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MODERN ASPECTS OF DIFFUSION-CONTROLLED REACTIONS

COOPERATIVE PHENOMENA IN BIMOLECULAR PROCESSES

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Preface

> He used to talk so much and so fast that – the following day – he was hardly able to remember what he had said – much less analyze it.
>
> V. Klyuchevsky, old Russian historian

A wide range of condensed matter properties including viscosity, ionic conductivity and mass transport belong to the class of thermally activated processes and are treated in terms of *diffusion*. Its theory seems to be quite well developed now [1–5] and was applied successfully to the study of radiation defects [6–8], dilute alloys and processes in highly defective solids [9–11]. Mobile particles or defects in solids inavoidably interact and thus participate in a series of *diffusion-controlled reactions* [12–18]. Three basic bimolecular reactions in solids and liquids are: dissimilar particle (defect) recombination (annihilation), $A + B \rightarrow 0$; energy transfer from donors A to unsaturable sinks B, $A + B \rightarrow B$ and exciton annihilation, $A + A \rightarrow 0$.

This theory, as originated from the early work of Smoluchowski [20], nowadays has numerous applications in several branches of chemistry, such as colloidal chemistry, aerosol dynamics, catalysis and the physical chemistry of solutions as well as in the physics and chemistry of the condensed state [21–24]. Until recently, its branch called *standard chemical kinetics* [12, 15, 16] based on the law of mass action seemed to be quite a complete and universal theory. However, because of their entirely phenomenological character, theories of this kind always operate with the *reaction rates* K which are postulated to be time-independent parameters.

Since the 1960s the first attempts were undertaken to develop a more rigorous theoretical formalism employing different techniques: the hierarchy of equations for many-particle distribution functions [25–28], field theory [29–32], and multiple scattering [33, 34]. Both theoretical studies and computer simulations [35–40] carried out in the 70s–80s have clearly demonstrated the principal shortcoming of the Smoluchowski-type theories (which are the basis of the standard chemical kinetics): they are two-particle approaches and thus neglect any effects related to *fluctuations in the reactant densities*. As an example of the limitations of these over-averaging theories we would mention the formation of such quite complex spatial structures as *fractal clusters* and reactions in restricted geometries [41, 42]. A very general review of a role of fluctuations in physical, chemical and biological processes has been

presented recently in review articles [43, 44]. The aim of our book is to consider the kinetics and peculiarities of *fluctuation-controlled bimolecular reactions.*

The treatment, done for the first time in the 70s at the intermediate *mesoscopic* level (concentration distributions are continuous but fluctuating) by Balagurov and Vaks [45] and Ovchinnikov and Zeldovich [46] for the $A + B \rightarrow B$ and $A + B \rightarrow 0$ reactions, respectively, has demonstrated their considerable deviations from the generally-accepted laws of the standard chemical kinetics resulting in an essentially non-Poisson spectrum of density fluctuations. Such a mesoscopic level of theory as well as macro- and microscopic approaches are discussed in detail in the book for the two above-mentioned kinds of fundamental bimolecular reactions in condensed matter, corresponding, e.g., to Frenkel defect recombination (annihilation) and energy transfer, respectively as well as for a third type of reactions of exciton annihilation. We will demonstrate that careful analysis of the kinetics of these simple bimolecular reactions, based on the second step in the cut-off of the infinite hierarchy of equations for many-particle densities, reveal their capability for *self-organization* (*cooperative phenomena*) which could be described in terms of the correlation length and critical exponents in the very same way as is done in statistical physics.

