Kinetic theory of nucleation and coarsening

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Abstract
Classical theory of nucleation based on Becker-Doering equations and coarsening for a binary alloy.

1 Introduction
The purpose of this chapter is to explain the classical kinetic theory of nucleation in a context simpler than polymer crystallization. Many theories start by assuming that polymer crystallization is an activated process involving crossing of a free energy barrier. The latter separates two accessible stable states of the system such as monomer solution and crystal. This general setting for activated processes can be used to describe the formation of a crystal from a liquid cooled below its freezing point, precipitation and coarsening of binary alloys, colloidal crystallization, chemical reactions, polymer crystallization, etc. In all these cases, the theory of homogeneous isothermal nucleation provides a framework to study the processes of formation of nuclei from density fluctuations, and their growth until different nuclei impinge upon each other. In the early stages of these processes, nuclei of solid phase are formed and grow by incorporating particles from the surrounding liquid phase. There is a critical value for the radius of a nucleus that depends on a chemical drive potential, which is proportional to the supersaturation for small values thereof. In this limit, the critical radius is inversely proportional to the supersaturation. At the beginning of the nucleation process, nuclei have small critical radius and new clusters are being created at a non-negligible rate. As the size of existing
clusters increases, there are less particles in the liquid phase, the supersaturation decreases and the critical radius increases. Then it is harder for new clusters to spontaneously appear from density fluctuations. What happens is that supercritical clusters (whose radii are larger than the critical one) keep growing at the expense of subcritical clusters, that in turn keep losing particles. The size of the nuclei is still small compared to the average distance between them, so that impingement processes (in which two or more clusters touch and interaction between them dominates their growth) can be ignored. This stage of free deterministic growth is called coarsening [9].

A convenient framework to describe nucleation and coarsening is the classical Becker-Döring kinetic theory. We assume that the dominant processes for nucleus growth or shrinking are addition or subtraction of one particle. Nucleation is thus treated as a chain reaction whereby nuclei of \( n \) particles are created by adding one particle to a nucleus of \( n-1 \) particles, or subtracting one particle from a nucleus with \( n+1 \) particles. We can then write rate equations for the number density of nuclei of \( n \) particles by using the law of mass action. The kinetic rate constants for the processes of addition and depletion have to be determined by using specific information from the physical process we are trying to model. Typically we impose detailed balance which implies that the ratio of rate constants is proportional to the exponential of the free energy cost of adding one particle to a nucleus of \( n \) particles (in units of \( k_B T \)). This leaves one undetermined rate constant. There are different ways of finding the missing constant. One way is to postulate a microscopic theory for particle interaction and use Statistical Mechanics to determine the free energy of a cluster [8]. A different point of view is to impose that our rate constants should provide a description of coarsening compatible with the macroscopic description in terms of balance equations. We shall illustrate this second point of view and be led to a Smoluchowski equation from which the Lifshitz-Slyozov coarsening theory follows [10].

The structure of this paper is as follows. We present the Becker-Döring kinetic equations for cluster with \( n \) particles in Section 2. One relation between the two rate constants of this theory follows from detailed balance. The other rate constant has to be determined by comparison with the known macroscopic equation for the growth of cluster radii. In the small supersaturation limit, the Becker-Döring equations can be approximated by a Smoluchowski equation for the distribution function of cluster radii. Its drift term yields the growth of cluster radii in terms of the missing rate constant. To compare with experimental data, we consider the case of coarsening of a binary alloy [3]. In Sections 4 to 6, we review phase equilibria, macroscopic kinetics of precipitate and matrix atoms and the quasistatic limit of the kinetic equations, respectively. As a result, we find the growth of the radius of a supercritical cluster in terms of macroscopic parameters. Comparison with the results in Section 2 yields the sought rate constant; see Section 5. Numerical values for all the parameters involved in our theories can be calculated from experimental data as explained in Section 6. A discussion of our results constitutes the last Section.
2 Kinetics of clusters

Let us assume that we have two stable phases characterized by different values, $c_1$ and $c_2$ of the number density $c$. Phase 1 is solution and Phase 2 precipitate. Or Phase 1 is the liquid and Phase 2 the crystal phase. Initially all precipitate particles are in Phase 1. Classic Becker-Döring (BD) kinetics treats nucleation as a *chain reaction* whereby nuclei (assumed to be *spherical*) of $n$ precipitate particles are created by adding one particle to a nucleus with $n-1$ particles, or subtracting one particle from a nucleus with $n+1$ particles. This chain reaction scheme is natural for the situation that BD has in mind, in which bulk precipitate phase consists only of precipitate particles so distinction between particles in nucleus or in solution is clear.

Let $\rho_n$ be the number density of nuclei of $n$ particles. The monomer density $\rho_1$ represents the concentration of precipitate particles in solution and as such it will be identified with the concentration $c_\infty$ of the macroscopic theory in Section 5. Consider the reaction

$$n + 1 \rightleftharpoons (n + 1).$$

The forward reaction proceeds at a rate proportional to $\rho_1 \rho_n$ with some rate constant $k_a$. The backward reaction proceeds at a rate proportional to $\rho_{n+1}$ with rate constant $k_d$. Hence the net rate of creation of $(n + 1)$-clusters from $n$-clusters per unit volume is the flux

$$j_n \equiv k_{a,n} \rho_1 \rho_n - k_{d,n+1} \rho_{n+1}.$$  \hfill (1)

The fact that the rate constants depend on cluster size has been explicitly indicated in (1). Net rate of creation of $n$-clusters is due to their creation from $(n-1)$-clusters minus the rate of creation of $(n + 1)$-clusters from $n$-clusters,

$$\dot{\rho}_n = j_{n-1} - j_n \equiv -D_- j_n, \quad n \geq 2.$$  \hfill (2)

This formulation specifies the evolutions of $\rho_2$, $\rho_3$, ... with $\rho_1 = c_\infty$ given. The number density of precipitate particles in $n$-clusters is $n \rho_n$ and the density $c$ (equal to the initial concentration of precipitate particles in the solution) of all precipitate particles is

$$c \equiv \sum_{n=1}^{\infty} n \rho_n,$$  \hfill (3)

or equivalently,

$$c - c_1 = \gamma_\infty + \sum_{n=2}^{\infty} n \rho_n,$$  \hfill (4)

where we have defined $\gamma = c - c_1$, $\gamma_\infty = c_\infty - c_1$. There is conservation of all precipitate particles so $c$ or $\gamma_0 = c - c_1$ are constant. (4) establishes that the constant initial concentration disturbance $\gamma_0$ is sum of the disturbance of
precipitate particles, $\gamma_\infty$, and the number density of particles in all cluster sizes $n \geq 2$. Given the constraint (4), the evolution of all $\rho_n$, including $\rho_1$, is specified.

A most essential point of BD kinetics is identification of rate constants $k_a$ and $k_d$. Ideally, this would be based on basic energetics and dynamics at the microscopic level, but a complete realization of this ideal is clearly elusive. Here is what is done: The ratio is determined by detailed balance. Equilibrium, if achievable, is described by a zero flux. Setting $j_n = 0$ in (1) implies

$$\frac{k_{a,n}}{k_{d,n}} = \frac{\rho_{n+1}}{\rho_1 \rho_n}.$$  

(5)

Standard equilibrium physicochemical theory states that

$$\frac{\rho_{n+1}}{\rho_n} = e^{-\mu_n},$$  

(6)

where $\mu_n$ is the free energy cost of creating an $(n+1)$-particle nucleus from an $n$-particle nucleus relative to the state of no nucleus. $\tau = k_B T$ is the temperature measured in units of energy. Clearly, $\mu_n = G_{n+1} - G_n$ ($G_n$ is the free energy of a $n$-cluster), so (6) becomes

$$\frac{\rho_{n+1}}{\rho_n} = e^{-\frac{G_{n+1} - G_n}{\tau}},$$

and (5) now reads

$$\rho_1 k_{a,n} = e^{-\frac{G_{n+1} - G_n}{\tau}} k_{d,n+1}.$$  

Thus formula (1) for the flux is now

$$j_n = k_{d,n+1} \left\{ e^{-\frac{G_{n+1} - G_n}{\tau}} \rho_n - \rho_{n+1} \right\}.$$  

(7)

The equilibrium considered in the detailed balance argument is achievable only if $G_n \to +\infty$ as $n \to \infty$, whereas in a supersaturated solution, $G_n$ achieves a maximum for finite $n$ and then $G_n \to -\infty$ as $n \to \infty$. The determination of the ratio $k_a/k_d$ is assumed to hold regardless.

