

ON MARIAN SMOLUCHOWSKI'S LIFE AND
CONTRIBUTION TO PHYSICS* ,**

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The first part presents the life and historical contributions of Marian Smoluchowski to the foundations of atomic theory of matter. Remaining parts are devoted to the presentation of the original derivation and present applications of the *Smoluchowski equations*. Commonly used in various physical, chemical, *etc.*, problems is the *kinetic* Smoluchowski equation, being the high-friction limit of the full Fokker-Planck equation. Of less use so far has been the *functional* Smoluchowski (called also Chapman-Enskog or Bachelier) equation. Within the scope of modern theory of stochastic processes this equation is an identity equivalent to the definition of a Markovian process. It is argued that, in the view of the growing interest in non-Markovian stochastic processes, the functional Smoluchowski equation may become the most natural and effective tool for checking the Markovian vs. non-Markovian character of a considered process, especially when applied to experimental data. Some examples are given.

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1. Introduction

Marian Smoluchowski¹ was born May 28th, 1872 in Vorderbrüchl near Vienna. His father was a high official in the chancellery of emperor Franz Joseph I. Smoluchowski studied at Vienna University, where he received his Ph.D. — with highest honours (*sub auspiciis imperatoris*) — in 1894. After that, he spent two years at universities in Paris, Glasgow and Berlin. In 1898 he returned to Vienna, where obtained *veniam legendi* (“Privatdozent”).

In 1900, at the age of 28, Marian Smoluchowski got the chair of theoretical physics at the Lvov University, becoming the youngest university professor (from 1903 — full professor) in the whole Habsburg Empire. He married Zofia Baraniecka in 1901. In 1913 he took the chair of experimental physics at the Jagellonian University. Just before his premature death he was elected for the Rector of our University. Died September 5th, 1917 in Kraków.

One of his lifelong passions was musics, other one — mountains. I am devoting a few words to his achievements in that field, because “To Smoluchowski, mountain climbing was more than a sport, it was an essential part of life. It was in the mountains that he could face unspoiled nature and acquire strength for his scientific endeavours. Mountains meant to him three things, he wrote to his alpine club: They accustomed him to undertaking difficult tasks, they gave him satisfaction when he overcame the challenge and they embellished his life with what he believed to be the highest poetry, the poetry of mountains” [7].

During his studies at Vienna University he was an outstanding alpinist and rock climber, one of the pioneers of modern alpinism. In their students’ years, in 1890’s, brothers Tadeusz and Marian Smoluchowski traced 24 new record ascents in Dolomite and Ortler Alps. Their generation revolutionized alpinism — inaugurated the climbing without the help of local highlander guides. Later on, till 1909, Marian Smoluchowski spent several climbing seasons in Central Alps, ascending several highest and difficult peaks, including legendary in that time Matterhorn. He climbed also in Scotland.

¹ Material about life and work of Marian Smoluchowski can be found in several books. His biography by A. Teske was published in Polish and in German [1]. Ref. [2] contains the reproduction of all Smoluchowski’s published papers. In Ref. [3] are reproduced (in original and in English translation): his fundamental paper about Brownian motion [4], and “Three lectures [given at Göttingen Univ.] on diffusion, Brownian motion and coagulation of colloids” [5], being a recapitulation of his work on these problems. Besides, this book gives also the chronological table of Smoluchowski’s life, and full bibliography of his publications as well as a bibliography of works about Marian Smoluchowski. Ref. [6] presents essays discussing Smoluchowski’s contributions to experiments, to statistical physics, and to didactics.

In the Lvov times Smoluchowski brothers took part in pioneer ski expeditions in East Carpathians. Later on, Marian Smoluchowski was an active member of Polish mountaineering (Climbing) Club in Tatra Mts.

