ON STOCHASTIC DYNAMICS IN PHYSICS — REMARKS ON HISTORY AND TERMINOLOGY*

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We discuss the early investigations of Brownian motion as a stochastic process by surveying contributions by Fick and Rayleigh developed later in works of Einstein, Smoluchowski, Langevin, Fokker, Planck, Klein, Kramers and Pauli. In particular, we are interested in the influence of the theory of probability in the development of the kinetic theory and we briefly analyze the origin of fundamental equations used in the mathematical description of the stochastic processes.

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1. Introduction

Due to the increasing role of stochastic processes in physics — we mention just their importance for the dynamics and functionality of biological macromolecules — more and more researchers enter the field. Just to give an example, the Smoluchowski Symposia have collected over 20 years leading and young researchers in the field and give summaries of the latest results and achievements. In this connection our experience shows, that there is some need to go back to the roots and make clear, who was involved in the most important ideas and to whom we should give the credits for the developments of the most important concepts and equations.

The observation of an erratic motion of small particles imbedded into liquids goes back already to Ingenhousz and Brown [1, 2]. These observations led to the concept of Brownian motion which is fundamental to Statistical

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Physics [6]. Moreover, the discussion of Brownian motion introduced quite new concepts of microscopic description, pertinent to stochastic approaches. The description put forward by Einstein in 1905/1906, Smoluchowski in 1906 and Langevin in 1908 is so much different from the one of Boltzmann and Gibbs: it dispenses from the description of the system's evolution in phase space and relies from the very beginning on probabilistic concepts [7]. Mark Kac, in an essay about Smoluchowski, put it as follows: *"... while directed towards the same goal how different the Smoluchowski approach is from Boltzmann's. There is no dynamics, no phase space, no Liouville theorem — in short none of the usual underpinnings of Statistical Mechanics. Smoluchowski may not have been aware of it but he begun writing a new chapter of Statistical physics which in our time goes by the name of Stochastic processes"* [6]. The synthesis of the approaches leading to the understanding of how the properties of stochastic motions are connected to deterministic dynamics of the system and its heat bath were understood much later in works by Mark Kac, Robert Zwanzig and others. Stochastic processes are growing in importance. Further, we are having in mind the anniversaries of the fundamentals of stochastic theory to be noticed in the years 2005–2008. And for all these reasons we will discuss now the history of these important concepts here in some more detail, however as we have to say, not from the point of view of professional historians and being aware of other useful surveys with related aims [3–6, 8].

2. Early works on Brownian motion

The perpetual erratic motion of small particles immersed in a fluid was first observed as early as in 1785 by a Dutch physician Jan Ingenhousz; however, the phenomenon remained unknown to the non-Dutch speaking community until it was rediscovered and studied in some detail by the Scottish botanist Robert Brown in 1827. Working on mechanisms of fertilization in plants, he turned his attention to the structure of pollen and concentrated at their microscopical characterization. Having observed the unceasing motion of the pollen in water, he thought at first that the movement must be due to the living nature of the particles under observation. However, being a cautious scientist, he repeated his experiments with pollen kept in alcohol for several months (presumably dead) and with nonorganic particles, which all showed similar behavior. One can find one of the Brown's original reports "Additional Remarks on Active Molecules" (1829) in the Internet [1]. A discussion of the first observations was given by Ford [2].

A next step of progress coming from a different direction was the work of Fick on diffusion which led to the diffusion equation

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2} n(x,t)\,, \tag{1}$$

where D is the diffusion coefficient [9] and $n(x,t)$ describes time-dependent concentration of the solute at the distance x from the solvent. We mention the structural (mathematical) identity to Fourier's law of heat conduction [10] (which was a guideline for Fick when putting down the theory of molecular diffusion) and the extensive mathematical literature on this equation. Fick's approach was purely phenomenological, and did not relate molecular diffusion to a Brownian motion discussed above.

The qualitative explanation of the Brownian motion as a kinetic phenomenon was put forward by several authors. In 1877 Desaulx wrote: "In my way of thinking the phenomenon is a result of thermal molecular motion in the liquid environment (of the particles)." In 1889 G. Gouy gave an account of detailed qualitative studies of the phenomenon [11]. He found that the Brownian motion is really a phenomenon which is not due to random external influences (vibration, electric or magnetic fields) and that the magnitude of the motion depends essentially only on the two factors: on the particles' size and on the temperature. In 1900 F.M. Exner undertook the first quantitative studies, measuring how the motion depends on these two parameters.

