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Kinetics of nucleation and growth

Part II *Diffusion controlled growth*

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The kinetics of nucleation and diffusion controlled growth have been re-examined; this includes the most commonly assumed nucleation laws. The square size distributions and the time dependence for the average square size were obtained from previous solutions for nucleation and reaction controlled growth. The solutions for the size distributions and average particle size were also derived.

1. Introduction

Some solutions for particle nucleation and growth have already been reported in Part I [1]. These solutions were derived for growth controlled by interfacial reaction. However, growth in a multicomponent solid matrix is often expected to become diffusion controlled. Therefore, a similar set of solutions for different nucleation laws and diffusion controlled growth is useful.

The simplest solutions are for constant nucleation rate, but realistic models for nucleation may have to account for an induction time [2], consumption of active nucleation sites or multistep nucleation [3, 4]. In addition, nucleation sites may be swallowed by growing particles, as described by the Johnson–Mehl–Avrami (JMA) theory [5–9].

A simple solution is known for diffusion controlled growth from zero [10], but numerical methods are usually needed to obtain solutions for growth from finite initial size [11–15]. In this case, numerical methods are also needed to combine the kinetics of nucleation and growth and to obtain the size distributions and the time dependence of the average particle size. Nevertheless, this limitation may be avoided by using a simple and relatively accurate solution for growth [13]. Numerical methods will thus only be needed when the kinetics of growth is described by a transient regime, as expected for a mixed diffusion + reaction growth mechanism and for the effects of interfacial energy. Self stresses and elastic interactions between particles are also believed to affect the diffusion controlled behaviour of particles [16, 17].

The kinetics of diffusion controlled growth may also depend on particle to particle distances; this occurs because the concentration profile around a particle may be affected by the nearest neighbours, as suggested for diffusion controlled coarsening [18, 19]. Note that the average distance between the nearest particles is related to the volume fraction of precipitate, and this may be effective even for precipitate volume fractions lower than 1%. In addition, oversaturation decreases with increasing precipitate volume fractions and the driving force for diffusion controlled growth also decreases.

2. Solutions for nucleation and diffusion controlled growth

Several nucleation laws will be treated as previously shown for reaction controlled growth [1]; this includes the linear law (Equation 1), the exponential law for consumption of nucleation sites (Equation 2) and Kashchiev's law to account for an induction time (Equation 4). Two alternative solutions are also used to describe multistep nucleation, (Equation 6 or Equations 7 and 8).

$$N_T = kt \tag{1}$$

$$N_T = N_0(1 - e^{-\tau}) \tag{2}$$

$$\tau = t/t_N \tag{3}$$

$$N_T = kt\, V(t/t_I) \tag{4}$$

$$V(\xi) = 1 - \pi^2/(6\xi) - 2\sum_{n=1}^{\infty}(-1)^n/[n^2\xi\exp(n^2\xi)] \tag{5}$$

$$N_T = kt^p \tag{6}$$

$$dN_T/dt = k_2 t^p \exp(-t/t_N) \tag{7}$$

$$N_T = k_2 t_N{}^{p+1} M(p, t/t_N) \tag{8}$$

$$M(p,\xi) = p! - [\xi^p + \sum_{j=0}^{p-1} p \times (p-1)\ldots(p-j)\,\xi^{p-j-1}]\,e^{-\xi} \tag{9}$$

where N_T is the total number of particles, t_N is a decay time and t_I is an induction time. The solutions for $V(\xi)$ are shown in Table I.

The following alternative equations can be used to compute the size distribution function $f(a, t)$

$$f(a,t) = N_T^{-1}(\partial N/\partial t)/(da/dt) \tag{10}$$

$$f(a,t) = -N_T^{-1}(\partial N/\partial a) \tag{11}$$

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TABLE I Solutions for $V(\xi)$, $V_1(\xi)$, $V_2(\xi)$, $E(\xi)$, $H(\xi)$

