

CONVEXITY REQUIREMENT IN THE GEOMETRIC-PROBABILISTIC APPROACH TO HETEROGENEOUS CHEMICAL KINETICS

A. Korobov

Kharkov University, P.O.Box 10313, Kharkov 310023, Ukraine

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Abstract

The convexity of localization forms, strictly required by conventional geometric-probabilistic formalism, is not in agreement with many experimental observations concerning solid-phase chemical reactions. In a discussion of the essence of this requirement, it is shown that it may be weakened for non-convex localization forms consistent with the symmetry of a solid reagent and described within the geometric-probabilistic approach in terms of planigons and Wigner-Seitz cells.

Keywords: kinetics, solid-phase reactions

Introduction

There are a fair number of examples of the non-convex localization forms of solid-phase chemical reactions, both convex and non-convex forms being observable even at the same crystal face, depending on the reaction type [1].

At the same time, the conventional geometric-probabilistic approach, widely used to describe these reactions in the kinetic regime [2-5], requires the strict convexity of the localization forms. Otherwise, the calculated probability appears to be an upper estimation rather than the exact solution to the degree of conversion $\alpha(t)$ [6]. (Not infrequently, another material requirement of the same form and orientation of the nuclei is satisfied simply by taking this form to be spherical and the convexity requirement remains in the shadow.)

With the aim of adapting the geometric-probabilistic formalism to a more subtle simulation of the chemical regularities by representing the solid reagent as a chemical individual in terms of Dirichlet domains [7, 8], we again face the convexity requirement, but now in another context: the planigons and Wigner-Seitz cells describing the symmetry of a solid reagent must be convex.

Naturally, the question arises of whether the experimentally observed non-convex localization forms may be described in terms of the geometric-probabilistic approach. It will be shown that the convexity requirement may be

weakened without loss of rigour in the particular case of nuclei formation at the lattice points alone. And due to this, the non-convex localization forms, made up of convex planigons, win the 'right of citizenship' within the discussed approach. (It is worth noting in this respect that the experimentally observed reaction front does not always coincide with the implied front of the redistribution of chemical bonds [1].)

The problem of convexity is basically the problem of the interrelation between a complex probability, calculated in the framework of the geometric-probabilistic approach, and the main variable of heterogeneous chemical kinetics, the degree of conversion $\alpha(t)$. The latter is associated with the probability $P(t)$ that an arbitrary point A of the original phase will be taken up by the new phase of growing and impinging nuclei up to time t . This probability P is the exact solution to α only if definite conditions are satisfied, including the convexity requirement [6].

From formal mathematical considerations, connected with use of the theorem of multiplication of mutually independent probabilities, the geometric-probabilistic approach is based on calculation of the probability $(1-P)$ that the above point A will not be taken up by the new phase up to the given instant of time. The main steps in the conventional case of a homogeneous and continuous original phase are as follows. Let the nucleus with point B as center have the form shown in Fig. 1a. Of course, this non-centrally symmetric form is not typical of an isotropic medium, and is chosen for illustration purposes alone. A nucleus is characterized by its radius $R(\tau, t)$, where τ is the instant of its appearance and t is the current time. The radius may be read in any direction from the center, but this direction must be one and the same for all nuclei. The particular form of a nucleus also determines a certain metric: the distance $\rho(A, B)$ from the nucleus center B to some point A is defined as the radius $R_B(\tau, t)$ that must be reached by the nucleus B , appearing at the instant τ , to take up the point A up to the instant t . The set of points for which the distance from point A does not exceed some value r is termed the r -neighborhood of point A . This region is centrally symmetric relative to the nucleus with center at A and is characterized by the same quantity $R(\tau, t)$, but read in the opposite direction (Fig. 1a). If this region is free from nuclei up to the instant τ , its central point A will not be taken up by the new phase up to the instant t . It is clear that, at fixed t , the r -neighborhood is maximum for $\tau=0$, tightening towards point A as $\tau \rightarrow t$. The absence of nuclei in the r -neighborhoods of point A at the successive instants of time $\tau_1=0, \tau_2, \dots, t$ are just the mutually independent events. The product of probabilities of these events, calculated with regard to the intensity of nucleus appearance and the area (or volume) of r -neighborhoods, gives at the limit $\Delta\tau \rightarrow 0$ the desired probability that the point A will not be taken up by the new phase up to the instant t .

However, it is essential to emphasize that, in the general case, the appearance of a nucleus in the r -neighborhood ensures the uptake of point A , and the absence of nuclei ensures freedom for point A only if the nucleus is convex.

Otherwise, discrepancies are possible [6]. The discussed issues must be considered in terms of Dirichlet tessellations. In these terms, the process is described as the growth of the only nucleus inside the ever-decreasing averaged hexagon cell of the random mosaic [7]. In this context, the following nuance is connected with the convexity requirement: we must be sure that each cell of the random mosaic will be the 'rightful domain' for its nucleus at any instant of time, with regard to the permanent rearrangement of the random mosaic. Only with this condition being satisfied, will the statements of the geometric-probabilistic scheme in terms of coverings and tessellations [9] be equivalent. In this respect, the non-convexity of a nucleus may result in two misestimations.