In the history of physics Marian Smoluchowski will be remembered mainly for his work on the theory of Brownian motion and related problems. In his obituary, Arnold Sommerfeld [8] wrote: "His name will, forever, be associated with the first flowering of atomic theory". Let us remember that at the beginning of our century the "molecular hypothesis" was just a hypothesis, which needed proofs, and that the first experimental proofs — honoured in 1926 by Nobel prizes in physics (for Perrin) and in chemistry (for Svedberg) — were based on Smoluchowski's theory of Brownian motion, critical opalescence, sedimentation and coagulation.

However, Smoluchowski's name remains still alive in the modern physics. His papers are frequently cited in the literature. The theoretical basis and the methods established in his work, including the *Smoluchowski equations* derived within theories of Brownian motion, *etc.*, became the founding blocks of modern statistical physics, especially of the theory of stochastic processes. This aspect of Smoluchowski work has been appreciated earlier by Mark Kac and Subrahmanyan Chandrasekhar, who were certainly better equipped than me to judge these results. Therefore I shall use their words [9,10].

Mark Kac wrote [9]: "... while directed toward 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 times goes by the name of Stochastic Processes. It is the probabilistic point of view in contradistinction to the statistico-mechanical one that is also clearly present in Smoluchowski's first paper on Brownian motion [11] and in a paper on the mean free path which just preceded it [4]. [...] This is a remarkable paper in which as far as I know the relation between random walk and diffusion is first established (L. Bachelier who is usually credited with this discovery comes a little later). Equally remarkable is the fact that Smoluchowski uses here Fourier transforms to handle convolutions of probability distributions and is thus first to prove a special case of the central limit theorem of probability theory by means of characteristic functions. [...] The novelty and originality of the Smoluchowski approach lie in his bold replacement of an impossibly difficult dynamical problem (a Brownian particle in a gas or liquid) with the statistical element coming in through the lack of specification of the initial state by a relatively simple *stochastic process*. A dynamical event like a collision, for example, is thus treated as if it were the result of a toss of a coin or a die with the laws of mechanics determining (to some extent at least) the probabilities of various outcomes.

The underlying idea proved enormously fruitful and it gradually permeated much of statistical physics; permeated it, in fact, so well that few of us realize today that much of ‘modern’ problematics (notably that related to so called master equations) is directly traceable to ideas first promulgated by Smoluchowski in the early years of this century”.

Kac mentions also (quoting Chandrasekhar’s paper [12]) “... that it was Smoluchowski who first introduced fluctuations into Physics (as early as 1904 in the Boltzmann Festschrift) [13]”.

According to Chandrasekhar [7], “... a series of papers which Smoluchowski wrote during last five years of his life, [are] papers in which the foundations of the modern theory of stochastic processes were laid [...] Detailed comparisons of the predictions of the foregoing theory [of Brownian motion in a colloidal solution] with experimental results [...] confirm the basic premises of the theory in a most striking way. But what is perhaps of even greater significance is that we have here the first example of a case in which it has been possible to follow in all detail, both theoretically and experimentally, the transition between the macroscopically irreversible nature of diffusion and the microscopically reversible nature of molecular fluctuations”.

2. Smoluchowski’s equations

Marian Smoluchowski’s legacy for modern physics are equations bearing his name, and being still the useful tools, though these equations are nowadays derived in another manner, and different is the reconstruction of the general scheme of the theory.

The main point in the Einstein-Smoluchowski [14,11] theory of Brownian motion is the observation that the proper measure of the motion is not the mean velocity of the particle of the suspension, but the mean square of its shift $\Delta x = x - x_0$ from initial position x_0 . In these first papers $\langle(\Delta x)^2\rangle$ was calculated: by Einstein from general laws of diffusion and statistical mechanics, by Smoluchowski — by detailed analysis of the mechanism of motion of the Brownian particle. It is worth to mention that they both assumed the same property of probabilities (discussed in more detail below).