What is known about $G_n$? Microscopic models for $G_n$ (or, equivalently, the cluster partition function $Q_n \equiv \sum_K e^{U b(K)/\tau} = e^{-G_n/\tau}$, where $U$ is the binding energy per pair of particles in the cluster of $n$ particles, $b(K)$ is the number of nearest-neighbor pairs of particles in the cluster $K$, and the sum is over all translationally inequivalent $n$-particle clusters) are described in [8, 11, 12]. We would like to follow here a simpler approach, consisting of identifying the resulting expressions for large spherical nuclei with known facts about radius growth in the quasistatic approximation. For nuclei of macroscopic size $n \gg 1$, $n$ can be written in terms of the cluster radius $a$ by

$$n = \frac{4\pi}{3} c_2 a^3,$$  

(8)
and \( G_n \sim G(a) \), where \( G(a) \) is the free energy of a nucleus of radius \( a \) as determined by continuum theory. For nuclei of only a few particles, this asymptotic correspondence with continuum theory breaks down. But if the critical nucleus has \( n \gg 1 \) particles, the continuum approximation works for \( n \) on the order of critical cluster size.

In the limit \( |(G_{n+1} - G_n)/\tau| \ll 1 \), formula (7) for the flux reduces to

\[
 j_n = k_{d,n+1} \left\{ -\frac{(G_{n+1} - G_n)}{\tau} \rho_n + \rho_n - \rho_{n+1} \right\} = -k_{d,n+1} \left\{ \frac{1}{\tau} (D_+ G_n) \rho_n + D_+ \rho_n \right\}, \tag{9}
\]

where \( D_{\pm} h_n \equiv \pm(h_{n\pm 1} - h_n) \). The basic evolution equation (2) now reads

\[
 \dot{\rho}_n - D_- \left\{ k_{d,n+1} \left( \frac{1}{\tau} (D_+ G_n) \rho_n + D_+ \rho_n \right) \right\} = 0. \tag{10}
\]

This equation looks like a spatially discretized Smoluchowski equation. Asymptotic replacement of difference operators \( D_+ \), \( D_- \) by derivatives is justified if the relative changes in \( G_n \), \( \rho_n \) and \( k_d \) when \( n \) increases by one are small. Here we will follow the simple procedure of formulating the continuum limit an checking its validity a posteriori.

The space-like variable in (10) is \( n \). Experimental data usually contain histograms showing the distribution of nuclei in the space of their radii \( a \), so we adopt the radius \( a \) as a more convenient space-like variable. The dependent variable should be \( \rho = \rho(a,t) \), the distribution of nuclei in space of radius \( a \). Thus \( \rho(a,t) \, da \) is the number of nuclei per unit volume with radii in \((a, a + da)\).

Conversions \( n \to a \), \( \rho_n \to \rho \) are now determined. From (8), it follows that the change \( da \) in \( a \) when \( n \) increases by 1 is given by

\[
 1 \sim 4\pi c_2 a^2 \, da. \tag{11}
\]

In the general continuum theory of nuclei, the concentration of precipitate particles inside a nucleus, \( c_2 \), is a function of the radius \( a \). But for many experiments, deviations of \( c_2 \) from its equilibrium value for a planar interface are negligible, so in (11) any term arising from \( a \)-dependence of \( c_2 \) is dropped. \( \rho_n \) is related to \( \rho(a,t) \) by

\[
 \rho_n \sim \rho(a,t) \, da \sim \frac{1}{4\pi c_2 a^2} \frac{\rho}{a^2}. \tag{12}
\]

Given any sequence \( h_n \) with continuum approximation \( h(a) \),

\[
 D_+ h_n \sim D_- h_n \sim \frac{h_n}{4\pi c_2 a^2}. \tag{13}
\]

It follows from (12) and (13) that the continuum limit of (10) is

\[
 \rho_t - \frac{\partial}{\partial a} \left\{ \frac{k_d}{(4\pi c_2 a^2)^2} \left( \frac{\rho}{\tau} \frac{\partial G}{\partial a} + a^2 \frac{\partial}{\partial a} \left( \frac{\rho}{a^2} \right) \right) \right\} = 0. \tag{14}
\]
(Here \(k_d\) is a function of \(a\), to be specified). The constraint \(\text{(14)}\) can be written as
\[
\gamma_\infty + c_2 \int_0^\infty \frac{4\pi}{3} a^3 \rho(a,t) \, da = c - c_1 \equiv \gamma_0.
\]
(15)

As time elapses, it will be seen that the diffusive term in Eq. \(\text{(14)}\) becomes negligible in comparison with the drift term. The latter yields the following equation for radius growth:
\[
\dot{a} = -\frac{k_d}{(4\pi c_2 a^2)^{\frac{1}{2}}} \frac{\partial G}{\partial a}.
\]
(16)

We now present a macroscopic theory that gives an explicit expression for \(\dot{a}\) that can be compared to experimental data. Then \(k_d(a)\) can be determined and this will specify the limit of \(k_{d,n}\) for large \(n\).

3 Phase equilibria of a binary material

3.1 Phase equilibria of a binary material

Let us consider a medium consisting of two different particles. The more abundant type is called “matrix”, the other “precipitate”. Suppose that we have a uniform mixture at fixed temperature and pressure. Let \(\mu\) be the chemical potential, i.e., the free energy cost of adding one precipitate particle to a pre-existing solution. It is a function of the number density of precipitate particles, \(c\):
\[
\mu = \mu(c).
\]
(17)

Let us now derive the relationship of the chemical potential, \(\mu(c)\), to the bulk free energy density, \(g(c)\). We shall add one precipitate particle to a solution of total volume \(V\). Then the free energy changes from \(g(c)V\) to \(g(c)V + \mu(c)\), but the volume changes from \(V\) to \(V' = V + \nu(c)\), where \(\nu(c)\) is the specific volume of a precipitate particle in a solution of number density \(c\). The number density changes from \(c\) to \(c' \equiv (cV + 1)/(V + \nu)\), and therefore the new free energy is also expressed as \(g(c')V'\). Hence we get the identity
\[
g(c)V + \mu(c) = g \left( \frac{cV + 1}{V + \nu} \right) (V + \nu).
\]
(18)

Since \(cV \gg 1, \nu \ll V\), this identity reduces to
\[
\mu(c) = g'(c) + \nu(c) \{g(c) - cg'(c)\}.
\]
(19)

One can just as easily consider the chemical potential \(\overline{\mu}(c)\), which is the free energy cost of adding one matrix particle to the solution. Adding one matrix particle changes the free energy to \(g(c)V + \overline{\mu}(c)\). The volume of the solution changes now to \(V' = V + \overline{\nu}(c)\), where \(\overline{\nu}(c)\) is the specific volume of a matrix
particle in solution. The concentration $c$ of the precipitate changes to $c' \equiv cV/(V + \nu)$, and therefore the new free energy is $g(c')V'$. Hence we get an identity analogous to (18),

$$g(c)V + \mu(c) = g\left(\frac{cV}{V + \nu}\right)(V + \nu).$$

(20)

Again the conditions $cV \gg 1, \nu \ll V$ lead to an asymptotic reduction of $g(c)\nu(c) = \nu(c)\{g(c) - cg'(c)\}$.