(i) The appearance of a new nucleus is accompanied by the appearance of a new cell of the random mosaic at the expense of adjacent cells. This rearrangement must proceed in such a way as to ensure that the 'older' nucleus is located completely within its new cell. However, in the case of a non-convex nucleus, there is a chance that it will exceed the limits of its cell and occupy part of the adjacent cell. The heavy hexagon in Fig. 1b is the cell of nucleus *A* before the appearance of nucleus *B*. The latter event is accompanied by the appearance of a new cell (shown in Fig. 1b by a thin line), part of it being occupied by nucleus *A* (solid hatching). As a result, the calculated fraction of the new phase will be misestimated.

(ii) In relation to some nucleus (for example, nucleus *A* in Fig. 1c), its cell of random mosaic *E* singles out the immediate neighbors (nuclei *B* and *C*). In contrast, nucleus *D* has no common edge of the random mosaic with nucleus *A* and thus does not belong to the immediate neighbors. This means that in the course of a process it must not impinge with nucleus *A* and must not influence the dynamics of impingements of *A* with *B* and *C*: whereas the appearance of a new nucleus results in rearrangement of the random mosaic, the growth of nuclei without the appearance of new nuclei must preserve the random mosaic and the subdivision into immediate and non-immediate neighbors. Figure 1c reveals that this may not be the case for non-convex nuclei. Cell *E* is drawn (with a heavy line) on the assumption that nucleus *D* is absent and nucleus *B* grows without disturbances. However, it may be seen from the Figure that the non-convex nucleus *D*, a non-immediate neighbor, may prevent the growth of nucleus *B* in the direction of nucleus *A*. As a result, the corresponding edge of the random mosaic will be shifted (thin line *F*), introducing a mistake into the calculations.

The possibility of the above misestimations is connected with the non-convex form of nuclei as far as the homogeneous continuous medium is concerned. However, this is not the case if certain peculiarities of the approach suggested are taken into account, primarily the discrete character of the appearance and growth of nuclei [7, 8]. In accordance with the translation symmetry of a solid reagent, a definite number of convex planigons are added to the growing nucleus at each step. The result is a non-convex centrally symmetric figure. The form of the *r*-neighborhood coincides in this case with the form of the nucleus.

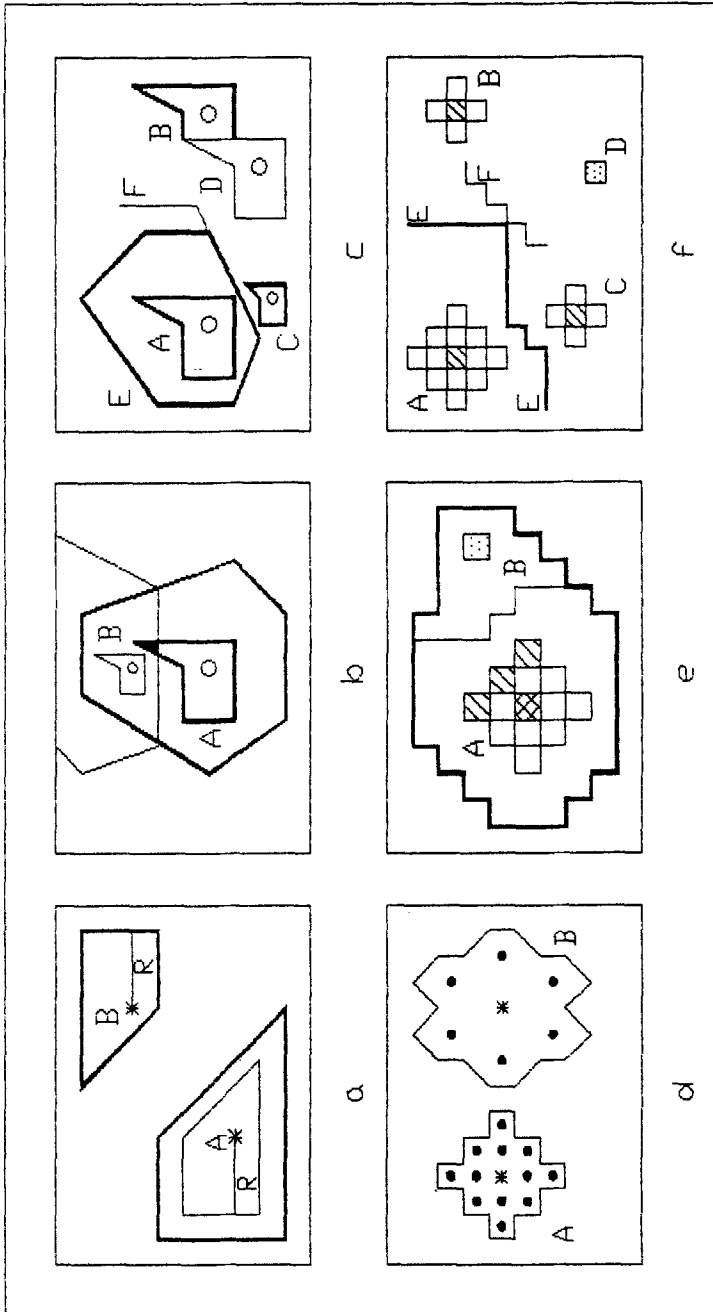


Fig. 1 Misestimations, that generally may result from the non-convexity of nuclei (b,c), are not the case for nuclei of peculiar form (d-f). (Explanations are given in the text)

