CENTENARY OF MARIAN SMOLUCHOWSKI'S THEORY OF BROWNIAN MOTION*

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Seminal ideas developed by Marian Smoluchowski in his 1906 papers on the diffusion and on the Brownian motion present the most creative application of the probability theory to the description of physical phenomena.

PACS numbers: 05.40.Jc, 05.20.Dd, 01.65.+g

The irregular persistent motion of small particles suspended in liquids has been observed by an English botanist Robert Brown in 1827 when the first achromatic microscopes became available. At this time Brown certainly could not foresee the importance of his discovery for further evolution of physical ideas on the constituents of material bodies. In his famous book "Les atomes" Jean Perrin who received in 1926 the Nobel prize in physics for "his works concerning the discontinuous structure of matter" describes this fascinating phenomenon in a picturesque way [1]:

> "Il suffit en effet d'examiner au microscope de petites particules placées dans de l'eau pour voir que chacune d'elles, au lieu de tomber régulièrement, est animée d'un mouvement très vif et parfaitement désordonné. Elle va et vient en tournoyant, monte, descend, remonte encore, sans tendre nullement vers le repos. C'est le *mouvement brownien ...*"

The theory of the Brownian motion has been elaborated independently by Einstein [2] and by Smoluchowski [4]. Both scientists explained the phenomenon as a result of collisions between the suspended particles and the molecules of the surrounding fluid and arrived at almost the same quantitative predictions. However, their approaches where so different, that they can be looked upon as two complementary studies reflecting the original ideas of each of the two authors.

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* Presented at the XIX Marian Smoluchowski Symposium on Statistical Physics, Kraków, Poland, May 14–17, 2006.

The papers published by Smoluchowski one hundred years ago turned out to be of fundamental importance not only to the theory of Brownian motion but above all to the victory of the atomistic theory of matter [3, 4]. This fact has been quickly recognised by the scientific community, and shows the scale of Smoluchowski's contribution to science. Already in 1917, just after Smoluchowski passed away, Sommerfeld wrote [5]:

> "His name will, forever, be associated with the first flowering
> of atomic theory."

Sommerfeld's statement has been recalled by Chandrasekhar in an essay entitled "Marian Smoluchowski as the Founder of the Physics of Stochastic Phenomena" [6]. Also Kac in his remarkable paper "Marian Smoluchowski and the Evolution of Statistical Thought in Physics" [6] stresses the fact that

> "...it was Smoluchowski whose work, perhaps more than that
> of any other man brought about the ultimate reconciliation of
> the seemingly irreconcilable and victory to the atomistic view."

In connection with these quotations it is worth recalling Feynman's reflection made in his lectures on physics [7]:

> "If, in some cataclysm, all of scientific knowledge were to be
> destroyed, and only one sentence passed on to the next genera-
> tion of creatures, what statement would contain the most infor-
> mation in the fewest words? I belive it is the *atomic hypothesis*
> ...that *all things are made of atoms — little particles that move
> around in perpetual motion, ...* "

The perpetual character of motion was one of the most striking features in the behaviour of the Brownian particles whose chaotic displacements persisted without noticeable changes at arbitrary long time scales. Some observations were carried out during more than one year revealing the ever continuing movements. The challenging problem for the molecular kinetic theory of matter was to explain how the behaviour of macroscopic systems subject to the second law of thermodynamics could be reconciled with the dynamics at the atomic scale where clearly no irreversibility was present. This is what Mark Kac meant by writing that Smoluchowski succeeded in the "reconciliation of the seemingly irreconcilable".

The two papers published in 1906 are representative of a creative approach to the most challenging problems of theoretical physics. The centenary of their publication which we commemorate today is an appropriate occasion to scrutinise the ingenious ideas and methods developed therein. Especially that they continue to exert an inspiring influence on the research in our time.

The most famous paper containing the outline of the kinetic theory of Brownian motion [4] begins by an exhaustive analysis of the theoretical ideas and of the available experimental evidence concerning the phenomenon under consideration. The author arrives then at a clear formulation of problems to be solved always in close relation to experiment. This last point is very important. Smoluchowski's great contribution in fighting the way for the atomic hypothesis was to reveal the role of both spatial and time scales in interpreting the results of physical measurements. It is owing to his insight into these questions that he could successfully repel attacks on the kinetic theory.