(21)

### 3.2 Phase equilibria in a dilute solution

Suppose that there are two stable phases characterized by different values, $c_1$ and $c_2$ of the number density $c$, and that these phases occupy adjacent half spaces separated by a planar interface. Imagine that one precipitate particle is removed from phase 1 and dropped in phase 2. The free energy cost is $\mu(c_2) - \mu(c_1)$. In equilibrium, the energy cost is to be zero, therefore

$$[\mu] \equiv \mu(c_2) - \mu(c_1) = 0.$$  

(22)

Similarly, the energy cost of removing a matrix particle from phase 1 and dropping it in phase 2 is also to be zero, so

$$[\mu'] = 0.$$  

(23)

The possible existence of multiple phases is determined by the structure of $g(c)$. Consider a dilute solution with $c$ much smaller than the total atomic density. In this case, the specific volumes $\nu$ and $\nu$ of precipitate and matrix particles should be nearly constants independent of $c$: “crowding” effects should be insignificant. In this case, $\mu$ and $\mu'$ imply

$$[g(c) - cg'(c)] \equiv [g - cg'] = 0.$$  

(24)

Given this result, it now follows from $\mu$ and $\mu'$ that

$$[g'] = 0.$$  

Hence,

$$g'(c_1) = g'(c_2) = M \quad \text{(common value)},$$  

(25)

and

$$[g] - [c] M = 0.$$  

(26)

Given $g(c)$ with $g''(c) < 0$ in some interval of $c$, and $g''(c) > 0$ outside, one discerns the standard geometrical construction of the solution to $g'$ for $c_1$ and $c_2$. This is depicted in Figure 7.
3.3 Critical nucleus

Consider a spherical nucleus of phase 2 surrounded by phase 1. The energy cost of adding one precipitate particle to this nucleus is

\[ [\mu] + 8\pi r\sigma \, dr. \]

Here \( r \) is the initial radius of the nucleus, \( dr \) is the change in radius due to adding one precipitate particle, and \( \sigma \) is the surface tension. One has

\[ 4\pi r^2 \, dr = \nu \]

so the energy cost can be written as

\[ [\mu] + \frac{2\sigma \nu}{r}. \]

For a nucleus in equilibrium, this energy cost is zero, therefore

\[ [\mu] = -\frac{2\sigma\nu}{r}. \] (27)

Now we add one matrix particle to the nucleus. No energy cost for this process implies

\[ [\mu] = -\frac{2\sigma\nu}{r}. \] (28)

After substituting for \( \mu \) from (21), this equation becomes

\[ [g - c\, g'] = -\frac{2\sigma}{r}. \] (29)
Now substitute (19) for \( \mu \) and (29) for \( 2\sigma/r \) in (27) to get

\[
[g'] = 0,
\]

(30)

which is the same as in the case of a planar interface, (25). Given the concentration \( c_1 \) of phase 1, this equation determines the concentration \( c_2 \) inside the nucleus, and then the Gibbs-Thomson relation (27) determines the radius of the nucleus, \( r \). This determination simplifies when the concentrations \( c_1 \) and \( c_2 \) are near “planar” values and \( \gamma_1 \) and \( \gamma_2 \) are deviations from the planar values. (30) together with (24) for the planar case imply

\[
[g'' \gamma] = 0.
\]

(31)

Let us denote the common values of \( g''(c_1) \gamma_1 \) and \( g''(c_2) \gamma_2 \) by \( m \). The variation of \( [g - c g'] \) in (29) is

\[
- [c g'' \gamma] = -[c] m.
\]

(32)

Hence (29) gives

\[
[c] m = \frac{2\sigma}{r}.
\]

(33)

4 Macroscopic kinetics

4.1 Balance equations and jump conditions

Let \( c(x,t), \tau(x,t) \) denote the macroscopic number densities of precipitate and matrix atoms. Local volume fractions of precipitate and matrix atoms are \( \nu c \) and \( \nu \tau \), respectively. Since matrix and precipitate atoms fill space leaving no gaps, we have the space filling condition

\[
\nu c + \nu \tau = 1.
\]

(34)

In conventional kinetics, the density of precipitate is locally conserved, with a flux proportional to the gradient of the precipitate chemical potential \( \mu(c) \),

\[
c_t + \nabla \cdot (-\delta \nabla \mu) = 0,
\]

or

\[
c_t = \nabla \cdot (D \nabla c), \quad D = \delta(c) \mu'(c).
\]

(35)

Here \( \delta(c) \) is a positive mobility coefficient and \( -\delta \nabla \mu = -D \nabla c \) is the flux of \( c \). This flux is formally a diffusion with diffusion coefficient \( D = \delta(c) \mu'(c) \). Given \( \mu(c) \) as in (19), and provided \( \nu \) and \( \tau \) do not depend on \( c \) (dilute solution),

\[
D = \delta(c) \mu'(c) = \delta(1-\nu c) g''(c) = \delta \nabla \tau g''(c).
\]

(36)

In the last equality, the space filling condition has been used to replace \( 1-\nu c \) by \( \nabla \tau \). For stable bulk phases, \( D \) must be positive, and (36) then implies \( g''(c) > 0 \).
The description of matrix transport is essentially the same. The flux of matrix concentration $\overline{c}$ is

\[ -\delta \nabla \overline{c} = -\overline{\delta \mu} \nabla = -\overline{D} \nabla \overline{c} \]  

(37)

where $\overline{\mu}(\overline{c})$ is the chemical potential of the matrix atoms as a function of the matrix concentration $\overline{c}$, $\overline{\delta}(\overline{c})$ is the mobility of the matrix atoms, and $\overline{D}$ is the matrix diffusion coefficient given by

\[ \overline{D} = \overline{\delta \mu} \cdot \overline{\nu} \].

Let $\overline{g}(\overline{c})$ be the free energy density as a function of $\overline{c}$. The space filling condition and $g(c) = \overline{g}(\overline{c})$ imply that

\[ \overline{\mu} = \overline{g}'(\overline{c}) + \nu \{ \overline{g}(\overline{c}) - \overline{g}'(\overline{c}) \}, \]

which is totally symmetric to (15). Then the diffusion coefficient $\overline{D}$ is related to $\overline{g}(\overline{c})$ by a formula symmetric to (36),

\[ \overline{D} = \overline{\delta \nu c \overline{g}''(\overline{c})}. \]  

(38)

The space filling condition leads to a relation between the mobilities $\delta$ and $\overline{\delta}$. The linear combination $\nu c + \nu \overline{c}$ is locally conserved with flux $-\nu \overline{D} \nabla c - \nu \overline{D} \nabla \overline{c}$. But $\nu c + \nu \overline{c} \equiv 1$, so this flux is divergence free. Let $C$ be any closed surface. Use of divergence theorem yields

\[ \int_C (\nu D_{cn} + \nu \overline{D}_{\overline{c}n}) da = 0. \]

The space filling condition implies $\nu c_n = -\overline{\nu c_n}$, so that we get $\int_C \nu (D - \overline{D}) c_n da = 0$. This holds for all concentration fields $c$ and closed surfaces $C$. Hence,

\[ D = \overline{D} \]  

(39)

and by (36) and (38),

\[ \delta(c) \nu \overline{c} g''(c) = \overline{\delta}(\overline{c}) \nu c \overline{g}''(\overline{c}). \]  

(40)

Now,

\[ g(c) = \overline{g}(\overline{c}) = \overline{g} \left( \frac{1}{\nu} (1 - c\nu) \right), \]

therefore, provided again that $\nu$ and $\overline{\nu}$ do not depend on $c$,

\[ g''(c) = \left( \frac{\nu}{\overline{\nu}} \right)^2 \overline{g}''(\overline{c}), \]

and (10) becomes

\[ \delta \nu \overline{c} = \overline{\delta \nu c}. \]  

(41)

