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STOCHASTIC PROCESSES IN PHYSICS AND CHEMISTRY

Revised and enlarged edition

N.G. VAN KAMPEN

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N.G. VAN KAMPEN

Institute for Theoretical Physics of the University at Utrecht

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STOCHASTIC PROCESSES IN PHYSICS AND CHEMISTRY

To the memory of

F. ZERNIKE

whose influence on this work
runs deeper than I can know

PREFACE TO THE FIRST EDITION

Que nous sert-il d'avoir la panse pleine de viande, si elle ne se digère? si elle ne se transforme en nous? si elle ne nous augmente et fortifie?

Montaigne

The interest in fluctuations and in the stochastic methods for describing them has grown enormously in the last few decades. The number of articles scattered in the literature of various disciplines must run to thousands, and special journals are devoted to the subject. Yet the physicist or chemist who wants to become acquainted with the field cannot easily find a suitable introduction. He reads the seminal articles of Wang and Uhlenbeck and of Chandrasekhar, which are almost forty years old, and he culls some useful information from the books of Feller, Bharucha-Reid, Stratonovich, and a few others. Apart from that he is confronted with a forbidding mass of mathematical literature, much of which is of little relevance to his needs. This book is an attempt to fill this gap in the literature.

The first part covers the main points of the classical material. Its aim is to provide physicists and chemists with a coherent and sufficiently complete framework, in a language that is familiar to them. A thorough intuitive understanding of the material is held to be a more important tool for research than mathematical rigor and generality. A physical system at best only approximately fulfills the mathematical conditions on which rigorous proofs are built, and a physicist should be constantly aware of the approximate nature of his calculations. (For instance, Kolmogorov's derivation of the Fokker–Planck equation does not tell him for which actual systems this equation may be used.) Nor is he interested in the most general formulations, but a thorough insight in special cases will enable him to extend the theory to other cases when the need arises. Accordingly the theory is here developed in close connection with numerous applications and examples.

The second part, starting with chapter IX [now chapter X], is concerned with fluctuations in nonlinear systems. This subject involves a number of conceptual difficulties, first pointed out by D.K.C. MacDonald. They are of a physical rather than a mathematical nature. Much confusion is caused by the still prevailing view that nonlinear fluctuations can be approached from the same physical starting point as linear ones and merely require more elaborate mathematics. In actual fact, what is needed is a firmer physical basis and a more detailed knowledge of the physical system than required for the study of linear noise. This is the subject of the second part, which has more the character of a monograph and inevitably contains much of my own work.

The bulk of the book is written on the level of a graduate course. The Exercises range from almost trivial to rather difficult. Many of them contain applications and others provide additions to the text, some of which are used later on. My hope is that they will not frustrate the reader but stimulate an active participation in the material.

The references to the literature constituted a separate problem. Anything even approaching completeness was out of the question. My selection is based on the desire to be helpful to the reader. To stress this aspect references are given at the bottom of the page, where the reader can find them without having to search for them. My aim will be achieved if they are sufficient as a guide to further relevant literature. Unavoidably a number of important contributions are not explicitly but only indirectly credited. I apologize to their authors and beg them to consider that this is a textbook rather than a historical account.

. . . .

I am indebted to B.R.A. Nijboer, H. Falk, and J. Groeneveld for critical remarks, to the students who reported a number of misprints, and to Leonie J.M. Silkens for indefatigable typing and retyping.

N.G. van Kampen

PREFACE TO THE SECOND EDITION

This edition differs from the first one in the following respects. A number of additions are concerned with new developments that occurred in the intervening years. Some parts have been rewritten for the sake of clarity and a few derivations have been simplified. More important are three major changes.

First, the Langevin equation receives in a separate chapter the attention merited by its popularity. In this chapter also non-Gaussian and colored noise are studied. Secondly, a chapter has been added to provide a more complete treatment of first-passage times and related topics. Finally, a new chapter was written about stochasticity in quantum systems, in which the origin of damping and fluctuations in quantum mechanics is discussed. Inevitably all this led to an increase in the volume of the book, but I hope that this is justified by the contents.

The dearth of relevant literature mentioned in the previous preface has since been alleviated by the appearance of several textbooks. They are quoted in the text at appropriate places. Some of the references appear in abbreviated form; the key to the abbreviations is given below.

N.G. van Kampen

ABBREVIATED REFERENCES

FELLER I: W. Feller, *An Introduction to Probability Theory and its Applications*, Vol. I (2nd edition, Wiley, New York 1957).
FELLER II: idem Vol. II (Wiley, New York 1966).
BHARUCHA-REID: A.T. Bharucha-Reid, *Elements of the Theory of Markov Processes and their Applications* (McGraw-Hill, New York 1960).
COX AND MILLER: D.R. Cox and H.D. Miller, *The Theory of Stochastic Processes* (Chapman and Hall, London 1972).
WAX: *Selected Papers on Noise and Stochastic Processes* (N. Wax ed., Dover Publications, New York 1954).
STRATONOVICH: R.L. Stratonovich, *Topics in the Theory of Random Noise*, Vol. I (R.A. Silverman transl., Gordon and Breach, New York 1963).
DE GROOT AND MAZUR: S.R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam 1962).
GARDINER: C.W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin 1983).
RISKEN: H. Risken, *The Fokker–Planck Equation* (Springer, Berlin 1984).

