THE TIME CONE METHOD FOR NUCLEATION AND GROWTH KINETICS ON A FINITE DOMAIN.

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Abstract

The Kolmogorov-Johnson-Mehl-Avrami theory is an exact statistical solution for the expected fraction transformed in a nucleation and growth reaction in an infinite specimen, when nucleation is random in the untransformed volume and the radial growth rate after nucleation is constant until impingement. Many of these restrictive assumptions are introduced to facilitate the use of statistics. The introduction of "phantom nuclei" and "extended volumes" are constructs that permit exact estimates of the fraction transformed. An alternative, the time cone method, is presented that does not make use of either of these constructs. The method permits obtaining exact closed form solutions for any specimen that is convex in time and space, and for nucleation rates and growth rates that are both time and position dependent. Certain types of growth anisotropies can be included. The expected fraction transformed is position and time dependent. Expressions for transformation kinetics in simple specimen geometries such as plates and growing films are given, and are shown to reduce to expected formulas in certain limits.

1 Introduction.

The Kolmogorov [1], Johnson-Mehl [2], and Avrami[3, 4, 5] (JMAK) theory of nucleation and growth reactions is the earliest example of an exactly solvable, although phenomenological and stochastic, kinetic model of a first order phase transformation. The model assumes an infinite specimen that is untransformed at time 0. It posits a given stochastic rate (number per unit untransformed volume per unit time) of creation of point nuclei that are randomly distributed in the remaining untransformed space. A grain is assumed to grow radially at a given constant rate from the moment of creation of each nucleus until impingement with other growing grains. Growth ceases at all points of impingement. Because of the statistical homogeneity, exact solutions were given for many aspects of the phase transformation; among them the volume fraction transformed as a function of time, the number of grains (equal to the number of nuclei), the unimpinged and impinged surface area, the length of triple junctions and the number of point junctions of four grains in the final structure[5, 6, 7, 8, 9, 10]. These assumptions are met approximately for a large number of first order phase transformations. The theory has been widely used. Its simplicity has also led to extensions for first order transitions where the theory is clearly not even approximately applicable. [11]

At least three general methods of deriving results are in the literature. Johnson and Mehl and Avrami focussed on computing the fraction transformed. This was done by calculating an extended volume fraction transformed X_e by assuming continued nucleation in the entire volume and unimpeded intergrowth, ignoring impingement, and making an exact statistical correction for the multiply counted transformed regions. Kolmogorov examined the probability that a point that had not transformed would transform in the time interval between t and $t + dt$ and integrated this expression over time. Jackson ([12] focussed on calculating the probability that a point x in one dimension is not transformed at a time t by computing the probability that no nucleus had formed earlier that would have led to transformation at that point. The method he used will be extended to finite specimens in this paper. Meijering also mentions this method briefly and did not make much use of it.[6]

Activities on extending the theory began with the original articles. The requirements for an exact theory permitted relaxing many of the assumptions with little modification of the theory; letting nucleation rates to be time dependent, which includes assuming that nuclei are present at time 0,[1, 13] confining nucleation to a set of randomly placed points, [4] letting the growth rate of a grain depend on time (but not on the time that the grain nucleated),[1, 2, 14] and allowing for some form of growth anisotropy (Some of the limitations on the functional form of anisotropy growth rates were correctly recognized,[1, 9] but the Kolmogorov's quantitative treatment was incorrect.). Kinetics during heating and cooling have been treated exactly by assuming that both the nucleation and growth rates depend on a time dependent temperature, in a specimen which is assumed isothermal at each instant. Such a theory for idealized cooling or heating experiments is widely used both for research purposes and for practical industrial applications.