This is the relation between mobilities.
The integral form of Equation (35) informs the upcoming discussion of
boundary conditions on a phase interface. Let \( R = R(t) \) be a time sequence of
closed regions in which \( c = c(x, t) \) is a smooth solution of (35). The number of
precipitate particles in \( R \) is
\[
N = \int_R c \, dx,
\]
and the time rate of change is
\[
\dot{N} = \int_R c_t \, dx + \int_{\partial R} Uc \, da,
\]
where \( U \) is the outward normal velocity of \( \partial R \). Using (35) to substitute for \( c_t \)
above, and then the divergence theorem, we obtain
\[
\dot{N} = \int_{\partial R} (U c + D c_n) \, da.
\]
The interpretation of this equation is clear: The influx of precipitate atoms per
unit area on \( \partial R \) is \( U c + D c_n \). (42)

Suppose now that there is a region \( R_1 \) of matrix surrounding a region \( R_2 \)
of precipitate. The influx of precipitate atoms per unit area on interface \( C \) is
given by (42) with \( c, c_n \) evaluated on the precipitate side of \( C \). The outflux
of precipitate atoms from the surrounding matrix into \( R_2 \) is also given by (42)
with \( c, c_n \) evaluated on the matrix side of \( C \). Since precipitate atoms do not
accumulate on \( C \) to form a surface density, the following jump condition holds
\[
[U c + D c_n] = 0 \quad \text{on} \quad C.
\]
(43)

In summary, conservation of precipitate is expressed by the diffusion equation
(35) and the associated jump condition (43). The matrix density \( \tau \) satisfies
the diffusion equation and jump condition with the same diffusion coefficient
\( D \). The space filling condition (34) is automatically upheld by this kinetics. In
addition there are “thermodynamic” jump conditions
\[
[g'] = 0, \quad \text{(44)}
\]
\[
[g - cg'] = -2\sigma\kappa, \quad \text{(45)}
\]
expressing local equilibrium about the phase interface. These are in fact Equations (29),
(30) with \( 1/r \) replaced by the mean curvature \( \kappa \). Equations (35),
(13), (44) and (15) constitute a free boundary problem for the evolution of
precipitate concentration \( c \) and the phase interfaces.

4.2 Time evolution of Gibbs energy

The total Gibbs free energy is
\[
G = G_1 + G_2 + \sigma S, \quad \text{(46)}
\]
where

\[ G_1 \equiv \int_{R_1} g \, dx \quad G_2 \equiv \int_{R_2} g \, dx \]  

are free energies of bulk matrix and precipitate phases, and \( S \) is the surface area of the phase interface, and \( \sigma \) the surface tension. The time evolution of \( G \) under the kinetics of the free boundary problem \( 35, 43, 44 \) and \( 45 \) is examined here. To compute the rates of change of \( G_1 \) and \( G_2 \), it is useful to formulate a transport equation for the free energy density \( g(c) \):

\[ g_t = g' c_t = g' \nabla \cdot (D \nabla c) = \nabla \cdot (D \nabla g) - D g'' |\nabla c|^2 \]

or

\[ g_t - \nabla \cdot (D \nabla g) = -D g'' |\nabla c|^2. \]  

In stable bulk phases, \( g'' > 0 \), therefore the source density in (48) is generally negative. Let us now look at the rate of \( G_2 \).

\[ \dot{G}_2 = \int_{R_2} g_t \, dx + \int_C U g \, da, \]  

where \( U \) is the normal velocity of the phase interface, positive if outward from precipitate. Inserting \( g_t \) from (48) and using the divergence theorem, (49) becomes

\[ \dot{G}_2 = \int_C (U g + D g_n) \big|_2 \, da - \int_{R_2} D g'' |\nabla c|^2 \, dx. \]  

In the surface integral, the subscript 2 means evaluation on precipitate side of interface. Similarly,

\[ \dot{G}_1 = -\int_C (U g + D g_n) \big|_1 \, da - \int_{R_1} D g'' |\nabla c|^2 \, dx, \]  

where subscript 1 means evaluation on matrix side of interface. The rate of change of the surface energy \( \sigma S \) in (46) is given by the standard formula of differential geometry,

\[ \sigma \dot{S} = 2\sigma \int_C \kappa U \, da. \]  

Adding Equations (50) to (52), we obtain the rate of change of the total free energy

\[ \dot{G} = -\int_{R_1+R_2} D g'' |\nabla c|^2 \, dx 
+ \int_C \{[U g + D g_n] + 2\sigma \kappa U \} \, da, \]  

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Here the jump [...] denotes values on precipitate side minus values on matrix side. Using the continuity condition \([g'] = 0\), it follows that
\[
[Ug + Dg_n] = U [g] + g' [Dc_n].
\]
In the right hand side, \(g'\) denotes a well defined value on the phase interface. By conservation jump condition (153), \([Dc_n] = -U [c]\), hence
\[
[Ug + Dg_n] = U [g - cg'].
\]
By the thermodynamic jump condition (155), \([g - cg'] = -2\sigma\kappa\), so finally,
\[
[Ug + Dg_n] = -2\sigma U\kappa,
\]
and the energy rate formula (53) reduces to
\[
\dot{G} = -\int_{R_1 + R_2} Dg'' |\nabla c|^2 \, dx. \tag{55}
\]
The integral is negative definite. Notice that surface integral contributions to \(\dot{G}\) cancel. This point is examined by direct physical argument to see what it really means.

Recall that influx of precipitate atoms into precipitate phase per unit area is
\[
U c + D c_n.
\]
The free energy of each precipitate atom changes by an amount \([\mu] = -2\sigma\kappa\nu\), according to (27), as it crosses from matrix to precipitate. Hence there is a contribution to \(\dot{G}\) of
\[
-2\sigma (U\nu c + D\nu c_n) \kappa \tag{56}
\]
per unit area of phase interface due to crossing of precipitate atoms. Similarly, influx of matrix atoms into precipitate phase per unit area is
\[
U \tau + D \tau_n
\]
and change in free energy for each matrix atom crossing into precipitate is \([\overline{\mu}] = -2\sigma\kappa\tau\), according to (28). Hence, crossing of matrix atoms gives another surface contribution to \(\dot{G}\), of
\[
-2\sigma (U\nu \tau + D\nu \tau_n) \kappa \tag{57}
\]
per unit area. Adding (56) and (57) yields surface contribution to \(\dot{G}\) due to crossing of both types of atoms,
\[
-2\sigma \{U (\nu c + \nabla c) + D (\nu c_n + \nabla c_n)\} \kappa = -2\sigma U\kappa
\]
per unit area. Here the space-filling constraint has been used. From (52) it is seen that \(2\sigma U\kappa\) can be identified as a rate of change of surface energy per unit area. Hence, the total rate of free energy production per unit area of phase interface is
\[
-2\sigma U\kappa + 2\sigma U\kappa = 0.
\]
5 Quasistatic nuclei

An isolated region $R_2$ of precipitate phase, called a nucleus is assumed spherical, and concentration field $c$ is assumed spherically symmetric. The kinetics is quasistatic if the time derivative in the diffusion equation (35) is negligible. Here kinetics is analyzed under the quasistatic assumption and regimes of validity are determined a posteriori by the criterion

$$\frac{Ua}{D} = \frac{a\dot{a}}{D} \ll 1. \tag{58}$$

Here $a$ is the radius of the nucleus, and the normal velocity $U = \dot{a}$. $a^2/D$ represents the characteristic time of diffusive transport in the matrix phase surrounding the nucleus. The characteristic time associated with the kinetics of the radius is $a/U = a/\dot{a}$. Kinetics is quasistatic if the time scale of the radius is much longer than the diffusion time in the surrounding matrix, as in (58).

