Function space theory of dynamic nucleation during solidification at high cooling rates

S K DAS

Computer Applications Division, National Metallurgical Laboratory, Jamshedpur 831 007, India

Abstract. An analytical theory is proposed to study the dynamic nucleation of crystals from melt at very high cooling rates (10^{-6} to 10^{-12} °K/sec). The mathematical framework is found to be isomorphic with the function space theory, wave and matrix mechanics, which enables application of various approximate methods of the latter disciplines. In principle, the mathematical apparatus and concepts of function space and wave mechanics can be utilized to study the time varying nucleation process. The Arrhenius law has been used to extrapolate the self-diffusion coefficient as a function of temperature above the melting point than those below. Since, applicability of Arrhenius equation at very high degrees of supercooling is not known and has to be substituted with appropriate constitutive relationship based on free volume theory of transport, the conclusion derived from the present analysis will not be unique with respect to the certainty of crystallization during the solidification process.

Keywords. Function space; wave and matrix mechanics; dynamic nucleation; orthogonal set; isomorphism; solidification.

1. Introduction

The rapid cooling of liquid metals (range $\sim 10^{-6}$ to 10^{-12} °K/sec), also known as rapid solidification (RS) has attracted a great deal of attention because of the wide range of opportunities it has opened for materials science and engineering (Collins 1986; Haour and Boswell 1987). A very important and also very difficult problem is the study of nucleation and crystal growth kinetics for RS processes coupled with phase transformation. Typically, the new phase forms by clustering or aggregation process that produces a definite distribution of nuclei with a wide variety of sizes (Christian 1975; Hirth 1978).

In RS process, one of the basic question concerns with the avoidance of homogeneous nucleation of the solid phase and the clue lies with the attainment of steady state distribution of embryos during kinetic process of nucleation (Turnbull 1948, 1950; Kantrowitz 1951; Abraham 1969; Shugard and Reiss 1976). For steady state, the rate of nucleation is given by the well known expression (Frenkel 1946)

$$\Omega = Be^{(-\omega/KT)}, \tag{1}$$

where, Ω is the number of nuclei produced per unit volume per unit time, B, a pre-exponential factor, ω the reversible work which must be expended to produce an embryo of the size of a nucleus, K the Boltzmann constant and T the temperature. If the cooling is linear with cooling rate η, then

$$T = T_0 - \eta t, \tag{2}$$

where t is time and T_0 the initial temperature. The total number of nuclei produced per unit volume by the time the temperature attains T is

$$N = \int_0^t \Omega(t)dt = -\frac{1}{\eta}\int_0^T \Omega(T)dT. \tag{3}$$

On the basis of the steady state theory of nucleation (Frenkel 1946), N (defined in (3)) can be evaluated which is based on system of differential–difference equation of the form

$$\frac{\partial \phi_j(t)}{\partial t} = -\kappa S_{j-1}N_{j-1}\left[\frac{\phi_j}{N_j} - \frac{\phi_{j-1}}{N_{j-1}}\right] + \kappa S_j N_j\left[\frac{\phi_{j+1}}{N_{j+1}} - \frac{\phi_j}{N_j}\right], \tag{4}$$

where $\phi_j(t)$ is the population per unit volume at time t of embryos composed of j molecules, and N_j the equilibrium concentration of embryos of the same size at the temperature under question. κ is the number of molecules which impact and stick to the unit area of embryo surface and S_j the surface area of an embryo size j. Earlier analytical work on dynamic nucleation problem (Abraham 1969; Shugard and Reiss 1976; Hirth 1978) addressed some of the aspects, such as temporal dependence of ϕ_j, the longest relaxation time and incubation time in a somewhat approximate manner.

In this paper, a methodology for exact solution of the dynamic nucleation process has been worked out and an attempt has been made to evaluate the lower bound of the relaxation time on the basis of eigen value analysis. The mathematical framework is isomorphic with that of wave and matrix mechanics which embodies the basic concepts of function space and inner product spaces (Hilbert space) (Morse and Feshbach 1953; Constant 1954; Margenau and Murphy 1956). This facilitates application of relevant mathematical apparatus of the discipline such as variational principle and perturbation techniques to obtain an estimate of ϕ_j and upper and lower bounds of relaxation times can also be derived with some additional effort.

2. Function space theory and solution formalism

The function space theory, matrix and wave mechanics are well known in the domain of functional analysis, topology and quantum mechanics. A complete set of 'n' orthogonal functions (sometimes normalized) defines a n-dimensional function space which has structurally similar properties as the n-dimensional vector space. The function space is called a Hilbert space with the additional definition of inner product for complex functions. To obtain matrix mechanics, a complete orthogonal set of functions are chosen to form the basis spanning the function space (Hilbert space) and all wave functions can be expanded in terms of this basic set of functions.

