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The application of the principle of least action to some self-organized chemical reactions

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Abstract

In contrast to the traditional viewing of reaction mechanism as a time-continuous progress of sequent intermediate states the feedback oscillatory self-organisation is investigated. Some cases of solid-state reactions are analyzed but main interest is directed to the ''principle of the least action'', introduced into the science by P.L.M. Maupertuis in 1744. It is used for the evaluation of diffusion action of propagating Belousov–Zhabotinsky (BZ) waves where the diffusion action is calculated as the product: $K \times \kappa \times m \times \lambda \times u$, K is the diffusivity factor ($K = 1$ for one-dimensional space, $K = 2$ for two-dimensional space, $K = 4\pi$ for three-dimensional space), κ is the tortuosity factor ($\kappa = 1$ for water non-restricted solutions, $\kappa > 1$ for gels, membranes, glasses, etc.), m is the mass of H^+ cations creating the propagating osmotic wave, λ represents a path necessary for the accumulation of H^+ in order to overcome the opposing pressure of the surroundings and u is the propagation speed of BZ waves. The examination of data available from literature revealed a strong tendency of successive target and spiral waves in water solutions ($\kappa = 1$) to minimize their action to a characteristic value $h = 6.63 \pm 0.06 \times 10^{-34}$ J s, having a striking coincidence with the Planck constant of microcosms.

Keywords: Chemical reaction; Reaction mechanism; Self-organization; Solidified lamellae; Belousov–Zhabotinsky waves; Diffusion action; Quantity of action; Tortuosity factor; Osmotic wave; Dispersion relation; Planck constant; One-dimensional propagation

1. Introduction

If an experimentalist would face chaotic trends in his resulting data while studying chemical reactions in an apparently closed system he would refuse such results reasoning that the experiment was not satisfactory completed due to not well enough defined reaction conditions, unknown disturbing effects from surroundings, etc. Such an attitude has habitual basis in traditional view common in classical thermodynamics that the associated dissipation of energy is steadily decelerated to reach its minimum (often close to zero) at a certain stable state (adjacent to equilibrium). In such a case we are examining the reaction mechanism as a time-continuous development of regularly successive states. In many cases, however, the reaction is initiated to start far away from its equilibrium or external contributions are effectual (partly open system) or reaction intermediates play a role of doorway agents (feedback catalysis) so that the seemingly chaotic (oscillatory) behavior is not an artefacts but a real scientific output worth of a more detailed inspection. In this case the reaction

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mechanism is understood not only in its traditional terms of time-continuous progress but also as a reflection of reaction time-rejoinder which feedback character yields rather complex structure of self-organization [1–3]. In most cases oscillatory trends are still sensed as a curiosity and the source of apprehension than an interesting phenomenon common in nature and thus worth of further investigation.

The best example is the basic occurrence of life as a self-replicating, mutable macro-molecular system capable to interact with its surroundings (supply of energy). It involves auto-catalysis that is a process in which the given compound serves as a catalyst of its own synthesis. Certain biopolymers exhibit such an inquisitive property that is basis for self-reproduction, i.e. the feature enabling agglomerates of molecules (possessing similar starting capability—concentration) to develop preferentially for those molecules that grow to become dominant (morfogenese) [4–6]. It means that a particular linear sequence of nucleotides must code for non-random sequences of aminoacids having auto-catalytic properties furthering their replication to provide a preferential reproduction. Other coding than provide less effective proteins and their replications are proceeding more slowly. By mutual co-operative actions of such autocatalytic reactions a larger self-regulating system can be created (gastrulation) to show the cyclic reproduction, exhibiting fixed time of repetition [4,6] as an important attribute of life. Enzymes that are big proteins molecules acting as biological catalysts and accelerating chemical reactions without being consumed by them play most important role. Their activity is specific for a certain set of chemical substrates and it is dependent on various boundary conditions (concentration and acidity-pH of reactants) and interactions with its surroundings (input fluxes of heat and mass and/or force fields such as gravity or temperature). The system is evidently far from its equilibrium and its fertile behavior cannot be explained by the classically viewed equilibrium thermodynamics that is sufficient to describe the formation of stable static structures (as crystals). Unlike ordinary static equilibrium states, such self-catalyzed states that are created away from the equilibrium are unstable because a small perturbation may lead precipitously to new states rich in their variety. It can be seen not only within the biological systems above mentioned but also in less known, but not less significant systems in physical and chemical world of inorganic substances [7–9].