Under assumptions of radial symmetry and quasistatic kinetics, the diffusion equation (35) reduces to

$$\partial_r (r^2 D c_r) = 0. \tag{59}$$

The conservation jump condition (43) reads

$$\dot{a} [c] = -[D c_r]. \tag{60}$$

The thermodynamic jump conditions (44) and (45) read

$$[g'] = 0, \tag{61}$$

$$[g - cg'] = -\frac{2\sigma}{a}. \tag{62}$$

Given the value $c_\infty$ of $c$ as $r \to \infty$, Equations (59) to (62) determine an ordinary differential equation (ODE) for the nuclear radius $a(t)$. The first integral of (59) is

$$r^2 D c_r = Q, \quad \text{or} \quad D c_r = \frac{Q}{r^2}. \tag{63}$$

Here $Q$ is a function of time on $r < a$ or $r > a$, but with a possible jump at $r = a$. Regularity of $c$ at $r = 0$ forces $Q \equiv 0$ on $r < a$. From (63) it is now evident that

$$[D c_r] = -\frac{Q}{a^2},$$

where $Q$ now refers to the value on $r > a$. The conservation jump condition (60) now reads

$$\dot{a}[c] = \frac{Q}{a^2}. \tag{64}$$
This is a differential equation for $a(t)$, once the dependence of $[c]$ and $Q$ upon the radius are determined. The two thermodynamic jump conditions (61) and (62) determine $c(a-)$ and $c(a+)$, hence $[c]$ as a function of $a$. Figure 2 shows the graphical construction of (61) and (62).

To determine $Q$, integration of (63) in $r > a$ is required. Let $h(c)$ be a function such that $h'(c) = D(c)$. (63) now reads

$$\partial_r h(c) = \frac{Q}{r^2},$$

and integration from $r = a$ to $r = \infty$ gives

$$h(c_\infty) - h(c_+) = \frac{Q}{a} \quad \text{or} \quad Q = a \{h(c_\infty) - h(c_+)\}.$$

Here $c_+$ means $c(a+)$. (63) now reads

$$\dot{a} = \frac{h(c_\infty) - h(c_+)}{a \left[ c \right]}.$$

(65)

Since $c_+$ and $[c]$ are definite functions of $a$ as determined by the thermodynamic jump conditions (61) and (62), (65) is the required ODE for $a(t)$.

5.1 Small supersaturation

A standard limit called *small supersaturation* is realized when the concentration is close to planar equilibrium values $c = c_1$ in matrix phase $r > a$ and $c = c_2$ in precipitate phase $r < a$. Let $\gamma$ denote disturbance of $c$ from planar equilibrium.
values: $\gamma = c - c_1$ in matrix phase, $\gamma = c - c_2$ in precipitate phase. For $|\gamma| \ll c_1, c_2$, (65) reduces to

$$\dot{a} \sim \frac{D_1 (\gamma_\infty - \gamma_+)}{a [c]}.$$  

(66)

Here $D_1 \equiv D(c_1)$ and $[c] = c_2 - c_1$. Also $\gamma_\infty = \gamma(r = \infty)$ and $\gamma_+ = \gamma(a+)$. $\gamma_+$ is determined from asymptotic limit of (65) and (66): Reduction of (65) is

$$[g''\gamma] = 0 \implies g''(c_1) \gamma_+ = g''(c_2) \gamma_- = m \text{ (common value)},$$

(67)

and given $m$, reduction of (66) is

$$[c] m = \frac{2\sigma}{a} \quad \text{or} \quad g''_{c_1} [c] \gamma_+ = \frac{2\sigma}{a}.$$  

(68)

Substituting this result for $\gamma_+$ into (63) gives the reduced ODE

$$\dot{a} \sim \frac{D_1}{|c| g''_{c_1} a} \left( g''(c_\infty) \frac{2\sigma}{a [c]} \right).$$  

(69)

This equation indicates that clusters whose radii are smaller than the critical value

$$a_c \equiv \frac{2\sigma}{g''_{c_1} \gamma_\infty [c]},$$  

(70)

shrink and disappear. Supercritical clusters of radius larger than the critical radius $a = a_c$ grow steadily according to (70).

Is this small supersaturation kinetics consistent with the quasistatic criterion (58)? Natural unit of $a$ is $a_c$ given by (70), which is the standard formula for critical radius in small supersaturation limit. Given $a = O(a_c)$, an order of magnitude estimate of $\dot{a}$ based on (69) is

$$\dot{a} = O \left( \frac{D_1 \gamma_\infty}{a_c [c]} \right)$$

which can be rearranged as

$$\frac{\dot{a} \dot{a}}{D_1} = O \left( \frac{\gamma_\infty}{[c]} \right).$$

(71)

The analysis here is based on $|\gamma| \ll c_1, c_2$. But for quasistatic kinetics, we need $|\gamma_\infty| \ll [c] = c_2 - c_1$.  

(72)

The reduced ODE (69) indicates natural units of $\gamma$, space and time. The limit (72) is embodied by measuring $\gamma = c - c_\epsilon$ in units of $\epsilon c_\epsilon$, where $\epsilon > 0$ is a gauge parameter and limit $\epsilon \to 0+$ is considered. Given this unit of $\gamma$, the order of magnitude of $a_c$ in (70) is $l/\epsilon$, $l \equiv \sigma/([c] g''_c c_\epsilon)$. $l/\epsilon$ is adopted as unit of length.
Finally, the unit of time which gives $\dot{a}$ as in (71) is $\tau_e/c^3$, $\tau_e \equiv (l^2/D_1)(\text{[c]/c}_e)$. This system of units is summarized in the following Table:

| Variable | Unit |
|----------|------|
| $\gamma \equiv c - c_e$ | $\epsilon c_e$ |
| $x \equiv \frac{\tau}{c^3}$, $l \equiv \frac{\sigma}{g''(c_e)}$ |
| $t \equiv \tau_e/c^3$, $\tau_e \equiv \frac{r^2}{D_1 c_e}$ |
| $G \equiv \frac{\sigma r^2}{c^3}$ |

Scaling Table for small supersaturation.

Given these units, the nondimensional version of (69) is

$$\dot{a} = \frac{1}{a} \left( \gamma_\infty - \frac{2}{a} \right).$$

(73)

### 5.2 Quasistatic energetics

Given evolution of precipitate concentration field $c$, corresponding changes in total free energy of medium are quantified by the rate formula (55). Now suppose concentration field $c$ corresponds to a nucleus undergoing quasistatic evolution as set by criterion (58). It seems reasonable to approximate the integral in (55) using the quasistatic approximation to $c$ which satisfies Equations (59) to (62). The rate formula (55) reduces to

$$\dot{G} = -\int_0^\infty Dg''(c_e')4\pi r^2 dr.$$

(74)

From (63), $r^2 Dc_r = Q$ for $r > a$, and $r^2 Dc_r = 0$ for $r < a$, so this reduces to

$$\dot{G} = -4\pi Q \int_{a+}^\infty g''(c_r) dr = -4\pi Q \{g'(c_\infty) - g'(c_+)\}.$$

Substituting for $Q$ from (64),

$$\dot{G} = -[c] \{g'(c_\infty) - g'(c_+)\}(4\pi a^2 \dot{a}).$$

(74)

In the right hand side, $[c]$ and $g'(c_+)$ are definite functions of radius $a$, determined by thermodynamic jump conditions (61) and (62). Hence, in quasistatic evolution, $G$ is effectively a function of the radius $a$. From (74), it is seen that $G(a)$ obeys the differential relation

$$dG = -[c] \{g'(c_\infty) - g'(c_+)\}(4\pi a^2 da).$$

(75)

In conventional descriptions of nucleus energetics, the Gibbs free energy cost of a nucleus regarded as a function of the instantaneous radius $a$, independent of past history. The specific formula is

$$G = 4\pi \sigma a^2 - \frac{4\pi}{3} a^3.$$

(76)
or in differential form,
\[ dG = 8\pi \sigma a da - g_b 4\pi a^2 da. \] (77)

Here \( \sigma \) is surface tension and \( 4\pi \sigma a^2 \) represents surface energy. \( g_b \) is a constant with units of energy density, sometimes called "chemical driving force". It is the free energy released per unit volume of increase of precipitate phase. In its present form (75) does not have obvious correspondence to (77). A correspondence is brought out by reformulation of (75) with help of thermodynamic jump conditions (61) and (62). By (61), it follows that
\[ g'(c_-) = g'(c_+) = \text{common value} \]
and hence (62) gives
\[ [g] - [c] m = -\frac{2\sigma}{a} , \]
or, equivalently,
\[ [c] g'(c_+) = [g] + \frac{2\sigma}{a} . \]

Hence (75) becomes
\[ dG = 8\pi \sigma a da + \{ [g] - [c] g'(c_\infty) \} (4\pi a^2 da) . \] (78)

The first term on RHS is differential of surface energy, same as in (77). An apparent correspondence between (77) and (78) is completed by identifying the chemical driving force
\[ g_b \equiv -[g] + [c] g'(c_\infty) . \] (79)
Recalling that \([g]\) and \([c]\) are functions of radius \( a \) as determined by thermodynamic jump conditions, it is evident that the chemical driving force (79) is generally a function of cluster radius, and not a constant as in conventional nucleus energetics.

