

Last time

Diffuse Interface Approximation

Functional Gradient

Kinetics for Non-conserved Order Parameters

Kinetics for Conserved Order Parameters

3.21 Spring 2002: Lecture 24

Nucleation

The transformation of a metastable material by the growth of initially small fluctuations (*e.g.*, composition fluctuations in the case of spinodal decomposition) was treated as a continuous transformation.

Some metastable systems are stable with respect to infinitesimal fluctuations, but are unstable to a perturbation in the form of a finite fluctuation. In such systems, the transformation

does not proceed until a finite fluctuation occurs. If the necessary fluctuation is so large that its probability of it occurring in any observable time is effectively zero, then the system is kinetically 'frozen' in its metastable state. Many, if not most, engineering materials are in such non-equilibrium states.

Each of these finite fluctuations is called a *nucleus*; the metastable medium is called the *matrix*. The minimum size nucleus required for continued spontaneous growth is called a *critical nucleus* and all the fluctuations smaller than the critical nucleus are called *sub-critical nuclei*. The process by which the sub-critical nuclei change their size by the (energetically favorable) loss of its atoms to the matrix and the improbable attachment of new matrix atoms onto the sub-critical nucleus is called *nucleation*.

Nucleation is commonly observed in carbonated beverages. When a beverage container is capped, the amount of dissolved CO₂ that is in equilibrium at capped pressure is greater than the amount of dissolved CO₂ in equilibrium at atmospheric pressure. The bubbles of CO₂ that form in an opened beverage and float to the top are the result of nucleation process.

Common experience also demonstrates that there are two different categories of nucleation. The nucleation of critical nuclei at defects such as surface imperfections is called *heterogeneous nucleation*; nucleation that occurs randomly throughout the volume of the metastable matrix is *homogeneous nucleation*.

Nucleation Regimes

Nucleation is what precedes growth by phase transformation. Consider the case of a solid solution of phase β at a composition that is metastable with respect to the creation of an α -phase.³⁴

³⁴It may be supposed that such a metastable composition comes about by cooling a stable composition into a two phase field. Such *supercooling* can occur because phase transformations are retarded by the time required to form a critical nucleus.

A prototypical case can be illustrated with a phase diagram and free energy curve.