The principle of detailed balance which is embedded in the governing equation (4) of nucleation process based on classical theory enables introduction of a self-adjoint formalism. This establishes a correspondence with function space theory and matrix mechanics.

The temporal variable can be transformed as:

$$\tau = \kappa t. \tag{5}$$

Equation (4) can be rewritten with the transformed variable as:

$$\frac{\partial \phi_j(\tau)}{\partial \tau} = S_{j-1}N_{j-1}\left[\frac{\phi_j}{N_j} - \frac{\phi_{j-1}}{N_{j-1}}\right] + S_j N_j\left[\frac{\phi_{j+1}}{N_{j+1}} - \frac{\phi_j}{N_j}\right]. \tag{6}$$

The above (6) can also be represented in matrix notation

$$\frac{\partial[\phi]}{\partial\tau} = [A] + [K][\phi],$$ (7)

where,

$$[\phi] = \begin{bmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_N \end{bmatrix},$$ (8)

$$[A] = \begin{bmatrix} K_{21}N_1 \\ \cdot \\ 0 \\ 0 \end{bmatrix},$$ (9)

where, N_1 is the concentration of monomers i.e. $N_1 = \phi_1$ and assumed to be constant in the system, and K_{21} an element of the matrix K. The elements of the matrix are:

$$K_{j,j-1} = S_{j-1}$$
$$K_{j,j} = -S_{j-1}\exp[\omega_j - \omega_{j-1})/KT] - S_j$$
$$K_{j,j+1} = S_j\exp[(\omega_{j+1} - \omega_j)/KT]$$
$$K_{M,M+1} = 0.$$ (10)

$\forall, j = 2, M$. In the system under consideration, the last of these equations reflects the fact that the production of M-mers is restricted through the loss of a molecule by $(M + 1)$-mers i.e. $(M + 1)$-mers are swept out of the system as soon as they form. A cluster of size M may be taken to mean an aggregate somewhat larger than a nucleus. Taking linear transformation of the form

$$[\phi] = [\xi] + [\gamma],$$ (11)

(7) can be rewritten as,

$$\frac{\partial}{\partial\tau}[\xi] = [A] + [K][\gamma] + [K][\xi].$$ (12)

γ is chosen such that

$$[A] + [K][\gamma] = 0.$$ (13)

The solution of the set of equations for the components of γ i.e. (13), can be obtained by utilizing (9) and (10)

$$\gamma_j = \phi_j(\infty) = N_j \left(1 - \frac{\displaystyle\sum_{i=1}^{j-1} \frac{1}{S_i N_i}}{\displaystyle\sum_{i=1}^{M} \frac{1}{S_i N_i}} \right).$$ (14)

Combining (12) and (13) gives:

$$\frac{\partial[\xi]}{\partial\tau} = [K][\xi].$$ (15)

2.1 *Transformation to Hermitian form*

Solution to (15) can be obtained by transforming matrix $[K]$ to its Hermitian form. A form 'f' on a real or complex function space F is called Hermitian (Kelly 1955; Halmos 1958) if,

$$f(\alpha, \beta) = \overline{f(\alpha, \ \beta)} \ \forall \alpha, \beta,$$

where, α and β are the basis vectors. This is accomplished as the elements of $[K]$ satisfy the condition:

$$K_{j,j-1} \exp(-\omega_{j-1}/KT) = K_{j-1, j} \exp(-\omega_j/KT). \tag{16}$$

A diagonal matrix $[D]$ is introduced whose elements are given as:

$$D_{nm} = \delta_{nm} \exp(\omega_n/KT). \tag{17}$$

Now, (17) can be expressed in matrix form as

$$[K]^T = [D][K][D]^{-1}, \tag{18}$$

where $[K]^T$ is the transpose of $[K]$. Let the matrix $[H]$ be constructed by the following similarity transformation

$$[H] = -[D]^{1/2}[K][D]^{1/2}. \tag{19}$$

Since $[D]$ is diagonal,

$$[D]_{nm}^{1/2} = \pm \delta_{nm} \exp(\omega_n/2KT), \tag{20}$$

$$[D]_{nm}^{-1/2} = \pm \delta_{nm} \exp(-\omega_n/2KT). \tag{21}$$

Without loss of generality the positive sign in (20) and (21) is chosen. Further derivation follows by using (18), (19) and using the fact that the diagonal matrix is its own transpose

$$\begin{aligned} [H]^T &= -[D]^{1/2}[K][D]^{-1/2} = [D]^{-1/2}[K]^T[D]^{1/2} \\ &= -[D]^{-1/2}[D][K][D]^{-1}[D]^{1/2} \\ &= -[D]^{1/2}[K][D]^{-1/2} = [H]. \end{aligned} \tag{22}$$

