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Heterogeneous chemical kinetics in two dimensions: two ways of discrete description[1]

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Abstract

Two different basically two-dimensional discrete approaches to describing solid-phase reaction kinetics are introduced and compared. These are the cellular automata approach and concentric belts approach, both in terms of Dirichlet tessellations. They have the same conceptual roots in the issue of representing the chemical individuality of a solid reagent in a mathematical model. Only deterministic aspects of solid-phase reaction kinetics are considered as originating largely from the suggested approaches.

Keywords: Cellular automata; Chemical individuality; Concentric belts; Dirichlet tessellations; Reaction dynamics

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1. Why in two dimensions? A geometric representation of chemical individuality

Attempts to make progress in simulating one or another phenomenon at the expense of reducing the dimensionality not infrequently implies that a mathematical model itself requires the appropriate simplification to become treatable. This is not so for the geometric–probabilistic formalism now in use in heterogeneous chemical kinetics [1–6]. One of its most distinctive features is its independence from dimensionality [5, 6] — in passing from three to two dimensions it becomes neither simpler nor more involved.

The main reasons why a mathematical description of a heterogeneous chemical reaction must be basically two-dimensional become explicit in analyzing the failures of experimental data interpretation. One of the conclusions is that the geometric–probabilistic approach is essentially ambiguous with respect to IKP (Inverse Kinetic

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[1] Dedicated to the memory of Professor I.V. Krivoshey.

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Problem) solution [7]. In thinking over the problem we arrive at the necessity to put forth special efforts for providing the "discriminability" of mathematical models through representing a solid reagent as the chemical individual. As far as the kinetics of chemical interactions are concerned, these are just the chemical considerations that could not be dispensed with. This leads us from conventional polydisperse polycrystalline samples to single crystals and further to a single crystal face as a chemical individual [8–10]. In its turn, this determines the need to operate not only with the concept of composition, but also with the concept of crystal chemical structure.

Though at first glance the arguments in favour of a 2D approach fall into "conceptual" and "formal mathematical" ones, in searching for a description of heterogeneous kinetics that is capable of taking the chemical individuality of a solid reagent into account one recognizes their deep interrelationship. The aim of this (and partly the next) section is not to add new arguments to those used previously [7–10] but to emphasize this interrelationship and try to get at its roots in the context of a geometrical representation of chemical individuality.

The chemical individuality of a (bulk) solid reagent may be taken into account in geometrical terms of the crystal lattice. In these terms, atoms of a particular type in the crystal structure occupy positions of the same regular system of points (RSP), i.e. equivalent positions [11]. However, these positions are equivalent only when there is no surface, and in the case of a localized solid-phase reaction, proceeding through the formation and growth of nuclei, one or another surface is always present; the reaction front advances along the surface and into the bulk which differs materially. Solid-phase reactions are multiform, and those proceeding within the bulk alone are mentioned in the literature along with those starting at a surface [4, 12]. From the present viewpoint the former are "more involved" than the latter in the sense that mathematical description of the former should be based on the mathematical description of the latter, and must anyway be basically two-dimensional. Using three-dimensional models we deprive ourselves of the possibility of taking into account the non-equivalence of surface and bulk positions of RSP with respect to the advance of the reaction front.

We should remind ourselves that a solid-phase reaction includes as an inherent stage the disintegration of the crystal structure of a solid reagent (the growth of a negative crystal) [9]. Hence its dynamics, as well as the way of formalizing it, depend to a considerable extent on factors which depend on which atoms of a solid reagent form this regular structure. Though these factors have been discussed intensively for quite a number of years, we still have no final answer. Thus, according to Ref. [13] the crystal symmetry cannot be represented in terms of quantum theory alone. In addition, we understand in the framework of synergetics how tremendous the distance is between the microscopic factors and the large-scale structure [14, 15]. In this context the increasing significance of the "geometrical outlook" becomes evident: now the geometrical model of a crystal may hardly be treated merely as the unavoidable limiting simplification of its physical model. (Note in passing that within this logic is the complete classification of all possible types of crystal symmetry, irrespective of particular details of composition.) With this in mind, we resort to the following consequence of the so-called local theorem [16–18]: from the viewpoint of geometry the regularity is determined by interactions between immediate neighbours, i.e. by *local interactions*.