As said before in chemical kinetics we are typically looking to reveal reaction mechanism within the inspection of the processes sequential progress (and for solid-state reactions also for its spatial distribution). For a simplified description we can use various equations suitable to globally monitor wide variety of auto-catalytic reactions (models suitable to match overall phenomenology) often completed by non-integral exponents acknowledged in the fractal geometry [10–12]. However, the aim of our contribution is contrary. We shall try to look at the reaction mechanism from another point of view not searching for the sequential progress but looking at the oscillation regularity and possible links that may join various oscillatory regimes and patterns by a generalized numerical constant, similarly to the Feingenbaum constant of convergence (equal to 4.6692016) determined to hold for various geometrical functions.

2. Oscillatory regimes in some inorganic systems

For example it is well known that resistors carrying large electrical current can exhibit negative differential resistance, i.e. currents that even decreases with increasing voltage supporting oscillations, rather than steady currents. Another example may be shown when studying instabilities that occur in thin wafers in certain semiconductors (GaAs). If the electrical potential across the semiconductor exceeds a critical value the steady current that is stable at lower potentials, abruptly gives way to periodical changes in the current, often called Gunn oscillations [13]. Statistics show that the stability of such a non-equilibrium steady state is reflected in the behavior of the molecular/atomic fluctuations that became larger and larger as the steady state becomes more and more unstable finally becoming cooperative on a long-range order. In many cases this effect is hidden by our insensitive way of observations, particularly for those reactions that we let start far from equilibrium first to exhibit non-equilibrium phenomena but latter either decaying (disappearing) close to its steadiness or abruptly stopped (freezed-in) by quenching (renowned amorphous state of non-crystallites).

Inorganic solid-state reactions are often assumed to proceed via branching [14]. Let us assume a simple case of synthesis known in the production of cement assuming ideal and real reactions hypothetically supposed to follow processes taking place during silicates formation [11,15]. There are two starting solid reactants A (CaO) and B (SiO_2) undergoing synthesis according the scheme shown below (left) to yield the final product AB ($CaSiO_3$) either directly or via transient products A_2B ($CaSi_2O_4$) and A_3B ($CaSi_3O_5$). The formation of these intermediate products depends, beside the standard thermodynamic and kinetic factors, on their local concentrations. If A is equally distributed and so covered by the corresponding amount of B the production of AB follows standard kinetic portrayal (left headed arrow). For a real mixture, however, the component A may not be statistically distributed everywhere so that the places rich in A may effect the reaction mechanism to prefer the formation of A_2B (or even A_3B) the latter decomposition of which is due to delayed reacting with deficient B that is becoming responsible for the time prolongation of reaction completion. If the component A tends to agglomerate the condition of intermediate synthesis become more favorable undertaking thus the role of rate controlling process. The entire course of reaction can consequently exhibit an oscillation regime due to the temporary consumption of the final product AB, which is limited to small neighboring areas. If the intermediates act as the process catalyst the oscillation course is pronounced showing yet more regular nature. Their localized fluctuation micro-character is, however, difficult to be detected by direct physical macro-observations and can be only believed upon secondary characteristics read from the resulting structure (final morphology):

$$\begin{array}{lcl} \mathrm{AB} \leftarrow \mathrm{A+B} \rightarrow +\mathrm{A} \rightarrow \mathrm{A_2B} \rightarrow +\mathrm{A} \rightarrow \mathrm{A_3B} & & \mathrm{dA} \rightarrow \quad \mathrm{diff} \quad \rightarrow \mathrm{dA} \\ +\mathrm{B}\downarrow \qquad +\mathrm{B}\downarrow & & \downarrow\mathrm{react} \quad \Downarrow \qquad \downarrow\mathrm{react} \\ \mathrm{AB} \leftarrow +\mathrm{B} \leftarrow \mathrm{A_2B} & & \mathrm{dB} \rightarrow \quad \mathrm{diff} \quad \rightarrow \mathrm{dB} \\ \textit{regular} \qquad \textit{autocatalytic} & & \textit{reaction} \Downarrow \textit{interface} \end{array}$$