Some sort of uniformly random spatial aspects (also called homogeneous in the statistics papers) of the nucleation seemed central to obtaining exact results in the original theory.[7] To avoid confusion in this paper, homogeneous nucleation and heterogeneous nucleation on randomly dispersed sites in a volume will be called "volume" nucleation, heterogeneous nucleation on surfaces and lines will be called "surface" and "line" nucleation. Homogeneous will denote uniform probability. Spatial homogeneity is met by the assumption of an infinite system with spatially uniform nucleation rates. But it can be easily shown that the theory can be extended to cases of surface or line nucleation if certain symmetries are present; each point on a surface or curve, to which the nucleation is confined, must have identical surroundings and nucleation rates. Thus, an exact theory can be made for nucleation on surfaces, such as planes, spheres, and on curves, such as lines, circles, and even helixes.[15] In an unpublished appendix to their original paper Johnson and Mehl gave an exact solution for a spherical specimen in which all nucleation was random but confined to the sphere surface.[16] In this finite domain example, exact results are obtainable because there is a stochastic homogeneity to the heterogeneous nucleation sites, and a related homogeneity in the same spherical boundary to the specimen that stops the growth. (Every grain nucleating at the same time has the same statistical shapes; the same chances of impingement with other grains and with the specimen surface.) It is apparent that the method Johnson and Mehl used would work equally well on nucleation confined to a single spherical surface in an infinite domain with inward and outward growth, or to outward growth from nuclei on the surface of a single void. This aspect of the theory permitted adaptation to random nucleation confined to a planar surface, either within an infinite space or bounding a half space, or to a line within an infinite space or at the apex of an infinite wedge, and these exact results were used in an approximate theory of grain boundary nucleated reactions.[17]

When there is a surface bounding the specimen domain the stochastic method of correcting the multiple counting in the extended volumes used by Johnson and Mehl fails for volume nucleation. Nonetheless good approximate solutions have been found for certain ratios of the parameters and for many specimen geometries that are accurate at short or long times. For example, at times that are long compared to the time it takes for a grain to grow across the thickness of a thin wire or thin film, one or two-dimensional JMAKs result becomes respectively valid approximations. Results for other geometries, such as spheres with volume nucleation, have been obtained by simulation[18] and for time dependent nucleation and growth.[19] Many of these geometries can be easily handled analytically by the theory presented in this paper.

Finite specimen geometries result in a spatial stochastic inhomogeneity. But since the nucleation is already inhomogeneous in time,[7] the insistence on spatial homogeneity would seem to be unwarranted. In this paper we explore an alternate way of derivation that allows for exact results under a much greater set of assumptions, including most cases of specimen geometry more complex than thin films and wires, and even cases where the specimen geometry changes with time as in the case of a growing film. To illustrate the method for dealing with problems in specimen geometry, we will keep other factors in this paper simple; nucleation and growth rates are kept constant in space, but not in time, and the growth rates is assumed isotropic as well. Results are expected to depend on position, which can be averaged to compare with experiments that measure averages or with results for infinite uniform systems. We will see that many approximations in the literature were unnecessary and some clearly wrong.

To demonstrate this method we begin with a rederivation of the classical JMAK result for volume fraction transformed in any dimension in an infinite specimen, and then extend the method for finite specimens. In a subsequent paper we will also include cases of spatial inhomogeneity, where nucleation and growth rates are functions of position as well as time and where growth rates can have a limited anisotropy.

2 A rederivation of the classical JMAK results for volume fraction transformed.

We assume that the system is an infinite line, planar surface, or a three or higher dimensional volume, in which there is no transformation at time 0, a constant (or time dependent) nucleation rate in the untransformed volume after time 0, and that each nucleus grows radially with a constant (or time dependent) rate until growth ceases at each point of impingement. The Johnson and Mehl method,[2] focusses on exact statistical estimates of the volume fraction transformed (which is $1-P$, where P is the fraction untransformed) by calculating the volumes transformed as if there were no impingement and no reduction in nucleation rate due to the reduction in P and then making exact statistical estimates for the corrections for impingement and the reduction in nucleation rate. In this section we calculate directly the estimate P that a point $\mathbf{x}$ in the volume will be untransformed at time t. This is done by computing the probability that no nuclei formed at all earlier times τ and positions $\mathbf{x}'$, that could have grown to reach point $\mathbf{x}$ at t. (It has to be none; if there are some, it does not matter how many.)