Among the important conclusions arising from this new formalism, we mention that, in contrast to what one might intuitively assume, similar particles (reactants), initially distributed at random and non-interacting with one other, after some reaction time become aggregated into domains containing particles of one kind only, A or B. Pattern formation results from the lateral interaction of similar particles (A–A and B–B) via their reaction with particles of another kind (A–B). This leads to a time-dependence of the reaction rate, not at short reaction times during the transient process (which is well known in chemical kinetics) but at *long times*. It occurs because similar particle aggregation leads to greater mean distances between dissimilar particles and thus hinders their reaction rate and concentration decay in time. This new theory reveals such previously *hidden parameters* as the ratio of diffusion coefficients, $D_A/(D_A + D_B)$, the spatial dimension $\bar{d}$, and the initial particle concentrations, $n_i(t = 0)$.

In the 70s, a new class of static long-range reaction in irradiated liquids, glasses and solids, called *tunnelling recombination* was discovered [47, 48]. Tunnelling recombination has a purely quantum-mechanical nature and results in the reaction between dissimilar particles separated by distances as

large as 20–30 Å, despite the fact that at sufficiently low temperature these particles are immobile. We will discuss how tunnelling reactions manifest themselves in self-organisation phenomena.

A number of quite different techniques have been presented in the last few years for studying self-organisation phenomena in the bimolecular reactions in condensed matter. At present those are covered in the review article [49] and Proceedings of the conference [50] only; we discuss their advantages and shortcomings, and the principal approximations involved (in particular, that by Kirkwood). Where possible, analytical results are compared with computer simulations, since very limited experimental data are known at present in this field. Those that do exist are also considered and the conditions for the experimental observation of cooperative effects under study are predicted theoretically. We hope that this book may stimulate new experimental studies in this very important field.

Until recently, only complex reactions with dozens of intermediate products were known to produce self-ordering effects characterized by a formation of *spatio-temporal structures* [51]; they were studied mainly in terms of the universal theory developed in the 1970s and known as *synergetics* [52–54]. A formation of these structures in active extended media is now of great interest for multidisciplinar studies in physics, chemistry and biology. Synergetics studies quite general laws determining the processes of creation, migration and recombination (decay) of particles (excitations) of arbitrary nature leading to the pattern formation [55]. Considerable success in this field has been achieved by making use of a *stochastic description* of irreversible processes far from equilibrium [18, 52–54, 56]. Among the main subjects of these studies are condensed media and diffusion-controlled reactions therein. The studies by means of stochastic methods are based on the standard approach of Markov chains with transition probabilities which are non-linear functions of stochastic variables [25, 26, 28, 52, 53]. As is known from statistical physics, the corresponding infinite set of coupled equations cannot be solved exactly. An approximate description of many-particle problems in terms of synergetics usually leads to a finite set of several non-linear partial differential equations. Their non-linearities arise from the same causes as in the Boltzmann equation, and often these equations have more than a single solution.

Self-organization manifests itself only in systems far from equilibrium and consisting of a large number of objects, whose cooperative behaviour is sometimes considered in terms of the *non-equilibrium critical phenomena*

(phase transitions) [53, 55, 57–62]. At present there are several complementary approaches to the physics of open systems far from equilibrium. A simple phenomenological description in terms of Langevin or Fokker–Planck equations was presented in [63]. Unfortunately, the structure and stationary distribution functions and the associated fluctuation-dissipative theorem are in general unknown, so these often represent an unwarranted extrapolation from some underlying deterministic approximation. An alternative scheme is provided by the stochastic master equations. Their additional linearization shows that the mentioned above phenomenological approach could be seriously in error. However, it is practically impossible to obtain systematic approximations in the vicinity of the critical points (see, however, [64, 65] where the *exact* Fokker–Planck or Langevin descriptions were derived from the master equation by means of the developed there "Poisson transformation"). Up to now the scaling and RG approaches [66–70] have not been used systematically because of the absence of a simple Landau–Ginsburg-type description. Their use requires modification of the statement of the problem, since only a rather limited class of stochastic problems defined by a set of the probability transitions could be solved by these methods alone. The formalism presented in [64, 65] seems to be in keeping with generalization of the scaling and RG approaches.

