# Benchmark problems for nucleation

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## 1 Problem setup

### 1.1 The phase-field model

For these benchmark problems I used the simplest possible phase-field model, which is for an isothermal pure substance with one liquid ($\phi = 0$) and one solid ($\phi = 1$) phase. The free energy of this system is defined by

$$F[\phi] = \int \left[ \frac{\epsilon^2}{2} (\nabla\phi)^2 + w g(\phi) - \Delta f p(\phi) \right] dV, \tag{1}$$

where $g(\phi) = \phi^2(1-\phi)^2$, $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ and $\Delta f$ is the driving force for solidification at the simulation temperature (positive below the melting point). The equation of motion for $\phi$ is

$$\frac{\partial \phi}{\partial t} = M \left[ \epsilon^2 \nabla^2 \phi - w g'(\phi) + \Delta f p'(\phi) \right], \tag{2}$$

and the equilibrium ($\Delta f = 0$) solid-liquid interface profile (1D solution) is given by

$$\phi(x) = \frac{1 - \tanh\left(\frac{x - x_0}{\sqrt{2}\delta}\right)}{2}, \tag{3}$$

where

$$\delta = \sqrt{\epsilon^2 / w} \tag{4}$$

$$\gamma = \frac{\sqrt{\epsilon^2 w}}{3\sqrt{2}} \tag{5}$$

are the width and the free energy of the interface.

Choosing the length and time units as $\xi = \sqrt{\epsilon^2/w}$ and $\tau = 1/(Mw)$, we can obtain the nondimensional form of the problem (the nondimensional quantities are denoted by tildes),

$$\tilde{F}[\phi] = \int \left[ \frac{1}{2} (\tilde{\nabla}\phi)^2 + g(\phi) - \tilde{\Delta f} p(\phi) \right] d\tilde{V} \tag{6}$$

and

$$\frac{\partial \phi}{\partial \tilde{t}} = \tilde{\nabla}^2 \phi - g'(\phi) + \tilde{\Delta f} p'(\phi) \tag{7}$$

with $\tilde{\Delta f} = \Delta f / w$, and the solid-liquid interface solution given by

$$\phi(\tilde{x}) = \frac{1 - \tanh\left(\frac{\tilde{x} - \tilde{x_0}}{\sqrt{2}}\right)}{2}. \tag{8}$$

### 1.2 The properties of the classical nucleus

According to the classical nucleation theory, the radius and the work of formation (excess free energy) of the critical size nucleus in 2D are

$$r^\star = \frac{\gamma}{\Delta f} \tag{9}$$

$$W^\star = \frac{\pi\gamma^2}{\Delta f}. \tag{10}$$

Using the same units as in the previous subsection, the nondimensional forms of these quantities are

$$\tilde{r}^\star = \frac{1}{3\sqrt{2}}\frac{1}{\tilde{\Delta f}} \tag{11}$$

$$\tilde{W}^\star = \frac{\pi}{18}\frac{1}{\tilde{\Delta f}}. \tag{12}$$

### 1.3 The Avrami plot

The basis of the Avrami plot is the transformed fraction vs. time function. According to the JMAK theory,

$$X(t) = 1 - \exp(-Kt^n), \tag{13}$$

where $K$ is a constant depending on the nucleation and growth rates, $n = d + 1$ for continuous nucleation and $n = d$ if nucleation happens only at $t = 0$, where $d$ is the number of spatial dimensions. If we plot $\log(-\log(1 - X))$ vs. $\log(t)$, then for the JMAK kinetics (Eq. 13) we get a straight line with slope $n$.

## 2 The suggested benchmark problems

From here, I will use only the nondimensional forms of the phase-field (Eqs. 6, 7, 8) and nucleation (Eqs. 11, 12) equations, but without the tildes, for simplicity.

