Towards a phase-field benchmark problem set on nucleation

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Introduction

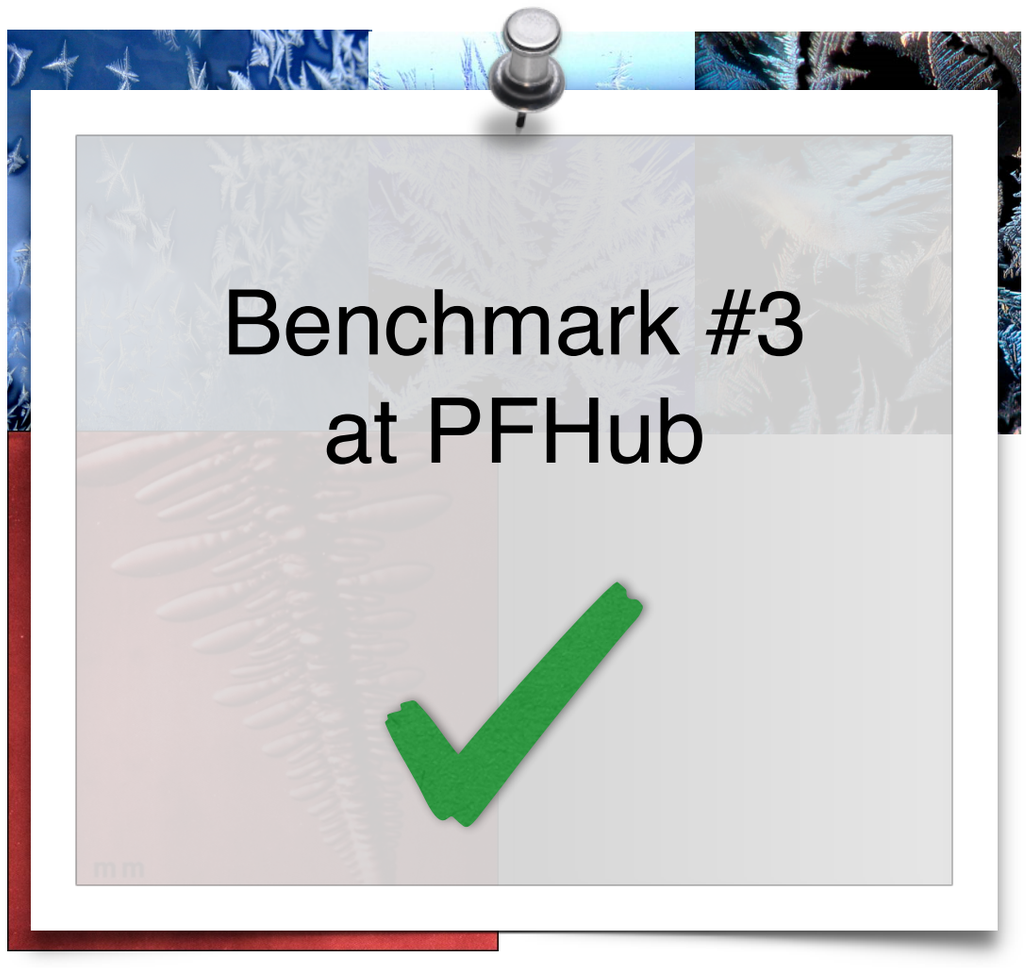
Solidification of an undercooled liquid

Nucleation

Molecular dynamics simulation: By courtesy of R. S-Aga & J. R. Morris

Embryos of the new phase appear via thermal fluctuation

Growth



Complex patterns evolve due to the interplay of capillarity, diffusion, and anisotropy.

