Domain size distribution in a Poisson-Voronoi nucleation and growth transformation

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Abstract

Random subdivisions of space originated in a nucleation and growth process are commonly observed in many scientific fields, such us metallurgy, geology, biology and ecology. One of the simplest of these processes is the one generated by an initial random distribution of seeds or nuclei, all growing at the same rate and fixed in space without pushing apart as they grow into contact. The final stage of this process is the well-known Poisson-Voronoi cellular structure or tessellation. Here, we present an analytical exact result for the evolution of the domain size distribution along the transformation process. The calculations are based on a differentiation of the domains by their different number of collisions with surrounding seeds. The method can be easily extended to the calculation of the probability distribution of any other geometrical characteristic, such as the free boundary fraction of the domains. As far as we know, it is the first time that an exact result is given for this classical system.

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The geometric characteristics of the structure generated in nucleation and growth processes have large influences on the properties of many different systems. This work deals with one of the simplest nucleation and growth processes, the so called "cell model"[1], where a certain homogenous medium is progressively occupied by growing domains or "crystals", all with the same isotropic growth rate and all emerging from an initial random point distribution of nuclei or "seeds". The collision of two domains with equal growth rate generates a flat border or face between them. Hence, the initial spherical domains become progressively changed to polyhedric cells as the number of collisions with neighbouring domains increases. When the domains occupy all the surrounding space left by their neighbours, the growth of the domains stops and they become Voronoi polyhedra. The final stage of this process is the well-known Poisson-Voronoi (PV) network or tessellation[2], and so we will call it here a PV nucleation and growth transformation. In spite of its simplicity, PV transformations and tessellations are commonly observed in a wide range of fields. Growth of pre-existing nuclei is observed in solidification and glass crystallization, leading to partially crystallized or polycrystalline materials[3][4], the macroscopic properties of these materials are dependent on the topological features of the crystals such as the size, the shape, the number of faces or the number of vertices. Moreover, PV transformations and tessellations are applied in other scientific fields including geology[5], biology[6][7], ecology[8], geography[9] and astrophysics[10].

The crystal size probability density function (PDF) of a PV tessellation, that is the final structure obtained in a PV transformation, is known to be accurately predicted by a gamma distribution[10][11]

$$f(a) \propto a^{\nu-1} \exp(-\nu\rho a), \tag{1}$$

where a is the size of the crystals and ρ is the density of seeds. The size a correspond to the length, the area or the volume of the crystals in one, two or three-dimensional tessellations and the mean value of a is obviously ρ^{-1}. The value of the exponent ν depends on the space dimension D with values of $\nu = 2$, 3.575 and 5.586 for $D = 1$, 2 and 3 respectively[13]. The gamma distribution of sizes in a PV tessellation was derived analytically for the one-dimensional case[1][14], while it was "empirically" obtained, fitting the results of computer simulations, for the two and three-dimensional cases[10][11]. The time evolution of the crystal size PDF along the transformation was analytically solved by Axe et al.[14] for the one-dimensional case. As far as we know, there are not analytical solutions for the

evolution of the crystal size PDF for two and three-dimensional PV transformations. Two semi-empirical approaches, based on a set of evolution equations for the size populations, were presented previously[15][16]. In this letter we present an analytical calculation of the temporal evolution of the crystal size PDF in a PV transformation. This calculation method allows the calculation of the size PDF to any desired accuracy at any finite time during the PV transformation, and it can be easily extended to the calculation of the probability distribution of any other geometric characteristic of the domains.

The two parameters determining completely a PV transformation are the density of seeds ρ and the growth rate of the crystals u. For the sake of simplicity, here we will assume $u = 1$, and so a crystal without collisions will be a sphere with radius equal to the time t elapsed since the beginning of the transformation. It should be noted that, at a certain value of the overall transformed fraction, the same geometrical configuration is obtained regardless of the specific growth rate function $u(t)$, provided that $u(t)$ is equal for all the growing crystals. The overall transformed fraction $x(t)$ is defined as the fraction of space already occupied by the growing crystals at time t. Therefore, the results obtained for the $u = 1$ system are representative of any PV transformation with the appropriate time scaling. Moreover, the results shown in this letter will be restricted to a transformation in a $D = 2$ space. Extension to $D = 1$ and $D = 3$ is straightly obtained and will be detailed elsewhere.