We do this in three steps:

1. It will be convenient to combine a d-dimensional space with time into a single space, and define a d+1 dimensional space Ω and a point ω in this space. In three dimensions, $\omega = (x, y, z; t) = (\mathbf{x}; t)$. We then construct for the point $(\mathbf{x}; t)$ a domain in this space that is the set of all points and earlier times $(\mathbf{x}'; \tau)$ that would have caused transformation at $(\mathbf{x}; t)$ had nucleation occurred. This domain will be a subset of Ω and will be designated by Ω_c. Since its shape is a cone, it will be termed an "influence cone" or "time cone." Its surface will be called an "event horizon."

2. Integrating the nucleation rate over the time cone to obtain the number of nuclei $< N >_c$ expected in Ω_c.

3. Making use of the stochastic independence of the nucleation events to estimate P

$$P = e^{-<N>_c}. \tag{2.1}$$

2.1 The time cone Ω_c when $V = V(t)$

At time t the radius of a grain that nucleated at time τ is

$$R(t, \tau) = \int_{\tau}^{t} V(t')dt'. \tag{2.2}$$

If the magnitude of the grain radius R exceeds the distance between $\mathbf{x}'$ and $\mathbf{x}$,

$$R(t, \tau)^2 - |\mathbf{x} - \mathbf{x}'|^2 \geq 0, \tag{2.3}$$

the point $\mathbf{x}$ will have transformed before time t. The time cone is the set of all points that satisfy this inequality.

The surface of the time cone, which is the event horizon are the nuclei points $(\mathbf{x}; t)$ that grow as grains that reach $\mathbf{x}$ exactly at time t. They are given by the points in Ω for which the inequality (2.3) is an equality. This allows the introduction of the method of characteristic applied to geometric growth [21, 22, 23] into the time cone theory. Such growth theories are based on the time $t(\mathbf{x})$ of arrival of a moving surface at a point $\mathbf{x}$. Thus t is a function of $\mathbf{x}$. The surface at any time t is a level surface of $t(\mathbf{x})$. If the surface is smooth, the direction of the gradient of t is parallel to the normal to the surface,$\mathbf{n}$, and its magnitude is $1/V$. Thus $\mathbf{n} = \nabla t/|\nabla t|$, and $|\nabla t| = |1/V|$. In a subsequent paper, we will use characteristics to construct time cones when V is a function of $\mathbf{x}, t$ and $\mathbf{n}$ with only a few restrictions, and derive relations for the kinetics for specimens that are anisotropic and inhomogeneous in space and time. One crucial corollary of the theory is that it can identify the assumptions necessary so that nuclei from points outside the time cone never grow into the time cone. [15]

If V is constant, equation(2.3) becomes the equation of the points in a cone,

$$V^2(t-\tau)^2 - |\mathbf{x}-\mathbf{x}'|^2 \geq 0. \tag{2.4}$$

Compare this equation with one for the time horizon for the point $(\mathbf{x};t)$ in the theory of relativity, $c^2(t-\tau)^2 - |\mathbf{x}-\mathbf{x}'|^2 = 0$, where c is the velocity of light. At any time τ the spaces in which any nucleation event will affect $(\mathbf{x},t)$ are thus: in 1-d, a line segment of length $2V(t-\tau)$; in 2-d a circle with radius $V(t-\tau)$; in 3-d a sphere with radius $V(t-\tau)$; etc., all centered on $\mathbf{x}$, and increasing in size the further back in time we go. With growth rates that depend on time, the event horizon is a conical surface of revolution in this space with apex at $(\mathbf{x};t)$ with its axis parallel to the time axis, and given by

$$\Omega_c(\mathbf{x};t) = \{(\mathbf{x}';\tau) : R(t,\tau)^2 - |\mathbf{x}-\mathbf{x}'|^2 \geq 0\}. \tag{2.5}$$

The time cone can be considered unbounded in the negative time direction, to times before the onset of nucleation, if a value is assigned to $V(t)$. Because $\alpha = 0$ there, the results do not depend on what is chosen for V.