Local effect of counter-diffusion would become another important factor that may not only accelerate above mentioned oscillations but can often outcome most of the interface reaction (see above scheme on right). As a result many of peritectic and eutectic reactions turn out to be in an oscillatory regime providing regularly layered structures. For example, the directional solidification of the $PbCl_2$–AgCl eutectic [16,17]] is driven by temperature gradient and provides lamellar structure separated repetitively at almost equal lamellae partition (see Fig. 1a). Solidification under microgravity starts with higher undercooling compared with that observed in terrestrial condition obviously due to the lack of convection. Typically gravity enhanced mass transfer leads to the effect of coarsening experienced at prolonged time and often increased temperatures. Similar pattern one can find on many other cases from shall ripening to sediments and variety of biological patterns and there arise a question why this separation is so regular and what are its grounds.

Oscillatory scheme is very important for all lively processes taking place far from equilibrium. The customary case often repeated are the curious circumstances emerging upon heating a thin layer of liquid from below (known as Rayleigh–Bénard hydrodynamic instabilities, see Fig. 2). First the heat passes through the fluid by conduction but at certain, well-defined critical point of intensified heating, the gradient pattern changes spontaneously but abruptly to a self-organized system of almost hexagonal cells. This high degree of their molecular organization becomes possible through the transfer of energy from microscopic thermal motion to macroscopic convention currents acting under the force field of gravity. Even more important is the domain of oscillatory processes common in chemistry, particularly known as the Belousov–Zhabotinsky (further abbreviated as BZ) reaction [7–9,18] (see Fig. 3).

These processes were successfully simulated by use of computers. Most famous is the scheme known as "Brussellator" [1,8,19] describing so called cross-catalytic reactions involving two reactants A and B and two products Z and P. The intermediates are X and Y and the catalytic loop is caused by multiplication of the intermediates X, see scheme below. Right graph

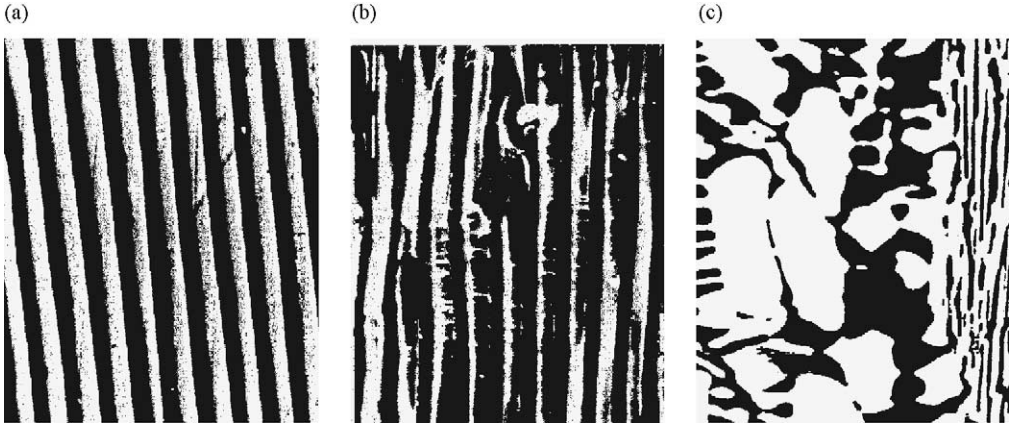
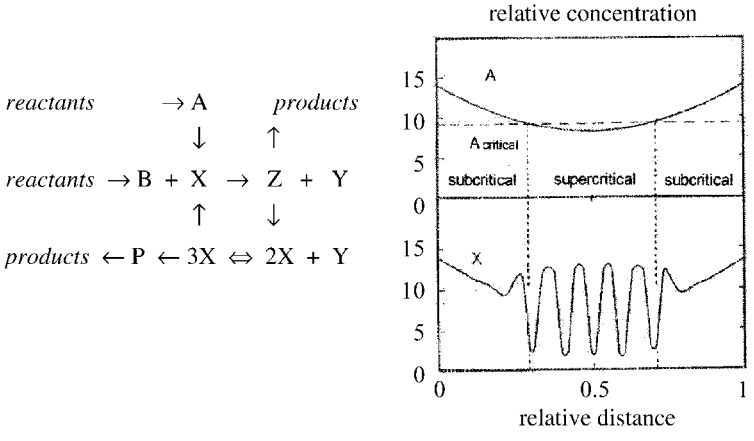