Motivated by the need to give a comprehensive description of Brownian motion and the increasing number of experiments, since 1905 several different (but strongly interconnected) approaches to Brownian motion were developed. The ingenious microscopic derivation of the diffusion equation by A. Einstein (which contained, in a nutshell, several different approaches) and the discussion by P. Langevin put forward the two different approaches: one based on the discussion of the deterministic equations for the probability densities, another one based on the discussion of single, stochastic realizations of the process. These approaches, refined both from physical and from the mathematical points of view build now the main instrument of description of both equilibrium and nonequilibrium processes on a mesoscopic scale.

3. Random walk approaches: Einstein, Smoluchowski, Pearson, Rayleigh, Bachelier

The first theory of Brownian motion was put forward by Einstein in 1905 [12]. Albert Einstein's first theoretical work was carried out during his employment at the Bern patent office. Einstein started his work on statistical physics in 1902–1903 with two very interesting papers published

in his favorite journal *Annalen der Physik*. Here, independently of Gibbs, Einstein developed the basic ideas of ensemble theory and the statistics of interacting systems. In 1906 he presented a dissertation to the Zürich University which contains a theory of Brownian motion. Einstein's work which appeared in 1905/1906 in the Annalen der Physik is the origin of stochastic theory in physics, one of the corner stones of modern statistical thermodynamics [12, 13].

In fact, Einstein's paper was a theoretical discussion of one of possible consequences of the molecular-kinetic theory of heat: *"Über die von molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen"*. In this work Einstein discusses that the kinetic theory of heat predicts the unceasing motion of small suspended particles [12]. He was not sure that the phenomenon discussed is exactly the Brownian motion, but considered this as a reasonable hypothesis. It was pointed out to him later (by Gouy) that the effect he discussed was really the Brownian motion, since not only the qualitative properties, but also the predicted orders of magnitude of the effect were correct, as discussed in the Einstein's second work [13]. Let us briefly discuss now the Einstein's approach. In his conjecture he has connected the motion of suspended particles with diffusion and showed that this diffusive behavior follows from the three postulates. First, the particles considered are assumed not to interact with each other: their trajectories are independent. Second, one assumes that the motion of the particles lacks long-time memory: one can choose such a time interval τ, that the displacements s of the particle during two subsequent intervals are independent. Third, the distribution of a particle's displacements s during the subsequent time intervals $\phi(s)$ possesses at least two lower moments. Moreover, for the force-free situation $\phi(s)$ is symmetric. The displacement of the particle can thus be considered as a result of many tiny, independent, equally distributed steps. The mathematical model behind this motion is thus a simple random walk with a given tact frequency of steps and a given, symmetric step length distribution.

The further line of his reasoning is very close to what we will call now a Kramers–Moyal expansion. For the simplicity, following Einstein, we analyze a one-dimensional problem:

The concentration of particles n in vicinity of point x is proportional to the probability density $f(x,t)$ to find one particle at this point. Comparing the probabilities at time τ and at time $t+\tau$ we get (due to the independence of the new displacement of the previous position and to the fact that $x(t+\tau) = x(t) + s$)

$$f(x, t+\tau) = \int f(x-s, t)\phi(s)\, ds\,. \tag{2}$$

Now, since both τ and s are both small compared to the time- and space-scales of interest, one can expand the function f in Taylor series on both sides of the equation. On the left-hand side it is enough to expand up to the first order in t, on the right-hand side we need the second order in s. We get:

$$f+\left(\frac{\partial f}{\partial t}\right)\tau+... = f+\left(\frac{\partial f}{\partial x}\right)\int s\phi(s)ds+\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}f\right)\int s^2\phi(s)ds+... \quad . \quad (3)$$

The integral $\int s\phi(s)ds$ vanishes due to the symmetry. In the lowest order we thus get:

$$\frac{\partial f}{\partial t} = \frac{\sigma^2}{2\tau}\frac{\partial^2}{\partial x^2}f\,, \quad (4)$$

where $\sigma^2 = \int s^2\phi(s)ds$. Here we recognize the Fick's diffusion equation, and associate $\sigma^2/2\tau$ with the diffusion coefficient D. The solution of Eq. (4) is, clearly, a Gaussian

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right), \quad (5)$$

so that the mean squared displacement of the particle along the x-axis would be

$$\langle x^2\rangle = 2Dt\,, \quad (6)$$

which gives the direct way of experimental measurement of D.

The derivation of the diffusion equation by Einstein was the very first step of statistical physics into the new domain of non-equilibrium phenomena. Note however, that it was not the derivation of the diffusion equation, which seemed to Einstein to be the main topic of this work: The discussion of the diffusion of particles in the solution gave the way to determine the Avogadro number $N_{\rm A}$ through the macroscopic measurements on large particles, the measurement performed by Perrin some 3 years later. Such measurements were necessary to provide solid basement for atomistic theory of matter. The corresponding theoretical considerations were summarized in Einstein's PhD thesis "Eine neue Bestimmung der Moleküldimensionen" (New method for determination of molecular sizes) presented on April 30, 1906 at the University of Zürich.

