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Kinetics of nucleation and growth

Part I *Reaction controlled growth*

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A number of solutions have been obtained to describe the size distributions and average particle size for nucleation and reaction controlled growth of precipitates; this includes the solutions for constant nucleation rate, the exponential nucleation law, Kashchiev's equation and some multistep nucleation models. The increase in the average particle size is related to increase in maximum size. Time-dependent effects occur if nucleation is affected by an induction time or a decay time.

1. Introduction

Particle nucleation and growth is relevant for a variety of processes in materials science and engineering; this includes crystallization of oxide glasses [1–7] and metallic glasses [8–11]. Precipitation by nucleation and growth from oversaturated liquids is also a promising technique for obtaining reactive and homogeneous powders.

The Johnson–Mehl–Avrami (JMA) theory [12–16] is probably the most cited model for the kinetics of nucleation and growth. It has been used to describe precipitation and decomposition of solids. The JMA theory describes the time dependence for fraction reacted but it does not describe the average particle size against time and size distributions; this might be as important as the fraction reacted. Note that particle counting and size measurements used to be tedious and time consuming, but this has been greatly improved by high resolution electron microscopy and by automatic image analysis.

The kinetics of nucleation is often complex. The simplest model is a linear law for constant nucleation rate, which corresponds to a very large number of embryos or active sites. The Kashchiev equation [17] includes the effect of an induction time. Consumption of embryos or active sites is expected to cause a decrease in nucleation rate and this leads to an exponential law. However, a number of systems do not fit any of these simple laws and multistep nucleation has also been proposed [18, 19]. Particle to particle impingement may occur for large volume fractions of precipitate and this corresponds to lower nucleation rates and a lower rate of transformation [20, 21].

Reaction controlled growth is usually described by constant growth rate of individual particles. However, high temperature observation is often nearly impossible and samples must be quenched and analysed at room temperature; this prevents observation of individual particles at firing temperatures and finding the laws that describe nucleation and growth must thus rely on the time dependencies found for particle counting, particle size distributions and average particle size. This also requires reliable mathematical methods.

2. Solutions for nucleation and growth

Constant nucleation rate is expected for a large number of potential nucleation sites or embryos; this gives the simplest nucleation law

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

where N_T is the number of particles nucleated, t is time and k is the rate constant. This law is most likely for the initial stage of nucleation. However, formation of a stable particle also corresponds to a decrease in the number of embryos or potential nucleation sites, $dN_T/dt = (N_\infty - N_T)/t_N$, where N_∞ is the maximum number of particles nucleated after a very long time and t_N is the nucleation time. Integration gives

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

where

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

In addition, a nearly linear nucleation law is often found only after an induction time t_I; this is given by Kashchiev's law [17]

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

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

A number of authors have also suggested solutions for multistep nucleation [18, 19]. These solutions are usually based on assuming that nucleation occurs by a series of elementary steps which can be written [18]

$$dN_i/dt = k_{i-1}N_{i-1} - k_i N_i \tag{6}$$

for $i = 1, 2, \ldots,$ and $dN_0/dt = -K_0 N_0$. Equation 6 can be solved for $k_0 = k_1 = k_2 = \ldots$ and initial conditions $N_0(0) = N_0$, $N_1(0) = N_2(0) = N_3(0) = \ldots = 0$.

This yields

$$N_i(t) = N_0/(i!)(t/t_N)^i \exp(-t/t_N) \quad (7)$$

However, the kinetic constants k_i may change for different cluster sizes and numerical methods are often required to obtain accurate solutions [22, 23]. An approximate solution for small times ($k_i t \ll 1$) is [19]

$$N_P = kt^p \quad (8)$$

For example, the solution $N_T = kt^3$ describes the kinetics of decomposition of BaN_6 [24].

Equation 7 predicts that the number of particles may decrease with increasing time when $t \gg t_N$; this is arguable, except during a coarsening regime. However, the rate of nucleation can be written $dN_T/dt = k_p N_p$ rather than Equation 6 on assuming that nuclei form on exceeding a critical size p, and combination with Equation 7 thus yields

$$dN_T/dt = (k/t_N)(t/t_N)^p \exp(-t/t_N) \quad (9)$$

where k is a kinetic constant and t_N corresponds to a decay time. Integration yields

$$N_T/(kt_N^{p+1}) = p! - e^{-\tau}[\tau^p + \sum_{j=0}^{p-1} p(p-1)\ldots \times (p-j)\tau^{p-1-j}] \quad (10)$$

where $\tau = t/t_N$, as previously defined for the exponential law.