The *Smoluchowski equations* were formulated in his later papers, containing the theory of Brownian motion, and of coagulation, in external force fields [5,15,16]. First, Smoluchowski finds that in the absence of external fields the probability (conditional) that the suspended particle starting from the point x_0 reaches the point x in the time t is:

$$W(x)dx = \frac{1}{2\sqrt{\pi Dt}} e^{-(x-x_0)^2/4Dt} dx, \quad (1)$$

where D denotes the “diffusion coefficient”. Next important step is the derivation of the general functional equation, valid for arbitrary external fields:

$$W(x, t|x_0, 0) = \int dx' W(x, t|x', \tau)W(x', \tau|x_0, 0) \quad (2)$$

determining the relations between the values of the conditional probabilities $W(x, t|x_0, 0)$ after subsequent (arbitrarily chosen) elapsed times τ , $t - \tau$, and t ($t > \tau > 0$). The crucial assumption (implicit both in Smoluchowski and in Einstein theories) here is that the motion in the (arbitrary) time segments from 0 to τ and from τ to t are independent². This equation will be discussed in detail in Section 3.

Next, Smoluchowski finds explicit forms of the conditional probability for the Brownian motion for a few simpler cases of external fields (the solutions for gravitational and/or centrifugal fields are of importance, among others, for the theory of coagulation). In particular, for the elastic force³ $f(x) = -\alpha x$:

$$W(x, t|x_0, 0) = \sqrt{\frac{\beta}{2\pi D(1 - e^{-2\beta t})}} \exp\left\{-\frac{\beta}{2D} \frac{(x - x_0 e^{-\beta t})^2}{1 - e^{-2\beta t}}\right\}. \quad (3)$$

where $\beta = k_B T \alpha / D$ (T — temperature, k_B — Boltzmann's constant), which gives *e.g.* the dispersion:

$$\sqrt{\langle x^2 \rangle} = (D/\beta)(1 - e^{-2\beta t}) + x_0^2 e^{-2\beta t}. \quad (4)$$

In turn, Smoluchowski realizes that the expressions (1), (3), (4), and like can be obtained as the solutions of the diffusion equation (with drift):

$$\frac{\partial}{\partial t} W = D \frac{\partial^2}{\partial x^2} W - \beta \frac{\partial}{\partial x} [W f(x)], \quad (5)$$

where $f(x)$ is related to the external force acting on the Brownian particle.

Eq. (5) is nothing but the continuity equation together with the first Fick's law (of diffusion in external field). However, in this case it is the *diffusion of probability* — it was Smoluchowski who first realized that the phenomenological laws of macroscopic diffusion can be applied to probability “because the process of diffusion is the superposition of Brownian motions of the molecules of the substance under consideration” [16].

² analogous equation, derived under analogous assumptions, can be found in Bachelier's paper devoted to the analysis of stock exchange fluctuations [17].

³ Smoluchowski pointed out earlier [18] that the *torsional Brownian motion* (molecular fluctuations of very small torsional mirror) can be measured.

Eq. (5) is the famous *Smoluchowski equation*, called also in the literature — improperly — the Fokker-Planck equation. The latter is, for the Brownian motion, the equation for the conditional probability $P(v, x, t)$ for both the position x and the velocity $v = \dot{x}$ of the Brownian particle and has the form:

$$\frac{\partial}{\partial t}P(v, x, t) = -\frac{\partial}{\partial x}vP - \frac{1}{m}\frac{\partial}{\partial v}[f(x) - \gamma]P + \frac{Q}{\gamma}\frac{\partial^2}{\partial v^2}P, \quad (6)$$

which corresponds to the equation of motion of the Brownian particle:

$$m\ddot{x} = -\gamma\dot{x} + f(x) + \xi(t), \quad v = \dot{x}. \quad (7)$$

The above is called the Langevin equation [19] — it is Newton's equation with the friction (damping) force $-\gamma v$, external force $f(x)$, and random force $\xi(t)$, the latter being the so-called white Gaussian noise:

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2Q\delta(t - t'). \quad (8)$$

The Smoluchowski equation can be obtained from the Fokker-Planck equation by the adiabatic elimination of the velocity (assuming that the Maxwell distribution of velocities is established in the time scale much shorter than the time scale of interest), or as the limit of Eq. (6) for the overdamped motion (neglecting the term $m\ddot{x}$ in Eq. (7)), by using the relation:

$$\int dv P(v, x, t) = W(x, t), \quad D = Q/\gamma, \quad \beta = 1/\gamma. \quad (9)$$

In other words, Smoluchowski equation is the reduced Fokker-Planck equation. One speaks frequently [20–22] about the *Smoluchowski limit* of the Fokker-Planck equation. The formally exact derivation of the Smoluchowski equation, Eq. (5), can be found in Refs [23].