We can now write Eq. (64) for \( \dot{a} \) in terms of \( G_a = -\{ g'(c_\infty) - g'(c_+) \} 4\pi a^2 [c] \) given by (75). The result is
\[ \dot{a} = -\frac{\int_{c_-}^{c_\infty} D(c) dc \ G_a}{g'(c_\infty) - g'(c_+)} \frac{4\pi [c]^2 a^3}{3} . \] (80)

### 5.3 Energetics at small supersaturation

In the small supersaturation limit, \( \int_{c_-}^{c_\infty} D(c) dc \sim D(c_1) (c_+ - c_\infty) = D_1 (\gamma_+ - \gamma_\infty) \), \( g'(c_\infty) - g'(c_+) \sim g''_1 (\gamma_+ - \gamma_\infty) \) and (80) reduces to
\[ \dot{a} = -\frac{G_a D_1}{4\pi g''_1 [c]^2 a^3} . \] (81)

Inserting the approximate chemical driving force \( g_b = [c] g'(c_\infty) - [g] \sim g''_1 \gamma_\infty \) from (79) into the free energy (75), we obtain
\[ G \sim 4\pi \sigma a^2 - [c] g''_1 \gamma_\infty \left( \frac{4\pi}{3} a^3 \right) . \] (82)
Notice that the asymptotic chemical driving force,
\[ g_b \sim [c] g''_1 \gamma_\infty, \]  
(83)
is in fact a constant independent of radius \( a \), as in the conventional wisdom. An alternative expression for \( g_b \) is useful: In certain experiments surface tension \( \sigma \) and critical radius \( a_c \) are measured observables, so it is convenient to represent \( g_b \) in terms of \( \sigma \) and \( a_c \),
\[ g_b = \frac{2\sigma}{a_c}. \]  
(84)
This formula follows from the condition \( G'(a_c) = 0 \). The natural unit of free energy is \( \sigma l^2 \). This is entered into the last column of the scaling table. Then the dimensionless version of the free energy formula (82) is
\[ G = 4\pi a^2 - \gamma_\infty \frac{4\pi}{3} a^3. \]  
(85)

5.4 Identification of rate constant in BD kinetics

We can now compare Eq. (16) for the growth of a (large) cluster radius in BD kinetics with the corresponding equations (80) and (81) obtained from our macroscopic description. We find
\[ k_d = \tau \int_{c_+}^{c_\infty} D(c) dc \left( \frac{c_2}{[c]} \right)^2 \frac{4\pi a}{g''_1} \]  
(86)
\[ \sim \frac{D_1 \tau}{g''_1} \left( \frac{c_2}{[c]} \right)^2 \frac{4\pi a}{a}, \]  
(87)
in the small supersaturation limit.

With this determination of \( k_d \), the continuum limit equation (14) of cluster kinetics is completely specified. It is easy to check that the corresponding microscopic rate constant determined by Penrose et al \[11, 12\] is also proportional to \( a \) for large clusters. One might wonder about the micromolecular basis of (87). While that requires further work, here is a curious observation which might become relevant to this question: Recall the mobility \( \delta \) defined in the formulation of the macroscopic transport theory of Section 4. It is related to the diffusion \( D \) by (36),
\[ D = \delta (1 - \nu c) g'' \]  
Hence the ratio \( D_1/g''_1 \) in (87) is given by
\[ \frac{D_1}{g''_1} = \delta_1 (1 - \nu c_1). \]  
(88)
In the next Section, we show that the volume fraction \( \nu c_1 \) of precipitate in matrix phase is small, \( \nu c_1 \sim (0.04521 \text{ nm}^3) (2.24 \text{ nm}^{-3}) \approx 0.10 \), for coarsening
experimental data in binary alloys \[3\]. Then \(D_1/g_1'' \approx \delta_1\) and formula (87) for \(k_d\) reduces to

\[
k_d \approx \delta_1 \tau \left( \frac{c_2}{|c|} \right)^2 4\pi a.
\]

Let us notice that this rate constant \(k_d\) is linear in the cluster radius so that it scales as \(n_1^3\) with cluster size. This contrasts with the usual Turnbull-Fisher rate constant that scales as \(n_2^3\) [6], but it agrees with the microscopic considerations of Penrose et al [11, 12]. The scaling \(n_1^3\) has been shown to yield the Lifshitz-Slyozov distribution function for cluster radii [10]. The latter is a roughly adequate description of coarsening [3, 4].

6 Material and energy parameters of kinetic theory determined from Xiao-Haasen data

6.1 Small supersaturation

The nucleation in Xiao-Haasen’s (XH) paper [3] takes place under low supersaturation: The initial sample has uniform composition, with mole fraction \(\chi \equiv 0.12\), or 12 % of Al in a Ni matrix. Equilibrium mole fraction of Al in matrix phase at annealing temperature of 773 K is \(\chi_1 = 0.101\), or 10.1 %. Equilibrium mole fraction of Al in precipitate phase is \(\chi_2 = 0.230\), or 23 %. Hence, supersaturation as a function of equilibrium concentration has initial value

\[
\frac{\chi - \chi_1}{\chi_1} \approx \frac{0.120 - 0.101}{0.101} \approx 0.19.
\]

Mole fractions are converted into number densities: XH report a molar volume of precipitate phase \(V_m \approx 27.16 \times 10^{-6} \text{ m}^3\). Conversion to an atomic volume by Avogadro’s number gives

\[
\nu_m = \frac{V_m}{N_A} \approx 4.51 \times 10^{-29} \text{ m}^3
\]

or \(\nu_m \approx 0.0451 \text{ nm}^3\).

XH also report a lattice constant of \(a \approx 0.356 \text{ nm}\) for the precipitate phase, and atomic volume corresponding to this lattice constant is \(\nu_m = a^3 \approx 0.0451 \text{ nm}^3\). It is clear that the molar volume \(V_m\) was derived from the lattice constant. A lattice constant for the matrix phase is not reported explicitly, so it is presumably close to the value \(a \approx 0.356 \text{ nm}\) of the precipitate phase. It seems there is an implicit assumption: Local structure of alloy in a lattice, with sites that can be occupied by Al or Ni atoms. In this case, atomic volumes of Al and Ni are de-facto the same, i.e.,

\[
\nu_m = \nu_m \approx 0.0451 \text{ nm}^3.
\]
Now number densities of Al and Ni easily follow. For instance, \( c_1 \), the equilibrium number density of Al in matrix phase is

\[
c_1 = \frac{X_1}{\nu} \approx \frac{0.101}{0.0451} \text{ nm}^{-3} \approx 2.24 \text{ nm}^{-3}.
\]

Table 1 gives initial concentration of Al in matrix phase, and equilibrium concentrations \( c_1 \) and \( c_2 \) of Al in matrix and precipitate phases.

| \( c_1 \) | \( c_1 \) | \( c_2 \) |
|---------|---------|---------|
| 2.66    | 2.24    | 5.10    |

Table 1: Number densities (nm\(^{-3}\)).