2.2 The expected number of nuclei in Ω_c

If the nucleation rate is given by $\alpha(\mathbf{x};t)$ (number of nuclei expected in unit time and unit d-dimensional "volume") the expected number of nuclei in the time cone is the integral of α over the time cone in space and time.

$$< N >_c = < N >_c (\mathbf{x};t) = \int_{\Omega_c} \alpha(\mathbf{x}';\tau) d\omega \tag{2.6}$$

When $\alpha = \alpha(t)$ and $V = V(t)$ for $t \geq 0$ and 0 for negative time, equation (2.6 can be integrated over space. For 3-dimensions, this gives

$$< N >_c (t) = \frac{4\pi}{3} \int_0^t \alpha(t') R(t,t')^3 dt'. \tag{2.7}$$

This form is useful for heating and cooling experiments.

Equation (2.7) simplifies even more when α is constant for positive time. Then $< N >_c$ becomes α multiplied by the "nucleation" volume $\|\Omega_N\|$, the volume in space-time of the cone where (and when) there is nucleation, or equivalently the volume of the intersection of the cone Ω_c with the constant nucleation rate domain of Ω. Thus when α is constant for positive time

$$< N >_c = \alpha \|\Omega_N\|. \tag{2.8}$$

For the classical JMAK theory this intersection of the cone with the nucleation space is a right truncated cone, whose volume $\|\Omega_N\|$ is the height t multiplied by the base B at $t = 0$ divided by $(d+1)$.

(2.9)
$$< N >_c = \alpha Bt/(d+1).$$

The bases B and the $\|\Omega_N\|$ are respectively in 1, 2 and 3 spatial dimensions: $2Vt$ and Vt^2; πV^2t^2 and $\frac{\pi}{3}V^2t^3$; and $\frac{4\pi}{3}V^3t^3$ and $\frac{\pi}{3}V^3t^4$.

2.3 The probability, $P(\mathbf{x}, t)$, that $\mathbf{x}$ is untransformed at t.

The postulated stochastic independence of the nucleation events make them Poisson distributed.[20] As a result

(2.10)
$$P(\mathbf{x}; t) = e^{-<N>_c}$$

This well-known result can be demonstrated in two ways:

1. By considering how P is changed when there is a change $d\omega$ in Ω_c,

(2.11)
$$-\,dP = P \cdot \alpha d\omega,$$

which is readily integrated to give

(2.12)
$$log P = -\int_{\Omega_c} \alpha d\omega = -< N >_c .$$

2. Alternatively we can use the Poisson distribution for finding n events when the expectation is N,

(2.13)
$$p(n, N) = N^n e^{-N}/n!.$$

Evaluated at $n = 0$ this gives $p(0, N) = e^{-N}$, which can be identified with P.

Equation (2.10) combined with equation (2.6), or when appropriate (2.7) or (2.8), are the basic equations of this paper. When α and V are constant, equation (2.6) may be replaced with equation (2.9), which is identical to the classical JMAK results for any dimension. In 3 dimensions this result is