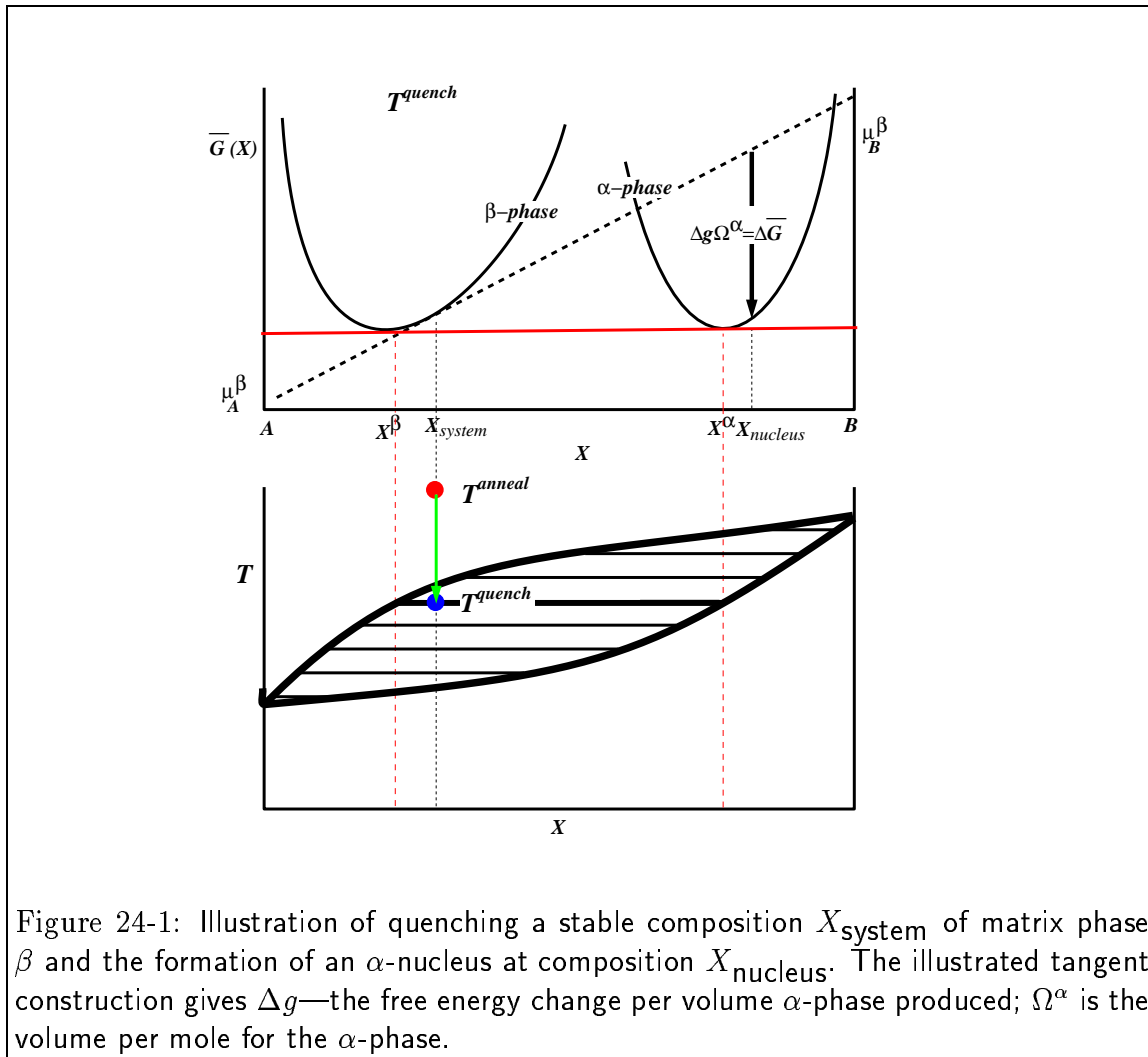


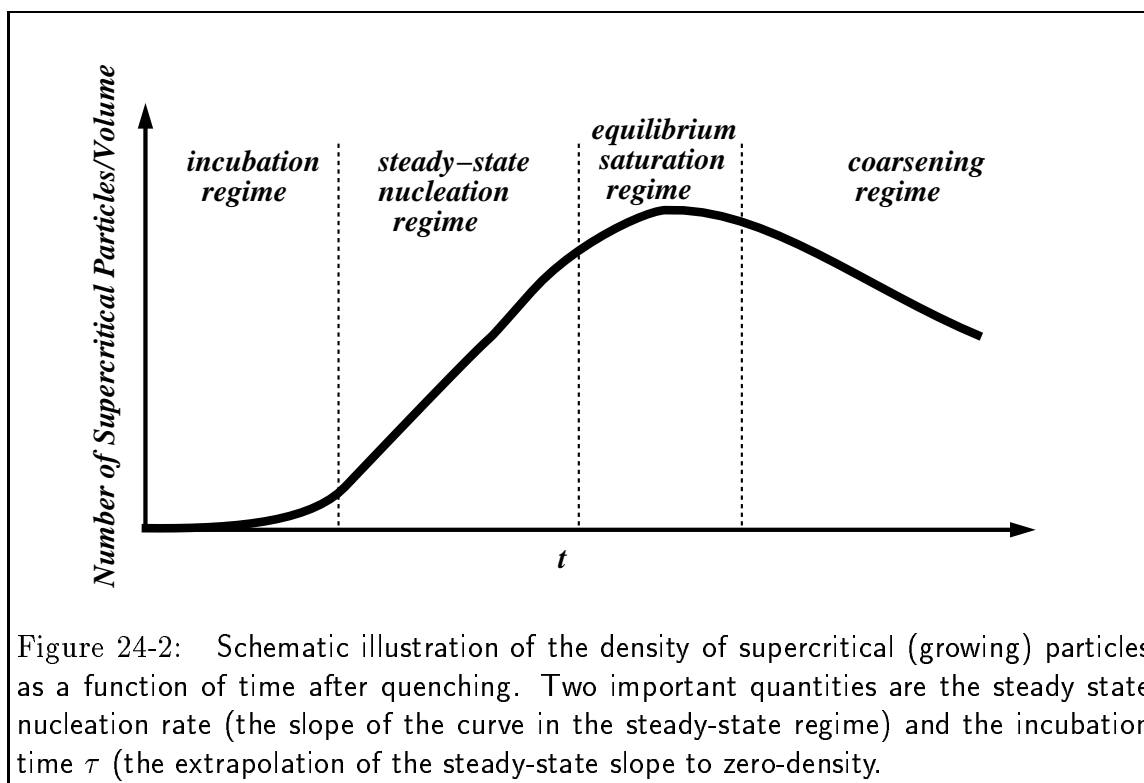
Figure 24-1: Illustration of quenching a stable composition X_{system} of matrix phase β and the formation of an α -nucleus at composition $X_{nucleus}$. The illustrated tangent construction gives Δg —the free energy change per volume α -phase produced; Ω^α is the volume per mole for the α -phase.

