $x = e^{\ln x} = (10^{0.4343})^{\ln x} = 10^{0.4343 \ln x}$, so that $\log x = \ln x / 2.303$. Conversely, $\ln x = 2.303 \log x$.

⁷Perrin was chemist enough to be concerned over the chemical nature of the substances involved. For example, he established that the yellow substance which was suspended in the case of gamboge, and which constituted about 80% by weight of the raw material, was apparently a pure chemical compound rather than a mixture, that it was an acid (which he named *gambogic acid*, from the French word for gamboge, *gomme-gaïe*), and that it had a molecular weight in the neighborhood of 540.

⁸Commonly, by extracting the raw latex with alcohol and diluting the resulting solution with water.

⁹Such sheets are commercially available for use in making blood counts.

¹⁰A correction factor of $\frac{1}{2}$, allowing for the fact that what was being measured was an *apparent* depth of water, had to be applied if an immersion objective were not used; Perrin, however, usually used the immersion objective.

¹²If a single counting of a quantity subject to random fluctuation gives the result n , the probable error of this result, which is roughly equal to the mean fluctuation, is \sqrt{n} ; the relative probable error is thus $1/\sqrt{n}$, which may be fairly large if n is only moderately large. For example, if the relative error is to be 1%, n must be 10 000.

¹³A few years later, Millikan was to discover that Stokes's law does indeed require modification when the diameter of the sphere becomes comparable with the average distance between molecules of the fluid. In liquids, however, this situation does not arise for visible, even microscopically visible, grains.

¹⁴In actuality, the positions of the grains were recorded on tracing paper by means of a camera lucida, an instrument which causes a virtual image to appear as if projected on a plane surface, such as a ground glass, so that a tracing can be made; in addition, the fluctuations mentioned were taken account of by averaging counts made on several vertical columns in a single cell, the columns being defined by square grills ruled on the microscope slide.

¹⁵For gamboge, the difference in density was in the range 0.2 to 0.3 gram per cubic centimeter, while for mastic it was only 0.065 gram per cubic centimeter.

¹⁶This work, and studies of the specific heat of solids, were at least as influential in the award of the Nobel prize to Einstein as was his work on relativity.

¹⁷The function of the camera lucida was described in footnote 13.

¹⁸The opponents of the atomic hypothesis, led by the chemist Ostwald, championed a doctrine that they called Energetics.

BIBLIOGRAPHY

This entire chapter is based on J. Perrin, *Annales de Chimie et de Physique* 18, 1-114 (1909), reprinted in J. Perrin, *Œuvres Scientifiques* (Service des Publications du Centre National de la Recherche Scientifique, Paris, 1950), pp. 171-239. This important work was translated into both English and German. The English translation is by Frederick Soddy, *Brownian Movement and Molecular Reality* (Taylor and Francis, London, 1910), and is excerpted in *The World of the Atom*, pp. 628-640.

5 *The Atomic Nucleus*

In 1911, the atomic hypothesis was on firm ground as a consequence of Perrin's work. True, the experiments of Rutherford and Soddy had robbed the atom of its immutability; but radioactivity was a rather special phenomenon. Neither study, however, had revealed anything about the structure of the atom. Of that, little was known. It was generally accepted that "corpuscles"—what we now know as electrons—played some role in the structure; but what that role was remained unknown, except that it was certainly related to the spectrum of light emitted by the atom.

At least three different suggestions had been put forward, however. The earliest (1902) was due to Lord Kelvin, but was championed principally by Sir J. J. Thomson and has become known as the Thomson atom; Thomson published an extensive paper on it in 1904 and continued to work with it for several years. The model regards the positive charge and the mass of the atom as being distributed uniformly throughout the atom, presumably in a sphere whose diameter would be of the order of 1 angstrom (10^{-8} centimeter). Electrons were thought of as being embedded in this sphere like raisins in a pudding; in consequence, the model is frequently referred to as the "plum pudding" atom. Thomson studied possible equilibrium arrangements of the electrons in the atom, and noted that there could be expected a sort of periodicity of atomic properties that was at least qualitatively similar to what was observed.

The second was put forth by a professor at the University of Kiel, Philipp Lenard, who conceived it as a result of his work on