ξ	$V(\xi)$	$V_1(\xi)$	$V_2(\xi)$	$E(\xi)$ $\times e^{-\xi}/\sqrt{\xi}$	$H(\xi)$
0	0	0	0	0	0
0.1	0.0000	0.0000	0.0000	0.0640	0.0320
0.2	0.0000	0.0000	0.0000	0.1232	0.0616
0.3	0.0002	0.0017	0.0000	0.1779	0.0890
0.4	0.0016	0.0117	0.0002	0.2285	0.1142
0.5	0.0058	0.0361	0.0007	0.2752	0.1376
0.6	0.0139	0.0749	0.0020	0.3185	0.1592
0.7	0.0261	0.1248	0.0041	0.3585	0.1793
0.8	0.0419	0.1814	0.0071	0.3956	0.1978
0.9	0.0607	0.2409	0.0110	0.4300	0.2150
1	0.0817	0.3006	0.0157	0.4619	0.2310
1.2	0.1278	0.4140	0.0269	0.5190	0.2595
1.4	0.1760	0.5142	0.0400	0.5682	0.2841
1.6	0.2238	0.5995	0.0541	0.6109	0.3054
1.8	0.2696	0.6709	0.0687	0.6478	0.3239
2	0.3128	0.7300	0.0834	0.6800	0.3400
2.5	0.4077	0.8359	0.1188	0.7437	0.3719
3	0.4849	0.9004	0.1511	0.7898	0.3949
3.5	0.5473	0.9396	0.1797	0.8238	0.4119
4	0.5979	0.9634	0.2049	0.8493	0.4247
5	0.6737	0.9865	0.2462	0.8843	0.4421
6	0.7267	0.9950	0.2783	0.9065	0.4532
8	0.7945	0.9993	0.3240	0.9324	0.4662
10	0.8355	0.9999	0.3544	0.9470	0.4735
12	0.8629	1.0000	0.3761	0.9363	0.4782
15	0.8903	1.0000	0.3988	0.9654	0.4827
20	0.9178	1.0000	0.4225	0.9743	0.4872
25	0.9342	1.0000	0.4372	0.9796	0.4898
30	0.9452	1.0000	0.4473	0.9830	0.4915
40	0.9589	1.0000	0.4601	0.9873	0.4937
60	0.9726	1.0000	0.4731	0.9916	0.4958
80	0.9794	1.0000	0.4797	0.9937	0.4969
100	0.9836	1.0000	0.4837	0.9950	0.4975
150	0.9890	1.0000	0.4891	0.9967	0.4983
200	0.9918	1.0000	0.4918	0.9975	0.4989
300	0.9945	1.0000	0.4945	0.9984	0.4992
500	0.9967	1.0000	0.4967	0.9990	0.4996
1000	0.9984	1.0000	0.4984	0.9995	0.4998

where a is the particle size and $N(a, t)$ is the number of particles with sizes equal to or larger than a. Those size distributions are used to compute the average size a_{av}

$$a_{av} = \int_{a_0}^{a_m} a f(a, t)\, da \qquad (12)$$

where a_0 is the minimum size and a_m is the maximum size.

Diffusion controlled growth from zero has been solved analytically and for an isolated spherical particle in a very large matrix this reduces to [10]

$$a = 2\beta\sqrt{(Dt)} \qquad (13)$$

$$(C_\infty - C_a)/[C_s(1 - v_A C_a)] = 2\beta^2 \int_0^1 \exp\{-\beta^2 \times [(1-x)^{-2} - 2\varepsilon x - 1]\} dx. \qquad (14)$$

where v_A is the solute partial molar volume in the matrix, C_a is solute concentration at the particle–matrix interface, C_∞ corresponds to the outer boundary condition, C_s is the concentration in the particle and $\varepsilon = 1 - v_A C_s$.

Cable and Frade [13] showed that the growth constant β is also reasonably suitable to describe diffusion controlled growth from finite initial size a_0. If the nucleation time is t_0 the age of the particle reduces to $t - t_0$ and growth is thus nearly described by

$$a^2 \approx a_0^2 + 4\beta^2 D(t - t_0) \qquad (15)$$

Transient effects for a mixed growth mechanism, interfacial energy, etc. are ignored.