In his later papers [5, 24] Smoluchowski discussed, among others, the coagulation processes, as processes related to the Brownian motion. Of his results, in use are nowadays the Smoluchowski kinetic equations [25], and the formulae describing the time dependence of concentrations of particles reacting with each other (coagulating, *e.g.*), for diffusionally limited processes:

$$C(t) \sim \begin{cases} t^{-1} & \text{for } d=3 \\ \ln t/t & \text{for } d=2 \\ t^{-1/2} & \text{for } d=1 \end{cases} \quad (10)$$

(d denotes the spatial dimension) called *Smoluchowski-type behavior* [26]. Smoluchowski equations, Eqs.(1) and (5), are nowadays ones of fundamental

equations of the theory of stochastic processes. Frequently used in many different fields (especially in chemical kinetics) is Eq. (5), its generalizations (especially for “position”-dependent “diffusion coefficient” $D(x)$, *i.e.*, for non-linear stochastic flows), and specialized equations derived from Eq. (5) (*e.g.*, coagulation equations) [20–22, 25, 26]⁴. We know now also the limits of applicability of Smoluchowski theory, especially we know that the underlying stochastic process needs to be the Wiener process, *i.e.*, that the driving stochastic force must be the white Gaussian noise [20, 21, 27–29].

3. Functional Smoluchowski equation

Less frequently used is the fundamental Smoluchowski equation, Eq. (1), which serves mainly for the derivation of other equations. In the present author opinion, however, this equation is also of fundamental importance for the determination of characteristics of stochastic processes and may gain more numerous applications in near future because of the increasing interest in non-Markovian stochastic processes. What is the character of this equation? What it describes?

Let us begin with the observation that implicit in the derivation of Eq. (1) are assumptions very similar to the assumptions implicit in the original derivation of Boltzmann's equation. Namely, one assumes that the value of the conditional probability W at a given time t depends only on the value of W at some (arbitrarily chosen) initial time t_0 , and not on the values of W at earlier times $t' < t_0$, *i.e.*, that $W(t)$ does not depend on the history of the stochastic process. Chandrasekhar [10] wrote: “In obtaining the expression for the transition probability, $W(n; m)$, [*i.e.*, the conditional probability] Smoluchowski makes the following two assumptions. *First* that the motions of the particles are not mutually influenced and are independent of one another; and *second* that all positions of a particle in the element of volume v have equal a priori probabilities. (It is clear that these assumptions enabled Smoluchowski to consider the fluctuations exhibited by n as derived from, what we should now describe as, a Markovian process)”⁵. It is worth to note that very similar (if not just the same) assumptions can be detected in Boltzmann's derivation of his equation, *i.e.* in the famous *Stosszahlansatz* — one assumes that the probability of collision between two particles is

⁴ The amount of papers using Smoluchowski's kinetic theory, and frequently citing explicitly his papers, esp. Refs [18] and [24], is vast — I cite here only some, rather randomly chosen examples.

⁵ In Chandrasekhar's interpretation, n is a number of Brownian particles in a volume v , $W(n; m)$ — probability that one observes m particles at an instant immediately following one in which n particles were observed. Moreover, $W(n) = e^{-\nu} \nu^n / n!$, $\nu = \langle n \rangle$, *i.e.*, the probability that one observes a number n of particles in volume v is given by Poisson process.

independent on the earlier history of the collisions of these particles (one neglects the correlations in the motion of particles). Similar assumptions are also in Einstein's work on Brownian motion. It seems that in early times the Markovianity assumption was taken for granted — perhaps because the paradigmatic random process was the series of throws of a coin or a die.