The suggested formalization of solid-phase reaction dynamics is based essentially on this statement. Also, this makes even more explicit the above arguments in favour of the 2D approach: surface and bulk atoms have nearest neighbours in different configurations, and surface RSP may not coincide (and often do not coincide) with bulk RSP.

Therefore, conceptual and formal arguments in favour of a two-dimensional approach converge in the context of a geometrical representation of the chemical individuality of a solid reagent, and it becomes clear that from both chemical and mathematical viewpoints the description of a solid-phase chemical reaction must be essentially two-dimensional.

One more aspect has to be taken into account here. In formalizing the dynamics we must agree the geometry representing the chemical individuality with the geometry determined by the existence of growing nuclei (that originally gave birth to the geometric–probabilistic approach). From this viewpoint an obvious shortcoming of a crystal lattice is the lack of a natural extensional measure. This may be eliminated by representing the crystal structure in terms of Dirichlet tessellations, which are also closely connected with the above geometrical considerations including the local theorem.

2. Dirichlet tessellations: from geometry to dynamics

Thus, the chemical individuality of a solid reagent finds proper representation in terms of the geometry of the crystal space. To integrate the chemical individuality into dynamic models, they must conform with this geometry. From general considerations, the way of doing this is not unique. *With the account of the above local character of interactions, we will use the notion of adjacency to link Geometry and Dynamics.* A single crystal with a surface will be treated as a set of crystallographic planes [19], each of them being represented in terms of Dirichlet tessellations [20–24]; this enables one to formalize the notion of adjacency: two points, p_j and p_k of a discrete set of points $\{p_i\}$ are termed adjacent if their Dirichlet domains have a common side.

In a real Euclidean plane, a tessellation is an arrangement of points, line-segments and simple polygons (called vertices, edges, and faces) such that every edge joins two of the vertices and is a common side of two faces [21]. Denote by D_k a geometric locus the points of which are closer to some point p_k than to any other point of $\{p_l\}$. This is just the Dirichlet domain or the domain of action of p_k; the point p_k itself is termed the centre of action. (In the case of three and more dimensions D_k is termed the Dirichlet–Voronoy domain.) A Dirichlet domain is always convex, and in totality these domains D_i form a tessellation, i.e. fill and cover the plane simultaneously. Note that a Dirichlet tessellation is normal: no vertex of a polygon is the interior point of a side of another polygon.

In our context a significant advantage of this mathematical notion is the possibility of treating fairly independent factors of solid-phase reaction dynamics in one and the same terms of Dirichlet domains using simultaneously their different varieties: planigons [21, 22], Wigner–Seitz cells [23], and random mosaics [24]. Thus, representing the (ideal) crystal structure in terms of planigons and point defects in terms of random mosaics, we thereby separate the deterministic part of the problem from its stochastic part [9, 10], which is one of the main steps in developing a formal description. Following the same logic, we associate the advance of the reaction front with the translational symmetry of a reagent, separating it in terms of Wigner–Seitz cells [9].

In so doing, we use the interrelationship between different varieties of Dirichlet tessellations constructed for the same single crystal face. They are illustrated in Fig. 1, which may be considered as a crystal face divided by heavy lines into the cells of a random mosaic.

The random mosaic is a Dirichlet tessellation for a random Poisson ensemble of points that in our context represent point crystal defects (both equilibrium and non-equilibrium). It is characterized by the typical polygon which is a hexagon (e.g. the central cell of Fig. 1). As many as three edges meet at each vertex of a random mosaic [24]. In the framework of the developed approach random mosaics are used for simulating the processes of nuclei origin.

The planigon is a finite figure associated uniquely with the corresponding RSP: a point of an RSP is the centre of action of a planigon. In the random cell (a) of Fig. 1 the planigon tessellation corresponds to the p3 symmetry group [22]. Planigons are not obligatory Dirichlet domains, but we will be interested in the Dirichlet domains, for