### 6.2 Nucleation energetics

In XH, the nucleus energy takes the classic form

\[
G = 4\pi \sigma a^2 - g_b \left( \frac{4\pi}{3} a^3 \right).
\]

(89)

Here \( \sigma \) is surface tension. A value \( \sigma \approx 0.014 \text{ J m}^{-2} = 1.4 \times 10^{-20} \text{ J nm}^{-2} \) is deduced from interpreting coarsening data with the Lifshitz-Slyozov (LS) theory. XH deals with chemical driving force \( g_b \) in two ways:

(i) “Experimental”. The distribution of nuclei in the space of their radii goes through a transient phase with two peaks, separated by a local minimum at about 1.2 nm. XH conjecture that the initial radius \( a_c \) is in fact this 1.2 nm. Estimate of \( g_b \) now follows from (83),

\[
g_b \approx \frac{2\sigma}{a_c} \approx 2.33 \times 10^{-20} \text{ J nm}^{-3}.
\]

Given an experimental estimate of the critical radius, \( a_c \approx 1.2 \text{ nm} \) at outset, one can estimate the number of atoms in the critical nucleus, both Al and entrained Ni:

\[
\frac{1}{\nu} \frac{4\pi}{3} a_c^3 \approx 160.
\]

Of these, 23\% are Al, so there are

\[
n_c = 0.23 \times 160 = 37
\]

Al atoms in the critical nucleus. It seems that the critical nucleus is “just big enough” so energetics based on continuum theory applies.

(ii) “Theory”. In standard theories, \( g_b \) is computed from both thermodynamic properties of precipitate and bulk phases. As such, it comes out as a constant independent of nucleus radius \( a \). These derivations do not face up to the fine points of the real situation, summarized in the formula (79) for \( g_b \). So our approach is to stick with the determination of \( g_b \) based on \( \sigma \) and \( a_c \),

\[
g_b \approx \frac{2\sigma}{a_c} \approx 2.33 \times 10^{-20} \text{ J nm}^{-3},
\]

21
and then see what can be said about \( g(c) \). In (83) one can determine \( g''_1 \) because all the other quantities are known. In fact, one gets

\[
g''_1 = \frac{g_b}{[c]^{\gamma_{\infty}}} \approx \frac{2.33 \times 10^{-20}}{(5.10 - 2.24)(2.66 - 2.24)} \approx 1.94 \times 10^{-20} \text{ J nm}^{-3}.
\]

The annealing temperature of 773 K defines a basic unit of energy,

\[
\tau = (773 \text{ K})(1.38 \times 10^{-23} \text{ J/K}) \approx 1.07 \times 10^{-20} \text{ J}.
\]

One now has

\[
\frac{g''_1}{\tau} \approx 1.81 \text{ nm}^3.
\]

This is just one number imposed upon free energy function \( g(c) \) by the XH data, but it is sufficient to establish the

**Nonideal character of Al solution in matrix phase.**

Suppose the solution is ideal. Then the chemical potential of an Al particle in matrix phase is given by

\[
\mu(c) = \mu_1 + \tau \ln \frac{c}{c_1},
\]

where \( \mu_1 \) is the chemical potential when \( c = c_1 \) is the planar solvability. Now the relation between \( \mu(c) \) and \( g(c) \) is given by (19), which is repeated here for easy reference,

\[
\mu(c) = g'(c) + \nu (g - c g').
\]

From this equation is evident that \( g''(c) \) gives information about \( \mu'(c) \). In fact, differentiation of (91) yields

\[
\mu'(c) = (1 - \nu c) g''(c) \Rightarrow \mu_1' = (1 - \nu c_1) g''_1.
\]

Numerical value of \( \mu_1' / \tau \) based upon previous value of \( g''_1 \) turns out to be

\[
\frac{\mu_1'}{\tau} \approx \{1 - (0.0451 \text{ nm}^3)(2.24 \text{ nm}^{-3})\} (1.81 \text{ nm}^3) \approx 1.63 \text{ nm}^3.
\]

If the ideal solution formula (90) were correct, one would get

\[
\frac{\mu_1'}{\tau} = \frac{1}{c_1} \approx \frac{1}{2.24 \text{ nm}^{-3}} \approx 0.45 \text{ nm}^3,
\]

which is 1/274 of value that follows from XH parameters. That the solution of Al in Ni phase is not ideal was already known to XH. They in fact considered that our chemical driving force \( g_b \) is sum of two terms: (i) a chemical driving force estimated from the activity of Al component at the concentrations \( \chi \) and \( \chi_1 \), and (ii) and the elastic strain energy per unit volume. With the corresponding
expressions, they obtained a value for the critical radius, $a_c \approx 1.7$ nm, which is not too far from the experimental value, $a_c \approx 1.2$ nm [3].

The experimentally derived values of surface tension $\sigma$ and chemical driving force $g_b$ in [30] set important parameters for macroscopic nucleation theory, namely: Energy barrier for nucleation, and typical free energy cost to add one Al particle to a nucleus.



Energy barrier is given by

$$G_{\text{nuc}} = G(a_c) = \frac{4}{3} \sigma a_c^3 \approx \frac{4\pi}{3} (1.4 \times 10^{-20} \text{ J nm}^{-2}) (1.2 \text{ nm})^2 \approx 8.4 \times 10^{-20} \text{ J}.$$  

Energy barrier in units of thermal energy is

$$\frac{G_{\text{nuc}}}{\tau} \approx 7.8.$$  

A reasonable looking number. Notice that exponential

$$e^{-\frac{G_{\text{nuc}}}{\tau}} \approx 3.7 \times 10^{-4},$$

which appears in the nucleation rate is not too small. This makes anthropomorphic sense: In XH experiment, nucleation kinetics unfolds in hours and days time scales, not unduly taxing to humans. Evidently, the annealing temperature is tuned so as to achieve a “reasonable” nucleation rate.

**Free energy cost to add one particle.**

The number $n$ of Al particles in nucleus is related to radius $a$ by

$$n = \frac{4\pi}{3} c_2 a^3 \implies a = \left( \frac{3n}{4\pi c_2} \right)^{\frac{1}{3}}. \quad (93)$$

Substituting (93) for $a$ in (89) gives nucleus energy as a function of $n$,

$$G_n = (36\pi)^{\frac{1}{3}} \sigma c_2^{\frac{2}{3}} n^{\frac{2}{3}} - g_b c_2^{-1} n. \quad (94)$$

Free energy cost to add one particle to nucleus of $n$ particles, in units of thermal energy $\tau$, is

$$\frac{\mu_n}{\tau} \equiv \frac{G_{n+1} - G_n}{\tau} = (36\pi)^{\frac{1}{3}} \sigma c_2^{\frac{2}{3}} \tau^{-1} \{(n + 1)^{\frac{2}{3}} - n^{\frac{2}{3}}\} - g_b c_2^{-1} \tau^{-1}.$$  

Since this formula is based on continuum theory, its validity requires $n \gg 1$, in which case it reduces to

$$\frac{\mu_n}{\tau} \sim \frac{2}{3} (36\pi)^{\frac{1}{3}} \sigma c_2^{\frac{2}{3}} \tau^{-1} n^{-\frac{2}{3}} - g_b c_2^{-1} \tau^{-1}. \quad (95)$$

Substituting XH parameter values in RHS,

$$\frac{\mu_n}{\tau} \sim 1.43 n^{-\frac{2}{3}} - 0.42. \quad (96)$$
In the limit $n \to \infty$, we get $|\mu_n/\tau| \sim 0.42$. While less than 1, one would not call this value “small compared to one”. For $n = 37$, corresponding to a critical nucleus, of course one gets $\mu_n/\tau = 0$. Hence there will be a range of $n$ about $n = n_c = 37$ in which $|\mu_n/\tau| \ll 1$. In particular, $|\mu_n/\tau| < 0.2$ in the rather generous interval $12 < n < 300$. In this range of $n$, asymptotic reduction of discrete kinetic models such as Becker-Döring to a Smoluchowski partial differential equation (PDE) should be reasonable.