3. Size square distributions and average size square

Equation 15 reduces to a linear relation between the square particle size and time

$$s = s_0 + R'(t - t_0) \qquad (16)$$

where $s = a^2$, $s_0 = a_0^2$ and $R' = 4\beta^2 D$; this gives a time dependence for the size square which is identical to the time dependence of the particle size for reaction controlled growth [1]. The solutions described in Part I can thus be useful also for diffusion controlled growth on replacing the size square $s = a^2$ for size a. The relevant solutions are shown in Tables II and III. The auxiliary functions are $V(\xi)$ (Equation 5), $M(p, \xi)$ (Equation 9) and

$$V_1(\xi) = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\xi) \qquad (17)$$

TABLE II Square size distributions for nucleation and diffusion controlled growth. The relevant rate constant is $R' = 4\beta^2 D$ and the solutions for $V_1(\xi)$ and $V(\xi)$ are shown in Table I

Nucleation law	Distribution function
1	$1/(s_m - s_0)$
2	$\dfrac{[(s - s_0)/(s_m - s_0)]\exp[(s - s_0)/(R't_N)]}{Rt_N\{\exp[(s_m - s_0)/(R't_N)] - 1\}}$
4	$V_1(x)/[(s_m - s_0)V(\tau)]$; $x = (s_m - s)/(R't_I)$, $\tau = t/t_I$
6	$p(s_m - s)^{p-1}/(s_m - s_0)^p$
7 and 8	$\dfrac{[(s_m - s)/(R't_N)]^{p+1}\exp[(s_m - s)/(R't_N)]}{(s_m - s_0)M(p, \tau)}$

TABLE III Average square size versus time for nucleation and diffusion controlled growth. The solutions for $V_2(\xi)$ and $V(\xi)$ are shown in Table I

Nucleation law	$(s_{av} - s_0)/(s_m - s_0)$
1	1/2
2	$1/(1 - e^{-\tau}) - 1/\tau$; $\tau = t/t_N$
4	$V_2(\tau)/V(\tau)$; $\tau = t/t_I$
6	$1/(p + 1)$
7 and 8	$1 - M(p + 1, \tau)/[\tau M(p, \tau)]$; $\tau = t/t_N$

$$V_2(\xi) = 1/2 - \pi^2/(6\xi) - 2\sum_{n=1}^{\infty}(-1)^n/[1 - \exp(-n^2\xi)]/(n^4\xi^2) \quad (18)$$

4. Size distributions and average particle size

4.1. Constant nucleation rate

The number of particles $N(a, t)$ for sizes equal to or larger than a may be related to nucleation time t_0 for the generic particle size a; this reduces to

$$N(a, t) = N_T(t_0) \quad (19)$$

where N_T is given by the required nucleation law. Therefore, combination with Equations 1 and 15 yields

$$N(a, t) = k[t - (a^2 - a_0^2)/(4\beta^2 D)] \quad (20)$$

From Equations 11, 12 and 20 and after rearranging

$$[(a_m^2 - a_0^2)/a] f(a, t) = 2 \quad (21)$$

$$a_{av}/a_m = (2/3)(a_m^3 - a_0^3)/(a_m^3 - a_m a_0^2) \quad (22)$$

Note that the time dependence has been replaced by the maximum size $a_m = (a_0^2 + 4\beta^2 Dt)^{1/2}$, which might be useful to assess if the same mechanism fits several sets of experimental data. The solutions for the size distributions are also suitable to test the agreement between theory and several sets of data.

4.2. Exponential nucleation law

The solutions for the exponential nucleation law can be obtained on combining Equations 2, 11, 12 and 15. This yields

$$N(a, t) = N_0 e^{-\tau} \exp[(a^2 - a_0^2)/(4\beta^2 Dt_N)] \quad (23)$$

$$(2\beta^2 Dt_N/a) f(a, t) = \frac{\exp[(a^2 - a_0^2)/(4\beta^2 Dt_N)]}{\exp[(a_m^2 - a_0^2)/(4\beta^2 Dt_N)] - 1} \quad (24)$$

$$a_{av}/a_m = [E(w) - E(y)]/[\sqrt{w}(e^{w-y} - 1)] \quad (25)$$

$$y = a_0^2/(4\beta^2 Dt_N)$$

$$w = a_m^2/(4\beta^2 Dt_N)$$

$$E(\xi) = \int_0^{\xi} \sqrt{x}\, e^x \, dx \quad (26)$$

The size distributions is again related to the maximum size rather than time, and some examples are shown in Fig. 1. The time dependence for the average particle size varies with the ratio $a_0/(4\beta^2 Dt_N)$ but can be computed by using the values of $E(\xi)$ shown in Table I. Some solutions are shown in Fig. 2.