Two alternative solutions can be used to compute the size distributions

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

$$f(a,t) = -[1/N_T]\cdot(\partial N/\partial a) \quad (11b)$$

where $N(a,t)$ is the number of particles with sizes equal to or larger than a. Note that $N(a,t)$ decreases with increasing particle size.

The time dependence for average particle size can also be computed as

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

where the maximum size a_m is that for the oldest particle nucleated at time $t = 0$ and the minimum size a_0 is for the nucleus. If the nucleation time of a particle is $t_0 < t$ its age reduces to $t - t_0$ which corresponds to growth. For growth controlled by interfacial reaction

$$a = a_0 + R(t - t_0) \quad (13)$$

Therefore, the number of particles $N(a,t)$ of sizes equal to or larger than a corresponds to all the particles nucleated before or at time t_0. For example, $N(a,t) = Kt_0$ for the linear nucleation law, etc.

3. Constant nucleation rate

The solutions for the number of particles of sizes equal or larger than a, size distribution $f(a,t)$, and average particle size a_{av} can be obtained on combining Equations 1, 11a, 12 and 13

$$N(a,t) = kt_0 = k(t - a/R + a_0/R) \quad (14)$$

$$f(a,t) = 1/(Rt) = 1/(a_m - a_0) \quad (15)$$

$$(a_{av} - a_0)/(Rt) = (a_{av} - a_0)/(a_m - a_0) = 1/2 \quad (16)$$

where $a_m = a_0 + Rt$ (Equation 13) is the maximum particle size. Equation 16 shows that the rate of increase in average size is half the growth rate for the largest particle.

4. Exponential nucleation law

Combination of Equations 2, 11b, 12 and 13 gives the solutions for decreasing exponential nucleation and growth controlled by interfacial reaction. Details of the required integration are omitted for easier reading.

$$N(a,t) = N_0 - N_0 e^{-\tau} \exp[(a - a_0)/(Rt_N)] \quad (17)$$

$$(a_m - a_0)f(a,t) = \frac{[(a - a_0)/Rt_N] \exp[(a - a_0)/(Rt_N)]}{\exp[(a_m - a_0)/(Rt_N)] - 1} \quad (18)$$

$$(a_{av} - a_0)/(a_m - a_0) = 1/(1 - e^{-\tau}) - 1/\tau \quad (19)$$

The time dependencies for the average particle size and for the size distributions are relatively simple. Fig. 1 shows that the size distribution is nearly constant for small times $\tau \ll 1$, as predicted by the solution for constant nucleation rate, and becomes increasingly narrower for large times.

5. Kashchiev's nucleation law

Combination of Equations 4, 5, 11b, 12 and 13 gives the relevant solutions when Kashchiev's equation is used to describe nucleation. Details of the integration are still more complex than for the previous cases, and are omitted for the sake of clarity.

$$N(a,t) = k[t - (a - a_0)/R] - kt_I\pi^2/6 - 2kt_I \sum_{n=1}^{\infty}(-1)^n n^{-2}\exp(-n^2\tau) \times \exp[n^2(a - a_0)/(Rt_I)] \quad (20)$$

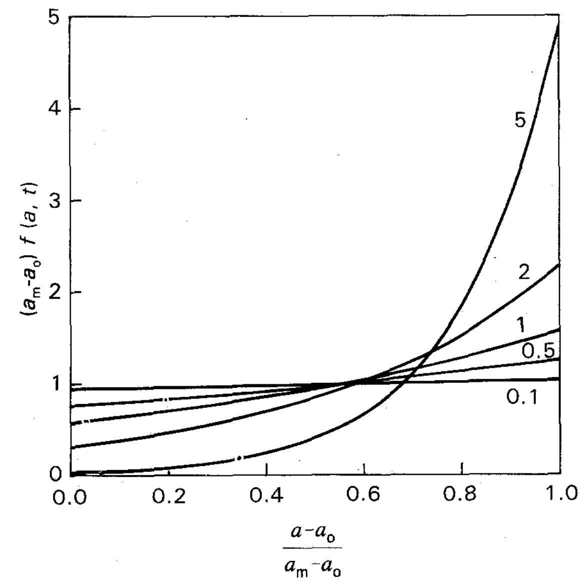

Figure 1 Size distributions for exponential nucleation (Equation 2) and reaction controlled growth. The values of τ are shown in the figure.