Fig. 1. (a) Quenched-in morphology of the directionally solidified dielectric eutectic of $PbCl_2$–AgCl processed at a high melt undercooling ($\Delta T = 50$ K) and growth rate ($v = 10$ mm/h) at both the terrestrial conditions ($G_0 = 1$, right) and microgravity ($G_0 \to 0$, left). It reveals the oscillatory growth of $PbCl_2$ lamellae in the crystallographic direction [1 0 0] parallel to the reaction interface (on the left-side of photos). (b) The lamellae that solidified directionally at terrestrial conditions exhibit, however, characteristic growth defects due to the interference of mass flow with gravitational field that is absent for the space experimentation. (c) Time-dependent effect of lamellae coarsening providing thus a common morphology pattern often achieved for prolonged equilibration (not in scale).

illustrates the input effect of reactant concentration within the given reaction mechanism (at the threshold concentration of A the steady subcritical region changes from the sterile to the fertile course of action capable of oscillations in supercritical region. Although first assumed hypothetically it enabled to visualise the auto-catalytic nature of many processes and gave to them the necessary practical dimension when applied to various reality situations:



Latter this scheme was associated to be close to the system of the glycolytic energetic cycles where the oscillatory intermediates are adenosintriphosphate (ATP) and adenosindiphosphate (ADP).

In concluding we would like to stress out that herewith we shall try to be consonant with familiar Prigogine's generalized ideas of self-organization dealt with on different levels [8,20]. The enormous collection of experimental data on the behavior of BZ waves published throughout the literature represents a very good opportunity for a better tuning of this concept as we attempt to do it in the forthcoming text although we are aware that any break in the traditional

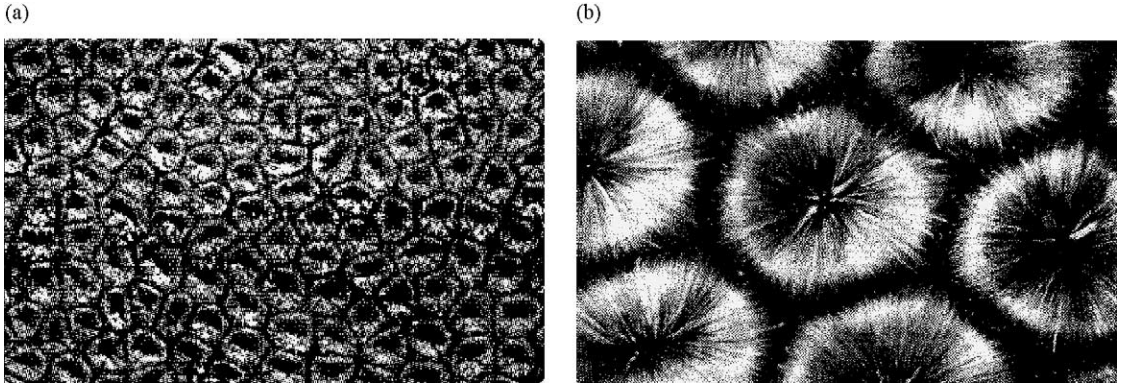


Fig. 2. The honeycomb Raylleigh–Bénard hydrodynamic temperature instabilities due to the interplay of macroscopic-scale currents driven by supply of heat (upwards convection) and gravitational field (downwards convection) and acting under the hindrance of viscosity: (a) global view of cells; (b) detailed view of a cell.