4.3. Kashchiev's nucleation law

The size distributions and average particle size for Kashchiev's law and diffusion controlled growth are derived from Equations 4, 5, 11, 12 and 15

$$N(a, t) = k[t - (a^2 - a_0^2)/(4\beta^2 D)] - k\pi^2 t_I/6 - 2kt_I \sum_{n=1}^{\infty}(-1)^n n^{-2} \times \exp[n^2(a^2 - a_0^2)/(4\beta^2 Dt_I) - n^2 t/t_I] \quad (27)$$

and

$$(2\beta^2 Dt_I/a) f(a, t) = V_1(x)/V(x_m) \quad (28)$$

where

$$x = (a_m^2 - a^2)/(4\beta^2 Dt_I)$$

$$x_m = (a_m^2 - a_0^2)/(4\beta^2 Dt_I)$$

and

$$a_{av} = (2/3)[(a_m^3 - a_0^3)/(a_m^2 - a_0^2)]/V(\tau) + 4a_m[\tau V(\tau)]^{-1}\sum_{n=1}^{\infty}(-1)^n n^2 H(n^2 w) - 4a_0[\tau V(\tau)]^{-1}\sum_{n=1}^{\infty}(-1)^n n^2 \times \exp(-n^2\tau) H(n^2 y) \quad (29)$$

where

$$H(\xi) = \int_0^{\xi} \sqrt{(x/\xi)}\, e^{x-\xi} \, dx \quad (30)$$

and

$$y = a_0/[2\beta\sqrt{(Dt_I)}]$$

$$w = a_m/[2\beta\sqrt{(Dt_I)}]$$

$$\tau = t/t_I$$

The solutions of $V(\xi)$, $V_1(\xi)$ and $H(\xi)$ are also shown in Table I. However, computing the solutions for the average particle size (Equation 29) is cumbersome, which explains the use of an alternative time dependence for the average size square as described in Table III and shown in Fig. 3. Some size distributions are exemplified in Fig. 4.

4.4. Multistep nucleation

The solutions for multistep nucleation can be obtained on combining Equations 6, 11, 12 and 15. This

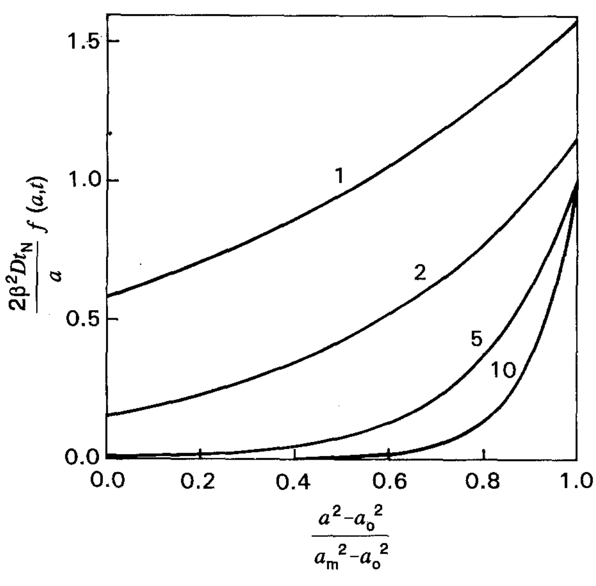

Figure 1 Particle size distributions for exponential nucleation (Equation 2) and diffusion controlled growth. The values of $\tau = t/t_N$ are shown in the figure.

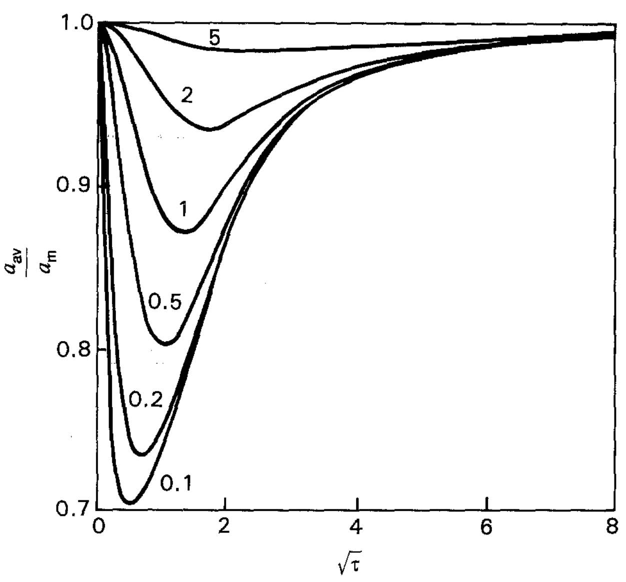

Figure 2 Time dependence for the average to maximum size ratio $a/(a_0^2 + 4\beta^2 Dt)$ when nucleation is given by the exponential law (Equation 2) and growth is diffusion controlled. The values of $a_0/[2\beta\sqrt{(Dt_N)}]$ are shown in the figure.