A well known example was the controversy around the velocity. At the atomic scale the velocity acquired by the Brownian particle of mass M at a single collision with a molecule of mass $m \ll M$ was estimated to be so small ($\sim 10^{-9}$m/s) that unobservable. This fact together with the idea that the cancelling effect of collisions coming from various directions will rule out building up of higher velocities seemed a serious argument against the kinetic theory. Smoluchowski replied by indicating a serious error in the reasoning analogous to that

> "...leading to the conclusion that a player in a game of chance (*e.g.* tossing of a die) would never loose or gain more than a single stake."

To illustrate this point he used the example of a random walk. He then recalled the equipartition law predicted by Maxwell and Boltzmann. The enormous number of collisions suffered by the Brownian particle, of the order of 10^{16} per second in a gas or 10^{20} in a liquid, will produce the thermalization with a typical velocity

$$V = \sqrt{\frac{m}{M}}\, v \,, \tag{1}$$

where v is the thermal molecular velocity. In other words, one should expect the Brownian particle to behave like a giant molecule in thermal equilibrium with the environment.

However, the difficulty persisted as this estimation of V lead to values three orders of magnitude larger than those deduced from sequences of displacements observed under microscope. Again Smoluchowski's insight into the scales involved was of crucial importance for a correct interpretation of this fact and for turning the apparent contradiction into an argument in favour of the molecular kinetic theory. He pointed out that the motion with the thermal velocity V was simply not accessible to observation under microscope. The only thing one could see was the sequence of mean positions of the Brownian particle resulting from adding up of an enormous number

of tiny, totally invisible segments, along which the particle performed rapid thermal motion. The visible outcome was the diffusive motion in the position space with changes of direction allowing the description in terms of an apparent mean free path.

In 1916, reviewing his theory of the Brownian motion from a perspective of a decade in a series of lectures given in Göttingen [8] Smoluchowski emphasised the importance of the scales of observation:

> " ...depending on the accepted standpoint, the same phenomenon appears in three different ways: from the macroscopic point of view it is called "diffusion", from the microscopic one it is called either a "Brownian molecular motion", when one follows the life history of an individual particle, or a "fluctuation of concentration", when one observes a fixed element of volume and the change of the number of particles contained in it at any time. Of course, there exist an interconnection between these three different aspects of the phenomenon."

Using the present language he clearly distinguished between the microscopic, the mesoscopic, and the macroscopic levels of description. It is the thorough analysis of their interconnections which led him eventually to the statistical interpretation of the second law of thermodynamics supporting strongly Boltzmann's basic ideas for explaining irreversibility.

Maybe the most important Smoluchowski's legacy in the thinking of contemporary physics is the description of many body dynamics in terms of stochastic processes revealing at the same time the fundamental role of fluctuations. The fact that the microstates of macroscopic amounts of matter were not accessible neither to control nor to observation was enough to him to justify the use of the theory of probability as a proper mathematical tool. He was persuaded that the statistical way of reasoning supported by the calculus of probability was the adequate method for theoretical investigations. Smoluchowski presents probabilistic reasonings in a most natural way, constructing the stochastic dynamics so that it corresponds as faithfully as possible to what one knows from experiment.

The need for a close relation to experiment is seen in article [3] devoted to the mean free path. There was no doubt that the concept introduced by Clausius and analysed by Maxwell was very important and useful in the kinetic atomic theory of gases. But the quantitative determination of the mean free path required establishing its relation to observable phenomena, and this was for Smoluchowski of primary importance. At the very beginning of the article he thus inquires about the relation of this quantity to viscosity, thermal conductivity and diffusion.

Having formulated a problem Smoluchowski often proceeded by adopting first simplifying assumptions which permitted to obtain qualitatively correct predictions together with an order of magnitude quantitative estimations without too many mathematical complications. Only then more precise calculations followed free of original approximations.

This kind of approach is well illustrated by his derivation of the probability density $p_n(\boldsymbol{x})$ for finding a molecule at some point $\boldsymbol{x}$ after having suffered n collisions with the surrounding molecules. Smoluchowski first assumes that the molecule moves always with the same speed c and that the distances covered between consecutive collisions are always the same equal to the mean free path λ. Moreover, after each collision the motion is supposed to start isotropically (a rather crude approximation). He thus begins by considering the simple version of the problem of random flights studied by Rayleigh. After that comes the more refined study assuming the Poisson distribution for distances separating collisional encounters. It turns out to qualitatively agree with the simple Rayleigh model. The obtained formula

$$p_n(\boldsymbol{x}) = \left(\frac{3}{4\pi n\lambda^2}\right)^{3/2} \exp\left(-\frac{3|\boldsymbol{x}|^2}{4n\lambda^2}\right) , \tag{2}$$