The basis of the present calculation is the distinction of the crystals by their number of "extended" collisions. The extended collisions include both actual collisions and collisions screened by a nearer crystal. In a PV transformation with $u = 1$, a domain without collisions would occupy all the space within a distance t from its seed. Therefore, any pair of domains with distance between their seeds smaller than $2t$ generates an extended collision. The number of extended collisions of a certain crystal corresponds to the number of neighbouring seeds found at a distance from the crystal origin smaller than $2t$. In the case of a two-dimensional PV transformation, the fraction of crystals with k extended collisions is given by

$$T_k(t) = \frac{(4\pi t^2\rho)^k \exp(-4\pi t^2\rho)}{k!}, \tag{2}$$

which is the probability of finding just k seeds in a $4\pi t^2$ area. It should be noted that the term $\exp(-4\pi t^2\rho)$ is the probability of finding no seeds in such area, and it corresponds to the fraction of crystals $T_0(t)$ that have not yet collided at time t.

At a certain time t, each individual crystal has a collision configuration which determines its size, free-boundary fraction and any other geometrical aspect. This collision configuration of a certain crystal is determined by the position of all the neghbouring crystals that may collide with it, that is the position of the k neighbouring seeds nearer than $2t$ from the crystal origin. These positions can be expressed by a distance $2t_i$ and an angle θ_i $(i = 1..k)$, with values of t_i ranging from 0 to t, and θ_i ranging from 0 to 2π. The probability of finding a crystal with k extended collisions disposed in a certain configuration $\{t_i, \theta_i\}$ is

$$P_k\left(t_1, \theta_1, .., t_k, \theta_k, t\right) = 4^k \rho^k \exp\left(-4\pi t^2 \rho\right) \prod_{i=1}^{k} t_i dt_i d\theta_i, \tag{3}$$

which is obtained multiplying the probabilities $4\rho t_i dt_i d\theta_i$ of finding an i-seed at a certain distance $2t_i$ and a certain angle θ_i, and the probability $\exp\left(-4\pi t^2 \rho\right)$ of finding no more seeds inside the sphere of radius $2t$. In the previous equation it is considered that $t_{i-1} < t_i < t_{i+1}$, this means that the time of the ith collision have to be between the times of the $(i-1)$th and the $(i+1)$th collisions. In case this temporal order of the collisions was not considered the probability in equation (3) would have to be divided by $k!$.

By a simple variable change $l_i = t_i/t$, P_k can be rewritten as

$$P_k\left(l_1, \theta_1, .., l_k, \theta_k, t\right) = T_k\left(t\right) \frac{k!}{\pi^k} \prod_{i=1}^{k} l_i dl_i d\theta_i, \tag{4}$$

where l_i can have values ranging from 0 to 1 corresponding to t_i ranging from 0 to t. Each particular set $\{l_i, \theta_i\}$ determines a collision configuration as the one shown in figure 1 for the case $k = 3$. Examination of the previous equation shows that the probability distribution of collision configurations $\{l_i, \theta_i\}$ for the crystals with k extended collisions is time-invariant. The term $T_k\left(t\right)$ is the probability of finding a crystal with k collisions at time t, while the time-invariant term

$$\frac{k!}{\pi^k} \prod_{i=1}^{k} l_i dl_i d\theta_i \tag{5}$$

is the probability of finding a certain collision configuration among the population of crystals with k collisions. Therefore, the probability distribution of any geometrical property dependent on the collision configuration is also time-invariant. For instance, in the case of the collision configuration of figure 1, a given set of values $\{l_1, \theta_1, l_2, \theta_2, l_3, \theta_3\}$ determines the shape of the crystal and its size. The probability of finding this specific geometrical

configuration among the population of crystals with $k = 3$ will be constant, while the total fraction of crystals with $k = 3$ will vary along the transformation.

