

## The theory of Brownian Motion: A Hundred Years' Anniversary

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The year 1905 was truly a miracle year, *annus mirabilis*, in theoretical physics. Albert Einstein published four important papers that year: Two papers laying foundations for the Special Theory of Relativity, one explaining the photoelectric effect that would win Einstein the 1921 Nobel Prize in physics, and one explaining the mechanism of Brownian motion<sup>1</sup>. An independent explanation of this last phenomenon was published the following year by a Polish physicist Marian Smoluchowski<sup>2</sup>. An explanation of the origin and properties of Brownian motion was a solution to a nearly 80 years old puzzle, a remarkable feat, but nobody expected it



Marian Smoluchowski (1872–1917)

to be a major breakthrough that would reshape the whole physics. This was, however, the case and we will try to explain why.



Robert Brown (1773-1858)

Brownian motion takes its name after a Scottish botanist, Robert Brown. Brown was a highly respected man in his time, not, however, for the discovery that he is now famous for, but for his classification of the plants of the New World. It was during this research that Brown noticed in 1827 that pollen in water suspension which he examined in his microscope displayed a very rapid, highly irregular, zigzag motion. Such motions had been observed even prior to Brown, but only in organic molecules, and their origin was delegated to some mysterious "vital force" characteristic of living matter. Brown was not satisfied with this explanation, which could possibly fit

the living pollen. Instead, he noticed that an identical motion was displayed not only by living pollen, but also by dead pollen and by fine inorganic particles.

<sup>&</sup>lt;sup>1</sup> A. Einstein, Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, Ann. Phys. 17, 549–560 (1905).

<sup>&</sup>lt;sup>2</sup> M. von Smoluchowski, Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen, Ann. Phys. 21, 756–780 (1906).

Incidentally, Brown used pulverized fragments of an Egyptian sphinx in his experiments, which did not influence the results, but nicely demonstrates the intellectual climate of the time. In conclusion, this motion must have had a physical origin. But which? Brown, limited by his laboratory equipment, was only able to show that this motion was not caused by currents (flows) in the liquid, nor by convection, nor by the evaporation of the solvent.



Albert Einstein (1879–1955)

The origin of the motion discovered by Robert Brown remained a mystery, one of the many scientific facts that did not have an explanation, but nobody doubted that sooner or later such an explanation would be provided. The problem of Brownian motion did not seem to be particularly important, but nevertheless, many people tried to solve it. First, the observations made by Brown himself, that neither flows in the liquid, nor convection or evaporation caused the motion, were confirmed. Next, chemical composition, the shape of the container, and several forms of external influence were eliminated as possible causes. After Maxwell and Boltzmann formulated the

so-called kinetic theory, people tried to describe the Brownian motion in terms of that theory, in particular by determining the velocity of Brownian particles. All those attempts failed.

Even though they are now only of historical interest, it was important in the time of Einstein and Smoluchowski that scientists had tried all those approaches with little success because the failure of conventional explanations prepared the ground for the revolutionary one proposed by these two men. We should remember that the remaining Einstein's achievements from his miracle year, the Special Theory of Relativity and the concept of a photon, were for many years heavily opposed by some leading physicists.

So what was the explanation proposed by Einstein and Smoluchowski? They realised that movements of Brownian particles were caused by collisions with molecules of the solvent. These molecules move erratically in display of their thermal energy, of which the temperature is a certain measure. Molecules of the solvent are too little to be observed directly, but particles of the suspension, even though they are tiny from a human point of view, are true giants in comparison with the molecules of the solvent, and can be observed directly. Today this explanation may seem to be trivial, but it was far from being trivial a hundred years ago. It is perhaps difficult to believe, but a hundred years ago the atomistic hypothesis, or the hypothesis that matter is grainy and cannot be continuously divided infinitely, was not commonly accepted. On the contrary, some researchers treated it merely as an unsupported working hypothesis, and others, including such eminent figures as Wilhelm Ostwald, the 1909 Nobel Prize in chemistry winner,

