Crystallization kinetics: A solution for geometrical impingement

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Starting from the wrong derivation by Erukhimovitch and Baram of an equation alternative to the classical Kolmogoroff-Johnson-Mehl-Avrami one for the transformed fraction in an infinite specimen, undergoing an isothermal first-order phase transformation, it is shown that a different exact solution of the geometrical problem of impingement can be obtained. Such solution is equivalent to the empirical one already presented by Austin and Rickett more than sixty years ago and allows to better fit experimental results for isothermal transformations. This also suggests that perhaps different statistical derivations could allow to reach the same result.

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The classical Kolmogoroff-Johnson-Mehl-Avrami (KJMA) equation,[1–5] for the transformed fraction in an infinite specimen undergoing a solid-solid or liquid-solid isothermal phase transformation, correctly describes the corresponding kinetic process when nucleation sites are randomly distributed and the linear-grain-growth rate is constant until impingement with neighboring ones. However, Erukhimovitch and Baram (EB) raised some doubts on the hypotheses underlying the KJMA equation and showed several examples in which their model better fitted experimental results in the case of isothermal amorphous to crystal transformations, polymer crystallization, etc.[6,7] Their works were an object of dure criticism by several authors because there actually were big mistakes in their derivation.[8–12] Anyway, even so, they were successful in calling attention on the lack of agreement with experimental results of KJMA solution, which, in general, predicts a transformed fraction as a function of time appreciably larger than the measured one after about 40% of the material had been transformed.

We will show the graphs that EB showed do not correspond to the equation they presented. Even more, the equation they showed as the base of their model does not arise from their initial assumptions. The plots they presented correspond to a different assumption that was already proposed as an empirical one by Austin and Rickett (AR) and already discussed by Avrami.[3,4,13] Similar empirical models for impingement have been frequently proposed and discussed in the literature, showing that better agreement with experimental results can be obtained, however, no strong physical justifications nor statistical arguments supported them.[14–18]

Here we want to show that AR model corresponds to a different exact solution of the geometrical problem of impingement, as formulated by Avrami, suggesting that perhaps statistical arguments, different from random distribution of nucleation sites, could allow to reach the same result.

Before rederiving the rigth EB equation, let us remember the KJMA one for isothermal first-order phase transitions. For the sake of simplicity let us limit the treatment to three-dimensional continuous nucleation with constant rate of grain production and constant interface velocity, the extension to two- and one-dimensional growth and inclusion of incubation time are straightforward. To this end, it is convenient to recall some of the quantities formulated in the first work of Avrami, starting from geometric considerations of a crystal aggregate of grains, of various shapes and sizes, resulting of growth beginning at various times in the past from nucleation sites.[3] Such considerations are totally independent of any hypothesis about the distribution of nucleation sites and the only assumption is that grain growth ceases where impingement occurs. Defining as extended the volume of any grain, had its growth been unimpeded by impingement, it is convenient to introduce $V_{1\,ex}=\int_0^t d\tau\sigma K(t-\tau)^3$ as the total extended volume fraction, which includes overlapped grains and also phantom nuclei (nuclei that are created in already growing nuclei and are completely embedded in them), σ being the shape factor ($4\pi/3$ for spheres) and K the rate production per unit volume of nuclei times the cube of their size derivative assumed constant. According to Avrami,[3] the portion of volume lying solely within the regions corresponding to m-overlapping extended grains is given by,

$$V'_m = V_m - V_{m+1}, \tag{1}$$

where V_m is the portion of volume corresponding to the sum of regions with degree of overlapping greater than or equal to m, counted only once,

$$V_m = \sum_{k=m}^{\infty} V'_k = \sum_{k=m}^{\infty} (-1)^{k-m} \frac{(k-1)!}{(m-1)!(k-m)!} V_{k\,ex}, \tag{2}$$

$V_{k\,ex}$ being the portion corresponding to the total volume of overlapping of all groups of k grains counted and added separately without regard to higher overlapping,

$$V_{k\,ex} = \sum_{m=k}^{\infty} \frac{m!}{k!(m-k)!} V'_m. \tag{3}$$

According to such definitions $V_1 = V$ is the usual transformed fraction.