A useful theory of nucleation should predict at least two quantities:

Incubation Time The expected delay τ , after quenching, before critical nuclei form in sufficient quantities for experimental observation.

Nucleation Rate The rate, J_{crit}^{ss} , at which critical nuclei form per unit volume after incubation.

These quantities are related to the so-called nucleation regimes:



Homogeneous Nucleation: Simple Theory

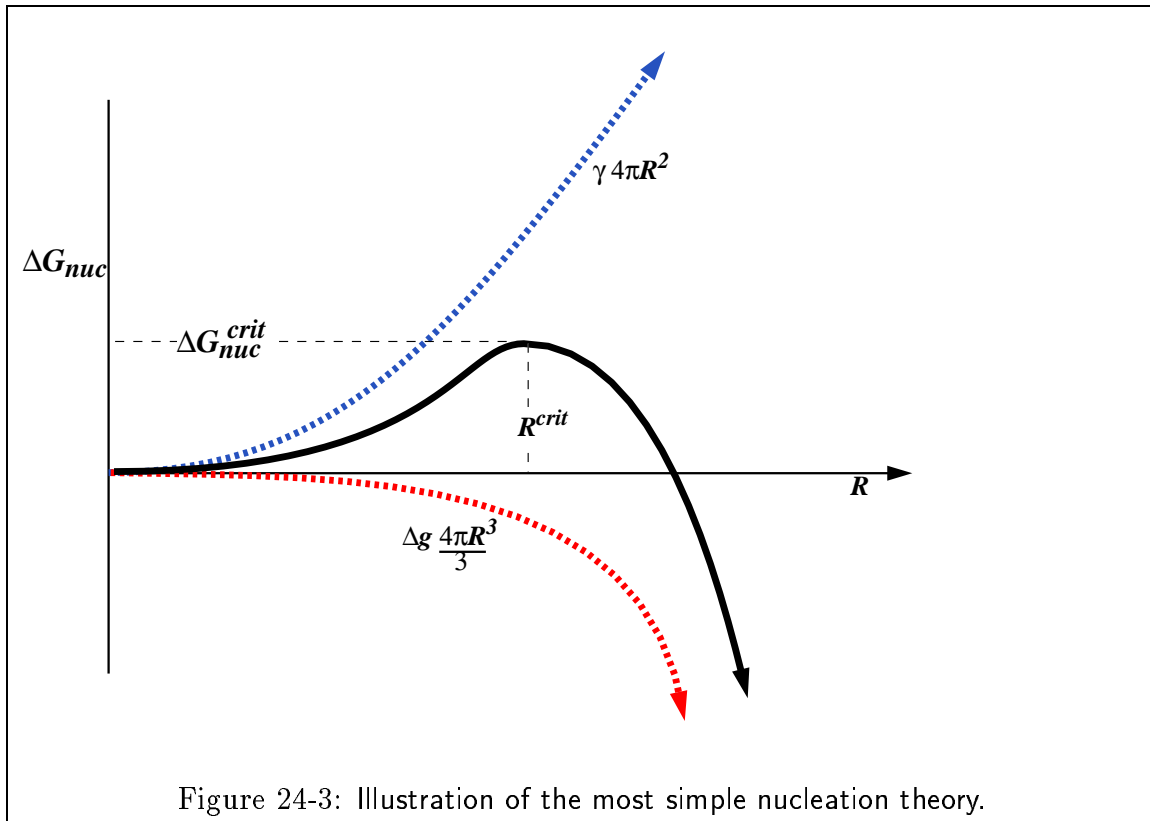
It is possible to formulate a very simple theory for the size of a critical nucleus from macroscopic thermodynamic quantities: interfacial surface tension $\gamma_{\alpha\beta}$ (energy/area), and free energy change per unit volume nucleus Δg (energy/volume). This simple theory works remarkably well despite the fact that, at the small sizes that critical nuclei are formed (10-50), extrapolation of $\gamma_{\alpha\beta}$ and Δg is questionable. Another advantage is that the model provides a useful understanding of the physical quantities that control nucleation.