(2.14)
$$P(\mathbf{x}; t) = e^{-\frac{\pi}{3}\alpha V^3 t^4}.$$

3 Generalizations of the theory to finite convex specimens.

The goal of this paper is to explore how the time cone theory can be made exact when the specimen is finite and convex and when α and V are functions of time alone. We let the time cone for the point $(\mathbf{x}; t)$ continue to be the set of all points in time and space $(\mathbf{x}'; \tau)$, including points outside the specimen, that, had nucleation occurred there and then, would have resulted in transformation at the point $(\mathbf{x}; t)$, if there were no interference from other grains. Extending the cone beyond the specimen boundary is tantamount to assuming that the grains that might have nucleated outside the specimen can grow into the specimen, which causes no problem if the nucleation rate is set to 0 outside the specimen and at times before the experiment began. By assuming that the specimen is convex in shape (and time), we insure that there is no interference from the specimen boundary from the nucleation event at $(\mathbf{x}'; \tau)$ to the point $\mathbf{x}$ at time t. With this assumption, time cones for finite specimens remain exactly as for an infinite specimen, equation (2.3); if V is constant, a cone in space-time with sides sloping by $1/V$, and if V is time dependent a conical surface of revolution with sides sloping by 1/V(t). We let the nucleation rate be whatever it is in the specimen and identically 0 outside the specimen. We then calculate the expected number of nuclei in the time cone by integrating the nucleation rate as before in equation (2.6). If the nucleation rate is constant in the specimen, the expected number of nuclei remains simply proportional to the "volume" of the intersection $\|\Omega_N\|$ of the nucleation time period in the space of the specimen with the time cone. $\|\Omega_N\|$ will be a function of the position $(\mathbf{x};\mathbf{t})$ of the apex, and the time period of the nucleation and the geometry of the specimen. The expected fraction untransformed will then be given by equation 2.10.

3.1 Specific Geometries.

Let us next examine some specific geometries.

1. Transformation near the planar surface $z = 0$ of a semi-infinite solid, half plane or half line.

If we look at the transformation for points on the surface, we have exactly halved the expected number of nuclei. Thus the expected fraction untransformed at the surface is the square root of what it would be deep in the interior. For 3-d this would be

$$P(0;t) = e^{-\frac{\pi}{6}\alpha V^3 t^4}. \tag{3.1}$$

Indeed $P(0;t)$ equals the $\sqrt{P(\mathbf{x};t)}$ as given in equations (2.14). More generally for any (z,t) we compute the volume of a cone truncated by a plane parallel to its axis. If $z \geq Vt$ the cone is not truncated and the surface has no effect on reducing the amount of transformation. If $z < Vt$ the cone is truncated and its volume is $(\pi/6V)[(Vt)^4 + 2z(Vt)^3 - 2z^3Vt + z^4]$. Defining a reduced distance from the specimen surface $Z = z/Vt$ we obtain for $0 \leq Z \leq 1$

$$P(Z;t) = e^{-\frac{\pi}{6}\alpha V^3 t^4[1+2Z-2Z^3+Z^4]}, \tag{3.2}$$

which may be rewritten

$$P(Z;t) = f_1(Z;t)e^{-\frac{\pi}{3}\alpha V^3 t^4}, \tag{3.3}$$

If $0 \leq Z < 1$ the correction factor

$$f_1 = e^{\frac{\pi}{6}[1-2Z+2Z^3-Z^4]\alpha V^3 t^4}; \tag{3.4}$$

when $Z \geq 1$, $f_1 = 1$. Because the lead term in the correction factor has the same Avrami exponent of 4 a plot of $log\ log P(z)$ versus $log t$ will have two parallel asymptotes. At any time a plot of $log P$ will show a surface zone of reduced transformation with limiting values in the square root relation.