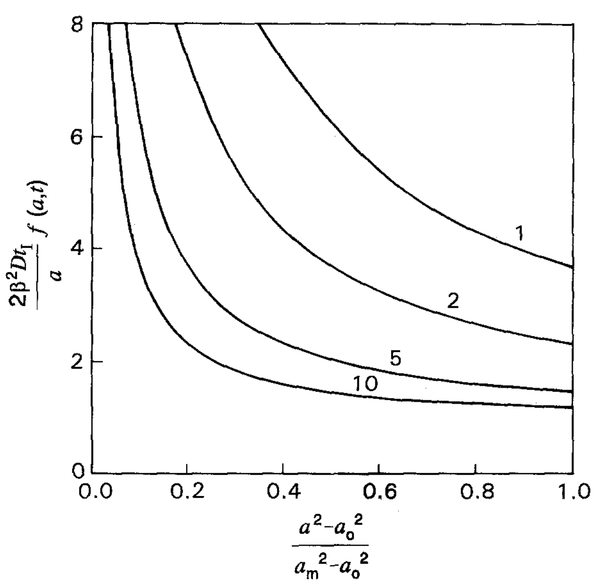

Figure 4 Size distributions for Kashchiev's nucleation law and diffusion controlled growth. The values of t/t_I are shown in the figure.

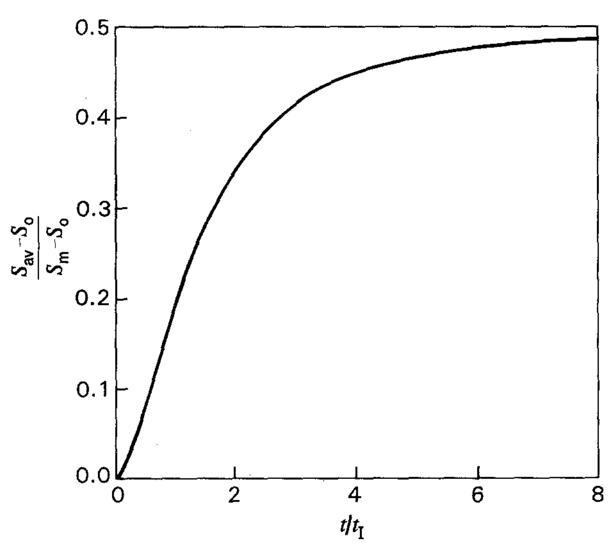

Figure 3 Time dependence for the average square size if nucleation is given by Kashchiev's law (Equations 4 and 5) and growth is diffusion controlled.

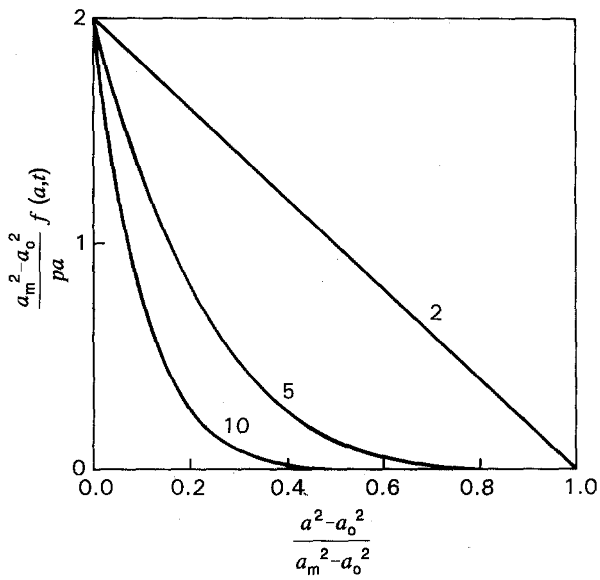

Figure 5 Size distributions for multistep nucleation (Equation 6) and diffusion controlled growth. The order p is shown in the figure.