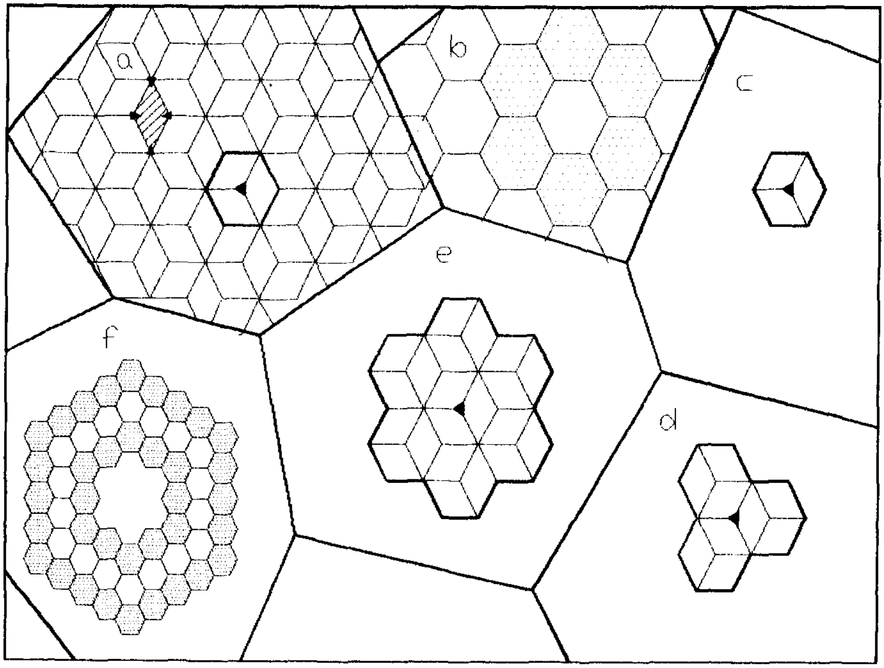

Fig. 1. Interrelation between different types of Dirichlet tessellation for a single crystal face, and their use in describing solid-phase reaction dynamics. The random mosaic is shown by heavy lines. The random cell (a) shows the planigon tessellation; the random cell (b) shows the Wigner–Seitz tessellation. A separate nucleus in cells (c–e) is growing according to the cellular automaton rule stated in Section 3. Three concentric belts in cell (f) illustrates the alternative approach (Section 4).

general RSP alone. The complete theory of planigons may be found in Ref. [22] including the necessary and sufficient conditions for a planigon to be a Dirichlet domain. A planigon is the fundamental region of one of two-dimensional Fedorov groups and may have three to six edges. As many as 46 types of planigon tessellation correspond to only 17 two-dimensional Fedorov groups. Planigon tessellations are always regular. Symmetry elements may be situated at planigon boundaries and never inside a planigon. Any infinite planigon tessellation is characterized completely by its finite part which is a consequence of the local theorem [16–18] and, in its turn, is used for formalizing the solid-phase reaction dynamics.

The parallelogon is a polygon consisting of planigons according to their symmetry and such that a tessellation of the plane may be obtained by translating it in two directions [11]. In Fig. 1a the parallelogon is shown with a heavy line. Only parallelograms of all types and hexagons, each side of which has an opposite equal side, may serve as parallelogons. Note that a parallelogon is associated with no centre of action and hence is not a Dirichlet domain.

The Wigner–Seitz cell is the Dirichlet domain for a lattice (not RSP) point [11, 18, 23]. It is one of possible (and widely used) elementary cells possessing the symmetry of a Bravias lattice. Its role in the present context is determined by the fact that the translational symmetry is represented completely in terms of Wigner–Seitz cells. A Wigner–Seitz cell may be either hexagon or rectangle, and each type of translationally non-equivalent point is represented by one point inside it. For some crystal structures the Wigner–Seitz tessellation may coincide with the parallelogon tessellation. Fig. 1 shows one example: the hexagonal cells of the Wigner–Seitz tessellation shown in Fig. 1b coincide with the parallelogon shown with the heavy line in Fig. 1a. But this situation is not general, which is material for formalizing the solid-phase reaction dynamics. One example of a mismatch will be given below; another may be found in Ref. [9].

Within the developed approach the main conceptual emphasis is on the planigons. In addition to the above considerations this is due to the important possibility of taking into account the combinatorial–topological structure of a crystallographic plane along with its symmetry [18, 21, 22]. It is this peculiarity that provides the detailed classification (46 types of planigon tessellations vs 17 2D Fedorov groups) and hence the adequate enough representation of the wide variety of crystal structures. The combinatorial structure is represented by 1-skeleton or net $N(T)$ corresponding to a tessellation T. This is the graph consisting of nodes, or vertices (where three or more faces meet) and edges (where two faces intersect). Two objects with the same net may not have the same symmetry (e.g. quadrate and parallelogram). But even if the symmetry is the same, symmetry operations may act in different ways on different nets [17, 22]. Each of 46 planigon types is a definite combination of the symmetry and combinatorial–topological structure. This feature of planigon tessellations enables one to start with the topological aspects of dynamics, bearing in mind the further metrization in the logic of measure assignment.