An α -phase nucleus forming in a β -matrix has only two contributions to its energy: the decrease in energy due to the volumetric driving force, Δg , and an increase in energy due to surface tension, $\gamma_{\alpha\beta}$.³⁵

For a spherical isotropic nucleus of radius R , the total free energy is:

$$\Delta G^{nuc}(R) = \frac{4}{3}\pi R^3 \Delta g + 4\pi R^2 \gamma_{\alpha\beta} \quad (24-1)$$

³⁵The volumetric term Δg can be determined from the construction in Fig. 24-1 and is necessarily negative for nucleation ($\Delta g < 0$). Other contributions to free energy, such as stress or composition gradients may exist, and are not included in this simple theory. The surface tension may also vary from absorption of solutes or the existence of interface dislocations—these effects are also ignored here.



Suppose nuclei are formed by random fluctuations and a distribution $f(R)$ of nuclei sizes R develops. Any one of the nuclei having a radius R such that $\frac{d\Delta G}{dR} < 0$ can decrease its free energy continuously by growing (i.e., increasing its radius); all other nuclei cannot grow continuously, but may grow by improbable events such as random attachment of add-atoms. Thus, the size of the critical nucleus must satisfy $\frac{d\Delta G}{dR} = 0$; it is the radius that maximizes $\Delta G(R)$ ³⁶

³⁶Further reflection shows that the critical nucleus is *not* the one that maximizes $\Delta G(R)$. In the spherical example, it was assumed that the particle is *always* in its most energetically favorable state. In other words, other nuclei shapes would give larger critical nucleus volumes for the same driving forces. Because the shape is energy-minimizing, the critical nucleus size corresponds to the lowest saddle point of ΔG that separates subcritical nuclei from supercritical nuclei.

$$\begin{aligned} \left. \frac{d\Delta G^{nuc}(R)}{dR} \right|_{R_{crit}} &= 0 \\ R_{crit} &= \frac{-2\gamma_{\alpha\beta}}{\Delta g} \\ \Delta G_{crit}^{nuc} &= \frac{16\pi(\gamma_{\alpha\beta})^3}{3\Delta g^2} \end{aligned} \quad (24-2)$$

Ignoring differences in heat capacities between the two phases and any temperature dependence of surface tension, $\Delta g = \Delta h(T_{eq} - T)/T_{eq}$ so that the critical size decreases as ΔT^{-1} and the nucleation barrier decreases as ΔT^{-2} .