Essential contributions, independently of Einstein, to this line of research we owe to the work of the great Polish physicist Marian Smoluchowski (1872–1917) published in subsequent contributions to the *Annalen der Physik* beginning with 1906 [14–17].

Marian Smoluchowski was born May 28, 1872 near Vienna as the son of a high Polish official in the chancellery of emperor Franz Joseph [3]. He studied at the Vienna University where he received his Ph.D. in 1894. Afterwards

he was traveling and spent two years in Paris working with Lipmann, next in Glasgow where he met Lord Kelvin, and eventually in Berlin where he spent several months working in the laboratory of Prof. Warburg. In 1899 Marian Smoluchowski accepted a position of a lecturer at the University of Lwów (at the time part of the province Galicia of Austria, now Lviv in Ukraine). In 1900, at the age of 28 he was promoted there a professor of theoretical physics. In 1913 he got an appointment from the Jagellonian University in Kraków where he served up to his premature death in 1917, just after being elected to the honorable post of the rector of the University.

As pointed out by Stanislaw Ulam, *"... It is interesting to see how it was possible for a person of his exceptionally high ability, to get to the forefront of European thought in physics, even though the milieu in which he worked as a young professor was relatively isolated and without tradition in science"*. Smoluchowski's most significant achievements regarding the kinetic theory of matter concentrated on what we now know as the theory of stochastic processes, where his contributions were of central importance. Apart from his pioneering works on the theory of Brownian motion, he made other important contributions to the theory of nonequilibrium processes, and can be considered as one of the founding fathers of modern theory of chemical kinetics, where his line of thought was continued by Lars Onsager and Hendrik Anthony Kramers.

The formulation of the quantitative theory by A. Einstein and by M. Smoluchowski motivated new, quantitative experiments performed by J.-B. Perrin (starting from 1908), A. Westgren, E. Kappler and many others. Perrin's work was crowned by the Nobel prize in 1926. The macroscopically measurable fluctuations gave new experimental possibilities and a series of famous experimentalists were attracted by the behavior of mesoscopic particles (Perrin measured Loschmidt's number and determined Planck's constant, Millikan and Ehrenhaft made experiments to define the elementary charge, Houdijk and Zeeman observed the motion of platinum wires). These works put the firm fundament to the modern understanding of both equilibrium and non-equilibrium phenomena. Further theoretical developments were given in the dissertations of two young scientists, L. Ornstein and G. Uhlenbeck, presented in 1908 and 1927, respectively, to the University of Leiden as well as their subsequent publications.

Let us mention another line of investigations which lead to the very similar models which did not lose their popularity in physics and in mathematics during the whole century afterwards. This one starts with the question to the readers of *Nature* put by Karl Pearson in 1905 ("The problem of random walk"):

> *Can any of your readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution provide me with an original one? I should be extremely grateful for aid in the matter.*
>
> *A man starts from point 0 and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r + \delta r$ from his starting point 0.*

The question was answered within a week by Rayleigh, who pointed out that essentially the same problem, encountered in the theory of oscillations, was solved by him in 1880, and that the result was given by a Gaussian $(2/n)e^{-r^2/n}rdr$ for n large enough. Pearson's inquiry was motivated by a problem of animal motion, and in his reply he admits that "one does not expect to find the first stage in a biometric problem provided in a memoir on sound". This reply is also the first source where the description of the walk model is connected with a metaphor of a drunken man's motion [18,19]. The fact, that on the very dawn of stochastic methods so much different practical problems ought for the same, revolutionary type of descriprion, stresses the power and universality of the approach.

However, still another source of our knowledge has to be mentioned, now laying far outside of physics. This is connected with the name of Louis Bachelier (although also he seems to have a predecessor in person of Thorwald Nicolai Thiele, the inventor of the method of least squares (in 1880), who formulated clearly some mathematical aspects of the problem). Indeed the first random walk model was put forward five years before Einstein's and Smoluchowski's work in the doctoral thesis of Louis Bachelier (1870–1946), defended and published in Paris in 1900. The thesis worked out mathematically the idea that the stock market prices with their unceasing ups and downs are essentially sums of independent, bounded random changes [20]. The report on this thesis written by H. Poincaré can be found in the article by Taqqu [21]. It is sometimes claimed that the thesis was written under the supervision of H. Poincaré; this statement does not seem to be, however, true: Bachelier worked and studied at the same time, he took courses occasionally, and probably presented his thesis as the "external" candidate. On the other hand, Poincaré, who disliked probabilistic approaches, made a positive note that the author "does not exaggerate the range of his results, and I do not think that he is deceived by his formulas". The range of Bachelier's results was hard to exaggerate.