$$(a_m - a_0)f(a, \tau) = V_1(x)/V(\tau) \quad (21)$$

$$(a_{av} - a_0)/(a_m - a_0) = V_2(\tau)/V(\tau) \quad (22)$$

where

$$\tau = t/t_I = (a_m - a_0)/(Rt_I) \quad (23)$$

$$x = (a_m - a)/(Rt_I) \quad (24)$$

$$V_1(\xi) = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\xi) \quad (25)$$

and

$$V_2(\xi) = 1/2 - \pi^2/(6\xi) - 2\sum_{n=1}^{\infty}(-1)^n[1 - \exp(-n^2\xi)](n^4\xi^2) \quad (26)$$

The solutions of functions $V(\xi)$, $V_1(\xi)$ and $V_2(\xi)$ are shown in Table I, and Fig. 2 shows the time dependence for the average particle size and for the number of particles. The corresponding asymptotic solution corresponds to constant nucleation rate (Equation 16). Fig. 3 shows that size distributions also tend to the corresponding solution for constant nucleation rate (Equation 15).

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

ξ	$V(\xi)$	$V_1(\xi)$	$V_2(\xi)$
0	0	0	0
0.2	0.0000	0.0000	0.0000
0.3	0.0002	0.0017	0.0000
0.4	0.0016	0.0117	0.0002
0.5	0.0058	0.0361	0.0007
0.6	0.0139	0.0749	0.0020
0.7	0.0261	0.1248	0.0041
0.8	0.0419	0.1814	0.0071
0.9	0.0607	0.2409	0.0110
1	0.0817	0.3006	0.0157
1.2	0.1278	0.4140	0.0269
1.4	0.1760	0.5142	0.0400
1.6	0.2238	0.5995	0.0541
1.8	0.2696	0.6709	0.0687
2	0.3128	0.7300	0.0834
2.5	0.4077	0.8359	0.1188
3	0.4849	0.9004	0.1511
3.5	0.5473	0.9396	0.1797
4	0.5979	0.9634	0.2049
5	0.6737	0.9865	0.2462
6	0.7267	0.9950	0.2783
8	0.7945	0.9993	0.3240
10	0.8355	0.9999	0.3544
12	0.8629	1.0000	0.3761
15	0.8903	1.0000	0.3988
20	0.9178	1.0000	0.4225
25	0.9342	1.0000	0.4372
30	0.9452	1.0000	0.4473
40	0.9589	1.0000	0.4601
60	0.9726	1.0000	0.4731
80	0.9794	1.0000	0.4797
100	0.9836	1.0000	0.4837
150	0.9890	1.0000	0.4891
200	0.9918	1.0000	0.4918
300	0.9945	1.0000	0.4945
500	0.9967	1.0000	0.4967
1000	0.9984	1.0000	0.4984

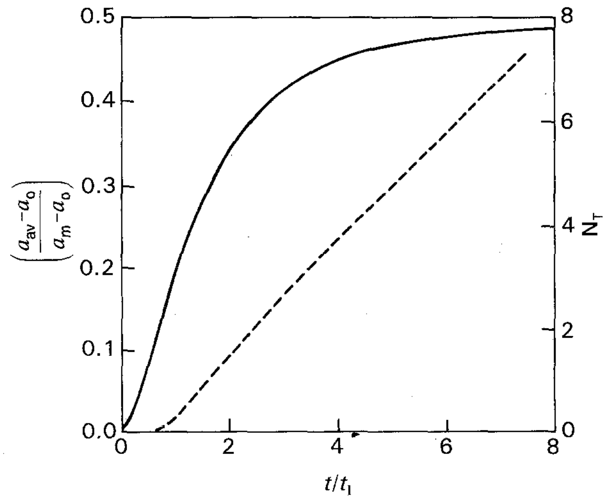

Figure 2 Time dependencies for the average particle size when nucleation is given by Kashchiev's law (Equation 4) and reaction controlled growth. The dashed line represents the number of particles.