Two conceptually different ways of formalizing the solid-phase reaction dynamics are connected with the use of Dirichlet tessellations: in terms of cellular automata and in terms of concentric belts. Both of them are discrete and have their roots in the deterministic part of the problem [9], i.e. concern first of all the unrestricted growth of a separate negative crystal (prior to the very first impingement with an edge of its random cell in Fig. 1).

3. Cellular automata approach

This approach may be considered as an alternative to the conventional continuous description of solid-phase reaction dynamics. Cellular automata (CA), first introduced by von Neumann and Zuse in the late forties, are mathematical idealizations of physical systems in which space and time are discrete, and physical quantities take on a finite set of discrete values. Main distinctive features of CA are uniformity and distributivity [25–29].

What are the reasons for expecting progress in simulating and understanding solid-phase reaction dynamics using CA? From a broad spectrum of arguments, from philosophical to computational, that may well constitute the subject of a separate discussion, the following seem to be mostly sound in the present context.

(1) The credo of the present approach is to deal with the chemical individual. In formalizing this concept the idea of discreteness is one of the axioms [11, 17, 18].

(2) Cellular automata are discrete spatially distributed dynamic systems the behaviour of which is determined completely in terms of local interactions [25, 26], which is in line with the above considerations. Chemical processes in which a single crystal face participates as one of the reagents are the peculiar example of such dynamic systems in the sense that the crystal lattice is the creation of Nature.

(3) If a mathematical model is sufficiently involved, one cannot exclude that it demonstrates the expected behaviour partly because this behaviour itself is "embedded" into it [26]. This is the case to a degree for conventional geometric–probabilistic models now in use for demonstrating the sigmoid form of α–t curves. But this cannot be the case for a CA the construction of which is extremely simple: the state of a cell is determined by a simple rule depending on the state of neighbouring cells.

(4) Despite the simplicity of their construction, CA are found to be capable of very complicated and interesting behaviour [25, 26] and hence are adequate for simulating the wide variety of observed localization forms (in contrast with continuous models).

(5) CA are used efficiently for simulating the kinetic aspects of phase transitions [27, 28] that always accompany solid-phase chemical reactions. (In passing we remind ourselves that continuous geometric–probabilistic formalism was developed originally for first-order phase transitions, with no chemical transformations being implied).

At first glance, the analogy between a regular two-dimensional crystal lattice and a regular lattice of sites of a conventional CA seems to be not only obvious but also trivial. Nevertheless, in describing the processes under discussion in terms of CA, one faces essential difficulties at the very first step. In our terms, an atom of a crystal structure is represented by a planigon in the centre of action of which it is situated. But planigon tessellations are not uniform (except that for the p1 symmetry group). The required uniformity is inherent to two more large-scale tessellations: Wigner–Seitz and parallelogon tessellations. Their cells may be treated as the cells of CA. Therefore, these are only superimposition of tessellations, each cell of which consists of planigons, that possesses the required features for describing the solid-phase reaction dynamics in terms of CA. These CA will be referred to as planigon tessellation cellular automata (PTCA).

The PTCA thus introduced are more involved than conventional CA in respect of both rules and neighbourhoods. Along with this it is worth emphasizing that they are not defined formally as some arbitrary cells on an abstract plane but are derived from a single crystal face with the account of its symmetry and combinatorial–topological structure. The p1 symmetry group serves in this context as a link with conventional CA: it is represented by quadrangle and hexagonal polygons that are planigons, parallelogons and Wigner–Seitz cells at the same time.

The state of a CA is completely specified by the values of the variables at each site. A cellular automaton evolves in discrete time steps τ, with the value of the variable at one site being affected by the values of variables at sites in its "neighbourhood" on the previous step. The above *local interactions* are represented in terms of CA as a set of rules according to which a unit or a group of units (a planigon or a cell consisted of planigons) may enter an evolving pattern. By in essence a rule R is the dynamic law, i.e. a function that takes the current configuration $C(\tau)$ as the argument and returns the next configuration $C(\tau + 1)$:

$$C(\tau + 1) = RC(\tau)$$

Most frequently it is represented as a Boolean function of the site within the neighbourhood. The neighbourhood of a site is typically taken to be the site itself and all immediately adjacent sites. An example is shown by dots in Fig. 1b.