2. Transformation at a point z in an infinite thin film of thickness ζ.

Without loss of generality we let $0 \leq z \leq \zeta/2$, and compute the volume of a cone truncated at $t = 0$ and by up to two planes parallel to its axis. If z (and $\zeta - z$ as well) is greater than Vt the film surfaces have no effect on reducing the transformation and equation (2.14) holds. If $z < Vt$, but $(1-z) > Vt$), the cone intercepts only one surface, and the reduction in transformation is as in the semiinfinite case, equation (3.2). If $(1-z) < Vt$ we have to subtract the effects of two planar truncations and obtain an equation whose domain of validity spreads from the center of the film when $Vt = \zeta/2$ and reaches the surfaces when $Vt = \zeta$

$$\|\Omega_N\| = \frac{\pi}{3}V[\zeta(Vt)^3 - (z^3 + (\zeta - z)^3)Vt + (z^4 + (\zeta - z)^4)/2]. \tag{3.5}$$

Although the Avrami time exponent of 4 has disappeared when $Vt = \zeta$, the behavior has not quite become 2-dimensional since there remains a correction factor as seen in the remaining terms with lower time exponents.

$$P(z;t,\zeta) = f_2(z;t)e^{-\frac{\pi}{3}\alpha\zeta V^2 t^3}. \tag{3.6}$$

The product $(\alpha\zeta)$ can be considered the nucleation rate per unit area of film; then the time dependent factor f_2 is a correction for the true three- dimensionality of the problem. Letting $X_1 = z/\zeta$, $X_1 + X_2 = 1$, and a reduced time $\theta = Vt/\zeta > 1$ we obtain

$$f_2 = e^{\frac{\pi}{3}[\alpha\zeta^4/V][(X_1^3+X_2^3)\theta+(X_1^3+X_2^3)/2]}. \tag{3.7}$$

While this correction factor to P increases with time, its effect on $logP$ decreases. (Although the lead time exponent is that of two-dimensional kinetics, the results are bracketed between the two and three dimensional JMA expressions.)

In many experiments an average over z or P is wanted

$$< P >= \frac{1}{\zeta}\int_0^\zeta P(z)dz. \tag{3.8}$$

This is readily computed numerically from the above expressions. However since $P(z)$ is a smooth curve, Simpson's Rule, with three points, $z = 0, \zeta/2, \zeta$,

$$< P >= \frac{1}{3}(P(0) + 2P(\zeta/2)) \tag{3.9}$$

should be an adequate approximation. Until $t = \zeta/2V$, this approximation takes on the form

$$< P >= \frac{1}{3}((1 + e^{-\frac{\pi}{6}\alpha V^3 t^4})^2 - 1).$$

Thereafter equations (3.2 and 2.14) must be used.

3. Transformation after deposition of a continuously growing specimen.

To illustrate that there is no need to fix specimen boundaries in time, we consider steady continuous deposition followed by transformation. We assume steady deposition of a one phase, say a glass, since infinitely long ago, and that this phase transforms, say devitrifies, with JMA kinetics. Let the surface of the specimen be given by $z_s = V_s\tau$ with $V_s > V = \beta V_s$, and consider the transformation at $z \leq V_s\tau$. The time cone is now truncated with a sloping hyperplane $z = V_s\tau$. When V_s is infinite this plane becomes the base, $\tau = const = 0$, of a right truncated cone and the result should correspond to the classic JMA. When $V \geq V_s$ the cone volume is infinite and transformation is complete everywhere in the specimen. (When $V_s = 0$ the plane is one of the truncation planes of the half space problem.)

The volume of the truncated time cone is $(\frac{\pi}{3})V^3(t-z/V_s)^4/(1-\beta^2)^2$. Because of the translational invariance we need only study $z = 0$ for $t \geq 0$, and

$$P(0;t) = e^{-\frac{\pi}{3}\alpha V^3(\frac{t}{\sqrt{1-\beta^2}})^4}. \tag{3.10}$$

Something like a Lorenz time dilation by a factor of $\sqrt{1-(V/V_s)^2}$ is showing up in this problem with V_s, instead of V, behaving like the velocity of light in relativity. As V approaches V_s, the intersection of the time cone with the nucleation domain diverges, and the transformation goes to the completion at the growing surface. This parallel with the Lorenz factor fails in surface nucleation in which the time dilation is $(1-(V/V_s)^2)^{3/4}$.[15]