### 2.1 Explicit nucleation, single seed

Make a 2D simulation domain of size $100 \times 100$ units. Set the driving force to $\Delta f = 1/(15\sqrt{2})$, which corresponds to the critical radius $r^* = 5$ (Eq. 11). Place a circular seed in the center of the domain using the profile $\phi(r)$ given by Eq. 8 with radius $r_0 = r^*$. This seed is the diffuse interface approximation of the classical sharp interface nucleus corresponding to the given $\Delta f$, and therefore it should be fairly close to (an unstable) equilibrium. Now follow the time evolution of the system for $t = 100$ units, and plot the solid fraction $X$ and the total free energy $F$ as function of time. Now make two more simulations starting from seeds with $r_0 = 0.99r^*$ and $r_0 = 1.01r^*$. Compare the results to the previous one.

For this benchmark, I used a simple finite difference code with forward Euler time stepping. I used the time step $\Delta t = 0.01$ and the spatial resolution $\Delta x = \Delta y = 0.4$ with periodic boundary conditions. The resulting transformed fractions and free energies are shown in Fig. 1.

### 2.2 Explicit nucleation, multiple seeds at t=0

To obtain reasonable statistics for this problem, we need a larger simulation domain and a large number of smaller nuclei. Increase the domain size to $1000 \times 1000$ and the driving force to $\Delta f = 1/(6\sqrt{2})$ to which a critical radius $r^* = 2$ belongs. Generate random positions with uniform distribution for 100 supercritical seeds with $r_0 = 1.1r^*$. (*We may decide to share these random positions to make simulations fully comparable.*) When adding a new seed, simply add the $\phi$ values given by the $\phi(r)$ profile (Eq. 8) to the $\phi$ values already in the domain, and handle the possible overlaps by setting $\phi = 1$ for all cells where $\phi > 1$. Run the simulation until $t = 400$. By this time the whole domain should be transformed to solid. Show the snapshot of the phase-field at $t = 80$, plot the time evolution of the transformed fraction and the total free energy, and make the Avrami plot.

Here I used the same FD code as in the previous problem. To make the simulation faster, I decreased the spatial and temporal resolution by setting $\Delta x = \Delta y = 0.8$ and $\Delta t = 0.04$. The results are shown in Fig. 2.

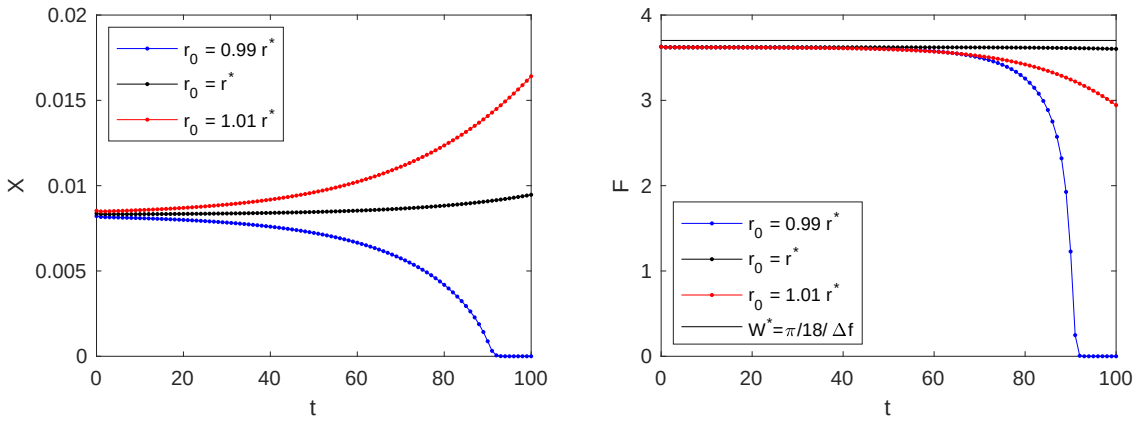


Figure 1: The time evolution of the transformed fraction $X$ and the total free energy $F$ starting from seeds close to the critical size $r_0$. $W^*$ is the work of formation according to the classical nucleation theory.