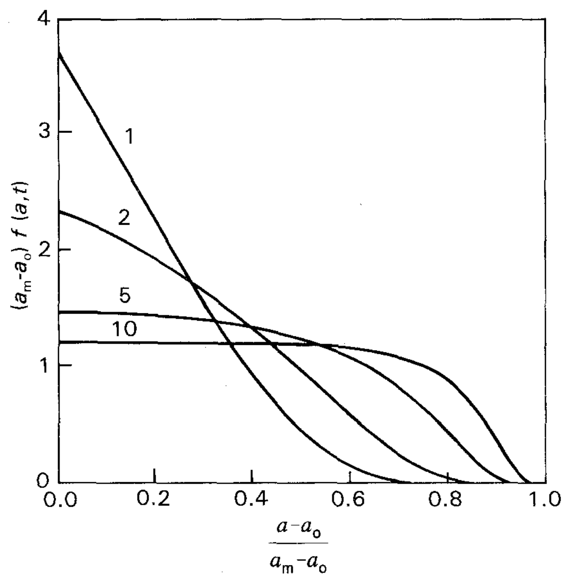

Figure 3 Size distributions for Kashchiev's nucleation law and reaction controlled growth. The numbers show the values of t/t_I.

6. Multistep nucleation

Equations 8, 11b, 12 and 13 also give relatively simple solutions for multistep nucleation

$$N(a,t) = kt_0^p = k(t + a_0/R - a/R)^p \quad (27)$$

$$(a_m - a_0)f(a,t) = p[(a_m - a)/(a_m - a_0)]^{p-1} \quad (28)$$

$$(a_{av} - a_0)/(a_m - a_0) = 1/(p + 1) \quad (29)$$

Complex alternative solutions are obtained on assuming consumption of first order embryos and irreversible change from order p to $p + 1$ (Equation 9 or 10). From Equations 9 and 13

$$(\partial N/\partial t) = k_2(t + a_0/R - a/R)^p \times \exp[(a - a_0)/(Rt_N) - \tau)] \quad (30)$$

In addition, combination of Equations 10, 11a, 13 and

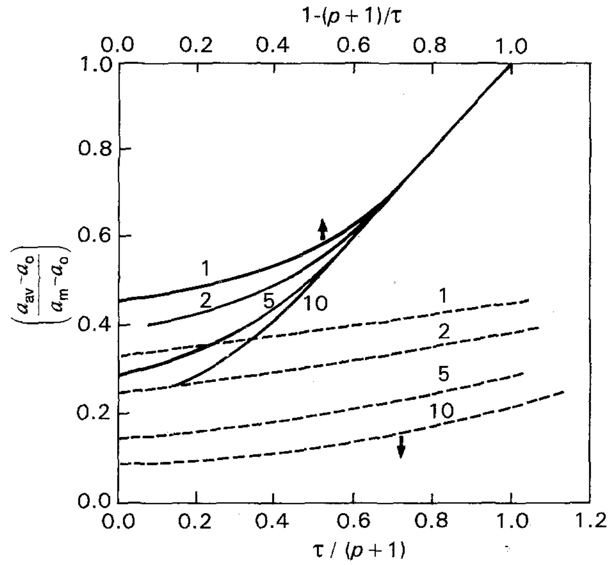

Figure 4 Average particle size for multistep nucleation (Equations 9 and 10) and reaction controlled growth. The numbers are the values of p. Alternative representations are shown to demonstrate the asymptotic solutions for short times (dashed lines) and for longer times (full lines).

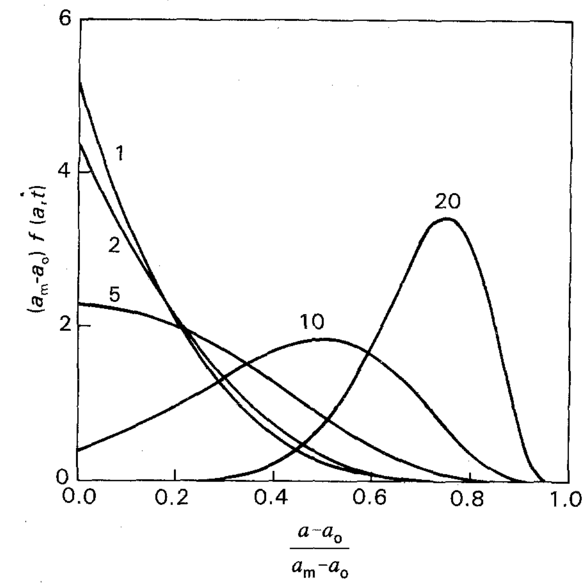

Figure 5 Particle size distribution for multistep nucleation (Equations 9 and 10) and reaction controlled growth. The numbers are the values of $\tau = t/t_N$.