We shall say nowadays that Eq. (1) defines the *Markov process*, *i.e.*, the stochastic process with independent increments. In the formal theory of stochastic processes (formulated mainly by Kolmogorov), Eq. (1) is derived as the identity resulting from the definition of the Markov process [27–29]:

$$\begin{aligned} P_{1|n}(x_\alpha, t|x_\beta, t_1; \dots; x_\gamma, t_n) &= P_{1|1}(x_\alpha, t|x_\beta, t_1) \\ &= W(x_\alpha, t|x_\beta, t_1), \quad t > t_1 > \dots > t_n, \end{aligned} \quad (11)$$

from the formal definitions of conditional probabilities:

$$P_{1|k}(x_\alpha, t_1|x_\beta, t_2; \dots; x_\gamma, t_{k+1}) = \frac{P_{k+1}(x_\alpha, t_1; \dots; x_\gamma, t_{k+1})}{P_k(x_\beta, t_2; \dots; x_\gamma, t_{k+1})}, \quad (12)$$

and from normalization conditions:

$$\int dx_\beta P_{2|1}(x_\alpha, t; x_\beta, t_1|x_\gamma, t_2) = P_{1|1}(x_\alpha, t|x_\gamma, t_2). \quad (13)$$

Eq. (1), called the functional Smoluchowski (Chapman-Kolmogorov, Bachelier) equation, is thus equivalent to the definition of the Markov process (is an identity following from the definition of the Markov process), and therefore can serve as the quantitative criterion whether a given process is Markovian⁶. Why this property seems to be important? In most cases we have the situation — *e.g.*, when some quantity X is measured experimentally — that the process $\dot{X}(t) = f(X, t)$ macroscopically *deterministic* is disturbed by some random process $\xi(t)$ (thermal noise, fluctuations of some external parameter, *etc.*), so that the effective kinetic equation has the form of the generalized Langevin equation:

$$\dot{X}(t) = f(X, t) + g(X, t; \xi(t)). \quad (14)$$

The process $X(t)$ becomes in this case also a stochastic process. If the noise $\xi(t)$ is linearly coupled and is effectively "white", *i. e.*, when its correlation

⁶ it is to be noted that there are non-Markovian processes which fulfill Eq. (1), but not Eq. (11) — cf. ref. [16], just as there are processes which fulfill Eq. (11) but not Eq. (1). This means that both these relations are the necessary conditions for the process to be Markovian, but they are not the sufficient conditions. In other words, it is sufficient that one of these conditions is not fulfilled to classify the process as non-Markovian.

time is much shorter than the characteristic time of the process $X(t)$, then the process $X(t)$ will in general be Markovian [28]. Therefore, when we find that $X(t)$ is of non-Markovian character, we may conclude that the stochastic disturbance is not "white", *i.e.*, that its correlation time is comparable with the characteristic time of the measured process. Let us note that direct observation of the disturbance $\xi(t)$ is frequently difficult, if not impossible. Measuring $X(t)$ we may thus find some information about $\xi(t)$. And vice versa: if some stochastic process is non-Markovian, we may suspect that it has some admixture of a deterministic process. In other interpretation [30], the noise $\xi(t)$ represents the residual effect of fast variables eliminated during the process of obtaining the macroscopic description from the microscopic description. Therefore $\xi(t)$ can be treated as Markovian when there are well-separated time-scales, *i.e.*, when the eliminated fast microscopic processes are indeed much faster than the macroscopic ones. When this condition holds no longer, the elimination still can be done, but the process $\xi(t)$ must be treated as non-Markovian. Let us note that the Markovian process is completely defined — via Eqs.(11)-(12) — by the knowledge of one- and two-point distributions only. On the other hand, for the complete definition of a non-Markovian process all probability distributions are needed.