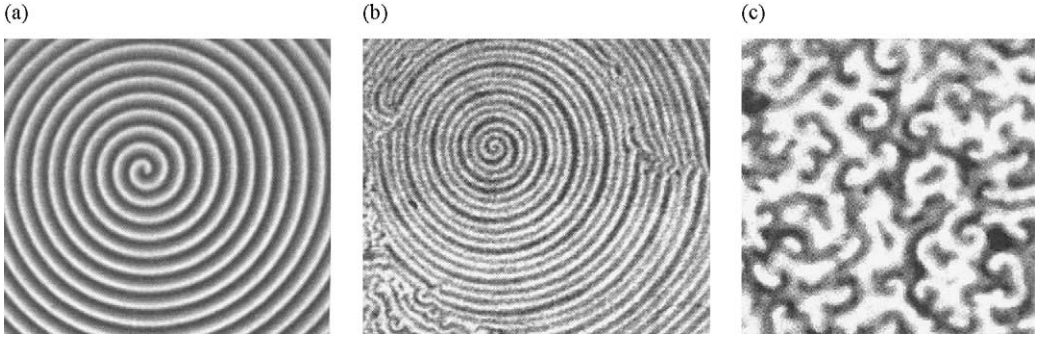


Fig. 3. The rotating spiral wave as a simple case of a reaction–diffusion pattern a kind of BZ two-dimensional waves experimentally observed for the system H_2SO_4–$NaBrO_3$–$CH_2(COOH)_2$. Illustrative example shows co-rotating (retrograde) meandering wave shaped in spirals to appear at low malonic acid concentration: (a) the spirals undergo retrograde meandering which for higher concentration turns opposite. At low sulfuric acid concentration the spiral are stable while for higher concentrations the distance between the successive wavefronts starts to vary spatially until a large number of small spirals around the edge of the stable spiral emerge; (b) this process can lead to the turbulent state beyond the convective instability of the spiral; (c) enlargement of the turbulent region is called as the Eckhous instability which is a quite common phase instability of yet periodic pattern (not in scale).

world of physics would be extremely difficult as it was not accepted yet despite several attempts during the past decades. We ventured to coin here the term *diffusion action, which* expresses the quantity of action induced by diffusion process of Brownian particles. The experimental values of the diffusion actions of the one-dimensional BZ waves might support the theoretical approach that attempts to interpret the concepts of quantum mechanics based on the behavior of Brownian particles [21,22]. The variety of its description about finding mutual links is the goal of this article while the mathematics of non-equilibrium thermodynamics was discussed by us elsewhere [23].

3. Historical views

The non-linear coupling between reaction and diffusion of ions with their concentrations in the range from $\sim 10^{20}$ to $\sim 10^{23}$ ions per dm^3 leads under some circumstances to the appearance of chemical waves. When a Russian scientist B.P. Belousov discovered in the year 1952 such a spontaneous product of self-organization

in the form of coaxial rings taking place in some chemically reacting system it took him several years to persuade officials to believe it. He was able to publish his finding in an obscure non-reviewed journal [24] only and later stopped his further scientific research at all. The reaction was followed and improved by Zhabotinsky et al. [25].

We should remind that the basic system consists from one/electron redox catalyst [Ce(III)/Ce(IV)], an organic substrate that can be easily brominated and oxidized (citric acid), and bromate ions in the form of $KBrO_3$ dissolved in sulfuric or nitric acid. It is worth to mention that colloid chemists obtained the defined periodic precipitation patterns a long time ago. Ord [26] prepared one-dimensional precipitation patterns in 1879, Pringsheim [27] introduced the concept of osmotic pressure to this field in 1895, Liesegang [28] prepared two-dimensional patterns in 1896, Leduc [29] developed the concept of osmotic pressure waves, as well as many other researchers contributed significantly to understanding of this subject. Nikiforov [30] in 1931 proposed to characterize the spatial and temporal development of chemical waves by the principle of the least action expressed by Maupertuis [31] in 1744, citing: ''*when some change takes place in nature, the quantity of action necessary for the change is the smallest possible. The quantity of action is the product obtained by multiplying the mass of the bodies by their velocity and the distance traveled*''. So far more than hundred different combinations of cations and anions were employed to approve so called Liesegang's ring formation [32,33] in the liquid phase all of them matching the quantities of action in the order of $\sim 10^{-34}$ J s. Accounting for the experimental difficulties in the estimation of mass of diffusing units (irreversible formation of clusters) the coincidence with the Planck quantum constant is striking but yet assumed accidental. It was not discussed properly enough as the Planck constant is firmly associated with microcosms of fundamental particles thus difficult to believe that its soundness can be extended to the macrocosms of diffusing molecules and even further on formation of deposits.