Types of nucleation to model by phase-field

1. Homogeneous nucleation

- Inside the volume, without the aid of foreign particles
- Extremely rare in nature

2. Heterogeneous nucleation

- On surfaces and foreign particles
- Practically much more relevant

Fluctuations required

3. Athermal nucleation (Greer et al.)

- Dormant particles, free growth condition: $\Delta f > \Delta f_{\text{crit}}(R)$

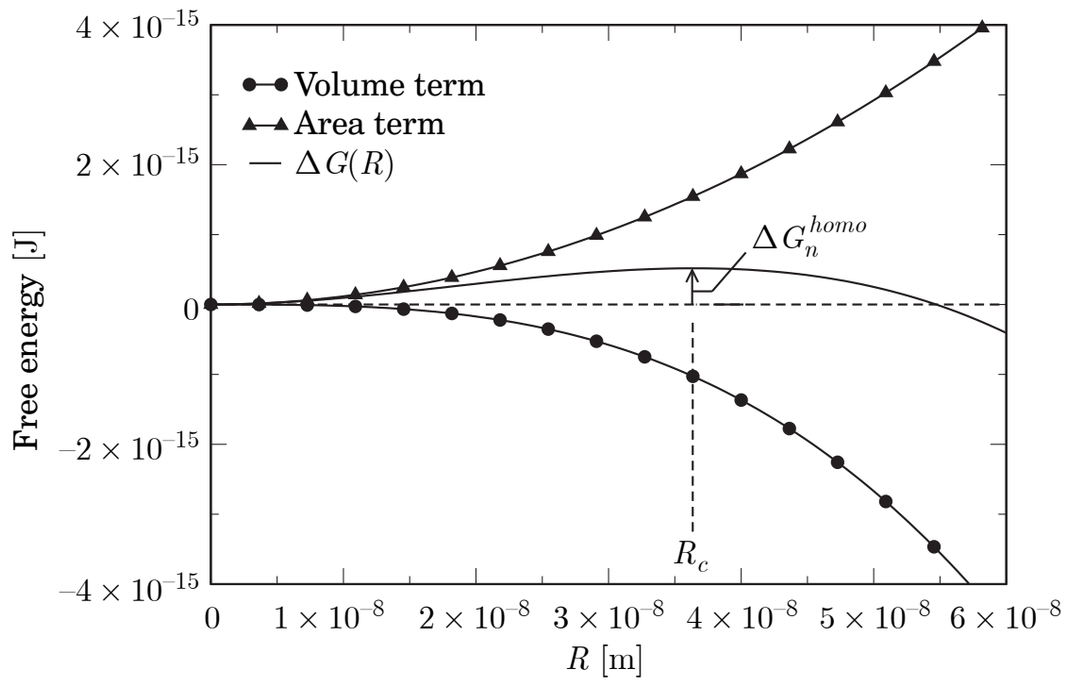
Fluctuations not required

Homogeneous nucleation

Classical nucleation theory (CNT):

Assumptions:

- sharp interface
- isotropic, curvature independent surface energy → spherical shape
- bulk properties inside



M. Rappaz: Solidification

Free energy of a spherical solid particle of radius r:

3D	2D
$\Delta F_{3\mathrm{D}}(r) = 4r^2\pi\,\gamma_{\mathrm{SL}} - \frac{4}{3}r^3\pi\,\Delta f$	$\Delta F_{2\mathrm{D}}(r) = 2r\pi\,\gamma_{\mathrm{SL}} - r^2\pi\,\Delta f$
$r^*_{3D} = \frac{2\gamma_{\mathrm{SL}}}{\Delta f}$	$r^*_{2D} = \frac{\gamma_{\mathrm{SL}}}{\Delta f},$
$W^*_{3D} = \frac{16\pi\gamma^3_{\mathrm{SL}}}{3\Delta f^2}$	$W^*_{2D} = \frac{\pi\gamma^2_{\mathrm{SL}}}{\Delta f}$

$$\left(\text{Gibbs-Thomson:}\quad \Delta f = 2\Gamma_{sl}\kappa, \quad \kappa = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \quad \kappa_{3\mathrm{D}} = \frac{1}{r} \quad \kappa_{2\mathrm{D}} = \frac{1}{2r}\right)$$

Heterogeneous nucleation

Classical nucleation theory (CNT):

Assumptions:

- sharp interface
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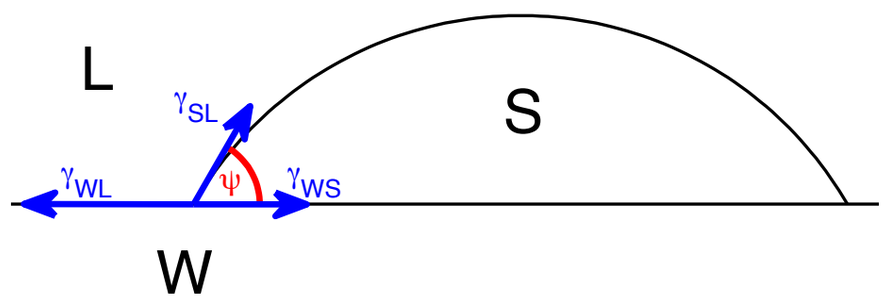
- bulk properties inside



Young equation: $\cos(\psi) = \dfrac{\gamma_{wl} - \gamma_{ws}}{\gamma_{sl}}$

$$\Delta F_{2\mathrm{D}}(r,\psi) = 2r\psi\gamma_{\mathrm{SL}} + 2r\sin\psi(\gamma_{\mathrm{SW}} - \gamma_{\mathrm{LW}}) - r^2\pi\, S_{2\mathrm{D}}(\psi)\,\Delta f$$

$$S_{2\mathrm{D}}(\psi) = \frac{(\psi - \cos\psi\sin\psi)}{\pi}$$

$$\Delta F_{3\mathrm{D}}(r,\psi) = 2r^2\pi(1-\cos\psi)\gamma_{\mathrm{SL}} + r^2\pi(1-\cos^2\psi)(\gamma_{\mathrm{SW}} - \gamma_{\mathrm{LW}}) - \frac{4}{3}r^3\pi\, S_{3\mathrm{D}}(\psi)\,\Delta f$$

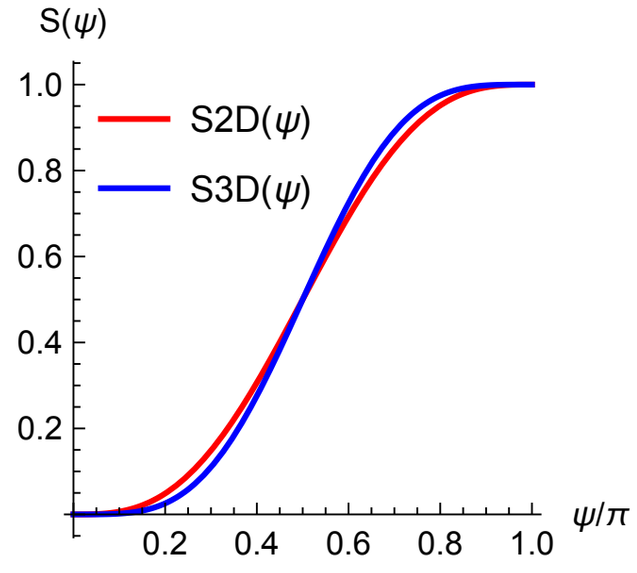
$$S_{3\mathrm{D}}(\psi) = \frac{2 - 3\cos\psi + \cos^3\psi}{4}$$

Results:

$$r^* = r^*_{\mathrm{het}} = r^*_{\mathrm{hom}}$$

$$W^*_{2\mathrm{D,het}} = \Delta F_{2\mathrm{D}}(r^*,\psi) = S_{2\mathrm{D}}(\psi) W^*_{2\mathrm{D,hom}}$$

$$W^*_{3\mathrm{D,het}} = \Delta F_{3\mathrm{D}}(r^*,\psi) = S_{3\mathrm{D}}(\psi) W^*_{3\mathrm{D,hom}}$$