Note once again that the laws of CA are local and the same at each site. PTCA offer broad possibilities for formulating fairly different rules that are adequate to the wide variety of the observed localization forms. With the view of peculiar construction of PTCA, the composite rules [26] are of especial interest, when the first step is made according to R_1 rule, the next step is according to R_2 rule, and so on in a definite sequence. The result is the "superrule" possessing properties differing materially from that of R_i. *According to the above considerations we will be interested first of all in the rules that are capable of taking into account and making explicit the distinctions between translational and non-translational (point) symmetry of a crystal lattice in respect of the advance of the reaction front.*

Let us refer again to Fig. 1 showing one of two possible planigon tessellations for the p3 symmetry group. Planigons in this case are rhombs [22]. All vertices of the planigon tessellation bear triad axes but fall into two types depending on whether three or six planigons meet at the given vertex. Wigner–Seitz cells and parallelogons coincide in this case, each containing three planigons. One of the simplest possible rules may be formulated, for instance, as follows.

(1) Two values, $p = 0$ and $p = 1$, are possible for a planigon depending on whether it (or, more accurately, an atom situated in its centre of action) has entered a reaction.

(2) Only two values, 0 or 1, are allowed for a hexagonal cell also.

(3) The value c of a cell is determined by the values p_i of component planigons, e.g.

$$c = p_1 \oplus p_2 \oplus p_3 \tag{1}$$

where $\oplus$ denotes addition modulo 3.

(4) If a planigon or a cell has taken on the value 1, no further changes are possible for it (monotony condition).

(5) If a cell with the value 0 has in its neighbourhood, shown in Fig. 1b by dots and specified as a set of displacement vectors in the form

$$N = \left\{ \begin{bmatrix} 2 \\ 0 \end{bmatrix}; \begin{bmatrix} 1 \\ 1 \end{bmatrix}; \begin{bmatrix} -1 \\ 1 \end{bmatrix}; \begin{bmatrix} -2 \\ 0 \end{bmatrix}; \begin{bmatrix} -1 \\ -1 \end{bmatrix}; \begin{bmatrix} 1 \\ -1 \end{bmatrix} \right\} \tag{2}$$

at least one cell with the value 1, the reaction front is advanced towards the boundary planigon (Fig. 1d).

(6) Note that this rule preserves the symmetry and "keeps" the reaction front inside the cell until all planigons of this cell have entered a reaction (Fig. 1c). As a result, we get two alternating forms of the evolving pattern (Fig. 1d, e).

Wigner–Seitz cells and parallelogons may coincide (as in the above example) but may note coincide, in which case an essential novelty arises concerning the declaration of neighbourhoods. This is illustrated in Fig. 2. The planigon tessellation (Fig. 2a) corresponds to p2 symmetry group and consists of quadrangles [22]. Two of them connected by a twofold axis of symmetry form the hexagonal parallelogon (line hatching) differing from the rectangular Wigner–Seitz cell (solid line). This suggests that the reasonable neighbourhood of a hexagonal PTCA cell in this case is as shown in Fig. 2a by dots (cf. Fig. 1b where cells are also hexagons). Applying the rule similar to that above, we obtain, after a sufficient number of steps, the pattern shown in Fig. 2b.

In addition to the vast variety of rules that may be formulated for two-dimensional CA [28], and so many more for introduced PTCA with the account of possible mismatch between parallelogons and Wigner–Seitz cells, note also the possibility of obtaining patterns from various nuclei. In the context of simulating the solid-phase