Bernard Bru comments the situation as follows: ''It was a thesis on mathematical physics, but since it was not physics, it was about the Stock Exchange, it was not a recognized subject" [21]. We note here that application of physical methods to analysis of economical systems is now a rather well established branch of statistical physics and a word "Econophysics" was coined to describe this field. The results put forward by Bachelier were of highest importance, and (partly used, partly rediscovered by later workers) lead to a flash of interest to stochastic processes and corresponding probabilistic approaches in mathematics. The mathematical approaches (culminating in work by Norbert Wiener, Paul Lévy and Andrei Nikolaevich Kolmogorov) in the direction of formulating and refining stochastic approaches lead to a large body of knowledge giving a solid basis for modern applications in statistical physics.

4. Stochastic differential equations: Langevin's legacy

Smoluchowski, who followed essentially the same random walk line of argumentation as Einstein, claimed that his approach is more direct and therefore simpler than the one of Einstein. Still, Paul Langevin in his article published in *Comptes Rendus* in 1908 proposed a completely different approach to description of Brownian motion, than the ones of Einstein and Smoluchowski, and also claimed it to be "infinitely simpler" than the Einstein's one. Here we repeat the main argumentation of his original work [22]:

Let us consider the motion of the Brownian particle in fluid. On the average this motion is governed by the Newtonian dynamics under friction, $m\dot{v} = -\gamma v$, where γ is the friction coefficient (for a macroscopic spherical particle this friction follows the Stokes law, so that $\gamma = 6\pi\eta r$, where r is the particle's radius). However, this equation, leading to the continuous decay of the particle's velocity, holds only on the average. In order to describe the erratic motion of the particle, resulting from random, uncompensated impacts of the molecules of surrounding fluid, we have to introduce additional, fluctuating force $\xi(t)$ (called otherwise "noise"). We assume only that this force has a zero mean (so that it does not lead to the net motion on average), and that it is independent on x, which reflects the homogeneity of the whole system. We thus write

$$m\dot{v} = -\gamma v + \xi(t)\,. \tag{7}$$

Our first task will be to find the mean squared displacement of the particle. Let us now multiply both sides of Eq. (7) by $x(t)$ and use the evident fact that $x\dot{v} = x\ddot{x} = \frac{d}{dt}(x\dot{x}) - \dot{x}^2$. We thus get

$$m\frac{d}{dt}(x\dot{x}) = m\dot{x}^2 - \gamma x\dot{x} + x\xi\,. \tag{8}$$

Let us now average this equation over the realizations of the process. Dividing both parts of the equation by m we arrive at:

$$\frac{d}{dt}\langle x\dot{x}\rangle = -\frac{\gamma}{m}\langle x\dot{x}\rangle + \left\langle \dot{x}^2\right\rangle + \frac{1}{m}\langle x\xi\rangle \ . \tag{9}$$

The last mean value vanishes due to the (assumed) independence of x and ξ and due to the fact that the mean value of ξ is zero: $\langle x\xi\rangle = \langle x\rangle\langle\xi\rangle = 0$. Moreover, by use of the equipartition theorem, the mean squared velocity of the particle in our one-dimensional model fulfills the relation $m\left\langle \dot{x}^2\right\rangle/2 = kT/2$, *i.e.*

$$\left\langle \dot{x}^2\right\rangle = \frac{kT}{m}\,. \tag{10}$$

Thus, for the mean $\langle x\dot{x}\rangle$ one has

$$\frac{d}{dt}\langle x\dot{x}\rangle = -\frac{\gamma}{m}\langle x\dot{x}\rangle + \frac{kT}{m}\,. \tag{11}$$

Let us now assume that the initial particle's position is taken to be at the origin of coordinates. Then $\langle x(0)\,\dot{x}(0)\rangle = 0$. Under this initial condition Eq. (11) can easily be solved and delivers

$$\langle x(t)\dot{x}(t)\rangle = \int_0^t \exp\left[-\frac{\gamma}{m}(t-t')\right]\frac{kT}{m}dt' = \frac{kT}{\gamma}\left[1-\exp\left(-\frac{\gamma}{m}t\right)\right]\,. \tag{12}$$

As a next step, we note that $\langle x(t)\dot{x}(t)\rangle = \frac{1}{2}d/dt\left\langle x^2(t)\right\rangle$, so that the mean squared displacement of the particle can be found by an additional integration of Eq. (12):

$$\left\langle x^2(t)\right\rangle = 2\int_0^t \left\langle x(t')\dot{x}(t')\right\rangle dt' = 2\frac{kT}{\gamma}\left[t - \frac{m}{\gamma}\left(1-\exp\left(-\frac{\gamma}{m}t\right)\right)\right]\,. \tag{13}$$

For large time the leading term corresponds to

$$\left\langle x^2(t)\right\rangle = 2\frac{kT}{\gamma}t\,, \tag{14}$$

i.e. to the diffusive behavior, Eq. (6) with the diffusion coefficient $D = kT/\gamma$.