Latter such a self-organization attracted deserved attention in a wider analysis of time-symmetry breaking associated with the emergence of time-periodic solutions known as limit cycles whose period and amplitude are stable and independent of the initial conditions. The importance of self-organization was approved as they can constitute models of rhythmic phenomena observed in nature, beside such chemical clocks in [9] more important biological or other evolution processes [4,6,34,35]. It became a model focus in generalized theory of chaos expressing its minute ordering. Curiously even the attempt to imagine a self-organizing ether (primeval matter) became also source of a related ''reaction-diffusion model of space-time creation'' [36] based on 1887 Cu-t'ung subatomic wave theory (bipolar ether of mutually transmuting states of opposites) to recently even compete the traditional idea of ''Big Bang'' theory.

Such stable rotating waves observed in this classical (ZB) reaction results from the possibility of cascade splitting (called bifurcation) which opens the way to gradual increase of complexity by a mechanism of successive transitions, leading either to the loss of stability of a primary branch and the subsequent evolution to a secondary solution displaying asymmetry in space and/or in time. It is worth mentioning that such transitions are sometimes accompanied by some remarkable trends, e.g. certain classes of reaction-diffusion systems under zero-flux boundary conditions may exhibit no net entropy production change when the system switches from the thermodynamic branch to a dissipative structure [22]. On the other hand there is a systematic decrease in entropy in the vicinity of bifurcation points known in the associated fields chaos [37,38] touching even traditional field of predicting weather. It is clear that a lot of research was given to the detailed observation of properties of these chemical waves and a great number of theories were proposed in order to characterize the behavior of these structures. From the mathematical point of view such systems becomes localized at the thermodynamic branch and the initially stable solution of the appropriate balance equation bifurcates and the new stable solution(s) suddenly appear (likely to overlap) [8,22].

4. Diffusion action of Brownian particles

There were many attempts to interpret the concepts of quantum mechanics based on the behavior of Brownian particles [39,40]. Several groups of colloidal chemists started to evaluate Liesegang rings formation by the principle of the least action after the

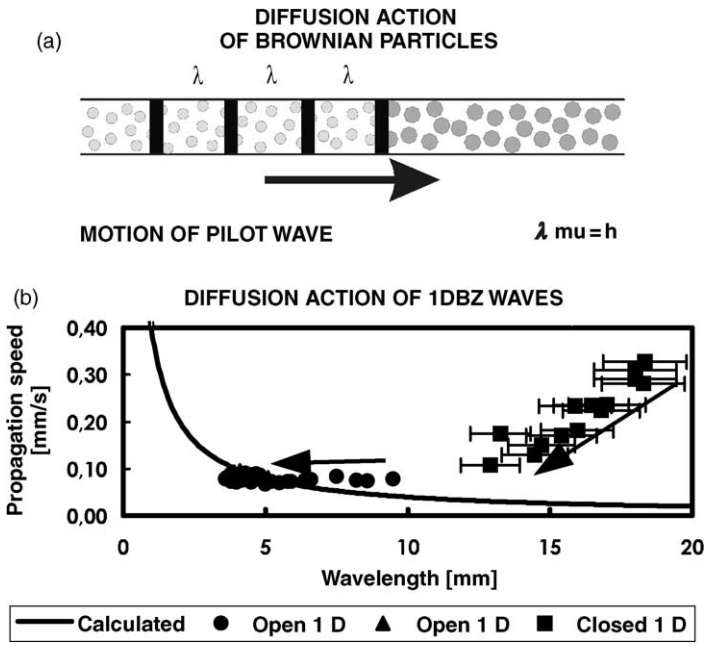


Fig. 4. (a) Self-organized wave of Brownian particles diffusing into the surroundings; (b) one-dimensional propagation of BZ waves in thin tubes in water solutions (●) open glass and Plexiglas tubes (Tatterson and Hudson, [44]) (■) closed glass tubes (Winfree, [45]). The arrows show a tendency to minimize diffusion action of successive waves during the prolonged time. The solid curve was calculated from the principle of least action ($K = 1$, $\kappa = 1$) and approaches the numerical value very close to the Planck constant for given system (product of wavelength and diffusion speed).

year 1931. Liesegang rings precipitate from collections of cations and anions in liquid phase in the presence of some gel forming agents in order to stabilize patterns in the reaction space. Liesegang patterns could be formed from vapor and solid phases and ordered layered and lamellar microstructures can be obtained during the eutectic and peritectic solidifications [16] (cf. Fig. 1).

