

Diffusion-limited Cluster Growth during Nucleation

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Introduction

Nucleation of clusters of a stable phase from a metastable phase is the initial stage of numerous phase transformations. Nucleation is often modeled by classical nucleation theory (CNT), but CNT is only applicable when growth of nucleating clusters is collision (or interface) limited. Therefore, CNT has recently been adapted by Slezov for growth limited by long-range diffusion of molecules to clusters in non-polymorphic transformations [1]. Slezov's model describes, e.g., precipitation of oxygen in silicon, and, more generally, crystallization in alloys.

However, Slezov's model is applicable only in 3D due to its reliance on quasi-steady-state growth, which does not occur in lower dimensions.

Generalizing the model requires using the general relationship between growth rate and cluster size in place of the quasi-static one, but is difficult because the former has no analytic solution. Exact solutions are available only for fixed concentration of the source phase at the cluster surface [2]. However, this situation does not arise in real systems. Instead, the surface concentration varies with the cluster's size through the Gibbs-Thomson capillarity effect [3]. In this case, growth rates can only be computed numerically. We therefore obtain diffusion-controlled growth rates with the COMSOL Multiphysics® simulation software. Such growth rates will be used to extend Slezov's model to 2D.

Scope

For simplicity, we model spherically symmetric growth, which occurs in isotropic systems, limited by Fickian diffusion with homogeneous diffusivity. To focus on filling the gap in Slezov's model, we modeled capillarity effects in 2D only.

In our model, the concentration of the stable phase c_{stable} is larger than the bulk concentration of the metastable phase c_{∞} . Then, cluster growth requires depletion of the parent phase.

We further require that only a small fraction of space is transformed from one phase to another, e.g., in dilute systems with $c_{stable} \gg c_{\infty}$ or in the early stages of phase transformations. In such a scenario, most clusters are far enough from one another that

depletion or enrichment of the original phase by one cluster does not affect the concentration near another. Then, a cluster's growth is independent of others' and can be simulated without including other clusters. Since we are interested only in growth during nucleation, clusters are assumed to be so small relative to the separation between clusters that an effectively infinite untransformed space surrounds each cluster, and the concentration approaches c_{∞} as the distance from the cluster increases.

More general models with anisotropic growth, non-diffusion-limited growth, or growth affected by neighbor clusters are possible, but will be deferred to future work.

Governing Equations

When growth is diffusion controlled, molecular exchange between a cluster and the parent phase is so much faster than diffusion to the cluster that concentration immediately outside the cluster is in local equilibrium with concentration in the cluster. Also, heat exchange is relatively instantaneous, so temperature is uniform throughout the system. Then, clusters' growth rate is wholly determined by the rate at which molecules diffuse to clusters, via mass conservation:

$$\dot{R} = \frac{D}{c_{stable} - c_R} \left. \frac{\partial c}{\partial r} \right|_{r=R} \quad (1)$$

where c is concentration, r is radial distance from the cluster and D is diffusivity. In this equation, the concentration gradient at the cluster surface must be determined from concurrently solving the diffusion equation

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (2)$$

with boundary conditions

$$c(R, t) = c_R \quad (3)$$

$$c(\infty, t) = c_{\infty} \quad (4)$$

A concentration profile satisfying these constraints is shown in Figure 1. If c_R were constant, these

equations would admit the solution in [2]. However, capillarity causes c_R to be higher for smaller clusters [3]:

$$c_R = c_{eq} \exp\left(\frac{\gamma}{RkTc_{stable}}\right) \quad (5)$$

where γ is surface tension, k is Boltzmann's factor and T is temperature.