Recent stochastic studies of the role of reactant density fluctuations in the bimolecular kinetics revealed an unexpected appearance of *microscopic* patterns characterized by a short-range and intermediate-range order, thus not violating the homogeneity of a system, rather than the long-range ordered structures which are the usual object of studies in synergetics. The effects in which we are interested are to be accounted for by the violation of the large number law [52] when the description of a system in terms of average quantities is no longer sufficient. It is so because the self-organizing systems are characterized by anomalous fluctuations which govern the behaviour of the average quantities and *qualitatively* change their time development. For the reactions controlled by reactant motion, coherent behaviour of the fluctuations is typical, i.e., the existence of spatial correlation of closely spaced reactants in a system. An analogy between the fluctuations in a system far from the equilibrium and such critical phenomena as the phase transitions at equilibrium has been pointed out more than once [54, 55]. It is well known that the fluctuation terms cannot be neglected in the equations for average quantities in the vicinity of instability points, since after a long enough time the non-Poisson fluctuation spectrum determines the behaviour of the average quantities [69, 71]. Here one cannot neglect a perturbation which equals

the deviation of the fluctuation spectrum from the Poisson one and thus increases in time. For systems with asymptotically unstable solutions (e.g., the well-known Lotka–Volterra model in its stochastic statement with interacting populations [52–54]) the *fluctuation dispersion cannot be neglected.* Thus the cut-off of the infinite hierarchy of equations for the distribution functions, which is of our interest, permits to obtain the approximate solution which is valid only at *short reaction times.* Higher-degree approximations are of key importance and often allow us to "discover" the latent degrees of freedom (e.g., dispersions) characterizing the kinetic behaviour of a system. Recent pioneering studies [45, 46] in fact discovered a *new class of self-organization phenomena.*

The key questions arose in this book are – are three above mentioned simplest bimolecular reactions complex enough to expect the appearance of self-organization or not? What is a marginal complexity for step reactions with several products?

For example, the standard synergetic approach [52–54] denies the possibility of any self-organization in a system with with two intermediate products if only the mono- and bimolecular reaction stages occur [49]; it is known as *the Hanusse, Tyson and Light theorem.* We will question this conclusion, which in fact comes from the qualitative theory of non-linear differential equations where coefficients (reaction rates) are considered as constant values and show that these simplest reactions turn out to be complex enough to serve as a basic models for future studies of non-equilibrium processes, similar to the famous Ising model in statistical physics. Different kinds of auto-wave processes in the Lotka and Lotka–Volterra models which serve as the two simplest examples of chemical reactions will be analyzed in detail. We demonstrate the universal character of cooperative phenomena in the bimolecular reactions under study and show that it is reaction itself which produces all these effects.

The considerable progress made in the studies of simple bimolecular reactions (which has led to such fundamental conclusions) was achieved by a more rigorous mathematical treatment of the problem, avoiding the use of the simplest approximations which linearize the kinetic equations. We focus main attention on the *many-point density formalism* developed in [26, 28, 49] since in our opinion it seems at present to be the only general approach permitting treatment of *all* the above-mentioned problems, whereas other theoretical methods so far developed, e.g., those of secondary quantization [19, 29–32], and of multiple scattering [72, 73], as well based on

the electrostatic analogy [74] could be applied to particular problems only. For example, the diagrammatic perturbation technique, being based on the analogy between the master equation and the quantum field theory with non-Hermitian Hamiltonian describing Bose particles, could be applied only to the steady-state of a system with particle source [32, 75, 76]. Moreover, this approach allows us to clarify the analogy between the kinetic equations derived for description of bimolecular diffusion-controlled reactions [25, 77] and those commonly used in the self-organization theory and its applications. We will use widely the analogy between our problems and physics of critical phenomena and treat kinetics under study in terms of *correlation lengths and critical exponents.*

We restrict ourselves to the case of classical particles and we thus disregard all quantum effects. The particle motion (if any) occurs by thermally-activated hops in continuum medium.

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