As each collision configuration $\{l_i, \theta_i\}$ determines unequivocally a normalized crystal size

$$s = \frac{a}{\pi t^2}, \tag{6}$$

this implies that the population of crystals with a given k has a time-invariant size PDF $g_k(s)$. The first of these size PDFs, corresponding to $k = 0$, is easily obtained as

$$g_0(s) = \delta(s - 1), \tag{7}$$

where δ is the Dirac delta function. This means that all the crystals without collisions have the original circular shape and $s = 1$ or equivalently a size $a = \pi t^2$. Defining a function $S_k(l_1, \theta_1, .., l_k, \theta_k)$ which calculates the normalized size of a crystal with a given $\{l_i, \theta_i\}$ configuration, the calculation of $g_k(s)$ for $k \geq 1$ can be performed by means of

$$\begin{aligned} g_k(s)\, ds &= \frac{k!}{\pi^k} \int_{l_1=0}^{1} \int_{\theta_1=0}^{2\pi} \cdots \int_{l_k=l_{k-1}}^{1} \int_{\theta_k=0}^{2\pi} \delta(s - S_k(l_1, \theta_1, .., l_k, \theta_k)) \prod_{i=1}^{k} l_i dl_i d\theta_i = \\ &= \frac{1}{\pi^k} \int_{l_1=0}^{1} \int_{\theta_1=0}^{2\pi} \cdots \int_{l_k=0}^{1} \int_{\theta_k=0}^{2\pi} \delta(s - S_k(l_1, \theta_1, .., l_k, \theta_k)) \prod_{i=1}^{k} l_i dl_i d\theta_i. \end{aligned} \tag{8}$$

Explicit details of the $S_k(l_1, \theta_1, .., l_k, \theta_k)$ functions will be given elsewhere. As an example, the size of a crystal with just one collision in a two-dimensional system is given by $S_1(l_1, \theta_1) = 1 - \pi^{-1}\left[\arccos(l_1) - l_1(1 - l_1^2)^{\frac{1}{2}}\right]$.

For small numbers of k and simple S_k functions, the previous expressions can be integrated analytically. A numerical integration using a Monte Carlo method is possible for any value of k. Obviously, the larger the k the longer the time consumed by the numerical integration. Figure 2 shows the calculated $g_k(s)$ for $k = 1, 2, 3, 4$ and 5. These functions correspond to the time-invariant probability densities of finding a domain with normalized size s among the population of domains that have k neighbouring seeds at a distance smaller than $2t$ from their origin. In the case of $k = 1$, $g_1(s) = 0$ for any $s < 0.5$ because the crystals with just one collision must have at least one half of their initial circular shape still not in contact with neighbouring domains. As it is expected, the mean value of s given by the $g_k(s)$ functions decreases progressively as the number k of extended collisions increases.

Now, the total PDF of normalized sizes at a certain time t can be calculated as

$$g(s,t) = \sum_{k=0}^{\infty} g_k(s)\, T_k(t)\,, \tag{9}$$

and the total size PDF $f(a,t) = g(s,t)\,\frac{ds}{da}$ is obtained using the variable change in equation (6). Figure 3 (Up) shows the calculated size PDF at a time where the overall transformed fraction is $x(t) = 0.5$, that is when a half of the overall space is already occupied by the domains. The total size PDF $f(a,t)$ of figure 3 (Up) is computed adding the contributions of the $g_k(s)$ distributions with $k \leq 7$. At $x(t) = 0.5$, more than 99% of the crystals have $k \leq 7$, the biggest contribution corresponds to the crystals with $k = 2$, which constitute a 24% of the total, and just 6.2% of the crystals remain with $k = 0$ collisions. In figure 3 (Up), the contributions of the $g_k(s)$ functions with $k = 1, 2, 3, 4$ and 5 are also shown. In the figure, the $f(a,t)$ calulated from equations (7), (8) and (9) is compared with the size distribution obtained in a stochastic simulation of the transformation. Details of the stochastic simulations were given in refs. [13] and [15].

Figure 3 (Down) shows the temporal evolution of the size PDF. The solid lines correspond to the calculated $f(a,t)$ at overall transformed fractions of $x(t) = 0.3$ and $x(t) = 0.6$. The final gamma distribution of equation (1), corresponding to $x(t) = 1$, is also shown in dashed lines. From equations (2) and (9), the time evolution of the overall system can be considered an addition of crystal k-populations with time-invariant geometrical cahracteristics, weighted by the number of these crystals at a certain time t. At the initial stages of the transformation, the crystals with small k will constitute the main part of the total number of crystals. At $x(t) = 0.3$, 24% of the crystals have $k = 0$ and 94% of crystals have $k \leq 3$. In this case, the estimation of the total PDF of the size, or of any other geometrical characteristic, requires the evaluation of the invariant probability distributions for a small number of k values. As the transformation proceeds, the estimation of the overall properties will require to extend the calculation over larger k values. At $x(t) = 0.6$, the number of crystals with $k \leq 3$ is reduced to 50%, and it is necessary to reach $k = 7$ in order to cover 95% of the total number of crystals. At the final stages of the transformation $x(t) \to 1$ as $t \to \infty$, and the calculation becomes impractical. However, then the system tends to the configuration of the widely-studied PV tessellation[17][18][19]. In the case of the crystal size, this means that the size PDF at the final stages of the transformation is well-described by the gamma distribution of equation (1). It should be noted here that although the calculation of the integrals in

