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Random nucleation and growth kinetics

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The classical Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation for nucleation and growth transformations, which assumes random nucleation and cessation of growth where grains impinge, was originally derived by accounting for the ''extended volume'' that is obtained when overlap of the growing grains is (mathematically) permitted. Motivated by experimental and computational results that call into question the validity of this equation and by recent theoretical concerns about the appropriate content of the extended volume, a derivation of the KJMA equation is presented that does not rely on the concept of the ''extended volume.'' [S0163-1829(96)09042-X]

Solid-state transformations occur by nucleation and subsequent growth of second-phase particles in a volume or at an interface.[1] The reaction kinetics may be interface controlled as in the case of recrystallization in plastically deformed metals and crystallization in metallic glasses, or diffusion limited as in the case of second-phase precipitation. For either type of kinetics, researchers typically analyze the transformation according to the theory of nucleation and growth processes developed independently by Kolmogorov,[2] Johnson and Mehl,[3] and Avrami[4] (KJMA) nearly sixty years ago.

This theory requires that the nucleation sites be randomly distributed over the (infinite) volume V (or interface) and that growth cease where two second-phase particles impinge. The transformed volume V^{tr} obeys the relation

$$dV^{\mathrm{tr}} = [1-(V^{\mathrm{tr}}/V)]\,dV^{\mathrm{ex}}, \tag{1}$$

where the ''extended volume'' V^{ex} is the volume of all the particles if they grew unimpeded (see Fig. 1). Integrating this expression and normalizing to unit volume produces the familiar KJMA equation for the transformed volume fraction f,

$$f = 1-\exp(-f^{\mathrm{ex}}), \tag{2}$$

where $f^{\mathrm{ex}} = V^{\mathrm{ex}}/V$.

The particle growth mechanism is implicit in V^{ex} and so can be determined, in principle, from the slope of the line produced by plotting experimental values of $\log[-\ln(1-f)]$ against $\log(t)$, where t is time. For example, in the case of instantaneous nucleation of spherical particles with number density N and constant growth rate G, as may occur for an interface-controlled reaction, $f^{\mathrm{ex}} = (4/3)\pi N(Gt)^3$. The exponent of t, and thus the slope of the line, is 3. Cahn[5] and Christian[1] have showed that other exponents are expected

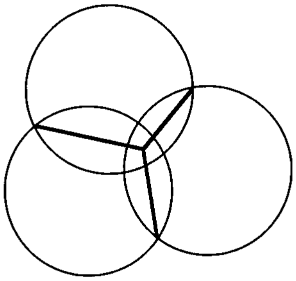

FIG. 1. In this two-dimensional representation, three particles (or grains) have grown together. Growth ceases where the particles impinge, here indicated by the heavy lines. The particle overlap that would occur in the absence of impingement is shown as well; this contributes to the ''extended volume'' that appears in the KJMA equation.

under other conditions such as continuous nucleation, growth in less than three dimensions, and heterogeneous nucleation on planar or linear defects.

In practice, many experiments show a deviation from the expected linear dependence on $\log(t)$, which can generally be ascribed to experimental conditions. As evidence of this, Rollett *et al.*[6] obtained the expected exponent of 3 from a computer simulation of instantaneously-nucleated recrystallization of uniformly deformed metal, and much smaller, time-varying exponents—in agreement with experiments—for corresponding simulations of nonuniformly deformed metal. Even so, the experimental deviations have called into question the correction for the ''extended volume'' given by Eq. (1); indeed, a motivation of the work by Rollett *et al.* was to test this ''basic assumption.'' [6] Price[7] has also simulated recrystallization kinetics under the conditions of instantaneous nucleation and linear growth, but concludes instead that ''the KJMA extended-volume relation overcorrects for impingement.''

For continuous nucleation of second-phase particles, which can occur only in the untransformed volume, Johnson and Mehl[3] and Avrami[4] derive an expression for V^{ex} which includes ''phantom'' particles that nucleate in the already-transformed volume. These ''phantom'' particles are in fact simply a mathematical artifice that is integral to the original derivation of Eq. (2). Nonetheless, their appearance in V^{ex} is a source of confusion. Recently, Erukhimovitch and Baram,[8] believing that these ''phantom'' particles actually contribute to the transformed volume as given by Eq. (2) [so that Eq. (2) overestimates the transformed volume fraction], have argued that they should not be included in V^{ex}, and have derived an integral equation for f from Eq. (1) that appears to provide a much better description of the amorphous-to-crystalline transformation in particular metal alloys.