gives

$$N(a, t) = k[t - (a^2 - a_0^2)/(4\beta^2 D)]^p \quad (31)$$

$$f(a)\,(a_m^2 - a_0^2)/a = 2p[1 - (a^2 - a_0^2)/(a_m^2 - a_0^2)]^{p-1} \quad (32)$$

$$a_{av}/a_m = p\int_z^{1+z} (1 + z - x)^{p-1}[x/(1 + z)]^{1/2}\,dx \quad (33)$$

$$z = a_0^2/(4\beta^2 Dt)$$

Some predictions for the size distributions are shown in Fig. 5. These predictions were made time-independent. On the contrary, the average size is time-dependent (Fig. 6), except for negligible initial size $a_0 \approx 0$. In this case

$$a_{av}/a_m = I(p) = p\int_0^1 (1 - x)^{p-1}\sqrt{x}\,dx \quad (34)$$

The solutions $I(p)$ are shown in Table IV.

4.5. Multistep nucleation with a decay factor

Combination of Equations 7, 8 and 9 for nucleation, Equation 15 for diffusion controlled growth and in addition Equations 10 and 12 gives

$$(2\beta^2 Dt_N/a)\,f(a, t) = [M(p, \tau)]^{-1}[(a_m^2 - a^2)/(4\beta^2 Dt_N)]^p \exp[(a_m^2 - a^2)/(4\beta^2 Dt_N)] \quad (35)$$

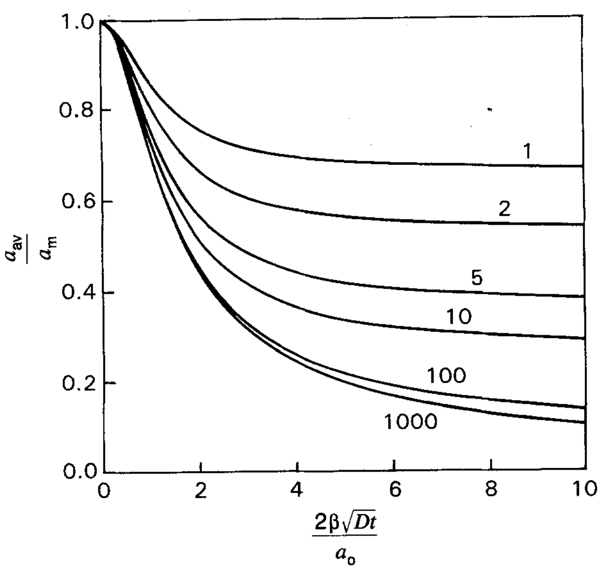

Figure 6 Increase in average particle size versus time for multistep nucleation (Equation 6) and diffusion controlled growth. The figure shows the order p of multistep nucleation.

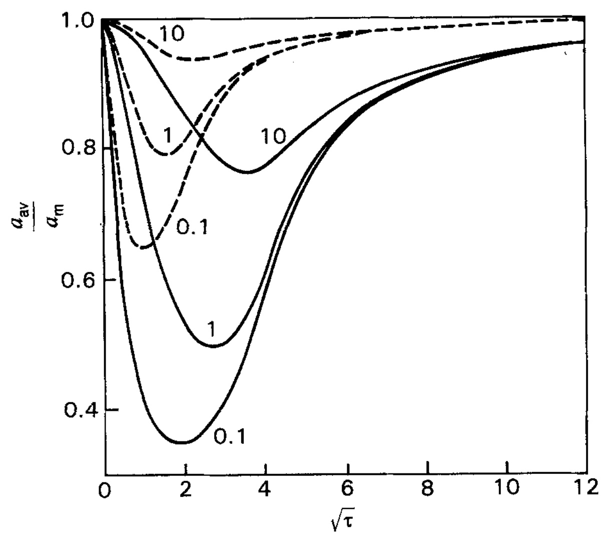

Figure 8 Average size for multistep nucleation (Equations 7, 8 and 9) and diffusion controlled growth. The values of $a_0^2/(4\beta^2 Dt_N)$ are shown. The dashed lines correspond to $p = 1$ and the full lines to $p = 10$.