equation (8) was performed using a numerical method, the derivation of equation (8) is fully analytic. In fact, the calculation of the $f(a,t)$ can be performed with any desired accuracy at any finite time t.

Another interesting property in a nucleation and growth transformation is the free-boundary of the crystals. In a two-dimensional space, the free-boundary of a crystal is determined by the fraction of the originally circular perimeter which is not in contact with other transformed domains. For the crystal configuration shown in figure 1 the free-boundary would correspond to the circular borders of the shadowed area. Similarly to any other geometrical property, each particular collision configuration $\{l_i, \theta_i\}$ determines a value of the free-boundary fraction; a procedure similar to the one described above by equations (8) and (9) allows the calculation of the free-boundary PDF of the crystals at any finite time during the transformation. Results of this calculation for PV transformations in 1, 2 and 3 dimensions will be presented elsewhere. Here, we focus our interest on the mean free-boundary fraction of the crystals. In the case of a two-dimensional transformation, a collision determined by the parameter l_i occupies a fraction of crystal perimeter equal to $\frac{\arccos(l_i)}{\pi}$, which is always smaller than 0.5. As any θ_i angle is equally probable, after each collision the probability that a certain point in the crystal's original boundary remains in contact with untransformed space is reduced by a factor $1 - \frac{\arccos(l_i)}{\pi}$. For a crystal with a given number k of extended collisions and a given set $\{l_i\}$ of collision distances, the average free-boundary fraction is

$$\prod_{i=1}^{k} \left[1 - \frac{\arccos(l_i)}{\pi} \right]. \tag{10}$$

And therefore, the mean free-boundary fraction of the crystals with k collisions is obtained as

$$\frac{k!}{\pi^k} \int_{l_1=0}^{1} \int_{\theta_1=0}^{2\pi} \cdots \int_{l_k=l_{k-1}}^{1} \int_{\theta_k=0}^{2\pi} \prod_{i=1}^{k} \left[1 - \frac{\arccos(l_i)}{\pi} \right] l_i dl_i d\theta_i \; = \tag{11}$$

$$2^k \int_{l_1=0}^{1} \cdots \int_{l_k=0}^{1} \prod_{i=1}^{k} \left[1 - \frac{\arccos(l_i)}{\pi} \right] l_i dl_i \; = \; \left(\frac{4-1}{4} \right)^k. \tag{12}$$

This result indicates that each extended collision provokes an average reduction of a 1/4 of the crystal free-boundary fraction. Furthermore, the overall free-boundary fraction of all

the crystals at a certain time t is then

$$\sum_{k=0}^{\infty}\left(\frac{4-1}{4}\right)^{k}T_{k}\left(t\right)=\exp\left(-\pi t^{2}\rho\right). \tag{13}$$

Taking into account that in a transformation with a random distribution of seeds the free-boundary fraction is equal to the untransformed fraction $1-x\left(t\right)$, the previous equation corresponds to the well-known Kolmogorov, Johnson-Mehl and Avrami (KJMA) equation[20][21][22] for a pre-existing nuclei transformation. This result can be extended to $D=1$ and $D=3$ transformations. In the case of a PV transformation in a D-dimensional space, the mean free-boundary fraction of the crystals with a given k is obtained to be $\left(\frac{2^{D}-1}{2^{D}}\right)^{k}$, this result leading to the KJMA equation for the evolution of the overall transformed fraction. Details of this derivation will be presented elsewhere.

Summarizing, in this letter we presented the following results:

- A calculation method for obtaining the probability density function of the geometrical characteristics of the domains in a Poisson-Voronoi transformation at any finite time t. The overall probability density function of any geometrical characteristic is demonstrated to be built-up by time-invariant probability distributions corresponding to the populations of domains with a certain number of extended collisions.