The use of the basic definition of Markovianity, Eq. (11), requires the knowledge of many-point probability distributions. On the other hand, the Smoluchowski equation, Eq. (1), contains two-point distributions only. Therefore the latter is simpler in practical use. For example, consider the stationary two-state process (dichotomous noise):

$$X(t) = \begin{cases} A & \text{for } t \in (t_{2m}, t_{2m+1}) \\ B & \text{for } t \in (t_{2m+1}, t_{2m+2}) \end{cases} \quad m = 0, 1, \dots, \quad (15)$$

such that the states A appear with the probability $P(A)$, states B with probability $P(B) = 1 - P(A)$. Smoluchowski equation has in this case the simple form⁷:

$$W(x, t|y, t_0) = \sum_{z=A,B} W(x, t|z, \tau)W(z, \tau|y, t_0), \quad t > \tau > t_0, \quad (16)$$

and the normalization gives

$$W(A, t|y, t_0) + W(B, t|y, t_0) = 1. \quad (17)$$

⁷ notation used here is as follows: $X(t)$ denotes the stochastic process, x, y, z — the values of this process (A, B in this case). $P(x, t, \dots)$, $W(x, t|\dots)$ are the probabilities that $X(t) = x$, *etc.* One-point probability distribution $P(x)$ does not depend on time, because the process is assumed to be stationary.

Let W satisfy the Master equation:

$$\dot{W}(A, t|y, t_0) = -\dot{W}(B, t|y, t_0) = -[\lambda_1 W(A, t|y, t_0) - \lambda_2 W(B, t|y, t_0)] \quad (18)$$

with obvious initial condition:

$$W(x, t_0|y, t_0) = \delta_{x,y}. \quad (19)$$

The solution reads:

$$\begin{aligned} W(A, t|y, t_0) &= e^{-\Lambda(t-t_0)} \left[\delta_{A,y} - \frac{\lambda_2}{\Lambda} \right] + \frac{\lambda_2}{\Lambda}, \\ W(B, t|y, t_0) &= e^{-\Lambda(t-t_0)} \left[\delta_{B,y} - \frac{\lambda_1}{\Lambda} \right] + \frac{\lambda_1}{\Lambda}, \end{aligned} \quad (20)$$

with $\Lambda = \lambda_1 + \lambda_2$. It is easy to check that this solution satisfies the Smoluchowski equation (16), therefore the considered process is Markovian⁸.

Define now another stochastic dichotomous process by the following Master equation:

$$\ddot{W}(A, t|y, t_0) + \nu \dot{W}(A, t|y, t_0) = -[\mu_1 W(A, t|y, t_0) - \mu_2 W(B, t|y, t_0)], \quad (21)$$

with the same initial conditions (19) and with $\dot{W}(x, t_0|y, t_0) = 0$. In this case the solution reads

$$\begin{aligned} W(A, t|y, t_0) &= \psi(t - t_0) \left[\delta_{A,y} - \frac{\mu_2}{M} \right] + \frac{\mu_2}{M}, \\ W(B, t|y, t_0) &= \psi(t - t_0) \left[\delta_{B,y} - \frac{\mu_1}{M} \right] + \frac{\mu_1}{M}, \end{aligned} \quad (22)$$

$$\begin{aligned} M &= \mu_1 + \mu_2, \quad \psi(t) = \frac{\theta_1 - \nu}{\Gamma} e^{-\theta_1 t} - \frac{\theta_2 - \nu}{\Gamma} e^{-\theta_2 t}, \\ \theta_{1,2} &= \frac{1}{2}(\nu \pm \Gamma), \quad \Gamma = \sqrt{\nu^2 - 4M}. \end{aligned}$$

It is easy to check that this solution does not satisfy the Smoluchowski equation, *i.e.*, that the process defined by (21) is not Markovian (for any definition of higher-order probability distributions). Let us note that the Markovian process (18) can be obtained from the non-Markovian process (21) in the limit $\nu \rightarrow \infty$ with the substitution $\mu_k = \nu \lambda_k$. This limit means that the “memory” of the process, described by the parameter $1/\nu$, becomes infinitely short (in the time scale of interest).