The deposition of a thin film growing with a velocity V_s beginning at $t = 0$ from a substrate at $z = 0$ followed by transformation, is computed with an additional truncation of the cone by the plane $z = 0$. There is no difficulty with this, but two expressions are obtained; one is equation(3.10) when $z \geq V_s t$.[15]

4 Discussion.

The classical JMAK results have been rederived using the time cone method, which does not make use of the conceptual artifacts of extended volume and ghost nuclei that are part of many earlier derivations of the exact theory. As expected the new method gives exactly the same result, but it permits the derivation of exact results for a whole class of inhomogeneous problems. In this paper we have illustrated this with the finite specimen examples of the last section.

It should not be surprising that identical results are obtained by two exact theories for the same model, JMAK and the time cone method. What is surprising is that two different physical concepts, extended volume and expected number of nuclei in the time cone, have identical expressions, i.e. we have found that $X_e =< N_c >$. That this equality is valid for a time dependent α and V can be seen by comparing equation (2.7) with the corresponding one for X_e in the literature.[1],[11]

In recent years there have been mistaken criticisms [24, 25] of the Johnson-Mehl and Avrami derivation, specifically that only nucleation in the untransformed volume should be used in computing the extended volume, that "ghost" nucleation should be excluded while keeping the correction for impingement. These recently "revised" calculations are purported to be the exact results of the same transformation model as JMAK and were shown to fit some experiments much better than JMAK at late times. However if an experiment does not fit the original JMAK we must look for physical reasons and try to create a new model that is valid for this experiment, rather than make an exact theory inexact. Because the time cone method does not rely on either of the two constructs that are part of the extended volume, the results can be viewed as an independent confirmation of the correctness of the original JMAK derivation.

The importance of an exact theory is that any disagreement between theory and experiment points to a failure of the experiment meeting one of the physical assumptions or vice versa; the construction and the use of the extended volume are not physical assumptions, but part of a technique of finding an exact solution for a particular set of physical assumptions. The agreement between the erroneous JMAK theory and experiment can only be fortuitous. Some physical assumption is not met in the experiment and understanding is advanced by tracking down the reason: nucleation may not be random or its rates may not be constant in time, growth rates may not be constant in time, grains may influence each other through diffusion or stress fields; etc. Because the time cone method does not rely on either of the two constructs that are part of the extended volume, the results can be viewed as an independent confirmation of the correctness of the original JMAK derivation.

Plotting $log\ logP$ versus $logt$ is an attempt to fit the transformation rate to a JMAK theory. The slope of such curves is the exponent of time in the classical theory, sometimes called the Avrami exponent, and equals the dimension plus one. In some analyses this exponent, determined from a linear fit to experiment, is used to attempt to ascertain information about the mechanism of the transformation, or to determine time exponents of algebraic fits to either the nucleation rate [13] or growth rate.[11] This is rarely valid without some independent measurement of nucleation or growth rates. Sometimes the analysis of the data is even used for experiments in which diffusion controls the rate of growth; overlapping diffusion zones from different grains affect growth and affects the nucleation process in ways that invalidate the stochastic independence. Nonetheless in the very early stages independent nucleation and growth can be assumed. The early growth rate is assumed time dependent, proportional to $t^{-1/2}$. For such processes, the exponent of 3/2 is interpreted as implying that all nuclei are present at the beginning, and 5/2 that nucleation continues at a constant rate (unlikely at best). Many ad hoc attempts to correct for such effects have been put forth.[27]