Avrami, in a beautiful piece of algebra, showed in the appendix of his second work,[4] that the assumption $V'_m/V_{m\,ex} = 1 - V_1$ allows to obtain a self-consistent solution of Eqs. (1)–(3), corresponding to $V'_m = (V_{1\,ex})^m \exp(-V_{1\,ex})/m!$, $V_{m\,ex} = (V_{1\,ex})^m/m!$, and $V_1(t) = 1 - \exp[-V_{1ext}(t)]$, in accordance with statistical deriva-

tions based on random distribution of nucleation sites.[1,2,5] Such a result allowed him to elaborate several reasoning to justify it from the very first principles, that can be summarized by the following relation for differential increments:[4]

$$dV_1=(1-V_1)dV_{1ext}. \tag{4}$$

EB questioned the inclusion of phantom nuclei in $V_{1\,ex}$ and proposed the following alternative relation for differential increments

$$dV_1=(1-V_1)dV^*_{1ext}, \tag{5}$$

with $V^*_{1ext}(t)=\int_0^t d\tau\sigma K[1-V(\tau)](t-\tau)^3$, which implies the occurence of nucleation sites only in the untransformed fraction. They stated, in both works they published, that the corresponding solution for V_1 should be given by[6,7]

$$V_1(t)=\int_0^t d\tau\sigma K[1-V_1(\tau)]^2(t-\tau)^3. \tag{6}$$

Michaelsen, Dahms, and Pfuff destroyed their claim showing that such a solution cannot be a bounded one.[8] This can be easily seen in the case of constant σK since, by repeatedly using Leibniz's rule for differentiation of integrals, it is possible to transform such integral equation to a simple differential one,

$$\frac{d^4V_1}{dt^4}=6\sigma K(1-V_1)^2, \tag{7}$$

which for initial condition $V=dV/dt=d^2V/dt^2=d^3V/dt^3=0$ has no limited solutions. However, from Eq. (5), in the case of constant σK, the following differential equation is the correct one:

$$\frac{d^3}{dt^3}\left(\frac{dV_1/dt}{1-V_1}\right)=6\sigma K(1-V_1). \tag{8}$$

It may be surprising but the solution of this last equation differs from KJMA solution in less than 1% also at high transformed fractions (this can be easily done using common commercial softwares for its integration), so it seems irrelevant to use the modified definition of the extended volume if the impingement is treated in a way analogous to Avrami. A similar result is mentioned in Ref. 9, where a numerical simulation of two-dimensional crystallization was done.

At this point what did EB really show in their graphs? We found the implicit answer in their second work where, *en passant,* in Eq. (19) they showed the differential equation they actually solved,[7] that in the case here examined reduces to

$$\frac{dV_1}{dt}=(1-V_1)^2\frac{dV_{1ext}}{dt}, \tag{9}$$

with V_{1ext} and not V^*_{1ext}. The solution of such equation is immediate and gives $V_{1\,ext}=V_1/(1-V_1)$ or alternatively

$$V_1=V_{1ext}/(1+V_{1ext}), \tag{10}$$

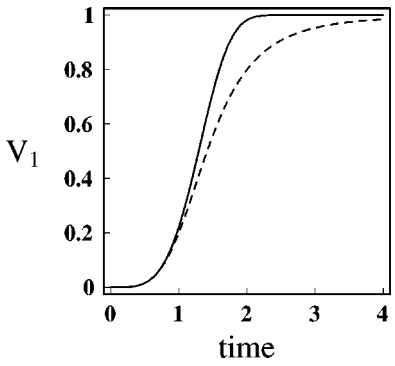

FIG. 1. KJMA (solid line) and AR (dotted line) solutions for the crystallized fraction as function of time in the special case $\sigma K=1$.