$[H]$ is found to be identical with its transpose $[H]^T$. Since, $[H]$ is a real matrix, it is 'Hermitian' or self-adjoint i.e. $H_{jk} = \overline{H_{kj}}$. The set of eigen vectors $[H]$ form a complete orthogonal set in the space of $[\phi]$. Now defining,

$$[\psi] = [D]^{1/2} [\xi]. \tag{23}$$

From (15), the following can be derived

$$\begin{aligned} \frac{\partial[\psi]}{\partial\tau} &= \frac{\partial}{\partial\tau}([D]^{1/2}[\xi]) = [D]^{1/2}\frac{\partial}{\partial\tau}[\xi] \\ &= ([D]^{1/2}[K][D]^{-1/2})[D]^{1/2}[\xi] = -[H][\psi], \end{aligned} \tag{24}$$

which can be written as

$$[H][\psi] = -\frac{\partial[\psi]}{\partial\tau}. \tag{25}$$

The above equation is somewhat similar to time dependent wave equation in quantum physics (Morse and Feshbach 1953; Margenau and Murphy 1956), which is given as

$$[H][\psi] = i\hbar \frac{\partial [\psi]}{\partial \tau},$$ (26)

where H is the total Hamiltonian, ψ the wave function and $\hbar$ the Planck's constant. Solution for ψ provides ϕ through the relation:

$$[\phi] = [\gamma] + [D]^{-1/2}[\psi].$$ (27)

Now, utilizing the concepts of eigen value problems in matrix mechanics (quantum mechanics), the eigen vectors of $[H]$ satisfy the equation

$$[H]\vec{u_k} = \lambda_k \vec{u_k},$$ (28)

where, u_k is the kth eigen vector and λ_k the kth eigen value. The eigen vector can be expressed in a form

$$u_k = C_k e^{-\lambda_k \tau},$$ (29)

where, C_k is a constant vector and time independent, then C_k satisfies it and also (25) is satisfied.

$$[H][u_k] = [H]C_k e^{-\lambda_k \tau} = C_k \frac{\partial}{\partial \tau}(e^{-\lambda_k \tau}) = -\frac{\partial}{\partial \tau}(C_k e^{-\lambda_k \tau}).$$ (30)

Since, the eigen vectors u_k form a complete orthogonal set of basis vectors for the function space, the general solution of (28) can be represented as a linear combination of u_k i.e.

$$\psi = \sum_k \alpha_k u_k = \sum_k \alpha_k C_k e^{-\lambda_k \tau}.$$ (31)

The set of relaxation times for the dynamic nucleation process is given as $\tau_k = 1/\lambda_k$ and the reciprocal of the smallest eigen value corresponds to a measure of time for attainment of steady state. Therefore, it is desirable to determine the upper bound of the smallest eigen value. The eigen value of $[H]$ are all greater than zero. For an eigen value equal to zero

$$[H]u_0 = 0.$$ (32)

For u_0 to represent a non-vanishing solution, $[H]$ must be singular. However, inspection of $[H]$ in the light of (19) and (20) indicates that $[H]$ is not singular and no non-trivial solution of (32) exists. This implies that, no zero value exists. The exponential term in (31) is indicative of the fact that all eigen values are positive. Since, $[u_k]$ are orthogonal set of vectors, α_k must also be orthogonal. Hence,

$$\alpha_j \exp(-\lambda_j \tau) = [u_k][\psi],$$ (33)

or,

$$\alpha_j = [u_k][\phi] \exp(\lambda_j \tau).$$ (34)

For normalization of α_k, it is required to have,

$$[\alpha_j][\alpha_k] = \delta_{jk}.$$ (35)

Since, $\lambda_k > 0$, the Rayleigh Ritz variational method can be applied to establish an upper bound for the smallest eigen value or, conversely, a lower bound for the longest relaxation time. An arbitrary trial vector $[\chi]$ in the space of ϕ can be constructed in the following manner

$$\lambda = \frac{[\chi][H][\chi]}{[\chi][\chi]}. \tag{36}$$

Then, $\lambda \geq \lambda_0$, where λ_0 is the smallest eigen value, and λ forms an upper bound to λ_0. An arbitrary vector χ is chosen with arbitrary components χ_n, to form λ, and then λ is minimized by partial differentiation with respect to various χ_j which constitute various variational parameters. Considering a typical case, where only two components are variables (say χ_k and χ_z) and differentiating with respect to χ_k and χ_z respectively yield