Although the Langevin's approach seems to be based only on the equipartition theorem, this is not quite true: Additional assumptions are hidden in the argumentation about correlations' decoupling. May be the pioneers overlooked the mathematical difficulties connected with this approach.

The Langevin's approach, however, is very popular in physics due to its intuitive transparency and beauty. The further development and mathematical refinement of this line of argumentation took place in the works of Kiyoshi Ito, Ruslan Leontievich Stratonovich, Yuri L'vovich Klimontovich and many others.

5. Partial differential equations in phase space — the work of Fokker, Planck, Smoluchowski, Klein, Kramers and Rayleigh

Adrian D. Fokker (1887–1972) was born as the son of the president of the Netherland Trading Society on Java. One of his cousins was the known aeroplane builder Fokker. Fokker studied mining technology in Delft and then physics at the Leiden University, where he earned his doctorate with Hendrik Lorentz. Later he left the field of Brownian motion and worked with Einstein, Rutherford and Bragg. After the second world war he devoted his life to music-theoretical research. The subject of Fokker's dissertation is connected with the publications of Einstein, who considered already, for the stationary case, the balance of probability currents in Brownian motion. Fokker studied in his dissertation directed by Lorentz in Leiden the a probability distribution $W(q,t)$ of a quantity which is influenced by fluctuations. Fokker was thinking about the angular momentum of a dipole but the consideration is so general that q could be any other fluctuating quantity as a coordinate or a velocity. In his dissertation which Fokker defended in 1913 he derived the equation

$$0 = -\frac{\partial}{\partial q} f(q) W(q,t) + \frac{1}{2}\frac{\partial^2}{\partial q^2} g(q) W(q,t)\,. \tag{15}$$

This equation was published in *Annalen der Physik* in a short paper without a detailed proof [23], which was announced for some later publication. Fokker's equation corresponds to a stationary process, it was shown that the coefficients are related as in Einstein's theory to the mean displacements

$$f(q) = \frac{\Delta q}{\Delta t}\,, \qquad\qquad g(q) = \frac{(\Delta q)^2}{\Delta t}\,. \tag{16}$$

Planck was interested in Fokker's work and waited for the announced longer publication containing a detailed proof of Fokker's equation. After waiting two years Planck made the decision to derive the equation on his own and published an equation which goes far beyond the work of Fokker [24]

$$\frac{\partial W(q,t)}{\partial t} = -\frac{\partial}{\partial q} f(q) W(q,t) + \frac{1}{2}\frac{\partial^2}{\partial q^2} g(q) W(q,t)\,. \tag{17}$$

By this time a similar equation was already proposed by Smoluchowski [15], as a continuation of his own line of thoughts and without evident connection to the Fokker's work.

The generalization of this equation to the phase space, *i.e.* taking into account both the coordinate and the velocity of the particles, whose mass cannot be neglected, was put forward in 1921 by Oskar Klein (the famous co-author of the Klein–Gordon equation and of the Kaluza–Klein theory) in his work "Zur statistischen Theorie der Suspensionen und Lösungen" [25]:

$$\begin{aligned}\frac{\partial W(x,v,t)}{\partial t} &= -\frac{\partial}{\partial x} v W(x,v,t) \\ &\quad -\frac{\partial}{\partial v}\frac{f(x)-\gamma v}{m} W(x,v,t) + k_{\mathrm{B}} T \gamma \frac{1}{2}\frac{\partial^2}{\partial v^2} W(x,v,t)\,, \end{aligned} \tag{18}$$

which is put here for exactly the same system as the one discussed by Langevin. The corresponding equation was rederived by Hendrik Anthony Kramers in his famous work *Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions* (1940) [26], where especially his highly nontrivial solution for the underdamped case has to be mentioned [27]. Eq. (18) is therefore often referred to as a Klein–Kramers equation.