and Ernst Mach, opposed it vigorously<sup>3</sup>. Albert Einstein and Marian Smoluchowski claimed that motion of the particles of the suspension provided a proof of existence of the molecules of the solvent, and what is more, that by examining the Brownian particles, one could get much insight into the properties of the molecules of the solvent. Einstein and Smoluchowski provided also a quantitative tool for assessing the Brownian motion: They discovered that the observed mean displacement of a particle (squared) was proportional to the duration of the observation, and that the proportionality constant was related to the so-called diffusion coefficient. These results rendered feasible many specific measurements; in particular it was now possible to experimentally determine the value of the so-called Avogadro constant. A French physicist Jean-Baptiste Perrin conducted such experiments a couple of years after the papers of Einstein and Smoluchowski were published, which won him the 1926 Nobel Prize.

It is worth noting that explaining the Brownian motion was not Einstein's intended goal. He did not know the experimental data on Brownian motion very well. Einstein aimed at establishing a connection between the diffusion coefficient and the temperature, in which he succeeded, but being a genius, he guessed what the thermal motion should look like. Smoluchowski, on the contrary, knew the experimental data on Brownian motion very well and intended to explain them. It is now clear from the surviving correspondence between Marian Smoluchowski and Albert Einstein that Smoluchowski obtained his results prior to Einstein but decided to publish them only after he was impressed by the work of Einstein.

The papers by Einstein and Smoluchowski discussed here have also answered several other questions. First, they provided a microscopical explanation of diffusion (molecules of the substance that diffuses are "pushed through" by the collisions with the molecules of the solvent), second, they provided a derivation of a differential equation known today as the diffusion equation<sup>4</sup>, and third, they explained why the previous attempts to describe the Brownian motion in terms of velocities had failed. Smoluchowski noticed that displacements of Brownian particles seen in a microscope resulted from a huge number of collisions with the molecules of the solvent: the displacements were *averaged* over many such collisions. It is now apparent that the mean time between two consecutive collisions is much shorter than the smallest time interval that we can measure even now, at the beginning of the 21<sup>st</sup> century. If this is the case, then neither in the time of Brown, nor in the time of Einstein and Smoluchowski, not even today, can we observe two

 $<sup>^{3}</sup>$  It is not surprising that Einstein, who esteemed Mach very much, immediately sent him a copy of his publication.

<sup>&</sup>lt;sup>4</sup> This equation, resulting from heuristic laws originally formulated by a German physiologist A. Fick, was already known at that time, but its derivation from first principles was lacking.

*consecutive* collisions. Any two observed zigzags of the trajectory are separated by a multitude of other zigzags that we have failed to observe. If this is so, we can assume that a collision takes place in every instant of time, and consequently, that a Brownian trajectory has a zigzag at every point, and that it is completely random. The velocity of a particle is undetermined at the moment of a sharp turn. We can of course measure the average velocity but this last quantity is of little importance from a fundamental point of view.

This point demands special attention. The Newtonian dynamics, commonly used in times of Smoluchowski and used today with great success in the analysis of many phenomena, says that a trajectory of every particle, of every "material point", can be described by a certain differential equation. To write down this equation, it is necessary and sufficient to know all forces acting on the particle. This is the essence of the Second Principle of dynamics. The forces may vary in space and time, but if their changes are continuous, the resulting trajectory is smooth, perhaps very complicated, but smooth in a mathematical sense. This was the canon of physics, and to attack this canon would nearly amount to a sacrilege. Smoluchowski claimed that a trajectory of a Brownian particle was not smooth, that it had many zigzags, indeed that it had a zigzag in every single point. This was a real revolution, a deviation from a well-established paradigm, but the point was that this approach led to results that agreed with the experiment while all the others did not. The diffusion equation mentioned above does not describe a trajectory of a single particle, but a mean, collective behaviour of a multitude of particles, like for example a drop of ink put into a water tank, or a lump of sugar used to sweeten the tea<sup>5</sup>. Even though the trajectory of a single particle, consisting entirely of zigzags, can be really awkward, the collective behaviour of many such particles can be quite decent if we only agree not to be bothered by *really* tiny details. This is the essence of a probabilistic approach.