A derivation of a nucleation and growth equation that imposes the KJMA conditions of random nucleation and growth cessation upon impingement but does not rely on the concepts of ''extended volume'' and ''phantom nuclei'' is thus useful. The straightforward derivation presented here, which in the end verifies the KJMA equation, considers the time-dependent *untransformed* volume and so avoids the issues of particle impingement/overlap and ''phantom'' nucleation altogether. The common criticism (e.g., Ref. 8), that the KJMA equation for continuous nucleation permits nucleation in the already-transformed region, is shown to be false.

In what follows, nucleation is assumed to occur in three dimensions, and particle growth is isotropic; the extensions to lesser dimensions and to different grain morphologies (by use of a geometric shape parameter) are then evident.

For a random distribution of point particles of number density N, let $w(r)dr$ denote the probability that the closest particle to the (arbitrary) origin resides a distance between r and $r+dr$ away. This probability is equal to the probability that no particles reside within the sphere of radius r, multiplied by the probability that a particle does reside within the spherical shell specified by the radii r and $r+dr$. Thus $w(r)$ must satisfy the relation[9]

$$w(r)=\left[1-\int_0^r w(r')dr'\right]4\pi r^2 N. \tag{3}$$

Taking the derivative of each side with respect to r and integrating produces the distribution function

$$w(r)=4\pi r^2 N\,\exp(-4\pi N r^3/3). \tag{4}$$

Now consider that the point particles are nuclei, and that at time t each growing particle has attained (ignoring impingement and not specifying a growth mechanism) a radius $R(t)$. Then the probability $\chi(t)$ that the origin is contained within a particle is equal to the probability that a particle resides within a distance $R(t)$ from the origin,

$$\chi(t)=\int_0^{R(t)} w(r)dr. \tag{5}$$

Because the location of the origin is arbitrary, $\chi(t)$ corresponds to the transformed volume fraction $f(t)$. Performing the integration in Eq. (5) gives the *untransformed* volume fraction

$$1-f(t)=\int_{R(t)}^{\infty} w(r)dr=\exp\{-\tfrac{4}{3}\pi N[R(t)]^3\}, \tag{6}$$

in agreement with the KJMA equation (2) for instantaneous (site-saturated) nucleation. [This derivation of Eq. (6) is due to Markworth.[10]]

To determine the untransformed volume fraction following *consecutive* instantaneous nucleation events, let $1-f_i(t-t_i)$ denote the untransformed volume fraction at time t due to particle nucleation at an earlier time t_i. In the case of two consecutive nucleation events at times t_1 and t_2, respectively, the untransformed fraction of the total volume at time t is

$$1-f(t)=[1-f_1(t-t_1)][1-f_2(t-t_2)], \tag{7}$$

since $[1-f_1(t-t_1)]V$ is the volume at time t that is left untransformed by the particles nucleated at time t_1, and, of that, $[1-f_2(t-t_2)]$ is the volume fraction which is untransformed by the particles nucleated at time t_2. Then for n consecutive instantaneous nucleation events, the untransformed volume fraction is

$$\begin{aligned}1-f(t)&=\prod_{i=1}^{n}[1-f_i(t-t_i)]\\&=\exp\left\{-\tfrac{4}{3}\pi\sum_{i=1}^{n}N_i[R_i(t-t_i)]^3\right\},\end{aligned} \tag{8}$$

where N_i is the number density of particles nucleated at time t_i and $R_i(t-t_i)$ is the radius at time t of those particles due to unimpeded growth over the time period $t-t_i$. Equation (8) thus accommodates multiple nucleation events (due to temperature changes,[11] for example), each generating a new collection of particles with different number density and different growth kinetics.

By converting the summation in Eq. (8) into an integral and the particle number density N into the nucleation rate $\dot{N}$, the untransformed volume fraction at time t due to *continuous* nucleation is found to be

$$1-f(t)=\exp\left\{-\tfrac{4}{3}\pi\int_0^t \dot{N}(\tau)[R(t-\tau)]^3 d\tau\right\}. \tag{9}$$

As in Eq. (8), the nuclei density and growth kinetics are permitted to vary with time.[12,13]

Equation (9) is precisely the KJMA equation (2). This derivation, which considers only the *untransformed* volume, thus effectively verifies the KJMA treatment[3,4] of the ''extended volume'' and shows that it allows particle or grain nucleation only in the untransformed region.

