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# DISCRETE RANDOM TESSELLATIONS WITH MOOR NEIGHBOURHOODS: A KINEMATIC STUDY

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Random tessellations with Moor neighbourhoods appear in investigating thermal decomposition kinetics of ammonium hydrocarbonate single crystals. The way is shown in which this variety of tessellations appears and its main kinematic properties are examined. Result obtained emphasizes the need to account for actual metric in kinetic data analysis in terms of geometric-probabilistic models.

Previously the concept of discrete random tessellations has been introduced for describing nucleation and growth to impingement processes in a metric determined by the crystal structure of a solid reagent [1,2]. In 1980th-1990th conventional continuous random tessellations, previously the object of pure mathematics, proved to be efficient in simulating disparate phenomena and processes [3]. Generally, a random tessellation is characterized by its typical element [4]. In [5] the kinetic representativity of the typical element has been shown for the first time in the continuous case. This means the possibility to describe kinetics of nucleation and growth to impingement processes in terms of random tessellations.

Currently, the Euclidian metric is implied when geometric-probabilistic models are used for simulating solid state reaction kinetics [6]. Actually, the metric is different and is determined by the crystal structure of a solid reagent and the peculiarities of the unrestricted nucleous growth [2]. There is no natural discrete analogs for continual Euclidian random tessellations. To interrelate them, continual analogous of discrete non-Euclidian tessellations have been compared with Euclidian one [7]. The difference between corresponding kinetic curves has shown to be significant, which means that a considerable error is introduced when the actual metric is not taken into account.

The simplest possible discrete random tessellation is the one with von Neumann neighbourhood. Its kinematic properties and geometric peculiarities are presented in [8]. The present paper deals with a different type of discrete random tessellations characterized by Moore neighbourhood which is described in terms of displacement vectors as

$$N_9 = \left\{ \begin{pmatrix} 0 \\ 0 \end{pmatrix}; \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \begin{pmatrix} -1 \\ 0 \end{pmatrix}; \begin{pmatrix} 0 \\ -1 \end{pmatrix}; \begin{pmatrix} 1 \\ -1 \end{pmatrix}; \begin{pmatrix} -1 \\ 1 \end{pmatrix}; \begin{pmatrix} 1 \\ 1 \end{pmatrix}; \begin{pmatrix} -1 \\ -1 \end{pmatrix}; \right\} \qquad (1)$$

This type of random tessellations arises from examination of the thermal decomposition of ammonium hydrocarbonate. Specially prepared single crystals of this compound are plate-like with only one face (001) entering the reaction [9]. Crystals of $NH_4HCO_3$ belong to the rhombic syngony; the spatial group is Pccn; parameters of the elementary cell: a = 7.255 A, b = 10.709 A, c = 8.746 A [10]. The projection of this crystal structure onto (001) face has the symmetry group c2mm; cell parameters a'=a and b'=b; coordinate origin is at ?, ?, z [11]. As many as 8 types of planigons correspond to this [12]. When the thermal decomposition proceeds in the kinetic regime, rhombic negative crystals oriented in one and the same manner are observed. Their stable unrestricted growth may be described using $P_{4A,23}$ planigon type. In this case one planigon encompasses two $NH_4 - HCO_3$ conjugated pairs of the ammonium hydrocarbonate, and its entrance into reaction means the transfer of two protons with the release of two $NH_3$ molecules and two $H_2CO_3$ molecules into the gaseous phase [13]. The kinetic stability of $H_2CO_3$ in the absence of water has been shown recently both experimentally and theoretically [14].

First steps of the unrestricted growth of rhombous negative crystals in terms of planigons are shown in Fig.1. They are shown with black circles and in light gray respectively. Upon impingements these negative crystals form a random tessellation. Topologically equivalent to this is the random discrete tessellation with the Moor neighbourhood (1) which determines the metric

$$dist = \max\left(|x - x_0|, |y - y_0|\right). \tag{2}$$

Fig.2 shows a small part of this tessellation in the assumption of Voronoi case, i.e. when all nuclei appear simultaneously. Three growth steps are shown for each of two nuclei (counting off the nucleation step). The boundary between them (circles with daggers) subdivides the plane into cells which are closer to the given nucleus than to any other nuclei. Peculiarities of the boundary are as follows.



Fig.1. Unrestricted growth of rhombous negative crystals in terms of $P_{4A,23}$ planigons.

–  the central part of the boundary is either horizontal (if the distance between nuclei along x-axis is smaller) or vertical (if the distance between nuclei along y-axis is smaller);

–  the number of sites in this linear part is equal to min ($|\Delta x|$, $|\Delta y|$);

–  The central part may be prolonged (ad infinitum if there are only two nuclei) in both direction with stepwise parts oriented along one of diagonals;

–  the central part may consist of only one cite if both nuclei are situated on the same diagonal;

–  under certain mutual situation of nuclei the boundary may form a two-dimensional array as is shown, for example, in Fig.3; the same is the case in regions where three or more growing nuclei meet.