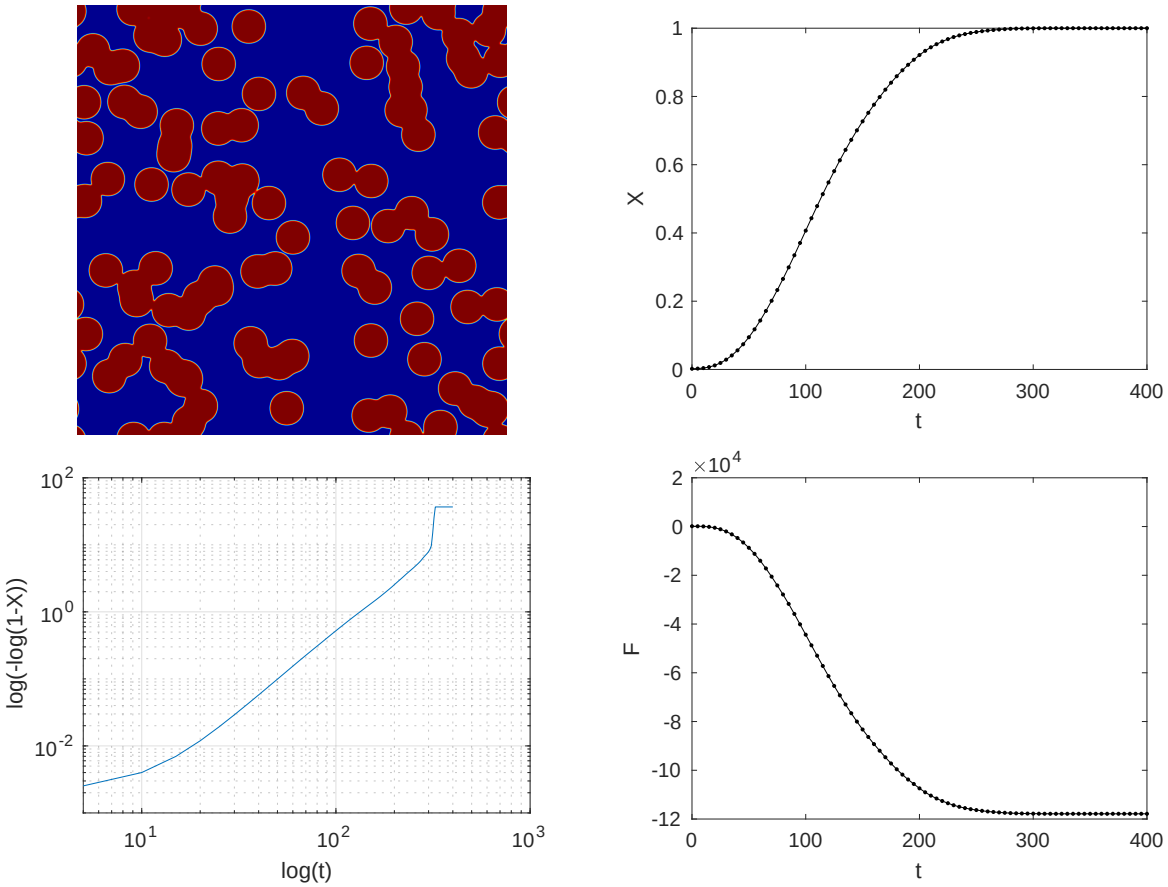


Figure 2: The snapshot of the phase field at $t = 80$, the time evolution of the transformed fraction $X$, the corresponding Avrami plot, and the time evolution of the total free energy $F$.