The number density $\rho(t)$ of particles (or grains) is of experimental interest as well, and may further distinguish between microstructures resulting from single and multiple instantaneous nucleation events and continuous nucleation. In the case of multiple nucleation events, there are N_1V particles after the first instantaneous nucleation event at time t_1; an additional $N_2[1-f(t_2)]V$ particles after the second instantaneous nucleation event at time t_2; an additional $N_3[1-f(t_3)]V$ particles after the third instantaneous nucleation event at time t_3; and so on. Thus the number density of particles after n consecutive nucleation events is

$$\rho(t)=\sum_{i=1}^{n} N_i[1-f(t_i)]. \tag{10}$$

In the case of continuous nucleation, the particle number density becomes

$$\rho(t)=\int_0^t \dot{N}(\tau)[1-f(\tau)]d\tau. \tag{11}$$

The average particle size is then given by $f(t)/\rho(t)$.

The interfacial area $S(t)$ between the transformed and untransformed regions following instantaneous (site-saturated) nucleation is found by substituting $S\ dR$ for dV and $S^{\text{ex}}\ dR$ for dV^{ex} in Eq. (1), where S^{ex} is the total surface area of the particles or grains comprising V^{ex}. Then the area

$$S(t)=[1-f(t)]S^{\text{ex}}(t), \tag{12}$$

and attains its maximum value $2\ (2\pi N)^{1/3}\ V\exp(-2/3)$ when $R=(2\pi N)^{-1/3}$, which occurs at the inflection point of the sigmoidal function $f(t)$.

The volume- and surface-reducing effects of particle impingement are evident in the expressions above; for example, the second term in Eq. (12) clearly accounts for the reduction of interfacial area as growing particles or grains coalesce. A more direct measure of the extent of impingement is given by the fraction $\chi'(t)$ of particles that have impinged as of the time t. For instantaneous nucleation, this is simply the probability that another nucleus resides within a distance $2R(t)$ of a given nucleus,[10]

$$\chi'(t)=\int_0^{2R(t)} w(r)dr=1-\exp\{-\tfrac{4}{3}\pi N[2R(t)]^3\}. \tag{13}$$

This sigmoidal function increases much more rapidly [inflection point at $R=\frac{1}{2}(2\pi N)^{-1/3}$] than $f(t)$, indicating the nearly immediate onset of impingement. Interestingly, the fractional quantities f and χ' at their respective inflection points, where their rate of increase is maximal, both equal $1-\exp(-2/3)$ $=0.48658$. [Note that $(d\chi'(t)/dt)dt$ is the fraction of particles that impinge during the time interval t to $t+dt$. For an instantaneously-nucleated population of particles, $(d\chi'(t)/dt)dt=(d\chi'(R)/dR)dR$, so that $(d\chi'(R)/dR)$ is seen to be the size distribution function for the population where growth of a particle stops completely upon impingement with another. The various moments of the distribution are easily calculated using $d\chi'(R)/dR$ obtained from Eq. (13). The transformed volume fraction comprised of these ''touching'' spheres is 1/8; the surface area, per unit volume, of the spheres is $\Gamma(\frac{5}{3})\ (\frac{9}{16}\pi N)^{1/3}=1.091\,41\ N^{1/3}$; and the average radius of the spheres is $\Gamma(\frac{4}{3})\ (\frac{32}{3}\pi N)^{-1/3}=0.276\,98$ $N^{-1/3}$.]

The transformation kinetics of a volume are reflected as well in the area transformed of any arbitrary plane through the volume and in the length of interfacial boundary and number of particles or grains intercepted by the plane. This areal data is generally easier to obtain experimentally than volumetric data. Because any slice through the volume can be made arbitrarily thin, the transformed area fraction $f_A(t)$ equals $f(t)$ (the subscript A signifies areal quantities). Similarly, the length $L_A(t)$ of interfacial boundary intercepted by the plane, per unit area of the plane, equals $S(t)/V$. Thus

$$L_A(t)=[1-f(t)]4\pi N[R(t)]^2 \tag{14}$$

following instantaneous nucleation. The areal number density $\rho_A(t)$ of particles or grains is given by Eq. (11) when the function $\dot{N}$ is replaced by the areal nucleation rate $\dot{N}_A$. For example, a population of instantaneously nucleated particles of number density N and constant growth rate G will provide a continuous nucleation rate $\dot{N}_A=2NG$ at the plane.