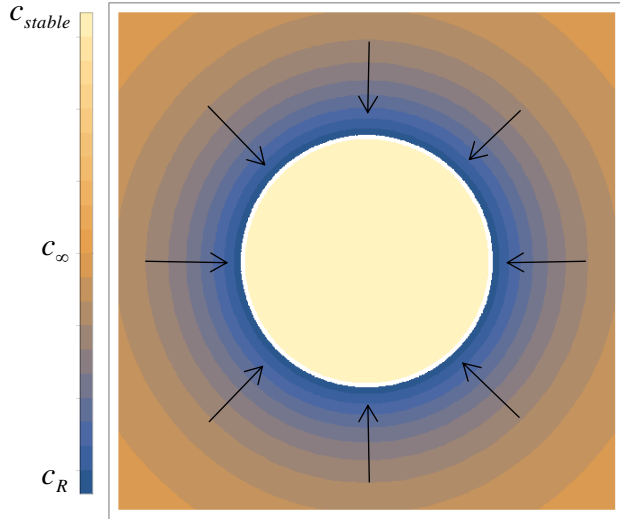


Figure 1. Concentration profile around growing cluster. Source phase is depleted near cluster, and rises in concentration away from cluster. Arrows show radial direction of molecular diffusion to cluster from far field.

Eqs. (1) - (5) must be solved together with initial conditions on c and R . $c(0, t)$ is randomly determined by concentration fluctuations and can affect \dot{R} . However, we expect the impact on \dot{R} to be transient, so that \dot{R} becomes independent of initial condition after sufficient time has elapsed. To rapidly obtain such growth rates, the initial condition should be chosen to minimize the transient time. Determining this initial condition is beyond the scope of this paper; however, $c(0, t)$ should vary smoothly and monotonically between Eqs. (3) and (4). A candidate $c(0, t)$ with this property is the solution in [2] with c_R fixed at its initial value. This solution also has the ideal potential of being a good approximation of the true solution at early times if growth is initially slow enough that c_R is approximately constant. We therefore model growth with this solution as initial concentration.

The choice of a monotonic $c(0, t)$ constrains initial R to be large enough for positive growth. In particular,

R must be so large that $c_R < c_{\infty}$, and the concentration gradient in Eq. (1) is positive so mass diffuses into the nucleus. Then, to obtain \dot{R} for the largest range of R , we start with R only 1% greater than the critical radius where $c_R = c_{\infty}$.

With these initial conditions, Eqs. (1) – (5) can be solved numerically to give \dot{R} and R at different t . Then, eliminating t gives $\dot{R}(R)$.

Computational Methods

Several techniques were attempted in COMSOL to solve the equations in the previous section. For expedience, each took advantage of radial symmetry to reduce the 2D problem to a 1D one. All were tested on the capillarity-free 1D case where $\gamma=0$, and checked against the solution in [2].

The most direct of these methods involves simulating the moving cluster surface using COMSOL's Moving Mesh interface. A less direct alternative sidesteps the issue of interface migration by changing to a moving reference frame with

$$\hat{r} = r - R \quad (6)$$

In either method, the far-field boundary condition, Eq. (4), can only be applied at a finite distance from the origin, leading to potential discrepancies with the test solution satisfying Eq. (4) exactly. We have found the discrepancy within tolerance when the boundary condition is applied at a distance at least around ten times the cluster's maximum size at the end of the simulation.

A third method avoids the problem of approximating an infinite system by switching to a coordinate system with $\hat{r} = R/r$. There, the parent phase is limited to $0 < \hat{r} < 1$.

Among these methods, the first and third were respectively found to be least accurate and slowest, while the second agreed well with the test solution and was reasonably fast. We therefore used the second method to compute growth rates of clusters subject to capillarity effects.

The chosen method amounts to adding a convective term to Eq. (2). We found it also necessary to introduce a source term in shifting and rescaling the concentration field by

$$\hat{c} = \frac{c - c_\infty}{c_R - c_\infty} \quad (7)$$

to fix $\hat{c}(R, t)$. The transformed equation was input in the Transport of Diluted Species interface and coupled to Eq. (1) at R by applying a linear extrusion to the dependent variable in a Domain ODEs and DAEs interface.

Eqs. (1) - (5) suggest the growth rate depends on many parameters. The number of degrees of freedom may be reduced to

$$n_{eq} = \frac{c_{eq}}{c_{stable}} \quad (8)$$

$$n_\infty = \frac{c_\infty}{c_{stable}} \quad (9)$$

by non-dimensionalization via

Quantity	Scale
Length	$\lambda = \frac{\gamma}{kTc_{stable}}$
Time	$\frac{\lambda^2}{D}$
Concentration	c_{stable}

Table 1. Scaling parameters.