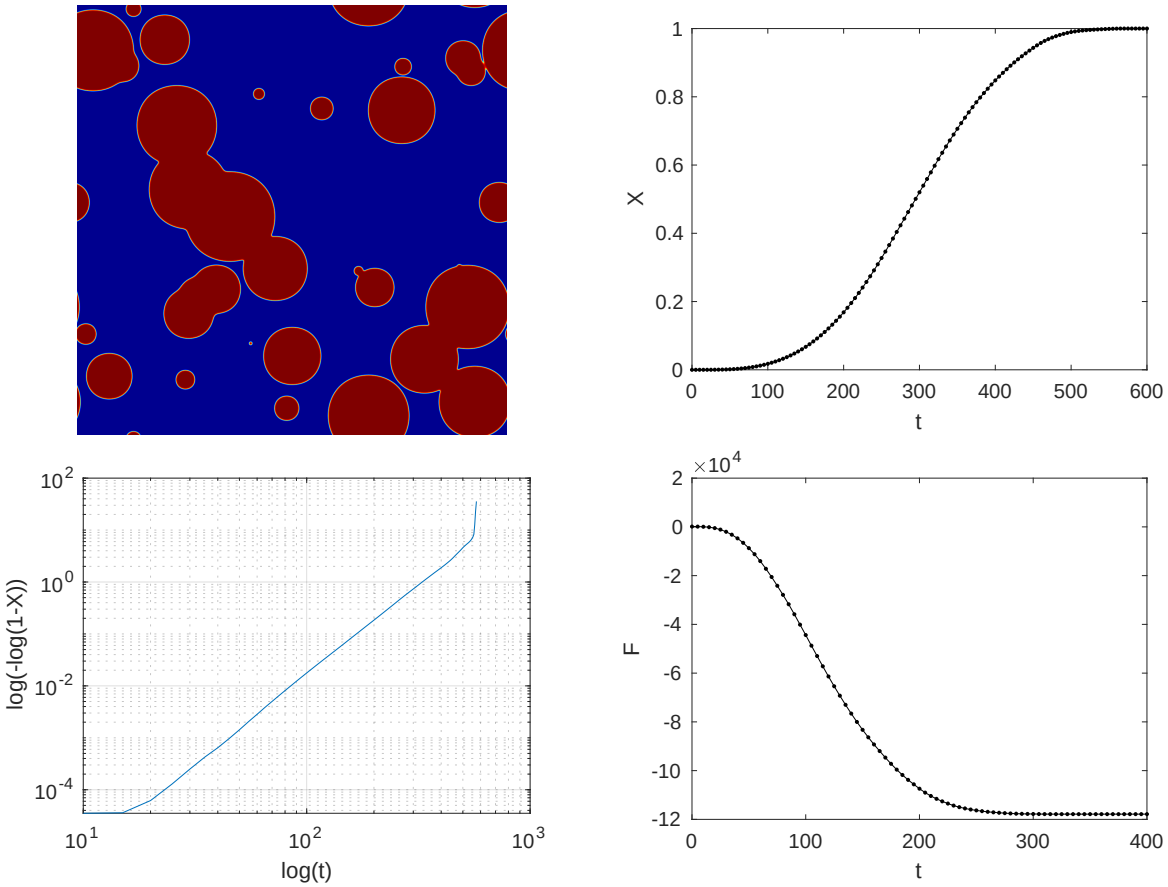


Figure 3: The snapshot of the phase field at $t = 100$, the time evolution of the transformed fraction $X$, the corresponding Avrami plot, and the time evolution of the total free energy $F$.

### 2.3 Explicit nucleation, multiple seeds at random times

Now instead of the fixed nucleation time at $t = 0$, generate 100 random nucleation times in the range $t = 0 \ldots 600$ for adding the 100 seeds to the simulation domain. Keep everything else just as in the previous problem, run the simulation for $t = 600$ and display the results.

My FD results are shown in Fig. 3. Please note the different slopes of the Avrami plot in Figs. 2 and 3.

### 2.4 Athermal nulceation

For the modeling of athermal nucleation, we need a surface with good wetting properties but of limited size. In the usual scenario, they are the surfaces of small, flat foreign particles. To simplify modeling, I suggest not to add additional boundaries (particles) to our simulations, rather to use one of the sides of our rectangular domain by making only a part of it good wetting. I also suggest to use the "Model B" approach described in Warren et al. PRB 79 014204 (2009), i.e., to set the wetting properties via the parameter $\phi_0$ used in the Dirichlet boundary condition $\phi = \phi_0$ along the surface. This has two advantages: (1) it is very simple to implement, (2) if we set $\phi_0$ high enough, solid will automatically appear at and grow from the surface (surface spinodal, for the details see the paper), so we can save the effort of inserting an appropriate seed in the beginning of the simulation.