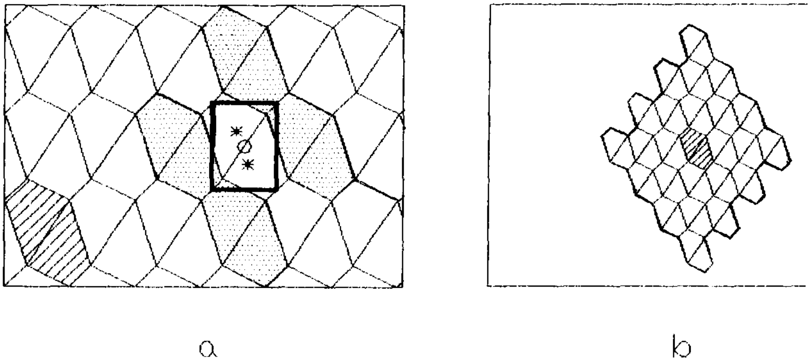

Fig. 2. An example of the mismatch between Wigner–Seitz cells and parallelogons. Explanations are given in the text.

reaction dynamics this is not only the source of even greater variety of patterns but also an important chance to get an insight into some subtle problems of nucleation that typically remain in the shadow within a conventional approach. This may be illustrated in brief with the two following questions.

(1) Can one and the same pattern be obtained from different nuclei? and

(2) Can a stable symmetrical evolution be obtained proceeding from a casual non-symmetric nucleus?

Fig 3a, showing the same planigon tessellation as in Fig. 1, shows the answers to be positive for both questions. Each of two different nuclei shown by the dots consists initially of three planigons and transforms after sufficient number of steps according to the above rule into one and the same pattern (shown on the right). In contrast to the nuclei this pattern possesses a twofold axis of symmetry, which, however, does not coincide with a vertex of the Wigner–Seitz tessellation. Fig. 3b shows one more example of a pattern that may be obtained from at least two different nuclei. Note that one possesses a threefold axis of symmetry. But this axis passes through the vertex of the planigon tessellation where six planigons meet, whereas the corresponding Wigner–Seitz tessellation is constructed around vertexes where three planigons meet. Because of this the resulting pattern has no axis of symmetry.

Finally, PTCA provides efficient possibilities for simulating the impingements of separate evolving nuclei. But their discussion concerns the probabilistic part of the problem and hence is not within the scope of this paper.

4. Concentrated models: topological aspects

The formalism of a cellular automata approach in terms of rules, represented as Boolean functions or even in the verbal form, is deeply dissimilar to the conventional

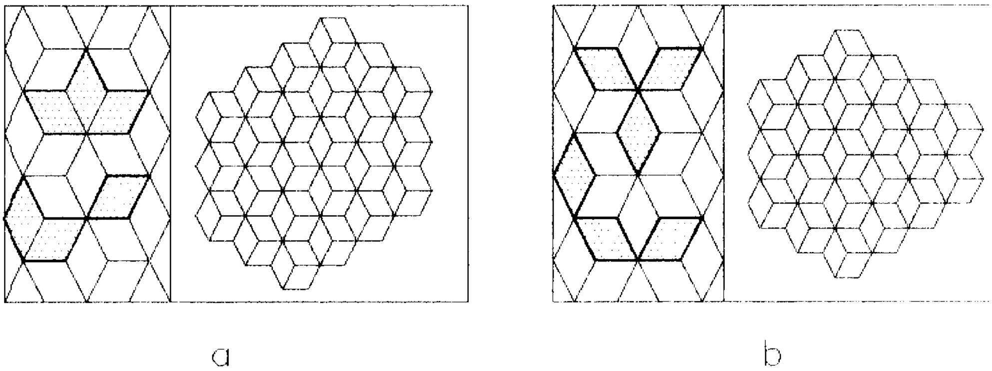

Fig. 3. The same patterns may be obtained from different nuclei using the same CA rule: (a) symmetric pattern obtained from asymmetric nuclei; (b) asymmetric pattern in the case when one of two nuclei is symmetric.

formalism based on a small number of aggregated variables determined on the continuum. At this point we face the philosophy of interrelation between distributed and concentrated models [26]. Nature itself hardly prefers one of these types. The choice is more likely determined by operational efficiency, aims, habits and a number of other similar considerations. On the one hand, the processes under discussion are closer by their character to the discrete distributed dynamic systems. In addition, the use of CA is promising with regard to computational efficiency [26, 28]. On the other hand, however, the way of integrating them into habitual logic of the inverse kinetic problem is far from clear.

In this connection, the possibility of developing another discrete approach, also in terms of Dirichlet domains but with the use of aggregated variables in the framework of more habitual logic of concentrated models, is worth emphasizing. Its conceptual aspects were discussed for the most part previously [9, 10]. Here we will restrict ourselves mainly to the topological aspects leading to difference equations for simulating solid-phase reaction dynamics.