⁸ strictly speaking, that it can be Markovian, if the remaining, higher-order probability distributions are defined in such a way that they satisfy also Eq. (11).

In general Smoluchowski equation (1) implies rather strong conditions which must be fulfilled by conditional probabilities of a Markovian process. It can be checked that the Gaussian distribution (3) satisfies Eq. (1). Besides, it seems that the only (almost?) admissible time dependence is the simple exponential form (20), although the proof of this conjecture is not known.

The Markovian character of a stochastic process determined by well-defined stochastic equations, or by well-defined (analytically) probability distributions, can be checked in several different ways. However, it is not so simple for a stochastic process defined by long numerical sequences, *e.g.* by experimental data. There are several propositions in the literature how to find whether such finite stochastic chains are Markovian [31]. It seems that the Smoluchowski equation is the simplest tool for this purpose. To illustrate this application, consider three dichotomous processes, the sample data of which are shown in Fig. 1 a, b, c. The processes a and b are stochastic, and at the first sight do not differ from each other. The process c is obviously periodic (deterministic). The analysis of these three processes via the Smoluchowski equation is shown in Figs. 2 and 3 (the cases a, b, c

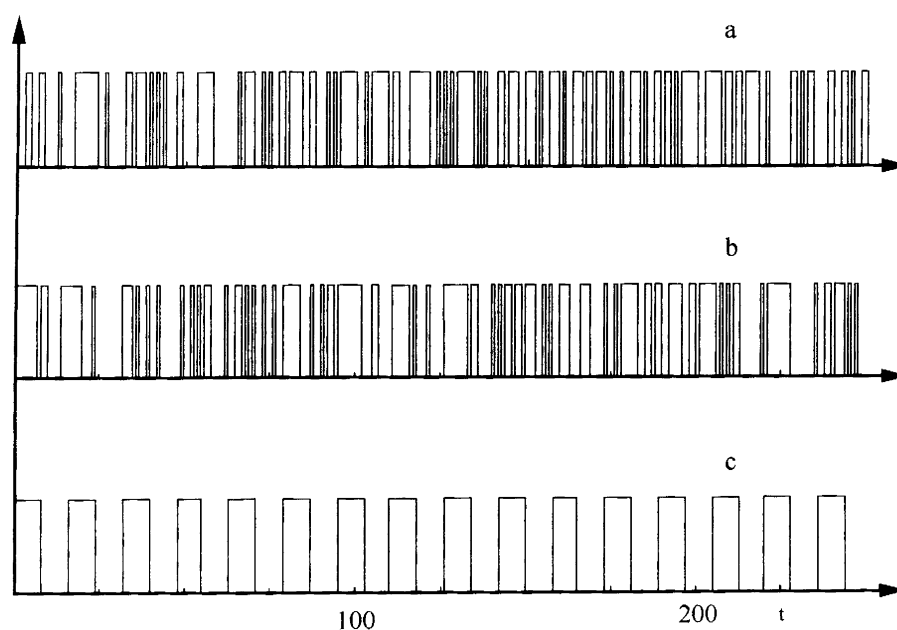


Fig. 1. Sample data of dichotomous series generated by the function (26). a: $\alpha = 1$, b: $\alpha = 0.5$, c: $\alpha = 0$.