The goal of this problem is to explore the behaviour around the free growth limit, which, in our 2D setting, is the half-circular configuration of solid on top of a straight surface of length $2r_0$, where $r_0$ is the radius of the homogeneous nucleus corresponding to the given driving force (Eq. 11).

A possible benchmark setup could be the following. Set the undercooling to $\Delta f_0 = 1/(30\sqrt{2})$, which corresponds to the critical radius $r^* = 10$. Use a simulation domain of width 40 and height 20. Use Dirichlet boundary conditions on the bottom side by setting $\phi = 0.9$ along the middle part of length 20 of the boundary and $\phi = 0$ outside. Starting from $\phi = 0$ everywhere, run the simulation for $t = 5000$. Plot the transformed

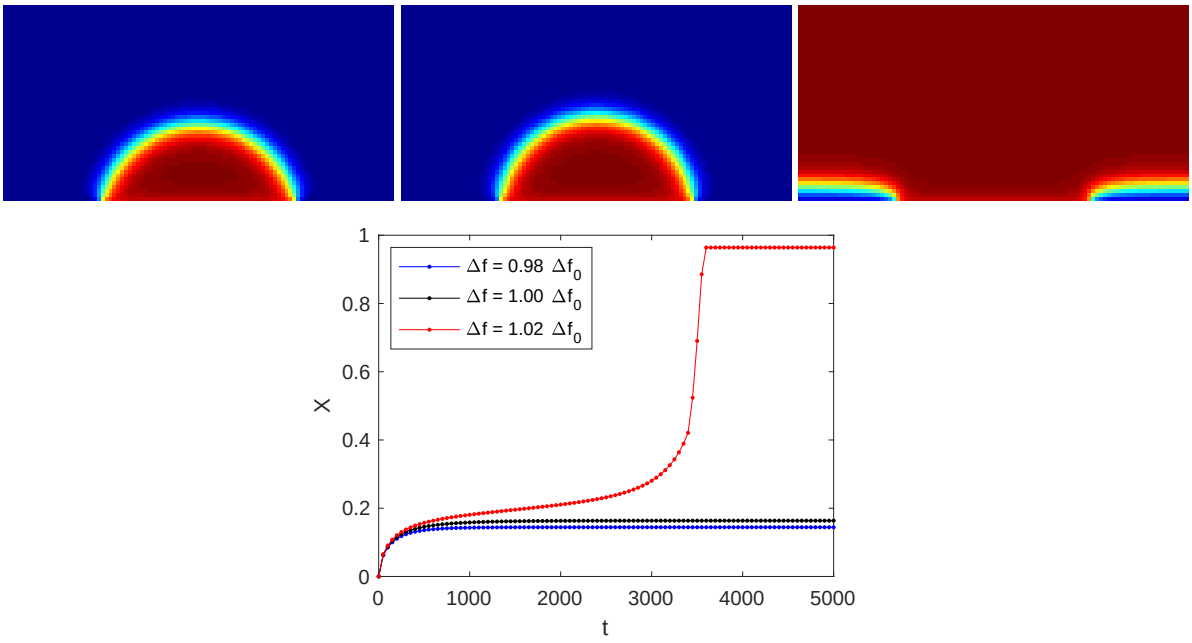


Figure 4: The snapshots of the phase field at $t = 5000$ for three different driving force values around the critical one, and the time evolution of the transformed fraction $X$.

fraction as function of time. Repeat the simulation with increasing/decreasing the driving force by 2%, and compare the results.

In my FD implementation I returned to the finer spatial and temporal resolution used in the first, single seed problem. The three final snapshots of $\phi$ and the transformed fraction curve are shown on Fig. 4. Only when the driving force was larger than the critical one ($\Delta f_0 = 1/(30\sqrt{2})$ corresponding to the $r^* = 10$ size of the wetting part of the bottom surface) did free growth occur. In the other cases growth stopped close to the half-spherical configuration.

*For this problem, I have not plotted the free energy curve by intention. To present it meaningfully, the result we obtain by simple integration has to be corrected for the effect of the surfaces, either via analytic calculations, or by making an empty, full liquid simulation (which is unfortunately impossible in the surface spinodal region) to have the free energy baseline. I may do this later.*