- The computation of the size probability density function of the domains at a given stage of the transformation, thus showing the applicability of the above result and its potential use for the calculation of different geometrical properties in Poisson-Voronoi transformations. As far as we know, it is the first time that an analytical exact result is obtained for this classical system widely found in several scientific fields. The method allows the calculations to an arbitrary accuracy at any finite time during the transformation.

- The analysis of the impingement process between domains in terms of extended collisions. It is found that each extended collision provokes the same average reduction of the free-boundary fraction of the domains. It is demonstrated that the presented formalism gives a detailed description of the space structure and includes the well-known Kolmogorov, Johnson-Mehl and Avrami model, whose results are reproduced.

In this letter, the calculation is restricted to a Poisson-Voronoi transformation in a two-dimensional space, however it can be easily extended to transformations in spaces of different dimensionality.

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FIG. 1: Possible collision configuration for a crystal with 3 extended collisions at normalized times l_1, l_2 and l_3.

FIG. 2: Time-invariant size distributions for crystals with a number of extended collisions $k = 1$, 2, 3, 4 and 5.

FIG. 3: (Up) Total crystal-size distribution in a PV transformation at a transformed fraction $x(t) = 0.5$. Calculated size distribution (thick line) compared with the results of a stochastic simulation (bars). The contribution of each of the $g_k(s)$ distributions (with $k = 0$, 1, 2, 4 and 5) is also shown. (Down) Calculated crystal-size distributions at $x(t) = 0.3$ and $x(t) = 0.6$. The dashed line corresponds to the final gamma distribution.

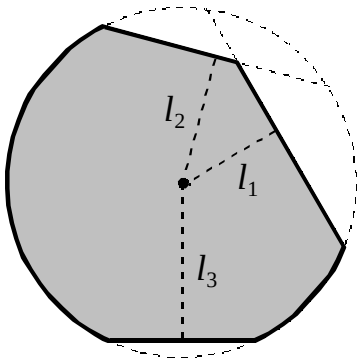

Fig1.

Figure 1

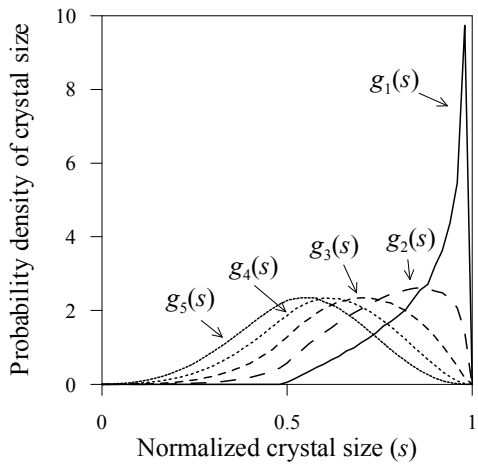

Fig 2.

Figure 2

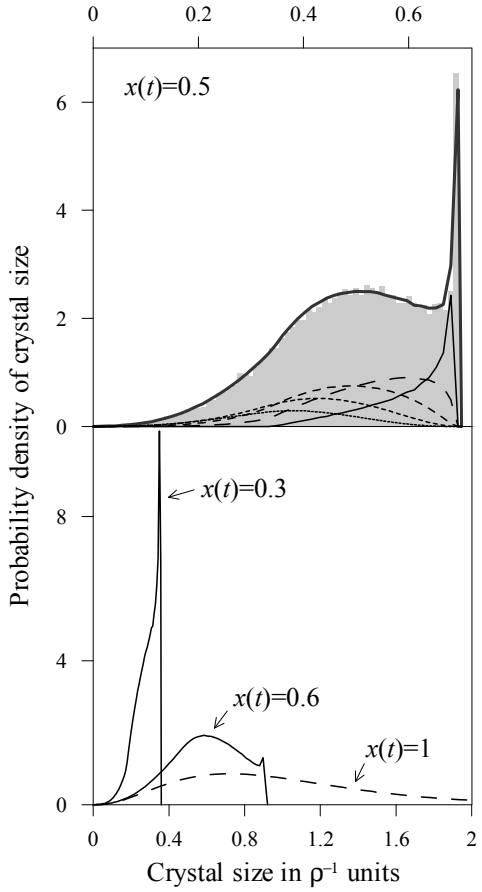

Fig 3.

Figure 3