Fig. 4a depicts the penetration of cations with their mass m into the surroundings containing anions. The concentration of cations increases along the diffusion path λ until the local osmotic pressure of these waves overcomes the pressure opposed by the surroundings. Thus, the symbol λ describes a path necessary for the accumulation of Brownian particles in order to overcome the pressure of the surroundings. The symbol λ was interpreted as a wavelength of individual Brownian particles in earlier interpretations in the period 1931–1939. In this contribution the symbol λ describes the collective properties of penetrating Brownian particles into their surroundings from their source. The value λ depends not only on the penetrating Brownian particles, but it can be influenced by the osmotic pressure of the surroundings (composed from both ions involved in the reaction and other active particles, temperature, pH, gravity, etc.) and geometrical arrangement of the diffusion process.

When the concentrations of cations and anions have been properly selected, then the local osmotic pressure (supersaturation) creates stable nuclei and starts their growth. The velocity, with which the diffusion field penetrates into the surroundings, is described as the propagation velocity u. The action of diffusing ions depends also on the geometrical arrangement of the experiment—on the dimension of the diffusion experiment K and this diffusivity factor describes the random Brownian motion in the space available for the chemical wave. For one-dimensional space (thin glass tubes) $K = 1$, for two-dimensional space (thin layer in a Petri dish) $K = 2$, in case of three-dimensional diffusion experiment the value of K depends on the space angle available for diffusion of Brownian particles

from their source. If the whole space is available for the propagation of the chemical waves, then $K = 4\pi$. The principle of the least action for collections of Brownian particles penetrating into their surroundings is expressed as the product:

$$K \times m \times \lambda \times u = h. \quad (1)$$

Field et al. [41] published a detailed study of the chemical mechanism behind the BZ reaction. This contribution revealed a complicated interplay among the individual components of the recipe. In 1974 Field and Noyes [42] measured the propagation velocities of bands in the BZ reaction in two-dimensional diffusion experiments. These rates were nearly proportional to the product $[H^+]^{1/2}$ $[BrO_3^-]^{1/2}$ and were almost independent of the concentrations of other species in the system. For the description of chemical waves by the principle of the least action the mass of diffusing units m, responsible for the appearance of the concentration waves, has to be exactly determined. The ion H^+ shows the highest mobility among the cations and anions of the BZ recipe and may create the osmotic wave in the direction from the center of the propagation of the observed bands and to start the wave propagation into the surroundings. Tockstein and Treindl [43] reviewed many variations of the original BZ recipe and concluded that the presence of the H^+ cation was necessary for the appearance of these oscillations. This idea can be easily experimentally confirmed or disprove because all quantities: K, diffusivity factor, m, mass of H^+ cations responsible for the osmotic wave, λ, distance between bands, u, propagation velocity of bands are for the BZ waves available with a reasonable experimental error.

5. One-dimensional diffusion action of the Belousov–Zhabotinsky waves

In excitable media periodic waves are known to travel at a propagation speed u that represents the product of the distance between patterns λ and their frequency ν (or its reciprocal value period T). The relation between propagation speed and period (wavelength, frequency) of successive BZ waves, known as the dispersion relation, is important to a better understanding of wave properties. The dispersion relation in the form of the dependence of the propagation speed u on the wavelength λ of that wave gives the best idea about the diffusion action of penetrating wave into the surroundings.

