Diffusion-limited cluster growth during nucleation

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Introduction:

- Nucleation is the formation of clusters of a stable phase from a metastable phase.
- Nucleation modeling requires cluster growth rates vs size.
- Exact rates are unavailable when
  1. growth is limited by rate of molecule diffusion to clusters in non-polymorphic transformations and
  2. molecule density on cluster surfaces is raised by Gibbs-Thomson effect.

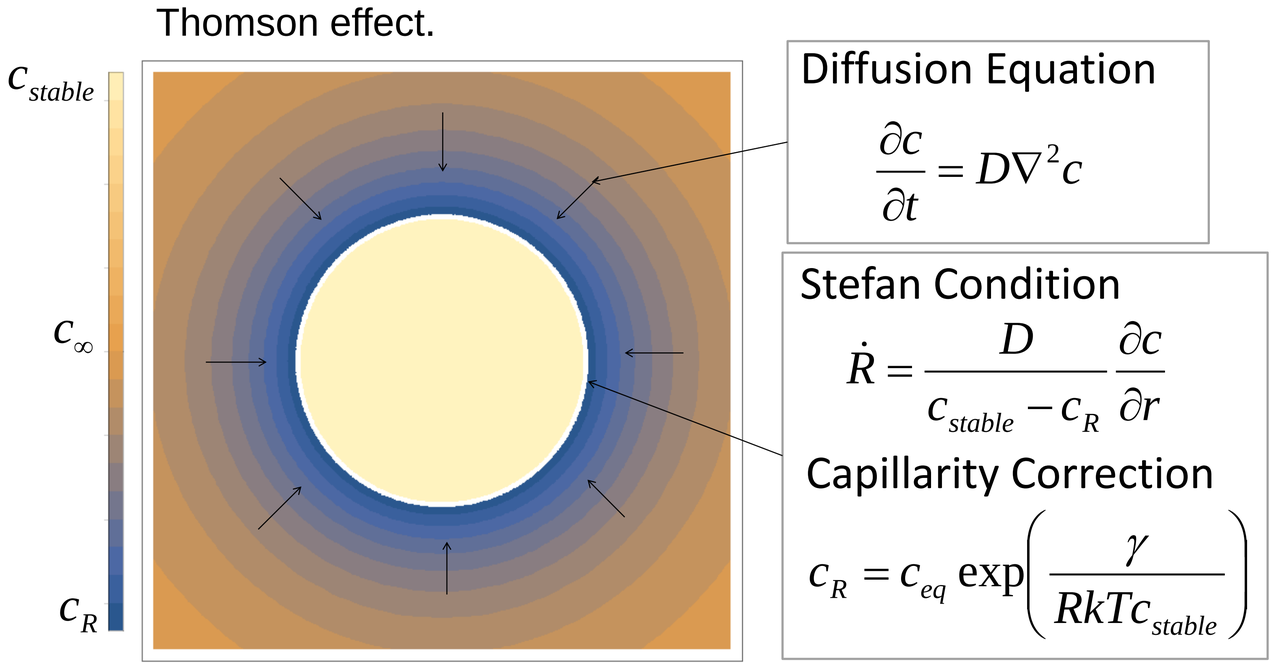

Figure 1. Radial diffusion-limited growth [1].

Computational Methods:

1. Change to a moving reference frame. $\hat{r} = r - R$
2. Shift and rescale density field to fix boundary densities. $\hat{c} = \frac{c - c_\infty}{c_R - c_\infty}$
3. Non-dimensionalize.
4. Restrict to 2D.
5. Sweep over the parameters $\frac{c_{eq}}{c_{stable}}, \frac{c_\infty}{c_{stable}} \in [0,1)$.

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

Table 1. Scaling parameters

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

- Growth rates decrease with size asymptotically.
- Growth rate approaches solution for $c_R = c_{eq}$ w/o capillarity correction [2] (dashed lines below) as growing interface becomes planar ($R \to \infty$).