The computational algorithm includes the following stages. A random tessellation was represented as a three-dimensional array of sites; the third dimension has been used for storing various characteristics. The required number of these sites was chosen at random as nucleation sites. To ensure the homogeneity of the tessellation, x-coordinates of all nuclei must be either even or odd and the same is required for y-coordinates. This is the main distinction of the computational algorithm from the previous one



Fig.2. Small part of random Voronoi tessellation with Moor neighbourhood.



Fig.3. The boundary between two nuclei may generally be two-dimensional.

[8] in which nuclei positions ware corrected to be only "black" or only "white". With the account of the above peculiarities boundaries were determined in the following way. For each site distances to all nucleation sites were computed and the minimal distance was identified. Then the number of these values in the array of distances was determined. This is the multiplicity of a site. It was stored together with the numbers of equidistant nuclei for further computations. Finally, the step number at which a given site would be reached by a growing nucleus was computed. After all sites have been processed, boundary cells of a tessellation were rejected. All statistical characteristics discussed below were computed for internal cells only. Discussed results were obtained for the 1500 x 1500 tessellations with 10000 nucleous.

In [5] the notion of kinematic curve was introduced for continual tessellations as the dependence of the actual boundary length with the account of impingements on the nucleous radius. This curve may be appropriately scaled to be compared with experimental rate-time curves. In the discrete case the kinematic curve is computed as the dependence of the number of sites forming the boundary on the step number. The curve computed in this way is shown in Fig.4. Similar curves may be computed separately for $\nu$-gons of the tessellation ($\nu$ = 4, 5, 6...). 3-gons were not found at all in this study. Qualitatively their mutual situation is as in the von Neumann case [8]: with the increase of $\nu$ the maximum is higher and is shifted
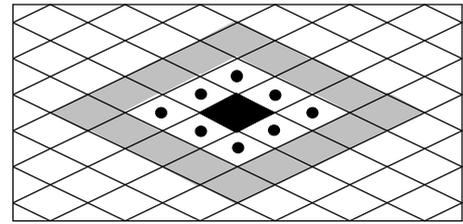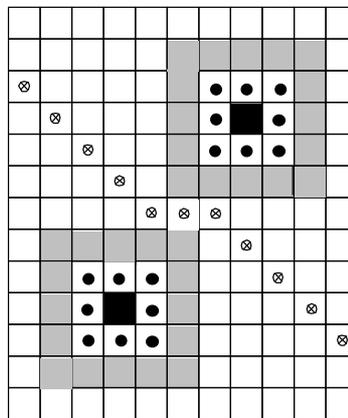
towards greater step numbers. Results obtained proved that 6-gons are prevailing in the tessellation, i.e. this mysterious regularity is preserved. The kinematic curve for 6-gons approximates reasonably well the total kinematic curve for the whole tessellation (Fig.4). As before [8] immediate neighbours were identified as nucleation sites that possess a common edge consisting of at least two neigbouring sites irrespectively to their multiplicity.

In Fig.4 the total kinematic curve for Moor tessellation is compared with that for von Neumann tessellation at the same nuclei density. The maximum for the former is 60% higher and is reached 30% quicker. This approach makes it possible to qualitatively estimate the mistake which is introduced into data analysis if the metric is chosen incorrectly. The situation of the maximum of rate-time curves is the main and not infrequently the only quantity which is used to judge about process parameters. Recall that the maximum in the Euclidian case is even lower than in the von Neumann case [7]. Therefore, in the case of Moore tessellations the mistake because of wrong metric choice is higher. In terms of discrete random tessellations the crystal structure of a solid reagent manifests itself in the stochastic regularities of nucleation and growth to impingements, which makes the geometric-probabilistic approach as a whole a more chemically specific one.
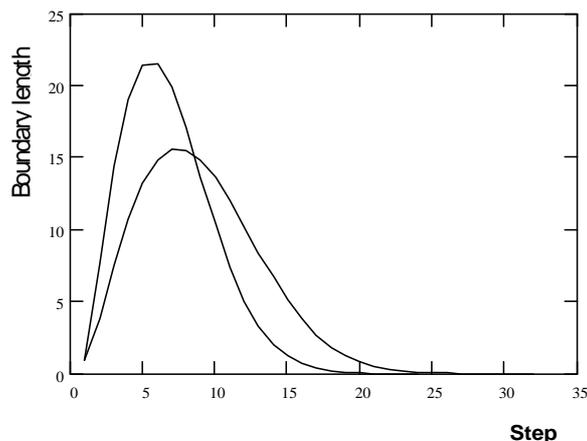


Fig.4. Comparison of kinematic curves for Moor tessellation (solid) and von Neumann tessellation (dash).

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Случайные мозаики с окрестностью Мура возникают при описании кинетики термического разложения гидрокарбоната аммония. Прослеживается логика их появления в моделях и изучены основные кинематические свойства. Полученные результаты дают представления об ошибке, которая вносится на стадии анализа данных при замене реальной метрики, задаваемой кристаллической структурой реагента, евклидовой метрикой.