yielded for the mean of the distance squared the diffusion law

$$\langle|\boldsymbol{x}|^2\rangle = 2n\lambda^2 . \tag{3}$$

Relating the number of collisions to the time t by $ct = n\lambda$ Smoluchowski obtained the desired relation between the mean free path and the diffusion coefficient

$$D = \frac{c\lambda}{3} . \tag{4}$$

In the case of the stochastic motion of Brownian particles in a gaseous medium the isotropy in the distribution of the velocities acquired at each collision had to be rejected even within the simplest approximation. But here again in order to take into account the unavoidable persistence of pre-collisional velocities Smoluchowski proposed a remarkably simple model. In his famous paper [4] he described the stochastic effects of encounters as deflecting the pre-collisional velocity by a small angle ε so that the particle continued its motion along a line segment of a cone whose symmetry axis was oriented along the pre-collisional velocity and whose opening angle was equal to 2ε. This illustrates his art of constructing appropriate simple models by retaining only essential information.

Smoluchowski belongs to the distinguished circle of physicists who have their equations. The Smoluchowski equation describes the evolution of the concentration W of Brownian particles of radius r and mass M suspended

in a viscous fluid with shear viscosity η and subject to an external force per unit mass $\boldsymbol{K}$

$$\frac{\partial W}{\partial t} = \mathrm{div}\left(D\,\mathrm{grad}\,W - \frac{\boldsymbol{K}}{\beta}W\right). \tag{5}$$

Here

$$\beta = \frac{6\pi r\eta}{M}, \qquad D = \frac{k_{\mathrm{B}}T}{\beta}.$$

In the absence of external forces Eq. (5) reduces to the diffusion equation

$$\frac{\partial W}{\partial t} = \mathrm{div}(D\,\mathrm{grad}\,W), \tag{6}$$

derived for the Brownian particles both by Einstein and by Smoluchowski with the fundamental solution

$$W(\boldsymbol{x},t|\boldsymbol{x}_0,0) = \frac{1}{(4\pi Dt)^{3/2}}\exp\left[\frac{(\boldsymbol{x}-\boldsymbol{x}_0)^2}{4Dt}\right]. \tag{7}$$

The more general equation (5) has been successfully applied to the phenomenon of sedimentation. It provided a particularly clear example of a case to which the formulation of the second law of thermodynamics in its conventional form used for macroscopic systems could not be applied.

A system of nonlinear equations has been derived by Smoluchowski to describe the dynamics of coagulation. In his Göttingen lectures [8] he writes:

> "Stimulated by Professor R. Zsigmondy, who informed me privately about his beautiful experimental investigations on coagulation of gold solutions and about the corresponding theoretical problems, I have worked out a mathematical theory of the kinetics of coagulation. This theory is a special application of the theory of Brownian motion ..."

The process of coagulation required the study of the relative motion of pairs of diffusing particles. Entering into a mutual sphere of influence the particles suffered a sticking reaction. The evolution of the system was described by a system of nonlinear equations for densities of m-fold particles, $m = 1, 2, \ldots$ resulting from the process of aggregation. This work of Smoluchowski had an important influence on the modern diffusion reaction theory. In fact he thought himself about this kind of applications [8]

> "The question arises whether the mechanism of coagulation is not related to that of chemical kinetics, and whether our theory does not perhaps open way towards a kinetic understanding of the processes in chemical reactions."

Coming back to the decisive role of Smoluchowski's work in the acceptance of the atomic hypothesis it seems appropriate to recall his way of understanding the status of physical theories. He was close in this respect to the attitude of Boltzmann. To quote Thirring [9]

> " ... Boltzmann was aware of the fact that the statements in physics are true only within a certain level of description. Indeed in one of his popular writings he says that by atomism he means that at the present moment the most fruitful assumption is that matter is made of indivisible constituents which he calls atoms."

Smoluchowski seemed to share this view. He would say that one could not consider a theory in physics as a true or even as a probable one. Only the statement about its usefulness could be reasonably formulated. However, he would add, there are some theories whose predictions are confirmed to such an extraordinary degree of accuracy that our confidence in them has a particularly sound basis. Clearly the kinetic theory of the Brownian motion discovered by Smoluchowski belongs to this category. His name appears together with the names of Maxwell, Boltzmann and Einstein in the history of creative applications of the theory of probability to the description of physical phenomena.

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