7 Discussion

In coarsening experiments, one starts from a situation of equilibrium at high temperature in which most clusters are monomers. Then the temperature is lowered to a value below the critical temperature, and kept there. Clusters are nucleated and grow, supersaturation changes with time so that nucleation of new clusters becomes unlikely, and the coarsening of clusters proceeds. As explained by Penrose et al [11, 12], this process is reasonably well described by the Becker-Döring model (better than by the Lifshitz-Slyozov distribution function), provided the volume fraction of precipitate is small. Let us describe the nucleation and coarsening processes in typical experiments such as XH and which parts thereof are mathematically understood.

The nucleation process described by the BD equations starts at $t = 0$ with some initial value of $\rho_1 = c_\infty$ and no supercritical clusters. According to the XH data, the energy barrier corresponding to the initial value of the critical nucleus is relatively high, $G_{nuc}/\tau \approx 7.8$, so that we may consider the clusters below critical size ($n < n_c$) to be in a quasistationary state. The flux across the energy barrier is then uniform and it supplies the source for coarsening of clusters larger than the critical size. As explained in Section 6 there is a range of sizes (about the critical size) for which we may approximate the discrete BD kinetics by a continuum Smoluchowski equation for the distribution function $\rho$. The latter will describe the coarsening process and it should be approximately solved with a boundary condition obtained by matching to the solution of the BD equations for $n < n_c$. For $t > 0$, supercritical clusters are created at the rate $j$ per unit volume given in Eq. (102) below, and $\rho_1$ starts to decrease. A small change of $\rho_1$, $O(1/n_c) = O(c^3 T^3/c_2)$, induces an $O(1)$ relative change of $j$. There is a transient situation during which $\rho$ becomes a bimodal distribution function with peaks at sub and supercritical sizes. As time evolves, the supercritical peak increases at the expense of the subcritical peak, which disappears given enough time. Then the resulting unimodal distribution evolves toward a function with the LS scaling.

Currently it is known that the LS distribution function [9] is a solution of the Smoluchowski equation for a very special boundary condition at small cluster size [10]. Although the stability properties of the LS distribution function are not completely elucidated, it seems clear that the Smoluchowski equation may have other stable solutions that may match the quasistationary distribution at small cluster sizes. The appropriate solution of the Smoluchowski equation
should then describe the transient stage of coarsening. As the time advances, the peak of the distribution function at subcritical sizes decreases and disappears while the peak at supercritical sizes takes over. The latter should have the LS scaling to explain experimental and numerical data. To carry out an asymptotic analysis of nucleation and coarsening providing the same qualitative description sketched here is a challenging future task.

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9 Appendix: BD kinetics for \( n < n_c \)

The quasistationary state is a solution of the BD equations characterized by uniform flux,

\[
j_n = k_{d,n+1} \left\{ e^{-\frac{G_{n+1} - G_n}{\tau}} \rho_n - \rho_{n+1} \right\} \equiv j,
\]

for \( n < n_c = c_2^2 \pi a_c^3 / 3 \). At high temperature, before the experiment starts, we have the following equilibrium solution

\[
\rho_{eq,n} = \frac{c e^{-\frac{G_n}{\tau}}}{\sum_{l=1}^{\infty} l e^{-\frac{G_l}{\tau}}} \sim c e^{-\frac{G_{n_c}}{\tau}}.
\]

To write the above approximation, we have assumed that \( G_n \) increases with \( n \) and that \( G_n \) is close to its equilibrium value [given by the approximate expression \( 2\pi \) at the correct temperature \( \tau \)], as \( n \ll n_c \). Thus \( \rho_n = O(c e^{-G_n - G_1} / \tau) \) if \( n < n_c \), and much smaller than this order if \( n > n_c \). This means that \( e^{\frac{G_n}{\tau}} \rho_n / c = O(e^{G_1} / \tau) \) if \( n < n_c \), and that \( e^{\frac{G_n}{\tau}} \rho_n / c = O(e^{G_1} / \tau) \) if \( n \gg n_c \).

Equation (97) can be written as

\[
e^{\frac{G_n}{\tau}} \rho_n + 1 - e^{\frac{G_n}{\tau}} \rho_n = -j k_{d,n+1} e^{\frac{G_{n+1}}{\tau}},
\]

and therefore easily integrated under the condition \( e^{\frac{G_n}{\tau}} \rho_n \rightarrow 0 \) as \( n \rightarrow \infty \):

\[
e^{\frac{G_n}{\tau}} \rho_n = j \sum_{l=n}^{\infty} \frac{G_{l+1}}{k_{d,l+1}}, \tag{99}
\]

The terms in this sum are largest for \( l \sim n_c \), at which \( G_l \) is maximum. For such integers, the continuum approximation holds, and we can write

\[
e^{\frac{G_{l+1}}{\tau}} \sim \frac{G_{n_c}}{k_{d,n_c}} \sum_{l=n}^{\infty} e^{-\frac{4\pi}{a_l-a_c} (a_l-a_c)^2} \tag{100}
\]
We have used $G_{t+1} - G_{nc} \sim -4\pi\sigma(a_l - a_c)^2$, for $l + 1$ close to $n_c$. We now approximate $a_l = a_c + x\sqrt{\tau}$ in (99), and $1 \sim 4\pi c_2 a_c^2 da_l = 4\pi c_2 a_c^2 \sqrt{\tau}/\sigma dx$, so that (99) becomes

$$e^{G_n} \rho_n \sim \frac{j}{D_1} \frac{c}{c_2} \frac{\sqrt{\tau}}{\gamma_\infty} e^{\frac{G_{nc}}{2}} 2 \int_\infty^{\infty} e^{-4\pi x^2} dx. \quad (101)$$

The equilibrium solution of the BD equations is (98). If we impose that $\rho_n \sim \rho_{eq,n}$ as $n \ll n_c$, (98) and (101) yield

$$j \sim \frac{\sqrt{\tau}}{\sigma} D_1 \gamma_\infty c_2 e^{-\frac{G_{nc} - G_1}{\tau}}. \quad (102)$$

This constant flux is exponentially small because $(G_{nc} - G_1)/\tau \sim G(a_c)/\tau \gg 1$. Notice that it is also proportional to the supersaturation $\gamma_\infty$. It is clear that a small change in the supersaturation, $\delta\gamma = O(\gamma_\infty/n_c)$, produces an $O(1)$ change in $n_c$ and in $G_{nc}$, $\delta n_c = -3n_c\delta\gamma/\gamma_\infty$ and $\delta G_{nc} = -2G_{nc}\delta\gamma/\gamma_\infty$, and hence a significant relative change of $j$ in (102):

$$\frac{\delta j}{j} \sim \exp\left(\frac{g''[c]n_c}{\tau} \delta\gamma\right). \quad (103)$$

Notice that, in the continuum limit, the flux $j_n$ becomes

$$j_n \sim \frac{-D_1 \tau}{g'_1[c]^2} \frac{e^{\frac{G(a)}{\gamma_\infty}}}{4\pi a} \frac{\partial}{\partial a}\left(e^{\frac{G(a)}{\gamma_\infty}} \frac{\rho}{a^2}\right)$$

$$= \frac{D_1 \tau}{g'_1[c]^2} \frac{1}{4\pi a} \left(\frac{\rho}{\tau a^2} \frac{\partial G}{\partial a} + \frac{\partial}{\partial a}\left(\frac{\rho}{a^2}\right)\right). \quad (104)$$

The relation between drift and diffusion coefficients here is $G_a/\tau$ in agreement with the formulas provided by Nonequilibrium Thermodynamics; see Ref. [6].

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