Then, the growth rate can be obtained by multiplying the non-dimensionalized growth rate by D/λ . In this way, all possible growth rates can be obtained by sweeping over the two degrees of freedom. Since growth requires $c_{eq} < c_\infty$, the parameter sweep is limited to

$$0 < n_{eq} < n_\infty < 1 \quad (10)$$

For each simulation in the sweep, the initial concentration profile was computed by a MATLAB function called through LiveLink. The concentration was defined on an arithmetically distributed mesh with number of elements equal 10x the non-dimensionalized length of the finite element domain and element ratio of 1000 to focus on capturing concentration variation closer to nuclei. Solution

accuracy was improved by adjusting the following solver options from their default values:

1. Automatic nonlinear (Newton) method was chosen.
2. Initial step size was fixed at 0.001.
3. Consistent initialization was switched off.

Results for $\dot{R}(R)$

Growth rates for different n_{eq} and n_∞ are shown in Figures 2. Growth rates always begin with a sharp decrease with cluster size, before peaking then gradually decreasing. The plunge at small sizes is likely transient, since it is sensitive to how close the initial size is to the critical size. The drop appears nearly linear on the log-log scale and is reminiscent of $\dot{R} \propto R^{-1}$ from depletion of the original phase near the nucleus in solutions uncorrected for capillarity. As R increases, capillarity lowers the concentration in the immediate vicinity of clusters via Eq. (5), increasing the concentration gradient and thus \dot{R} in Eq. (1). Further increase in R eventually brings c_R close enough to c_{eq} that c_R is practically constant, and \dot{R} follows the capillarity-uncorrected solution to decrease as R^{-1} .

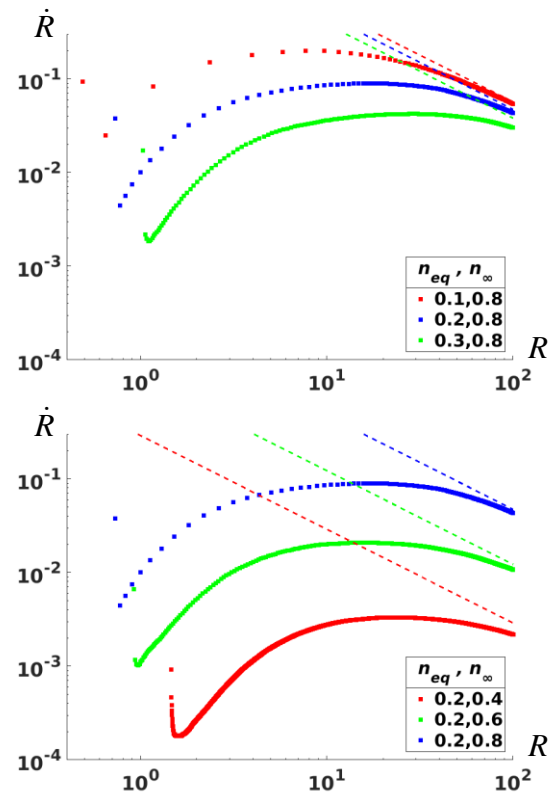


Figure 2. Growth rate decreases with n_{eq} (top) and increases with n_∞ (bottom). Growth rate approaches

solution for $c_R = c_{eq}$ without capillarity correction (dashed lines) as growing interface becomes planar ($R \rightarrow \infty$).

After the initial decline in \dot{R} , \dot{R} at the same cluster size is higher for smaller n_{eq} and larger n_∞ . This trend can be understood from how the concentration gradient in Eq. (1) is likely to be steeper the larger the separation between n_{eq} and n_∞ . The change in \dot{R} is less pronounced for decreasing n_{eq} because the increase in concentration gradient is partially offset by the increased local depletion, which boosts the denominator in Eq. (1).

Comparison with capillarity-uncorrected solution for $\dot{R}(R)$

Because the growth simulations are lengthy and have to be repeated to obtain growth rates for different conditions, it is expedient to have simple approximations of growth rates. Such approximations are especially useful in optimization applications where growth rates a variety of different processing conditions are needed. A natural choice for a trial approximation is the capillarity-uncorrected solution for surface concentration on a cluster fixed at its equilibrium value, shown as dashed lines in Figure 2. This solution is expected to agree well with the growth rate of large clusters, because the surface concentration approaches the equilibrium concentration as clusters grow, according to Eq. (5). However, the solution must overestimate actual growth rates of small clusters because the surface concentration is significantly larger than its equilibrium value due to capillarity.