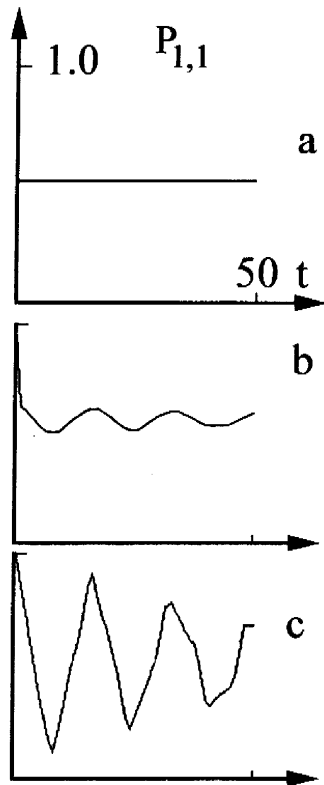


Fig.2

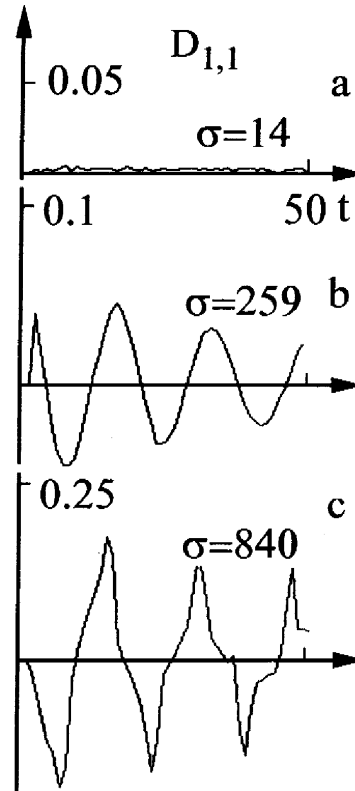


Fig.3

Fig. 2. Conditional probabilities $P_{1,1}(t) \equiv P_{1|1}(A, t|A, 0)$, calculated for three series shown in Fig.1.

Fig. 3. Deviations $D_{1,1}(t)$ from the Smoluchowski equation, calculated for conditional probabilities shown in Fig.2. σ denote mean squares of these differences, Eq. (25), multiplied by 10^4 .

correspond to the sample data from Fig. 1). For this purpose were generated three “experimental” series of data, each composed of 250 000 real numbers. These numbers were translated into dichotomous series of states A and B by assuming that a given number $x \in A$ if $x > x^*$, otherwise $x \in B$, with the threshold x^* chosen in such manner that the one-point (stationary) probabilities of both states were equal:

$$P(A) = P(B) = 1/2. \quad (23)$$

Fig. 2 presents the two-point conditional probability

$$P_{1,1} \equiv P_{1|1}(A, t|A, 0)$$

(state A is taken here as the state number 1). Note that for (23)

$$P_{1|1}(A, t|A, 0) + P_{1|1}(B, t|A, 0) = 1, \quad P_{1|1}(A, t|A, 0) + P_{1|1}(A, t|B, 0) = 1. \tag{24}$$

The Markovianity check is shown in Fig. 3. There $D_{1,1}$ denotes the difference between left-hand-side and right-hand-side of the Smoluchowski equation (16) calculated for the probabilities $P_{1,1}$ shown in Fig. 2. The numbers labelling the curves are the measures of the differences shown in Fig. 3 (multiplied by 10^4):

$$\sigma = \left\{ \frac{1}{T} \int_0^T dt D_{1,1}(t) \right\}^{1/2} \tag{25}$$

with $T = 50$ (the range of time shown in Fig.3). It is seen that all three “experimental” series behave very differently. Now, the analysed series are generated by the function:

$$f(t) = \alpha \text{rnd}(t) + \frac{1}{2}(1 - \alpha)[1 + \sin(10t)], \tag{26}$$

with $\text{rnd}(t) \in [0, 1]$ being the random number, and with $\alpha = 1, 0.5, 0$ for series a, b, c, respectively. Therefore the series a is obviously Markovian, the non-zero value of σ giving the numerical accuracy of the procedure (related, among others, to the finite amount of data). The series c is periodic, *i.e.*, “non-Markovian” with infinite “memory”. The series b, which at first sight is indistinguishable from the purely random series a, contains in equal shares both the deterministic and the random (Markovian) components. The analysis via the Smoluchowski equation shows easily the substantial difference between the purely random Markovian series a and the mixed non-Markovian series b.

Similar analysis was recently performed by us for the experimental data on the single-channel ionic currents [32], finding there the deterministic component.

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