In comparison with CA, the step of the independent variable s, acting as a discrete time, is slightly more large-scale. This enables one to single out the linear part of the problem. The dynamics will be described in terms of concentric belts consisting of the cells of Wigner–Seitz or parallelogon tessellations. Choose an arbitrary cell c_0 with the boundary b_0. All cells (except c_0) that have vertices on b_0 are termed the 1st belt; its external boundary being denoted b_1 (Fig. 1b may again serve as an example). The totality of cells, except that of the 1st belt, having vertices on b_1, is the 2nd belt, and so on.

We proceed from the premise that the propagation of a chemical reaction from the given cell to all its neighbours is equiprobable on this scale and, consequently, occurs simultaneously. The substantiation of this, as well as the explanation of what is the "propagation of interactions" were given in the previous paper [9]. Here we aim at finding the dependence of the number of cells, C, forming the belt on the step, s. It will be derived using the well-known Euler relationship [30]

$$V - E + F = \chi \tag{3}$$

interrelating the number of faces, F, the number of edges, E, and the number of vertexes, V, of an arbitrary graph. In the case of a planar graph the Euler characteristic, $\chi = 1$, if the outer face is not taken into account. Making use of Fig. 1, we will talk about hexagonal cells but will keep in mind that all calculations are also true for quadrangle cells.

Considering the growing nucleus as a planar graph, one may write

$$C(s) = F(s) - F(s-1) \tag{4}$$

By use of Eq. (3), i.e. expressing F in terms of V and E,

$$C(s) = [E(s - E(s-1)] - [V(s) - V(s-1)] \tag{5}$$

For the number of edges, E, the known relationship [30]

$$2E = vF + E_B \tag{6}$$

may be used, where v is the number of edges of a cell (in our context this is either six or four), E_B is the number of edges forming the external boundary of the graph. The second bracket in Eq. (5) is the number of vertices on the external boundary which is equal to the number of edges forming this boundary (since the boundary is a simple closed line). Hence

$$C(s)=\frac{v}{2}\left[F(s)-F(s-1)\right]-\frac{1}{2}\left[E_B(s)+E_B(s-1)\right] \tag{7}$$

Taking Eq. (4) into account and writing the number $E_B(s)$ of edges forming the external boundary on the step s as the same number $E_b(s+1)$ of the edges forming the internal boundary on the next step $(s+1)$ (see Fig. 1f in which three successive concentric belts are shown), one gets

$$C(s)=\frac{v}{2}C(s)-\frac{1}{2}[E_b(s+1)+E_B(s-1)] \tag{8}$$

To determine E_B and E_b, consider a separate belt (e.g. that not hatched in Fig. 1f), for which $\chi=0$ and

$$2E=vC+E_B+E_b \tag{9}$$

where subscripts B and b denote the external and internal boundaries of the belt, respectively. Note that whereas each of the inside vertices of the graph belongs to three faces, boundary vertices can be either two-valent or three-valent. A concentric belt may be considered as a "complex" of cells. Since only two cells may be adjacent in this complex, the number V_3 of three-valent vertices is the same for internal and external boundaries: $V_{3,b}=V_{3,B}$. For the two-valent vertexes this is the case only if the complex is linear (Fig. 4a). A bend results if two excess vertices are on the external boundary (Fig. 4b). Each of our belts includes v linear segments and v bends. Accordingly,

$$V_{2,B}-V_{2,b}=2v \tag{10}$$

Note further that

$$V_{2,B}=E_B-C \tag{11}$$

$$V_{2,b}=E_b-C$$

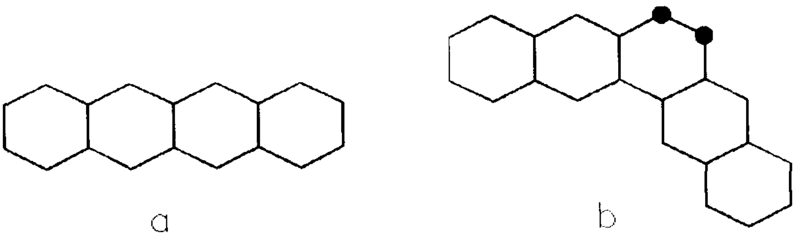

Fig. 4. Two solid circles are excessive two-valent vertexes of the bent complex (b) in comparison with the linear complex (a).