$$(H_{kk} - \lambda)\chi_k + H_{zk}\chi_z = -\sum_j H_{kj}\chi_j, \tag{37}$$

$$H_{zk}\chi_k + (H_{zz} - \lambda)\chi_z = -\sum_j H_{zj}\chi_j. \tag{38}$$

The terms on the right hand side of above equations are known by some prior choice. If the constant components are set to zero for these equations, then two simple homogeneous equations are obtained

$$(H_{kk} - \lambda)\chi_k + H_{kz}\chi_z = 0, \tag{39}$$

$$H_{zk}\chi_k + (H_{zz} - \lambda)\chi_z = 0. \tag{40}$$

The determinant of the coefficients of the above equations has to be zero and λ is eventually determined from the secular equation by using $H_{kz} = H_{zk}$.

$$\lambda^2 - (H_{kk} + H_{zz})\lambda + (H_{kk}H_{zz} - H_{kz}) = 0. \tag{41}$$

The lowest solution of this equation is

$$\lambda = \frac{1}{2}(H_{kk} + H_{zz}) - \left[\frac{(H_{kk} - H_{kz})^2}{4} + H_{kz}^2\right]^{1/2}. \tag{42}$$

This forms the least upper bound achievable with this simplest of all trial vectors. It is evident from (10), (17) and (19) that

$$H_{j,j-1} = -S_{j-1}\exp[\omega_j - \omega_{j-1}/2KT], \tag{43}$$

$$H_{jj} = S_{j-1}\exp[(\omega_j - \omega_{j-1})/KT] + S_j, \tag{44}$$

$$H_{j,j+1} = S_j\exp[(\omega_{j+1} - \omega_j)/2KT]. \tag{45}$$

3.   Illustrative example

As an illustrative example, (43), (44) and (45) can be applied to supercooled liquid copper at $690°$ K. Two different pairs of k and τ values, namely, $k = 2$, $\tau = 3$ and $k = M - 1$ and $\tau = M$. On the basis of physical reasoning, it is expected that the second pair will lead to a lower bound than the first one since, it invokes the properties of kinetic process associated with the largest embryos of significance whose formation is

associated with longer relaxation times or smaller λ. It is reasonable to have M correspond to the first embryo beyond the nucleus size. For ·.per at 690° K, the nucleus size can be calculated as:

$$n^* = \frac{32\pi\sigma^3 v^2}{3\left(\lambda\ln\left(\frac{T_0}{T}\right)^3\right)}, \tag{46}$$

where, n^* is the critical nucleus size, λ the enthalpy of fusion per mole, σ the interfacial tension between solid and melt, v the volume per molecule and T_0 the melting temperature. From (46), it is found out that the critical nucleus size, i.e. $n^* = 4\cdot28$, the non-integer value is stemming from the fact that continuum approximation has been used.·The second pair of values are: $k = 4, \tau = 5$. However, for the first pair of values, the relevant data for copper can be evaluated by using (45), Doolittle equation and the expression of Einstein-Stokes relating the fluidity with self-diffusion coefficient (Doolittle 1951; Cohen and Turnbull 1959). These are $H_{22} = 8\cdot84 \times 10^{-15}$ cm^2, $H_{33} = 10\cdot4 \times 10^{-15}$ cm^2 and $H_{23} = H_{32} = -4\cdot62 \times 10^{-15}$ cm^2. Substitution of these values in (43) and (44) gives $\lambda = 6\cdot67 \times 10^{-15}$. Therefore, $\tau_0 \geq \lambda^{-1} = 1\cdot499 \times 10^{14}$. Converting it to the standard unit of seconds (i.e. $t_0 = \tau_0/\kappa > 1/\kappa\lambda$, and κ for copper is $2\cdot93 \times 10^{25}$ at 690°K), it is found out that $t_0 \geq 5\cdot11 \times 10^{-12}$ sec. If the entire process is repeated with the second pair of values, it can be shown that $t_0 \geq 5\cdot10 \times 10^{-12}$. As it was predicted the latter pair gives closer relaxation time although the improvement is marginal. More sophisticated variational functions may give higher accuracy.

4. Conclusion

A theoretical framework is presented for studying the dynamic nucleation phenomena during solidification at high cooling rates. The mathematical apparatus is found to be isomorphic with the function space theory encompassing matrix and wave mechanics of quantum theory. The theoretical concepts have been applied to the problems of super cooled liquid copper as given in the illustrative example. It is expected that the theory probably gives fairly reliable results in certain nucleation problems of metallurgical interest. However, its applicability is severely constrained because of paucity of reliable data on self-diffusion coefficients and fluidities in supercooled metallic melts.

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