with $V_{1\,ext}=\sigma Kt^4/4$ in the case of constant σK, without any need for numerical methods. Expression (10) represents all the curves they showed in both works to better fit experimental results. Such an excellent agreement may be considered amazing at this point, however, it is quite an old result, already mentioned in Avrami's works, which Austin and Rickett empirically proposed the same expression for isothermal transformation of super-cooled austenite into bainite.[3,4,13] In Avrami's second work the Austin-Rickett formula was deduced as an approximated one. For illustrative purposes, in Fig. 1 the KJMA (solid line) and AR (dotted line) solutions are plotted as functions of time in the special case, $\sigma K=1$.

Equation (9) is a special case of the empirical expression $dV_1=(1-V_1)^i dV_{1ext}$ for differential increments formulated well long ago for better fitting experimental data.[14,15] The correction factor for impingement $(1-V_1)^i$ with $0<i<1$ is associated to some degree of order for the crystallization process that is completed in a finite time, while for $i>1$ clustering of nucleation sites should be responsible for the increasing slowness of the process.[18] Therefore, besides deviations from linear grain growth at the end of transformation and/or deviations from isothermal conditions, also deviations from random distribution of nucleation sites could account for the lack of agreement between KJMA predictions and experimental results.

KJMA solution is an exact one, arising from self-consistent assumptions satisfying the geometrical formulation of the problem [this means that the quantities defined by Eqs. (1)–(3) must all be expressed in terms of only V_{1ext}, which can be easily computed] and also satisfying a random distribution of nucleation sites. However, we will show that KJMA solution is not unique when the random hypothesis is relaxed and another solution, reducing to AR formula, satisfying the same geometrical requirements, can be obtained.

It can be easily proved that the assumption

$$\frac{V'_m}{V_{m\,ex}}=(1-V_1)^{m+1}, \tag{11}$$

allows to consistently satisfy relations (1)–(3) with

$$V_{m\,ex}=(V_{1\,ex})^m, \tag{12}$$

$$V_m=(1-V_1)^m V_{m\,ex}. \tag{13}$$

For instance, Eq. (2) reduces to the following identity:

$$\left(\frac{V_{1\,ex}}{1+V_{1\,ex}}\right)^m=\sum_{k=m}^{\infty}(-1)^{k-m}\frac{(k-1)!}{(m-1)!(k-m)!}V_{1\,ex}^k.$$

Correspondingly, $V_1=V_{1ext}/(1+V_{1ext})$ and $dV_1=(1-V_1)^2dV_{1ext}$ in agreement with AR formula and Eqs. (9) and (10). The relation between differential increments can also be written $dV_1=(1-V_1)(V_1/V_{1ext})dV_{1ext}$ and it can be interpreted as if the increment in the transformed fraction is proportional to the increment in the extended fraction, corresponding to the transformed fraction embedded in it, and corrected for the probability of happening in the already untransformed fraction. Such argument seems quite plausible and should be interpreted in terms of statistical considerations as in the case of KJMA solution.

Again some doubt may be raised regarding the validity of considering V_{1ext} or V_{1ext}^* in Eq. (9). It can be shown that if V_{1ext}^* is considered the following differential equation arises for V_1 when σK is constant:

$$\frac{d^3}{dt^3}\left(\frac{dV_1/dt}{(1-V_1)^2}\right)=6\sigma K(1-V_1), \tag{14}$$

and its corresponding numerical solution differs from $V_1=V_{1ext}/(1+V_{1ext})$ in less than 1%, showing again the irrelevance of making any distinction between V_{1ext} and V_{1ext}^*.

In conclusion, the AR empirical formula represents an alternative exact solution of the geometrical problem of impingement that allows to better fit experimental results on isothermal crystallization kinetics.

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