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Chapter I

STOCHASTIC VARIABLES

This chapter is intended as a survey of probability theory, or rather a catalogue of facts and concepts that will be needed later. Many readers will find it time-saving to skip this chapter and only consult it occasionally when a reference to it is made in the subsequent text.

1. Definition

A "random number" or "stochastic variable" is an object X defined by

a. a set of possible values (called "range", "set of states", "sample space" or "phase space");

b. a probability distribution over this set.

Ad **a.** The set may be *discrete*, e.g.: heads or tails; the number of electrons in the conduction band of a semiconductor; the number of molecules of a certain component in a reacting mixture. Or the set may be *continuous* in a given interval: one velocity component of a Brownian particle (interval $-\infty, +\infty$); the kinetic energy of that particle $(0, \infty)$; the potential difference between the end points of an electrical resistance $(-\infty, +\infty)$. Finally the set may be partly discrete, partly continuous, e.g., the energy of an electron in the presence of binding centers. Moreover the set of states may be *multidimensional*; in this case X is often conveniently written as a vector $\boldsymbol{X}$. Examples: $\boldsymbol{X}$ may stand for the three velocity components of a Brownian particle; or for the collection of all numbers of molecules of the various components in a reacting mixture; or the numbers of electrons trapped in the various species of impurities in a semiconductor.

For simplicity we shall often use the notation for discrete states or for a continuous one-dimensional range and leave it to the reader to adapt the notation to other cases.

Ad **b.** The probability distribution, in the case of a continuous one-dimensional range, is given by a function $P(x)$ that is nonnegative,

$$P(x) \geqslant 0, \tag{1.1}$$

and normalized in the sense

$$\int P(x)\, \mathrm{d}x = 1, \tag{1.2}$$

where the integral extends over the whole range. The probability that X has a value between x and $x + dx$ is

$$P(x)\,dx.$$

Remark. Physicists like to visualize a probability distribution by an "ensemble". Rather than thinking of a single quantity with a probability distribution they introduce a fictitious set of an arbitrarily large number $\mathcal{N}$ of quantities, all having different values in the given range, in such a way that the number of them having a value between x and $x + dx$ is $\mathcal{N}P(x)\,dx$. Thus the probability distribution is replaced with a density distribution of a large number of "samples". This does not affect any of its results, but is merely a convenience in talking about probabilities, and occasionally we shall also use this language. It may be added that it can happen that a physical system does consist of a large number of identical replicas, which to a certain extent constitute a physical realization of an ensemble. For instance, the molecules of an ideal gas may serve as an ensemble representing the Maxwell probability distribution of the velocity. Another example is a beam of electrons scattering on a target and representing the probability distribution for the angle of deflection. But the use of an ensemble is not limited to such cases, nor based on them, but merely serves as a more concrete visualization of a probability distribution. To introduce or even envisage a physical interaction between the samples of an ensemble is a dire misconception*).

In a continuous range it is possible for $P(x)$ to involve delta functions,

$$P(x) = \sum_n p_n\,\delta(x - x_n) + \tilde{P}(x), \tag{1.3}$$

where $\tilde{P}$ is finite or at least integrable and nonnegative, $p_n > 0$, and

$$\sum_n p_n + \int \tilde{P}(x)\,dx = 1.$$

Physically this may be visualized as a set of discrete states x_n with probability p_n embedded in a continuous range. If $P(x)$ consists of delta functions alone, i.e., if $\tilde{P}(x) = 0$, it can also be considered as a probability distribution p_n on the discrete set of states x_n. A mathematical theorem asserts that any distribution on $-\infty < x < \infty$ can be written in the form (1.3), apart from a third term, which, however, is of rather pathological form and does not appear to occur in physical problems.**)

Exercise. Let X be the number of points obtained by casting a die. Give its range and probability distribution. Same question for casting two dice.

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*) E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, Cambridge 1946).

**) FELLER II, p. 139. He calls the first term in (1.3) an "atomic distribution".

Exercise. Flip a coin N times. Prove that the probability that heads turn up exactly n times is

$$p_n = 2^{-N}\binom{N}{n} \quad (n = 0, 1, 2, \dots, N) \tag{1.4}$$

("binomial distribution"). If heads gains one penny and tails loses one, find the probability distribution of the total gain.

Exercise. Let X stand for the three components of the velocity of a molecule in a gas. Give its range and probability distribution.