TABLE IV Solutions for $I(p)$ (Equation 34)

p	$I(p)$	p	$I(p)$
1	0.6667	25	0.1746
2	0.5333	30	0.1597
3	0.4571	35	0.1481
4	0.4063	40	0.1387
5	0.3694	50	0.1243
6	0.3410	60	0.1135
7	0.3182	70	0.1052
8	0.2995	80	0.0984
9	0.2837	90	0.0928
10	0.2702	100	0.0880
12	0.2481	150	0.0717
14	0.2307	200	0.0619
16	0.2165	300	0.0502
18	0.2046	500	0.0386
20	0.1946	1000	0.0257

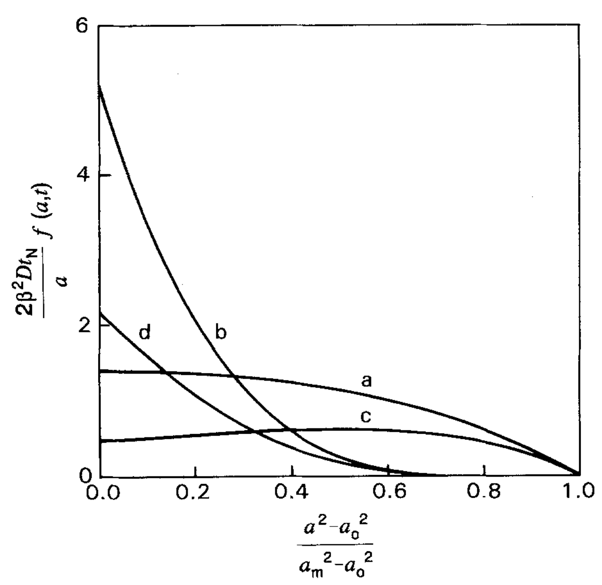

Figure 7 Size distributions for multistep nucleation (Equations 7, 8 and 9) and diffusion controlled growth. The relevant parameters are: (a) $p = 1, \tau = 1$; (b) $p = 5, \tau = 1$; (c) $p = 1, \tau = 2$; (d) $p = 5, \tau = 2$.

$$a_{av}/a_m = [(y + \tau)^{1/2} M(p, \tau)]^{-1} \times \int_0^{\tau} (\tau - x)^p e^{x-\tau} (x + y)^{1/2} dx \quad (36)$$

$$y = a_0^2/(4\beta^2 Dt_N)$$

$$\tau = t/t_N = (a_m^2 - a_0^2)/(4\beta^2 Dt_N)$$

These solutions for the size distribution and average particle size are both time-dependent (Figs 7 and 8). For $t \gg \tau$, Equation 36 converges to

$$a_{av} \approx \beta(Dt)^{1/2} [2 - (p + 1)/\tau] \quad (37)$$

5. Conclusions

The square size distributions and average square particle size for nucleation and diffusion controlled growth were worked out from size distributions and average size for nucleation and growth controlled by interfacial reaction. These solutions are relatively simpler than the corresponding time dependence for the average size when growth is controlled by diffusion.

The solutions for size distributions were normalized to assist the interpretation of experimental data and for easier testing of the agreement between theory and practice.

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References

1. J. R. FRADE, *J. Mater. Sci.* **28** (1993) 6715.
2. D. KASHCHIEV, *Surface Sci.* **14** (1969) 209.
3. C. BAGDASSARIN, *Acta Physicochim.* **20** (1945) 441.
4. A. R. ALLNATT and P. W. M. JACOBS, *Can. J. Chem.* **46** (1968) 111.

5. W. A. JOHNSON and R. F. MEHL, *Trans. AIME* **135** (1939) 416.
6. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
7. *Idem., ibid.* **8** (1940) 212.
8. *Idem., ibid.* **9** (1941) 177.
9. B. V. EROFEEV, *C. R. Acad. Sci. URSS* **52** (1946) 511.
10. L. E. SCRIVEN, *Chem. Engng Sci.* **10** (1959) 1.
11. D. W. READEY and A. R. COOPER, *ibid.* **21** (1966) 917.
12. M. CABLE and D. J. EVANS, *J. Appl. Phys.* **38** (1967) 2899.
13. M. CABLE and J. R. FRADE, *J. Mater. Sci.* **22** (1987) 149.
14. *Idem., Chem. Engng Sci.* **42** (1987) 2525.
15. *Idem., J. Mater. Sci.* **22** (1987) 1894.
16. F. C. LARCHÉ and J. W. CAHN, *Acta Metall.* **30** (1982) 1835.
17. A. J. ARDELL and R. B. NICHOLSON, *ibid.* **14** (1966) 1295.
18. A. J. ARDELL, *ibid.* **20** (1972) 61.
19. K. TSUMURAYA and Y. MIYATA, *ibid.* **31** (1983) 437.

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