However, also here the forgotten predecessors were in play. Evidently, the first researcher who studied Brownian motion as a stochastic process, and followed the lines very close to the ones discussed here, was Lord Rayleigh [28]: apparently, already in 1891 Rayleigh formulated an equation for the probability distribution $W(v,t)$ of the velocity v of a particle of mass m which is subject to friction γ and moves in a heat bath:

$$\frac{\partial W(v,t)}{\partial t} = \gamma \left[\frac{\partial}{\partial v} v W(v,t) + \frac{k_{\mathrm{B}} T}{m} \frac{\partial^2}{\partial v^2} W(v,t) \right] . \tag{19}$$

Rayleigh's equation which was not given credit for a long time up to a hint given to this forgotten work by another pioneer in the field, Nicolas van Kampen [29]. The reason for overlooking Rayleigh's contribution is perhaps related to the fact that the *velocity* of the Brownian particle could not be tracked experimentally at that time; in contrary, the Einstein's or Langevin's emphasis on the *displacement* changed the situation dramatically and gave rise to almost a flood of excellent experiments.

6. Stochastic description of transitions between discrete levels — Einstein and Pauli's master equations

Planck mentioned in the title of his work on stochastic processes "Über einen Satz der statistischen Dynamik und seine Erweiterung in the Quantentheorie" explicitely "quantum theory" but in fact there was not much

quantum theory in it. However the work that Albert Einstein presented even a bit earlier to the Physical Society and the Academy in Berlin was a real breakthrough in the quantum theory of stochastic processes. Trying to connect the Planck's formula for a blackbody radiation with the postulates of the quantum theory of atoms put forward by Niels Bohr, Einstein put down the balance equation for the numbers of atoms N_1 and N_2 being in the two quantum states 1 and 2 with energies E_1 and E_2 under the influence of the resonant electromagnetic field $E_2 - E_2 = h\nu$. This work lead to the discovery of induced radiation, the main ingredient of the modern physics of lasers. Nowaday we would describe the mathematics of this approach as a stationary master equation description of a two-level system in an external field [30].

The full master equation as we know it today was for the first time derived in 1928 by Pauli [31]. Pauli considered a quantum system with a discrete spectrum. His method is based on perturbation theory which he applied to a Hamiltonian

$$H' = H + \lambda V \,, \tag{20}$$

where H is the Hamiltonian of the unperturbed system with the eigenstates $|n\rangle$ and λV is the perturbation. An essential point is that H is dominant and is so simple that we can find the eigenstates. The perturbation should be small but sufficiently complicated to mix the unperturbed states so that it can give rise to irreversible behavior. Pauli defined the probabilities of being in the state n by

$$p_n(t) = |c_n(t)|^2 \,,$$

where c_n are the amplitudes of the quantum state at time t and derived the master equation

$$\frac{\partial p_n}{\partial t} = \sum_m \left[W_{nm} p_m - W_{mn} p_n\right] \tag{21}$$

with the transition probabilities given by the Fermi golden-rule rates

$$W_{nm} = \frac{2\pi}{\hbar} \lambda^2 \delta(E_m - E_n) |\langle m|V|n\rangle|^2 \,. \tag{22}$$

It is very essential that this matrix is symmetric, what is due to the microscopic reversibility. The procedure to derive Eq. (22) is rather simple but contains several essential assumptions, in particular we have to assume random phases at any time which amounts to dropping the non-diagonal terms. The Pauli master equation is the most commonly used model of irreversible processes in simple quantum systems. As mentioned, it can be derived from elementary quantum mechanics (with an additional Markov assumption). Despite a number of conceptual problems with the Pauli equation (like *e.g.* violation of the continuity equation), it is widely employed, in almost all semi-classical treatments of electron transport in semiconductors.

7. On terminology of stochastic dynamics

In a stochastic system (*i.e.* on the stochastic level of description of the physical system which might or might not have some underlying deterministic dynamics) the present state of the system, as described by the vector

$$\boldsymbol{x}(t) = [x_1(t), x_2(t), \ldots, x_n(t)] \tag{23}$$

of whatever relevant variables of the system, does not fully determine its future state. The dynamics is introduced as a map from the state at the initial time to a time later by a shift δt

$$\boldsymbol{x}(t_0 + \delta t) = \boldsymbol{T}(\boldsymbol{x}(t_0), \boldsymbol{u}, \delta t)\,, \tag{24}$$

where $\boldsymbol{u}$ is a set of parameters describing the process. The map $\boldsymbol{T}$ can be unique (so that the effective dynamics is deterministic) or probabilistic, meaning that there are several possibilities of the future state occurring with different probabilities. This kind of dynamics is called stochastic. A deterministic dynamics is often defined by a set of differential equations

$$\dot{x}_i(t) = F_i(x_1, ..., x_n(t))\,, \qquad i = 1, 2, ..., n\,. \tag{25}$$

Due to stochastic influences the future state of a dynamical system is in general not uniquely defined. In other words the dynamic map defined by Eq. (24) is non-unique. A given initial point $x(0)$ may be the source of several different trajectories. The choice between the different possible trajectories is a random event. The easiest way to introduce stochastic elements is to use the Langevin picture:

$$\dot{x}_i = F_i(x) + \sqrt{2D}\xi_i(t)\,, \tag{26}$$

where $\xi_i(t)$ is a delta-correlated Gaussian random variable

$$\langle \xi_i(t) \rangle = 0\,, \qquad \langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t - t') \tag{27}$$

and the coefficient $2D^{1/2}$ defines an amplitude (or intensity) of random pulses ξ_i. By averaging we find

$$\langle \dot{x}_i \rangle = \langle F_i(x) \rangle \simeq F_i(\langle x \rangle)\,. \tag{28}$$

This way, in average, the deterministic dynamics is reproduced at least approximately. In the case of nonlinear dynamics this could be problematic, as stressed by van Kampen [29].

In the stochastic case the state of the system at time t is described by a probability density $P(\boldsymbol{x}, t; \boldsymbol{u})$. By definition $P(\boldsymbol{x}, t; \boldsymbol{u})d\boldsymbol{x}$ gives the probability of finding the state of the system at time t in the domain $(\boldsymbol{x}, \boldsymbol{x} + d\boldsymbol{x})$

of state variables. Instead of the deterministic equation for the state, we may now try to derive an evolution equation for the probability density $P(\boldsymbol{x}, t; \boldsymbol{u})$. In the most general case such equations have the form of the integral equations representing the probability conservation in course of the temporal evolution of the system and connecting the probabilities at two different times t and $t + dt$. Such general integral equations (the Einstein's Eq. (2) being an example thereof) are called *Chapman–Kolmogorov* equations. In applications, it is much more convenient to work with the differential forms, which might be less general but better suited for applications.

As underlined by Einstein, Smoluchowski, Fokker, Planck, Klein and Kramers, probabilities are conserved quantities and their dynamics is given by balances of gain and loss. In a general case we may define $\boldsymbol{G}$ as the vector of the probability flow. Based on the conservation we have an equation of continuity and in consequence, we get

$$\partial_t P(\boldsymbol{x}, t; \boldsymbol{u}) = -\mathrm{div}\, \boldsymbol{G}(\boldsymbol{x}, t; \boldsymbol{u})\,. \tag{29}$$

In the special case when there are no stochastic forces, the flow is proportional to the deterministic field *i.e.*

$$\boldsymbol{G}_i(\boldsymbol{x}, t, ; u) = \boldsymbol{F}_i(\boldsymbol{x}, t; u) P(\boldsymbol{x}, t; u)\,.$$

Including now the influence of the stochastic forces we assume here *ad hoc* an additional diffusive contribution to the probability flow which is directed downwards the gradient of the probability

$$G_i(\boldsymbol{x}, t; \boldsymbol{u}) = F_i(\boldsymbol{x}, t; \boldsymbol{u}) P(\boldsymbol{x}, t; \boldsymbol{u}) - D \frac{\partial}{\partial x_i} P(\boldsymbol{x}, t; \boldsymbol{u})\,. \tag{30}$$

This is the simplest "Ansatz" which is consistent with Eq. (25) for the mean values. The "diffusion coefficient" D (the same as in Eq. (26)) is determined by the properties of the stochastic force, as first discussed by Langevin. Introducing the above relation into Eq. (29) we get a partial differential equation:

$$\partial_t P(\boldsymbol{x}, t; \boldsymbol{u}) = \sum_i \partial x_i \left[D \frac{\partial}{\partial x_i} P(\boldsymbol{x}, t; \boldsymbol{u}) - F_i(\boldsymbol{x}, t; \boldsymbol{u}) P(\boldsymbol{x}, t; \boldsymbol{u}) \right]\,. \tag{31}$$

which governs time evolution of the probability density function $P(\boldsymbol{x}, t; \boldsymbol{u})$.

With the historical background given in the previous sections the following notations with respect to Eq. (31) could be recommended:

(i) If the elements of $\boldsymbol{x}$ are usual mechanical coordinates, we call the equation *Smoluchowski equation* to honor the contribution of Marian Smoluchowski who was the first to put the corresponding balance equation exactly in the form discussed.

(ii) If $\boldsymbol{x}$ is comprised of the mechanical coordinates $x_1, \ldots, x_f$ and velocities $v_1, \ldots v_f$ (or the corresponding momenta) we refer to the corresponding balance equation as to a *Fokker–Planck equation*, since Fokker and Planck wrote down the first version. Alternatively we may call the equation a *Klein–Kramers equation* after the scientists who formulated the standard form used nowadays. Strictly speaking, we could also use the term *Rayleigh equation* for the case that $\boldsymbol{x}$ consists only of velocities, although this may be too confusing for the reader.