When the appearance of the nucleus is discussed in these terms, one deals not with continuous neighborhoods, but only with discrete sets of points at which a nucleus may appear. In Fig. 1d, these sets are shown for two possible topologically different cases: quadrangular (A) and hexagonal (B) Wigner-Seitz cells. It is worth emphasizing that in both cases these points form the convex sets determining the essential peculiarity of the considered non-convex figures. By virtue of this, a nucleus consisting of planigons may neither exceed the limits of its cell of random mosaic in the course of rearrangement, nor be converted from an immediate neighbor into a non-immediate one or vice versa.

We will consider the case of quadrangular Wigner-Seitz cells, similar considerations holding for hexagonal cells. It is worth emphasizing that the localization forms and, accordingly, the metrics associated with these forms, are determined ultimately by the symmetry of a solid-phase reagent: at each step, the process of nucleus growth propagates to all nearest translationally equivalent positions determined by the Wigner-Seitz cells, the total number of added planigons being determined by the number of translationally non-equivalent lattice points in a Wigner-Seitz cell. Using, as previously [7], the step number s for the discrete time, one may naturally associate integer coordinates with each Wigner-Seitz cell and characterize the growing figure by the radius $R = |x| + |y|$ (rather than $(x^2 + y^2)^{1/2}$, the corresponding metric being determined by the relationship $\rho(A, B) = |\Delta x| + |\Delta y| = \rho_x(A, B) + \rho_y(A, B)$).

In this metric, the boundaries of the random cell are straight lines only when they are parallel to the coordinate axis, being stepwise lines in the general situation. An example is the hexagonal cell of nucleus A , drawn in Fig. 1e with a heavy line (the absence of nucleus B is assumed). The situation shown in this Figure is similar to that in Fig. 1b: the appearance of a new nucleus B results in rearrangement of the random mosaic, and the new boundary (shown with a thin line) appears between nuclei A and B . Its stepwise part contains $n = \min(|\Delta x|, |\Delta y|) + 1$ steps and for this reason all Wigner-Seitz cells forming the side of nucleus A turned towards nucleus B (single hatching) are equidistant from the new boundary. Accordingly, our nucleus will in no case exceed the limits of its cell in the course of rearrangement of the random mosaic.

Finally, Fig. 1f shows a situation similar to that in Fig. 1c. Nuclei B and C are immediate neighbors of nucleus A . Heavy line E is part of the cell of A . Its maximum distance from A is $d = \max(\rho(A, B), \rho(B, C)) + \delta$, where $\delta = |\rho(A, B) - \rho(A, C)|$. The stepwise thin line F is part of the boundary between nuclei A and D . Nucleus D is not an immediate neighbor of A , i.e. $\rho(A, D) > d$. To block the way of nucleus B towards A , the situation of nucleus D must satisfy the inequality $\rho_y(B, D) \leq \rho_x(B, D)$. Additionally, the impingement of nuclei B and D must take place between E and B : $\rho_x(B, D) \leq \rho_x(A, B)/2$. With regard to the triangle inequality, these conditions are incompatible. This means that a situation similar to that in Fig. 1c is impossible because of the peculiarity of the metric.

Hence, it follows that the convexity requirement, strict in the case of a continuous original phase, may be considerably weakened when the discrete nu-

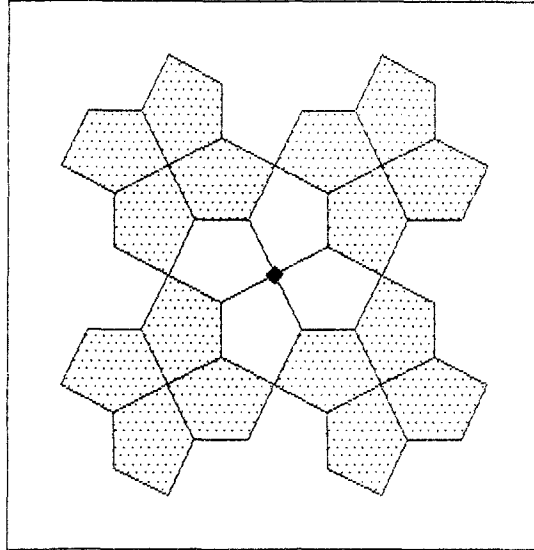


Fig. 2 An example of the non-convex localization form consistent with the geometric-probabilistic approach

cleus formation in the lattice points involves nucleus growth described in terms of planigons and Wigner-Seitz cells. One of the numerous examples of non-convex localization forms, which acquire the 'rights of citizenship' in the framework of the geometric-probabilistic approach, is shown in Fig. 2 (p4 symmetry group). In this context, the at first sight formal convexity requirement appears to be connected with material conceptual distinctions between solid-phase chemical reactions and conventional phase transitions.

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