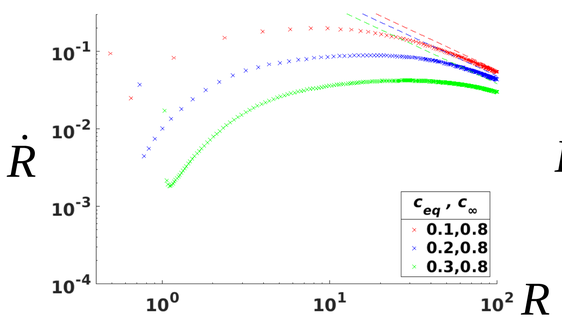

Figure 3. Growth rate decreases with c_{eq}.

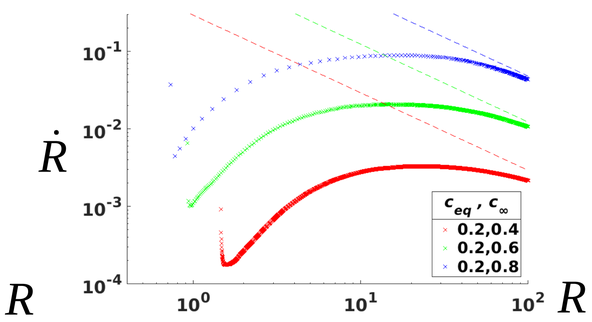

Figure 4. Growth rate increases with c_∞.

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

- Solution overestimates growth rate by underestimating actual c_R.
- Estimate may be improved by using different solution for each R, such that equilibrium density in solution for one R equals capillarity-corrected c_R at that R.

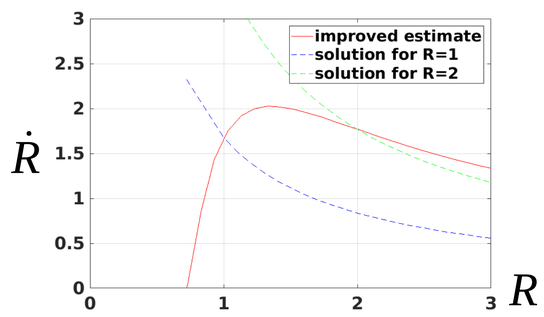

Figure 5. Improve estimate by joining solutions for different c_{eq} at corresponding R.

- Improved estimate still exceeds true rate because each solution assumes constant c_R.
- Relative deviation of estimates appears asymptotically linear in $\xi(R) - \xi(\infty)$, where $\xi(R) = \frac{c_\infty - c_R}{c_{stable} - c_R}$.

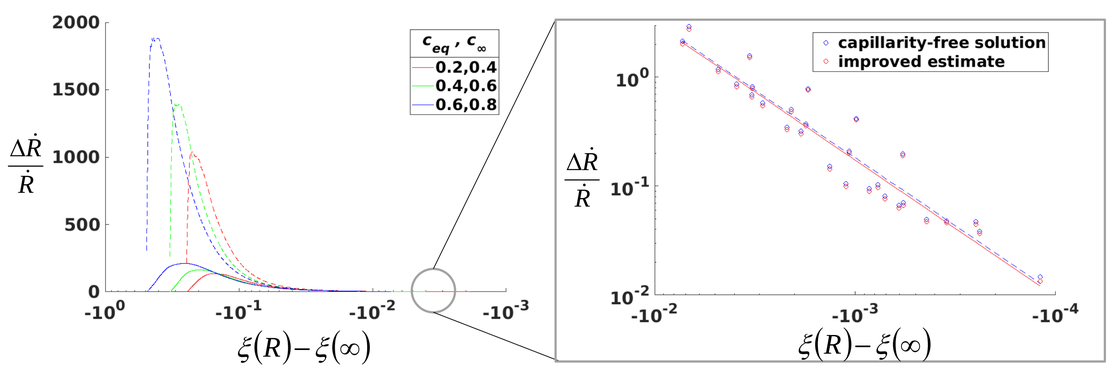

Figure 6. Relative deviation from capillarity-free solution (dashed) and improved estimate (solid).

Conclusions:

- We computed 2D diffusion-limited growth rates that are affected by capillarity.
- Estimate constructed from solutions for different equilibrium densities is a decent approximation for large clusters.
- Growth rate can be incorporated into nucleation model to better capture diffusion and capillarity effects.

References:

1. Ghez, R., Diffusion Phenomena, 60-74, (2001)
2. Zener, C., Theory of Growth of Spherical Precipitates from Solid Solution, JAP, 20, 950-953, (1949)