(iii) In the general case when the meaning of the $x_1, \ldots, x_n$ is not specified at all, we may speak about general Fokker–Planck equations or in the mathematical context about Chapman–Kolmogorov equations.

In common literature on the subject many authors use (for all variants mentioned above) only the term *Fokker–Planck equation* which seems historically not fully correct.

Let us now consider the case of a discrete state space, *e.g.* the levels in an atom or a molecule, which we denote by

$$i = 1, 2, 3, \ldots, n, \ldots .$$

A stochastic dynamics may be introduced by the transition probabilities

$$W_{nm} = \text{Prob}\ (m \to n)$$

per unit time. The condition of balance between gain and loss leads immediately to

$$\frac{\partial p_n}{\partial t} = \sum_m \left[W_{nm} p_m - W_{mn} p_n \right] . \tag{32}$$

Following the general use we propose to use the notation *Pauli master equation*, or simply a master equation.

All in all, we discussed here briefly the history and notation for several equations of the stochastic dynamics which describe the evolution of probabilities and we tried to give credit to the authors of the pioneering approaches.

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REFERENCES

[1] R. Brown, see
http//dbhs.wvusd.k12.ca.us/Chem-History/Brown-1829.html

[2] B.J. Ford, *Microscope* **40**, 235 (1992).

[3] A. Teske, *Marian Smoluchowski, His Life and Work*, PWN, Kraków 1955.

[4] S. Chandrasekhar, M. Kac, R. Smoluchowski, *Marian Smoluchowski, His Life and Scientific Work*, PWN, Warszawa 2000.

[5] S. Ulam, *Am. J. Phys.* **25**, 475 (1957).

[6] A. Fuliński, *Acta Phys. Pol. B* **29**, 1523 (1998).

[7] W. Ebeling, I. Sokolov, *Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems*, World Scientific, Singapore 2005.

[8] P. Hänggi, F. Marchesoni, *Chaos* **15**, 026101 (2005).

[9] A. Fick, *Ann. Phys.* **94**, 50 (1855).

[10] J.B. Fourier, *Theorie de la Chaleur*, Paris 1888.

[11] G. Gouy, *Comptes Rendus* **109**, 102 (1889.)

[12] A. Einstein, *Ann. Phys.* **17**, 549 (1905).

[13] A. Einstein, *Ann. Phys.* **19**, 371 (1906).

[14] M. v. Smoluchowski, *Ann. Phys.* **21**, 756 (1906).

[15] M. v. Smoluchowski, *Ann. Phys.* **48**, 1103 (1915).

[16] M. v. Smoluchowski, *Phys. Z.* **17**, 557 (1916).

[17] M. v. Smoluchowski, *Oeuvres*, ed. W. Natanson, PAU, Kraków 1924–1928.

[18] K. Pearson, *Nature* **72**, (1865) 294 (1905); **72**, (1867) 342 (1905).

[19] Lord Rayleigh, *Nature* **72**, (1866) 318 (1905).

[20] L. Bachelier, *Ann. Sci. Norm. Sup.* **17**, 21 (1900).

[21] M.S. Taqqu, in *Mathematical Finance — Bachelier Congress 2000*, Ed. H. Geman, Springer, Berlin 2001.

[22] P. Langevin, *C. R. Acad. Sci. (Paris)* **146** 530 (1908).

[23] A.D. Fokker, *Ann. Phys.* **19** (4), 810 (1914).

[24] M. Planck, *Sitzber. Preuss. Akad. Wiss.* , 324 (1917); M. Planck, *Physikalische Abhandlungen und Vorträge*, Vieweg, Braunschweig 1958, p. 435.

[25] O. Klein, *Arkiv für Matematik, Astronomi och Fysik*, **16** (5), 1 (1921).

[26] H.A. Kramers, *Physica* **7** (4), 284 (1940).

[27] P. Hänggi, P. Talkner, M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).

[28] Lord Rayleigh, *Phil. Mag.* **32**, 424 (1991); *Scientific Papers III*, Cambridge Univ. Press 1902; Reprinted Dover, New York 1964.

[29] N.G. van Kampen, *Physik. Blätter*, October, 14 (1997).

[30] A. Einstein, *Verh. Dtsch. Phys. Ges.* **18**, 318 (1916); *Mitt. Phys. Ges. Zürich* **18**, 47 (1916); *Phys. Z.* **18**, 121 (1917).

[31] W. Pauli, *Festschrift zum 60. Geburtstage A. Sommerfelds*, Hirzel Leipzig 1928.