whence

$$E_B - E_b = 2v \tag{12}$$

By using Eqs. (3) and (9) one may now calculate

$$\begin{aligned} E_b(s+1) &= \left(\frac{v}{2} - 1\right)C(s+1) - \frac{v}{2} \\ E_B(s-1) &= \left(\frac{v}{2} - 1\right)C(s-1) + \frac{v}{2} \end{aligned} \tag{13}$$

and substitute these into Eq. (8). The result is the second-order difference equation for C:

$$2C(s) - C(s+1) - C(s-1) = 0 \tag{14}$$

This equation just means the linearity of the unrestricted growth that previously [10] was noted without proof.

Using the standard procedure [31] one may pass from Eq. (14) to the "one-step" equation

$$U_s = M^s U_0 \tag{15}$$

where $U_s = (C(s), C(s+1))$, and M is the matrix $M = \left[\begin{smallmatrix} 0 & 1 \\ -1 & 2 \end{smallmatrix}\right]$. Finally, taking into account the initial conditions and reminding ourselves that each cell consists of η planigons, we arrive at the extremely simple equation

$$n(s) = (s-1)v\eta \tag{16}$$

that calculates the number n of planigons in the concentric belt at step s. It enables one to calculate also the total number N of planigons forming the graph:

$$N(s) = \frac{s(s-1)v\eta}{2} + \eta \tag{17}$$

This quantity is connected directly with one of two main variables of phenomenological heterogeneous kinetics, the degree of conversion α, the meaning of which is the part of the surface (volume) occupied by a new phase at the given instant s. In our terms

$$\alpha(s) = \frac{N(s)}{N_0} \tag{18}$$

where N_0 is the initial number of planigons. The second main variable, the rate $\dot{\alpha}$, is proportional to $n(s)$ considered as a measure of the reaction zone, but in contrast to Eq. (18) the corresponding relationship

$$\dot{\alpha}(s) = \kappa v\eta(s-1) \tag{19}$$

includes the coefficient κ that has no roots in the above considerations. Since its meaning cannot be explained in the above terms alone, we will consider it so far merely as a proportionality factor. This emphasizes the difference between α and $\dot{\alpha}$ (see also Ref. [32] for the discussion of this point).

The simple difference equation, Eq. (19), describes the linear unrestricted growth of a separate nucleus in terms of planigons and forms an adequate basis for more subtle understanding of the peculiarities of non-linearity in the case of heterogeneous chemical kinetics.

5. Conclusions

One of the main objectives of this paper was to advance the idea of separating the deterministic factors of solid-phase reaction dynamics [9] towards developing a more adequate mathematical description with due regard for the chemical individuality of a solid reagent. This point seems to be a lacuna within the modern geometric–probabilistic approach which pays predominant attention to its probabilistic part. Two approaches suggested seem to fill this lacuna partly and are considered as a basis for modifying the inverse kinetic problem with the intention of including the broad spectrum of chemical considerations into its logical framework. The main items may be summarized as follows.

(1) The chemical individuality of a solid reagent finds proper representation in terms of the geometry of a crystal space, suggesting that appropriate kinetic models must be two-dimensional and discrete to take this into account.

(2) The reaction dynamics are interrelated with this geometry using the notion of adjacency, which reflects the local character of chemical interactions and determines the use of Dirichlet tessellations.

(3) Two ways of formalizing the reaction dynamics, in terms of cellular automata and in terms of concentric belts, are connected with the use of Dirichlet tessellations. Their main common features are topological character and the possibility of taking the combinatorial–topological structure and the symmetry of a single crystal face into consideration simultaneously.

(4) At the same time they are conceptually different: distributed models in the form of CA rules versus concentrated models in terms of difference equations. Whereas for the CA introduced we have to restrict ourselves to separate rules alone, in terms of concentric belts the linearity of $\dot{\alpha}(s)$ and $\alpha(s)$ is proved for unrestricted growth, which enables further analysis of the non-linearity of heterogeneous kinetics.

(5) Originating largely from the deterministic part of the problem, both these approaches determine, in their turn, significant modifications of the probabilistic part with respect to the account of the energetic inhomogeneity of a sample as well as the impingements of nuclei. This will be the subject of a subsequent discussion.

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