The growth of subcritical nuclei increases the nucleus free energy with each increment of nucleus size. The process will be treated as a sequence of activated states similar to the activation process for a vacancy exchange as described in Chapter 6 of KPIM. Assuming that the nucleation occurs at constant pressure and temperature, the nuclei sizes will be distributed with a probability proportional to $\exp(-\Delta G^{nuc}(n^{nuc})/kT)$ where $\Delta G^{nuc}(n^{nuc})$ is the total free energy of a nucleus containing n^{nuc} atoms. Equation 24-2 can be converted using $n^{nuc}\Omega = \frac{4}{3}\pi R^3$ to

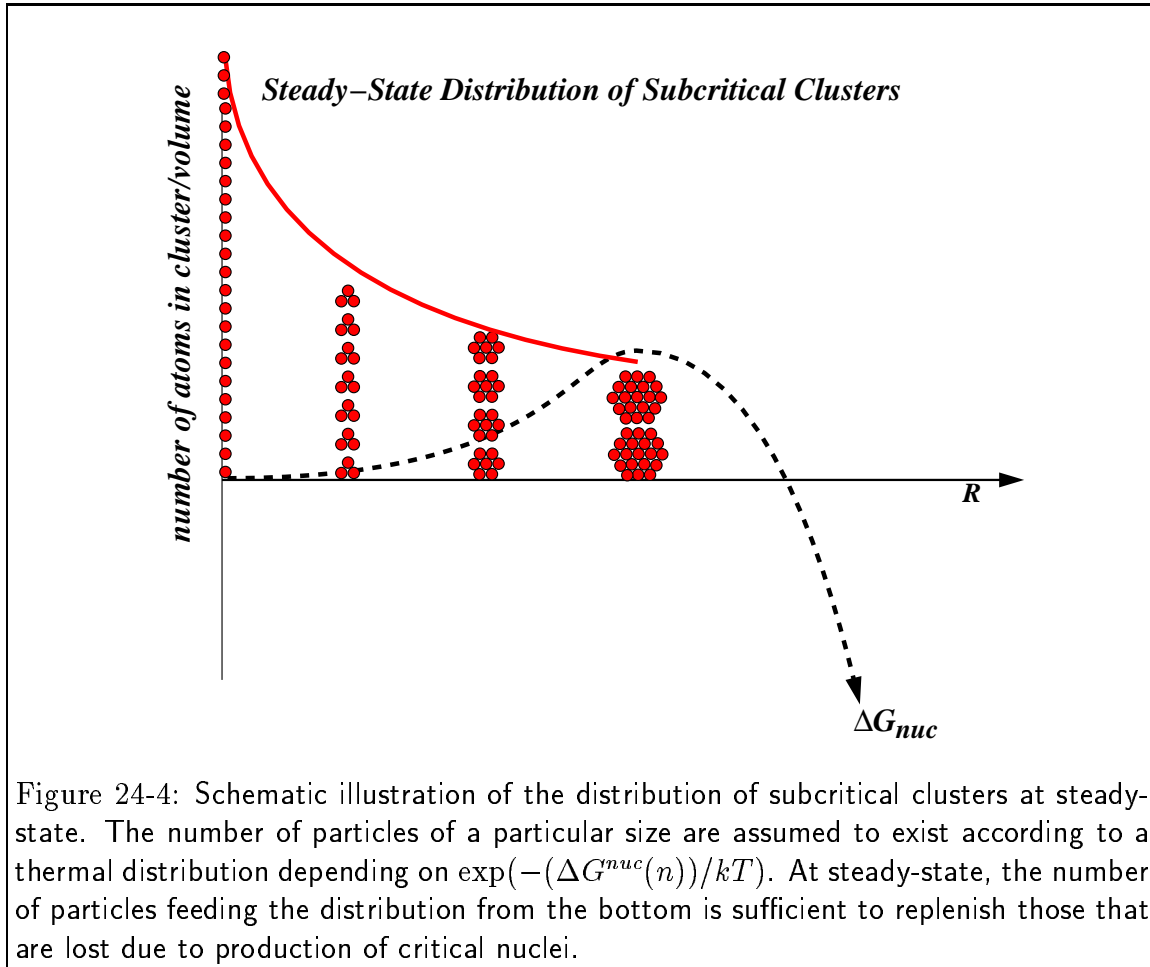
$$\begin{aligned} \Delta G^{nuc}(n) &= n^{nuc} \Delta \bar{G} + (6^2\pi)^{1/3} \Omega^{2/3} n^{nuc2/3} \gamma_{\alpha\beta} \\ n_{crit}^{nuc} &= \frac{-32\pi\gamma_{\alpha\beta}^3 \Omega^2}{3\Delta \bar{G}^3} \\ \Delta G_{crit}^{nuc} &= \frac{-80\pi\gamma_{\alpha\beta}^3 \Omega^2}{3\Delta \bar{G}^2} \end{aligned} \quad (24-3)$$