30 gives the size distribution

$$(a_m - a_0) f(a,\tau) = [(a_m - a)/(Rt_N)]^{p+1} \times \exp[(a_m - a)/(Rt_N)]/M(p,\tau) \quad (31)$$

$$M(p,\tau) = p! - e^{-\tau}[\tau^p + \sum_{j=0}^{p-1} p(p-1)\ldots \times (p-j)\tau^{p-1-j}] \quad (32)$$

where $\tau = t/t_N = (a_m - a_0)/(Rt_N)$. Note that Equation 32 is the same as Equation 10. The average particle can also be obtained on combining Equations 12 and 31. Integration yields

$$(a_{av} - a_0)/(a_m - a_0) = 1 - M(p+1,\tau)/[\tau M(p,\tau)] \quad (33)$$

The limiting solutions for small and for large times are

$$(a_{av} - a_0)/(a_m - a_0) = 1/(p+2) \quad \text{for } t \ll t_N \quad (34)$$

$$(a_{av} - a_0)/(a_m - a_0) = 1 - (p+1)/\tau \quad \text{for } t \gg t_N \quad (35)$$

Fig. 4 shows some typical results for this multistep nucleation mechanism. The limiting trend for large times (Equation 35) is nearly accurate for $t > 1.4$ $(p+1)t_N$ and the predictions for short times converge to Equation 34 for $t < t_N/2$. Fig. 5 also shows the evolution towards typical size distributions for longer times.

7. Conclusions

The dynamics of nucleation and reaction controlled growth of disperse particles has been examined. The time dependence for the average particle size is usually a simple solution, for several nucleation laws. The simplest cases give similar time dependence for growth of the largest particles and for the average particle size, except for a time-independent factor. This is possible for constant nucleation rate and for simple multistep nucleation laws. Analytical solutions have been derived for time-dependent effects when nucleation is given by the exponential law, Kashchiev's law or a multistep nucleation law with a decay factor.

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References

1. D. R. UHLMANN, *J. Non-Cryst. Solids* **7** (1972) 737.
2. R. W. HOPPER, *ibid.* **15** (1974) 45.
3. P. I. K. ONORATO and D. R. UHLMANN, *ibid.* **22** (1976) 367.
4. *Idem., ibid.* **41** (1980) 189.
5. E. D. ZANOTTO and A. GALHARDI, *ibid.* **104** (1988) 736.
6. E. D. ZANOTTO and M. C. WEINBERG, *ibid.* **105** (1988) 53.
7. M. C. WEINBERG and E. D. ZANOTTO, *Phys. Chem. Glasses* **30** (1989) 110.
8. K. JANSSON and M. NYGREN, *Mater. Res. Bull.* **19** (1984) 1091.
9. Q. C. WU, *J. Mater. Sci.* **21** (1986) 3581.
10. E. H. HENNINGER and D. S. EASTON, *ibid.* **20** (1986) 4298.
11. G. K. DEY, *ibid.* **21** (1986) 117.
12. W. A. JOHNSON and R. F. MEHL, *Trans. AIME* **135** (1939) 416.
13. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
14. *Idem., ibid.* **8** (1940) 212.
15. *Idem. ibid.* **9** (1941) 177.
16. B. V. EROFEEV, *C. R. Acad. Sci. URSS* **52** (1946) 511.
17. D. KASHCHIEV, *Surface Sci.* **14** (1969) 209.
18. C. BAGDASSARIN, *Acta Physicochim.* **20** (1945) 441.
19. A. R. ALLNATT and P. W. M. JACOBS, *Can. J. Chem.* **46** (1968) 111.
20. I. ORGZALL and B. LORENZ, *Acta Metall.* **36** (1988) 622.
21. B. LORENZ, *ibid.* **37** (1989) 2689.
22. E. RUCKENSTEIN and B. NOWAKOWSKI, *J. Colloid Interface Sci.* **137** (1990) 583.
23. B. NOWAKOWSKI and E. RUCKENSTEIN, *ibid.* **145** (1991) 182.
24. A. WISCHIN, *Proc. R. Soc. Lond.* **A172** (1939) 314.

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