Exercise. An electron moves freely through a crystal of volume Ω or may be trapped in one of a number of point centers. What is the probability distribution of its coordinate $\boldsymbol{r}$?

Exercise. Two volumes, V_1 and V_2, communicate through a hole and contain N molecules without interaction. Show that the probability of finding n molecules in V_1 is

$$p_n = (1+\gamma)^{-N}\binom{N}{n}\gamma^n, \tag{1.5}$$

where $\gamma = V_1/V_2$ (general binomial distribution or "Bernoulli distribution").

Exercise. An urn contains a mixture of N_1 white balls and N_2 black ones. I extract at random M balls, without putting them back. Show that the probability for having n white balls among them is

$$p_n = \binom{N_1}{n}\binom{N_2}{M-n}\bigg/\binom{N_1+N_2}{M} \quad \text{("hypergeometric distribution").} \tag{1.6}$$

It reduces to (1.5) in the limit $N_1 \to \infty$, $N_2 \to \infty$ with $N_1/N_2 = \gamma$.

Note. Many more exercises can be found in texts on elementary probability theory, e.g., J.R. Gray, *Probability* (Oliver and Boyd, Edinburgh 1967); T. Cacoulos, *Exercises in Probability* (Springer, New York 1989).

Excursus. As an alternative description of a probability distribution (in one dimension) one often uses instead of $P(x)$ a function $\mathbb{P}(x)$, defined as the total probability that X has any value $\leqslant x$. Thus

$$\mathbb{P}(x) = \int_{-\infty}^{x+0} P(x')\,\mathrm{d}x',$$

where the upper limit of integration indicates that if P has a delta peak at x it is to be included in the integral.*) Mathematicians call $\mathbb{P}$ the *probability distribution function* and prefer it to the *probability density* P, because it has no delta peaks, because its behavior under transformation of x is simpler, and because they are accustomed to it. Physicists call $\mathbb{P}$ the *cumulative distribution function*, and prefer P,

*) This is, of course, an arbitrary convention; one might also define $\mathbb{P}(x)$ as the probability that X takes a value $<x$.

because its value at x is determined by the probability at x itself, because in many applications it turns out to be a simpler function, because it more closely parallels the familiar way of describing probabilities on discrete sets of states, and because they are accustomed to it. In particular in multidimensional distributions, such as the Maxwell velocity distribution, $\mathbb{P}$ is rather awkward. We shall therefore use throughout the probability density $P(x)$ and not be afraid to refer to it as "the probability distribution", or simply "the probability".

A more general and abstract treatment is provided by axiomatic probability theory.*) The x-axis is replaced by a set S, the intervals $\mathrm{d}x$ by subsets $A \subset S$, belonging to a suitably defined family of subsets. The probability distribution assigns a non-negative number $\mathscr{P}(A)$ to each A of the family in such a way that $\mathscr{P}(S) = 1$, and that when A and B are disjoint

$$\mathscr{P}(A + B) = \mathscr{P}(A) + \mathscr{P}(B).$$

This is called a probability measure. Any other set of numbers $f(A)$ assigned to the subsets is a stochastic variable. In agreement with our program we shall not use this approach, but a more concrete language.

Exercise. Show that $\mathbb{P}(x)$ must be a monotone non-decreasing function with $\mathbb{P}(-\infty) = 0$ and $\mathbb{P}(+\infty) = 1$. What is its relation to $\mathscr{P}$?

Exercise. An opinion poll is conducted in a country with many political parties. How large a sample is needed to be reasonably sure that a party of 5 percent will show up in it with a percentage between 4.5 and 5.5?

Exercise. Thomas Young remarked that if two different languages have the same word for one concept one cannot yet conclude that they are related since it may be a coincidence.**) In this connection he solved the following "Rencontre Problem" or "Matching Problem": What is the probability that an arbitrary permutation of n objects leaves no object in its place? Naturally it is assumed that each permutation has a probability $n!^{-1}$ to occur. Show that the desired probability p as a function of n obeys the recurrence relation

$$np(n) - (n-1)p(n-1) = p(n-2).$$

Find $p(n)$ and show that $p(n) \to \mathrm{e}^{-1}$ as $n \to \infty$.

*) A. Kolmogoroff, *Grundbegriffe der Wahrscheinlichkeitsrechnung*. Ergebn. Mathem. Grenzgebiete **2**, No. 3 (Springer, Berlin 1933) = A.N. Kolmogorov, *Foundations of the Theory of Probability* (Chelsea Publishing, New York 1950). Or any other modern mathematical textbook such as FELLER II, p. 110; or M. Loève, *Probability Theory* I and II (Springer, New York 1977/1978).

) Philos. Trans. Roy. Soc. (London 1819) p. 70; M.G. Kendall, Biometrica **55, 249 (1968). But the problem goes back to N. Bernoulli (1714) and P.-R. de Montmort (1708), see F.N. David, *Games, Gods, and Gambling* (Griffin, London 1962).