The importance of the exact JMAK theory is for late stages; the failures of the assumptions show up only later. For the early stages, when nuclei are few and too far apart to affect each other, much simpler theoretical methods suffice, even for transformations that deviate significantly from JMAK assumptions. The exponents have some meaning during the early stages of the transformation when nucleation and growth of each grain proceeds independently of the others; when there is little impingement, corrections for it are unnecessary. The fraction transformed $1 - P$ equals the extended volume fraction X_e, and both equal $logP$, only when there is little transformation. Then if nucleation and growth rates can be expressed as algebraic functions of time, the time exponents will be a sum of the time exponent of the nucleation rate plus the dimension multiplied by the time exponent of the growth, regardless of whether the JMAK assumptions are met. But at late times the differences show up. For example, an exact theory for nucleation followed by diffusional growth in which V depends initially on $t^{-1/2}$ gives an Avrami exponent of 1 for the approach to equilibrium (neglecting surface energy and hence coarsening too) in any dimension, regardless of many assumptions about the nucleation rate (e.g. whether nucleation occurs at a constant rate or all nuclei are present at $t = 0$). The change of time exponent from 5/2 or 3/2 to 1 at late times is without a change in mechanism.[28]

Specimen boundaries introduce a spatial inhomogeneity into the problem whose influence spreads with time. Time inhomogeneity was inherent in the original JMAK problem, and indeed the JMAK methods could easily deal with nucleation and growth rates with arbitrary time dependencies. The cone method can handle time inhomogeneity as easily as a wide variety of spatial inhomogeneities. In this paper we kept the specimen convex in order to make the cone construction depend only on growth rate and not on the specimen boundary. We have allowed the specimen to change its surface in time as well. A more general cone method can allow for an anisotropic growth rate that depends on position and time in a specimen that is not convex in space and time.[15] In this paper we have made the boundary surface inactive as a nucleation site. The surface region has less transformation, small systems transform more slowly. Often the opposite is found when the surface is a source of nuclei. This was considered approximately forty years ago[17] and will be reconsidered with the cone method in a subsequent paper.[29]

What are the essential features of when the cone method can give exact results? For the construction of the cone, it is clear that the growth rate of a grain can be dependent on time, space and the orientation of the normal, but should not depend on the presence of any other grain until impingement. Here the assumptions that lead to geometric growth and the method of characteristics have much to contribute to the theory. For computing $< N_c >$ the nucleation rate at a point can be dependent on time and the coordinates of that point (space dependent). The properties of stationary or moving specimen boundaries matter; they cause no difficulty if they are is simply places where growth in certain directions is limited.

Many relaxed assumptions are still sufficient for the required stochastic independence for calculating P. The boundary simply defines the space outside the specimen where nucleation does not occur; again since nucleation can be space and time dependent, it does not matter whether the specimen boundary is stationary or moving, and whether or not it is a source of nuclei. In the JMAK assumptions a nucleation event should not depend on nucleation or growth of any other grain until the growth of some grain overruns that point. This apparent interdependence of nucleation events may have been at the heart of some of the erroneous rederivations.

For transformation for which all the JMAK assumptions are met, except for the finite size of the specimen, the cone method will provide rigorous results. But while the cone method will also permit obtaining exact results with other relaxations of the assumptions, many first order phase changes fall outside. Solidification when the matrix is fluid and the growing grains can settle, as in a casting or porphyritic mineral, is an obvious example where the JMAK results continue to be applied with doubtful validity. [10, 26] On the other hand settling may be negligible in spherulites growing from a viscous polymer, or spherical eutectics growing in a thin layer of organ pipe metal. A martensitic transformation in which the various components of the stress fields of existing plates or rods ("grains" of martensite) can both increase and decrease the nucleation of new plates is another example too far from the JMAK assumption.

Failure of some of the assumptions combined with the cone method may lead to exact bounds on some kinds of transformation. For diffusion controlled or disallowed anisotropic growth it may still be possible to construct the cone to include all points in time and space which will lead to transformation at $(\mathbf{x}, t)$ if no grains growing from nuclei outside the cone interfered. But such interference does occur through the diffusion fields and can only lead to a reduction of the amount of transformation. The general case of anisotropic growth provides another example of such a bound. Having statistical noise in $V(t)$ might be treated with a cone with a fuzzy surface. The method does seem to have enough flexibility to warrant reexamining my cases.

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