It should be emphasized that nonrandom nucleation, such as clustered nucleation or nucleation on a regular lattice, cannot be accommodated by this formulation of nucleation and growth kinetics. Clustering of nuclei can be simulated by partitioning the total volume into subvolumes, where each subvolume has a different nuclei density and transforms according to the equations above at early times; however, interactions between adjacent subvolumes at later times cannot be similarly treated. The difficult issue of clustering has inspired various phenomenological equations for $f(t)$ utilizing the concept of ''extended volume,'' that have little physical basis.[14]

The degree to which an experimentally-observed particle or grain distribution is random can be qualitatively ascertained, for the case of instantaneous (site-saturated) nucleation, by recognizing that the function $w(r)$ [Eq. (4)] gives the distribution of nearest-neighbor distances for a random population.[9] Thus the ''average distance'' D between nearest neighbors of a random distribution of particles or grains is

$$D=\int_0^{\infty} rw(r)dr=\Gamma(\tfrac{4}{3})(\tfrac{4}{3}\pi N)^{-1/3}=0.553\,96N^{-1/3}. \tag{15}$$

A more ordered arrangement of nuclei will produce a larger value for D ($D \geqslant N^{-1/3}$ for cubic arrays), while clustering of nuclei will produce a smaller value.

The classical KJMA equation is recovered from this derivation which has required only that nucleation occur randomly throughout a volume. By considering only the *untransformed* volume, impingement or overlap of the growing particles or grains may be ignored. The particle growth function $R(t)$, by expressing the growth mechanism, assumes a central role in this formulation of transformation kinetics.

For systems for which the assumption of random nucleation is well founded, poor fits of experimental data to Eq. (6) with linear growth may reflect more complex nucleation and growth kinetics that can be better described by Eqs. (8) or (9) and nonlinear $R(t)$ functions.

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[1] J. W. Christian, in *Physical Metallurgy*, 2nd ed., edited by R. W. Cahn (North-Holland, Amsterdam, 1970).

[2] A. N. Kolmogorov, Izv. Akad. Nauk SSSR, Ser. Matem. No. **1**, 355 (1937).

[3] W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Min. Metall. Eng. **135**, 416 (1939).

[4] M. Avrami, J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).

[5] J. W. Cahn, Acta Metall. **4**, 449 (1956).

[6] A. D. Rollett, D. J. Srolovitz, R. D. Doherty, and M. P. Anderson, Acta Metall. **37**, 627 (1989).

[7] C. W. Price, Acta Metall. **35**, 1377 (1987); Acta Metall. Mater. **38**, 727 (1990).

[8] V. Erukhimovitch and J. Baram, Phys. Rev. B **50**, 5854 (1994); **51**, 6221 (1995); J. Baram and V. Erukhimovitch, Innov. Mater. Res. **1**, 109 (1996). In addition to the flawed premise upon which their work is based, there is a mathematical mistake in their derivation [Eq. (8) in the latter paper] that renders their transformation equation incorrect in any case. C. Michaelsen, M. Dahms, and M. Pfuff [Phys. Rev. B **53**, 11 877 (1996)] have noted that the transformed volume fraction, given by that equation, does not converge to 1 as time goes to infinity.

[9] This argument was made originally by P. Hertz [Math. Ann. **67**, 387 (1909)], and more recently by S. Chandrasekhar [Rev. Mod. Phys. **15**, 1 (1943)].

[10] A. J. Markworth, Scr. Metall. **18**, 1309 (1984).

[11] P. Krüger, J. Phys. Chem. Solids **54**, 1549 (1993).

[12] Indeed, Erukhimovitch and Baram (Ref. 8) begin their derivation by simply replacing the integrand in Eq. (9) with $I(\tau)[G(\tau)]^3(t-\tau)^3[1-f(\tau)]$. Thus the factor $[1-f(\tau)]$ is included in either the particle nucleation rate at time τ, so that $\dot{N}(\tau)=I(\tau)[1-f(\tau)]$, or in the growth rate of those particles, so that $[R(t-\tau)]^3=[G(\tau)]^3(t-\tau)^3[1-f(\tau)]$. This phenomenological factor effectively slows the kinetics as the volume transforms, which may account for the improved fits to experimental data found in Ref. 8. (Note that $\dot{N}$ is the particle nucleation rate per unit volume, rather than per total volume, so that an explicit dependence on the transformed volume fraction f as shown above is unlikely.)

[13] E. Woldt, J. Phys. Chem. Solids **53**, 521 (1992); N. X. Sun, X. D. Liu, and K. Lu, Scr. Mater. **34**, 1201 (1996).

[14] See, for example, M. Hillert, Acta Metall. **7**, 653 (1959); A. M. Gokhale, C. V. Iswaran, and R. T. DeHoff, Metall. Trans. A **11A**, 1377 (1980).