As we can see, displacements of Brownian particles can be modelled by a random process. The works of Einstein and Smoluchowski have become one of the cornerstones of Probability Calculus and the theory of Stochastic Processes, which are now one of most prominent branches of mathematics. Stochastic modelling has become a key method in many areas of science and technology, ranging from physics, through engineering design, to biology, ecology and social sciences. Even this would not be possible without the works of Einstein and Smoluchowski.

Einstein and Smoluchowski have discovered that viscosity and other forms of dissipation are, on a molecular level, caused by thermal motion of particles; this law is now known as the Fluctuation-Dissipation Theorem. Some time later Marian Smoluchowski has shown that variables used to describe any sufficiently

<sup>&</sup>lt;sup>5</sup> Tea and sugar is a standard example, which is the sole reason for my using it, as I personally prefer the unsweetened tea.

large (or macroscopic), but finite, system in a thermal equilibrium must vary in time in a manner that we now call Gaussian White Noise; this is the very same noise that causes the Brownian motion. In other words, Brownian motions are necessarily displayed by any macroscopic physical system in equilibrium.

Since Brownian motions, or rather thermodynamical fluctuations that cause them, are common, we need to learn how to live with them. Thermal noise is usually detrimental: it is this noise that causes disturbances in communication lines. the measurement errors, the power loss in transfer lines and so on. However, it turns out that without the noise, the whole world as we know it would collapse. The noise can act constructively: it can sustain signals that would otherwise dissipate, it can amplify, not weaken, signals (this is known as the stochastic resonance), and finally, the noise is an indispensable component in many crucial biochemical reactions without which the biological life in its current form could not possibly exist. The thermal noise must be taken into account when designing nanorobots and molecular motors that have long been dreamt of by science fiction writers and are now becoming the subject of serious research. Nanorobots are, for example, supposed to travel through human body in blood and repair various microdefects. One needs to remember, though, that particles in the environment intended for nanorobots are in a ceaseless thermal motion. If a nanorobot were scaled up to the human size, the fluctuations would have to be similarly scaled up. Simple calculations show that thermal fluctuations would then reach the strength of a hurricane. Designing nanorobots and molecular motors is thus as difficult as designing machinery that would work seamlessly during Katrina<sup>6</sup>, or better still, that could use Katrina's force to their own benefit! But nature manages to do so: It has designed natural molecular motors, for example the kinesins, or proteins that move on intramolecular membranes. This example shows that science is, in fact, one and indivisible: Understanding many biochemical mechanisms would not be possible without this branch of theoretical physics that has been started with the works of Einstein and Smoluchowski a hundred years ago.

A group of physicists based in Jagellonian University in Krakow is active in research on this particular branch of physics and its applications not only in other branches of physics, but also in molecular biology, ecology, financial mathematics and social sciences.

Marian Smoluchowski is considered to be the most prominent Polish physicist. His papers are still quoted and an important equation used in physics is named after him. Jagellonian University Institute of Physics is named after him as well, and the most important prize awarded by the Polish Physical Society is called the Smoluchowski Medal. As we have said, Jean-Baptiste Perrin, who

<sup>&</sup>lt;sup>6</sup> Katrina was the name given to a Category 5 hurricane that drowned New Orleans in August 2005.

based his measurement of the Avogadro number on the theory developed by Einstein and Smoluchowski, received his Nobel Prize in 1926. Albert Einstein received the Nobel Prize in 1921. Even the arch-opponent of the atomistic hypothesis, Wilhelm Ostwald, received the Nobel Prize. We can only wish that Marian Smoluchowski belonged to the elite club of the Nobel Prize laureates. Alas, Marian Smoluchowski, professor of the University of Lvov and of Jagellonian University in Cracow, died of dysentery in 1917 aged only 45, when the Great War ragged the world and before the importance of his scientific achievements was fully recognized.



Kołłątaj Collegium, the old Physics Dept.

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