A Model for the Steady-State Nucleation Rate

A subcritical nucleus has a driving force which tends to make it shrink and dissolve back into the matrix. The development and incremental growth of subcritical nuclei is assumed to be a thermally activated process. The steady-state nucleation regime subsists by the development of a steady-state size distribution of subcritical clusters. At steady-state, the source of the

material to produce subcritical clusters is sufficient to replenish the material that is lost as a critical cluster becomes a stable precipitate and grows. The rate at which subcritical clusters reach their critical size must be the steady-state nucleation rate, J_{nuc}^{ss} and can be experimentally determined from the slope in Fig. 24-2.

The steady-state nucleation rate depends on the distribution of subcritical nuclei.



The rate of creation of critical nuclei can be extended to subcritical nuclei as follows. The rate at which subcritical nucleus of size n (per unit volume) are created must be related to the concentration of nuclei of size $n - 1$ that grow by one unit minus the rate at which those of size $n + 1$ lose one unit:

$$J_n^{nuc} = \Gamma_{\beta \rightarrow \alpha} S_{n-1}^\beta C_{n-1} - \Gamma_{\alpha \rightarrow \beta} S_{n+1}^\alpha C_{n+1} \quad (24-4)$$

where Γ is the rate of a successful jump across the nucleus interface and S is the number of atoms adjacent to the interface.

We assume that there is a steady-state distribution for which the “flux” J_n must vanish, so³⁷

$$0 = \Gamma_{\beta \rightarrow \alpha} S_{n-1}^{\beta} C_{n-1}^{ss} - \Gamma_{\alpha \rightarrow \beta} S_{n+1}^{\alpha} C_{n+1}^{ss} \quad (24-5)$$

where C_n^{ss} is the steady-state concentration of nuclei of size n . It is reasonable that the kinetic factors Γ do not depend on equilibrium, so Eq. 24-5 can be solved and one of the kinetic factors in Eq. 24-4 can be removed, and an expression for a system away from steady-state can be obtained:

$$J_n^{nuc} = \Gamma_{\beta \rightarrow \alpha} S_{n-1}^{\beta} C_{n-1}^{ss} \left(\frac{C_{n-1}}{C_{n-1}^{ss}} - \frac{C_{n+1}}{C_{n+1}^{ss}} \right) \quad (24-6)$$

and this can be approximated by a derivative of a continuous function:

$$J_n^{nuc} = -\Gamma_{\beta \rightarrow \alpha} S_n^{\beta} C_n^{ss} \frac{\partial(C_n/C_n^{ss})}{\partial n} \quad (24-7)$$

Therefore the rate of change of the concentration of nuclei of size n must be related to the divergence of this flux:

$$\frac{\partial C_n}{\partial t} = \frac{\partial}{\partial n} \left(\Gamma_{\beta \rightarrow \alpha} S_n^{\beta} C_n^{ss} \frac{\partial(C_n/C_n^{ss})}{\partial n} \right) \quad (24-8)$$

which is called the Zeldovich equation and is very similar to the diffusion equation except that the spatial variable \vec{x} is replaced with a nucleus size n .

³⁷This is the assumption of “microscopic reversibility.” It is a bit suspicious to find it in a theory of non-equilibrium processes...