Tatterson and Hudson [44] substantially improved both the recipe of BZ reaction and the technique for a well-documented observation of the dispersion relation in one-dimensional reaction space. They used a stirred tank as an oscillating source whose frequency could be controlled by the intensity of stirring. The waves, emitted from this tank, penetrated into the attached glass or Plexiglas tubes and one-dimensional propagation of waves were observed and measured potentiometrically. Their experimental arrangement served as a reproducible and controllable source for the waves from outside into the diffusion tube. Winfree [45] filled a capillary tube with BZ reagent and stimulated a random sequence of waves in the closed tube and measured the dispersion relation of the successive waves. The experimental results from both open and closed diffusion systems are summarized in Fig. 4b together with a theoretical curve calculated from the previous Eq. (1). The data obtained by Tatterson and Hudson in their open one-dimensional diffusion experiment give a surprising agreement with the value of the quantum of action. There is an observable departure of quantities of action of waves with longer wavelength from the curve because the detector was placed only 12 mm from the entrance and the diffusion field could not self-organize itself to reach the value of the least quantity of action. This type of observation of BZ waves appears to be very useful for an estimation of the concept of the diffusion action of chemical waves because all four parameters, which have to be determined experimentally, can be easily evaluated: $K = 1$, $m_{H+} = 1.674 \times 10^{-27}$ kg, λ and u are determined with an error of few percents. On the other hand, the spatial propagation of BZ waves in a close tube is different because the diffusion field of H^+ (self-organization of randomly moved Brownian particles) is not the same in closed and open systems. Moreover, the dataset of propagation of waves created in Winfree's one-dimensional experiment in closed glass tubes are available only from a secondary source and the details of experiments are not known. Nevertheless, the quantities of action of successive one-dimensional waves in their sequence tend to reach the attractor (quantum of action), as it was found for two-dimensional BZ propagation in closed systems, too.

The future experiments may bring more accurate data describing the quantities of action of successive one-dimensional trigger BZ waves. The analysis of two and three-dimensional cases verified the validity of the above concept and are the subject of our simultaneous communication elsewhere [46].

6. Discussion and conclusions

Under certain conditions the randomly moved collections of Brownian particles may self-organize themselves as propagating waves that penetrate into the surroundings in the form of stripes, circles, semicircles, spirals, etc. The principle of the least action, introduced into the science as early as in 1744, may be still considered appropriate for the interpretation of the propagation of those waves of Brownian particles. The product of diffusivity factor K, tortuosity factor κ, mass m of particles creating the expanding osmotic wave, propagation speed u with which the wave emanates, and the wavelength λ—a distance necessary for the accumulation of Brownian particles in order to overcome the opposing pressure of the surroundings—gives a value of the quantity of diffusion action of that propagating wave. The interpretation of the quantities of diffusion action of BZ waves by this concept supports some earlier contributions stated, that the Planck quantum of action could naturally emerge as a fundamental property of self-organized collectives of Brownian particles. The famous BZ waves represent a type of chemical waves driven by the osmotic wave of H^+ cations that have a very high mobility in water solutions. Cations H^+ do not create clusters in water solutions and keep its m_{H+} constant during the propagation of BZ waves.

The one-dimensional (thin tube, $K = 1$, $\kappa = 1$) arrangement of BZ wave propagation in water (non-restricted) media enables to tune the value of the quantum of action of BZ waves to the range $6.63 \pm 0.06 \times 10^{-34}$ J s. The experimental error of parameters of BZ waves obtained by recent techniques is about 1%. Dispersion relations of BZ waves show a strong tendency of successive waves to reach a minimal quantity of their diffusion action. The dimension of space, characterized by the diffusivity factor K, has to be taken into account in non-restricted media to characterize the space available for emanation of wave from its source. The path of Brownian particles becomes more tortuous in restricted media, so that the tortuosity factor κ of those media should be used together with the diffusivity factor K to express this more complicated geometry of space available for the penetration of BZ wave. The successive waves in restrictive media tend to reach to a minimal quantity of diffusion action, too. The principle of the least action may be helpful to interpret the behavior of perturbed BZ waves that return reversibly to the original value of their quantity of action, when the perturbation source is switched off. The observed shape transformation of BZ spiral wave into the target wave and the transformation of trigger target wave into the phase wave seem to be related to the least quantum of action in non-restricted media. It is somehow related to the long lasting discussion on intramolecular diffusion and calculation of unimolecular velocity constants factually analyzing quantum mechanics as a classical diffusion process [47–49]. Before the acceptance of this scenario within the frame quantum mechanics [50], some other systems should be evaluated by this principle of the least action. The next candidates of self-organized Brownian particles may be electrons forming stripes in Crookes tubes filled by inert gases and atomic waves prepared recently from atoms of alkali metals diffusing through tubes filled with inert gases.

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