A better approximation can be constructed from partly correcting the positive bias of the capillarity-uncorrected solution relative to the actual growth rate. To do so, we make use of how the growth rate of clusters of a particular size in one capillarity-uncorrected solution is smaller than that in another for larger surface concentration. Then, by using the solution for size-independent surface concentration equal c_R from Eq. (5) evaluated at size R of those clusters, we can decrease the bias for clusters of size R . By following the same procedure for each R , we construct a new estimate with decreased bias at all sizes. This estimate can be understood as a trajectory in \dot{R} - R space passing through a different capillarity-uncorrected solution at every R , as illustrated in Figure 3.

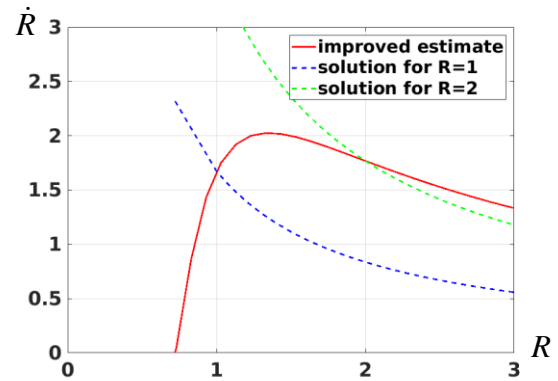


Figure 3. Improved estimate of growth rate from joining solutions without capillarity correction for different fixed surface concentrations on clusters at corresponding R . The estimate is able to capture the rise in \dot{R} from capillarity, unlike each capillarity-uncorrected solution, which can only predict the R^{-1} behavior.

The modified estimate will still be no smaller than the true growth rate by the following argument. The estimate will exactly equal the real rate at the smallest R , because the initial condition has been chosen to match the capillarity-uncorrected solution the estimate uses for that R . For slightly larger R , the estimate uses a capillarity-uncorrected solution that assumes a correspondingly smaller surface concentration and consequently faster growth at smaller R . Because cluster growth to slightly larger R is slower, diffusion has more time to occur, so the concentration profile is more quasi-steady, i.e. gentler near the cluster surface, resulting in slower \dot{R} in Eq. (1). By induction, clusters of even larger R will also grow at a slower rate than that predicted by the multi-solution estimate. Therefore, we can be sure the modified estimate does not increase the magnitude of the bias by overcorrection, as confirmed in Figure 4, which shows the decrease in error from the improved estimate.

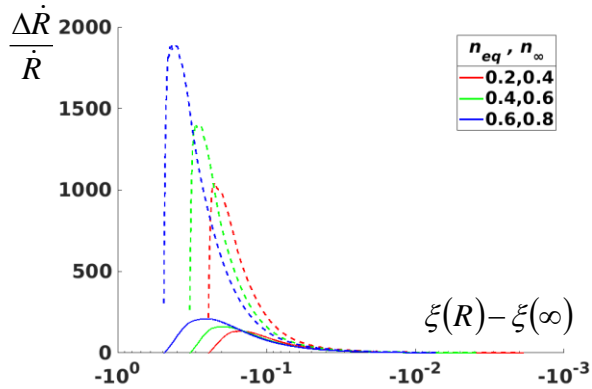


Figure 4. Relative deviation of growth rates from capillarity-uncorrected solution (dashed) and improved estimate (solid). For convenience, the abscissa is chosen as the difference of $\xi(R) = \frac{c_{\infty} - c_R}{c_{stable} - c_R}$ from its limiting value as a measure of the cluster's planarity. Initial surge originates from fall of actual growth rates detailed in previous section.

Conclusions

We computed 2D diffusion-limited growth rates that are affected by capillarity by multiphysics modeling in COMSOL. To facilitate modeling with these rates, we also constructed a simple estimate that agrees well with growth rates of large clusters. These growth rates can be incorporated into Slezov's nucleation model to better capture diffusion and capillarity effects. Furthermore, the methods developed can be used to study negative growth and growth in higher dimensions.

References

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