At steady-state, $\partial C_n/\partial t = 0$ can be integrated with respect to n . The integration constant must be $-J_{nuc}^{ss}$ and not a function of n :

$$J_{nuc}^{ss} = -\Gamma_{\beta \rightarrow \alpha} S_n^\beta C_n^{ss} \frac{\partial C_n/C_n^{ss}}{\partial n} \quad (24-9)$$

which can be integrated again from one particle (where it may be assumed that $C_1 \equiv C_1^{ss}$) to an infinite number of particles where $C_n/C_n^{ss} \rightarrow 0$ as $n \rightarrow \infty$.

$$J_{nuc}^{ss} \int_1^\infty \frac{dn}{\Gamma_{\beta \rightarrow \alpha} S_n^\beta C_n^{ss}} = \int_1^0 d(C_n/C_n^{ss}) = 1 \quad (24-10)$$

Several approximations must be made to replace the first integral in Eq. 24-10 with simple forms. The integrand over n is large only when $S_n^\beta C_n^{ss}$, which is small near $n = n_{crit}$ —so the limits of integration can be extended to $\pm\infty$ without addition of significant error. The thermally activated concentration $C_n^{ss} \approx N_v \exp(-\Delta G^{nuc}(n)/kT)$ where N_v is the number of possible homogeneous nucleation sites per volume and the nucleation barrier can be expanded around the critical size:

$$\Delta G^{nuc}(n) = \Delta G_{crit}^{nuc} + \frac{(n - n_{crit})^2}{2} \frac{\partial^2 \Delta G^{nuc}(n)}{\partial n^2} \Big|_{n=n_{crit}} \quad (24-11)$$

where, if the simple approximation in Eq. 24-3 is used

$$\Delta G^{nuc}(n) = \frac{-80\pi\gamma_{\alpha\beta}^3\Omega^2}{3\Delta\bar{G}^2} - \frac{\Delta\bar{G}^4}{64\pi\gamma_{\alpha\beta}^4\Omega^2} \frac{(n - n_{crit})^2}{2} \quad (24-12)$$

With these approximations and the integration can be carried out and

$$J_{ss}^{nuc} = Z\Gamma_{\beta \rightarrow \alpha} S_n^\beta N_v e^{\frac{-\Delta G_{crit}^{nuc}}{kT}} = Z\Gamma_{\beta \rightarrow \alpha} S_{n_{avg}}^\beta C_{crit}^{ss} \quad (24-13)$$

where Z is the Zeldovich factor given by the result of approximating the integral in Eq. 24-10

$$Z = \sqrt{\frac{-1}{2\pi kT} \frac{\partial^2 \Delta G_{crit}^{nuc}}{\partial n^2}} \quad (24-14)$$

For the simple model in Eq. 24-3:

$$Z = \frac{\Delta \bar{G}^2}{8\pi\Omega\gamma_{\alpha\beta}^2} \sqrt{\frac{1}{2kT}} \quad (24-15)$$

Typical experimental values of $Z \approx 1/20$.

Model for the Nucleation Incubation Time

Considerations of thermally activated subcritical nuclei resulted in a diffusion equation for the rate of change of the density of nuclei of size n in Eq. 24-8 with an effective diffusivity given by $\Gamma_{\beta \rightarrow \alpha} S_n^\beta$.

The incubation time is approximately the amount of time before particles begin reaching the critical size. The nucleation and growth process throughout all regimes implies that the particle size distribution is changing over time:

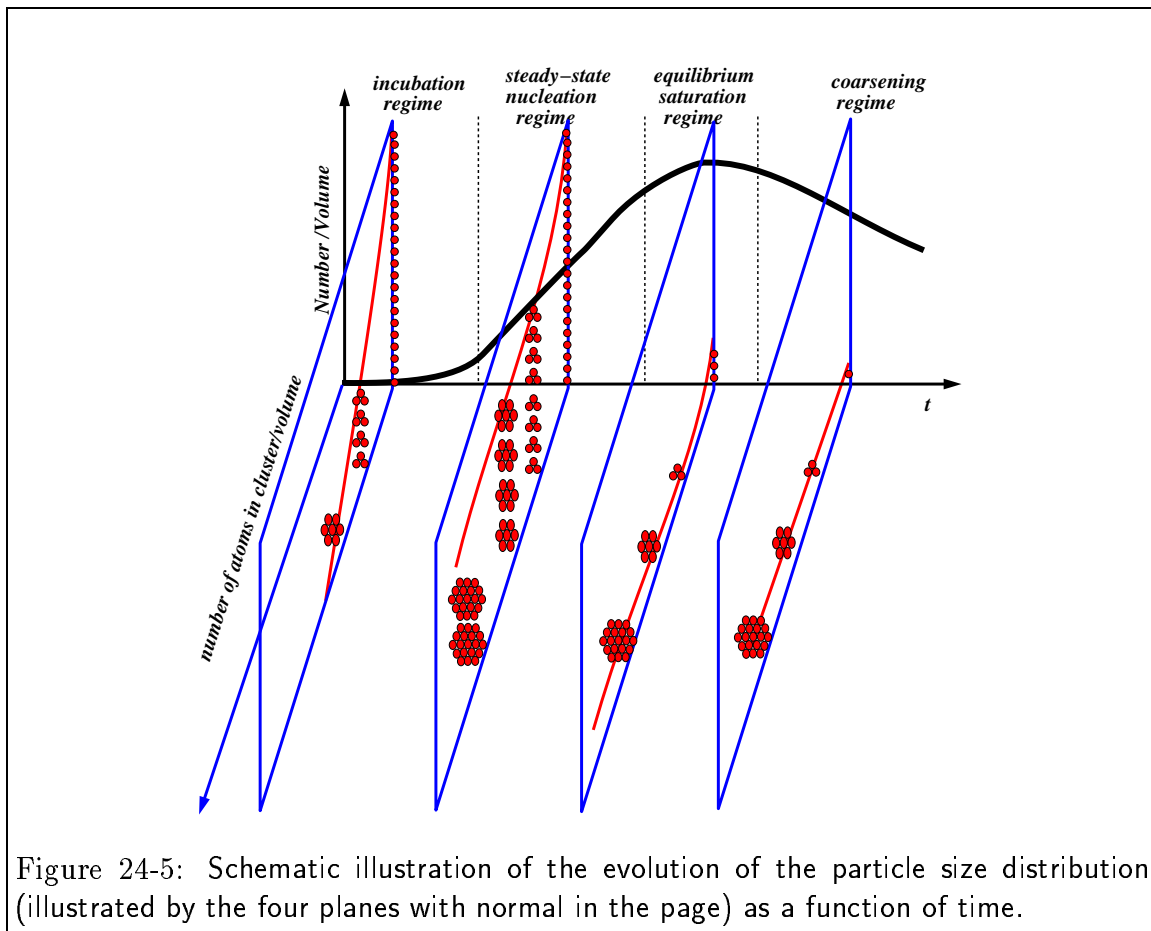


Figure 24-5: Schematic illustration of the evolution of the particle size distribution (illustrated by the four planes with normal in the page) as a function of time.

This diffusion equation could be solved for an initial distribution of clusters with a fixed concentration at small sizes ($n = 1$) and zero flux at $n = \infty$ to yield a characteristic time when appreciable concentrations appear at $n = n_{crit}$.

However, the incubation time can be approximated with a random walk model as follows. Near $n = n_{crit}$, ΔG^{nuc} is nearly flat and the rate of the number of particles crossing $n = n_{crit}$ can be approximated by the root-mean-square 'displacement' relation for a one-dimensional random walk: $\langle \delta n^2 \rangle = 2\Gamma_{\beta \rightarrow \alpha} S_n^\beta \tau$ where $\delta n/2$ is the 'distance' on either side of the maximum that ΔG^{nuc} can be considered to be flat. Approximating the $\delta n/2$ by the value at which

$$\Delta G^{nuc}(n_{crit} - \delta n/2) = G_{crit}^{nuc} - kT,$$

$$\tau \approx \frac{\delta n^2}{2\Gamma_{\beta \rightarrow \alpha} S^\beta} = \frac{256\pi kT \gamma_{\alpha\beta}^4 \Omega^2}{\Delta \bar{G}^4 \Gamma_{\beta \rightarrow \alpha} S^\beta} \quad (24-16)$$

so that the characteristic incubation time goes like $T/(\Delta T)^4$.