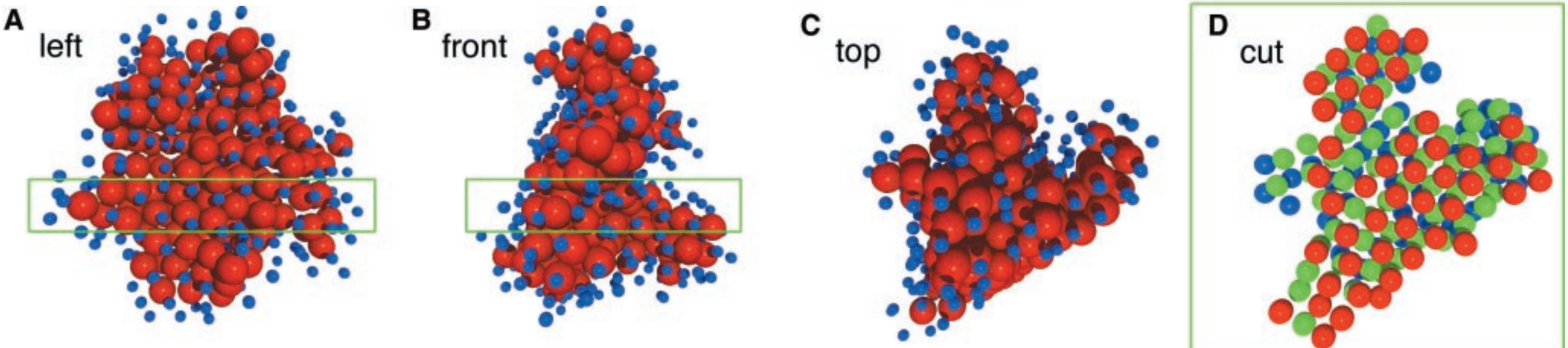
Nucleation rate and limits of the CNT

Nucleation rate:

$$J = J_0 \exp\left(\frac{W^*}{kT}\right)$$ extremely sensitive to W^* and T !

Limits of the classical theory:

- Nucleation rates corresponding to time scales of typical experiments may correspond to 10-100 molecules → the CNT fails miserably → a diffuse interface model is needed!
- The nucleus is not necessarily spherical



Gasser et al, Science, 2001

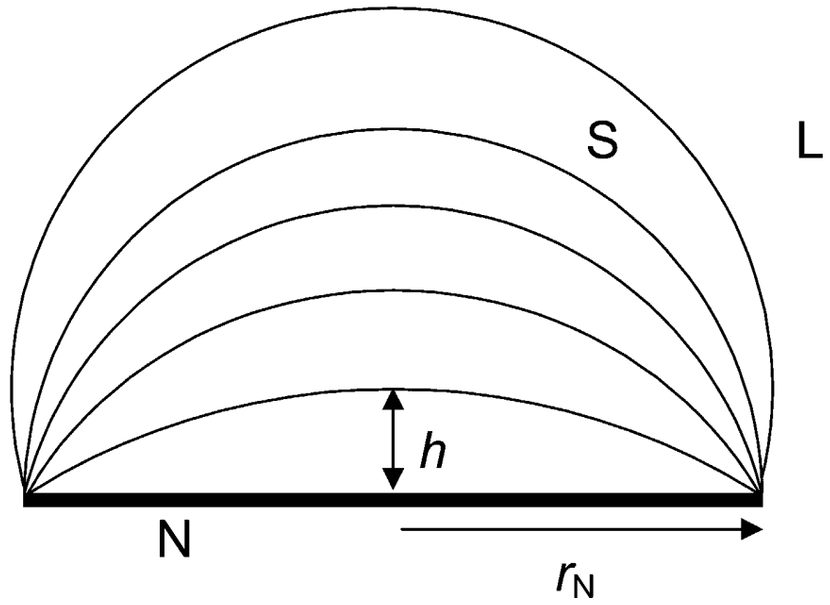
Athermal nucleation

Inoculant particles with good wetting properties, easy heterogeneous nucleation

particle grows as far as the substrate size allows, when growth must stop

further growth is possible if the radius can be decreased, i.e., the undercooling can be increased

critical radius (undercooling)?



Quested and Greer, Acta Mat. 2005

Think of pushing a ball through a hole of radius r_N in the wall...

$$r^* = r_N$$

$$r^* \rightarrow \Delta T^*$$

$$\Delta T^* = \Delta T^*(r_N)$$

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Fluctuations not required

With the PF theory, we do not have the strongly limiting assumptions of the CNT

Hope for being a better model for nucleation. (see László's presentation)

Two levels of benchmarking

1. Theoretical / model level

- How do different implementations of the same model compare?
- How do the results depend on e.g. the numerical resolution?
- How do different models compare?

2. Experimental level

- How do the different models compare to experiments?
- Model parameters?

How can we model nucleation in the PF theory?

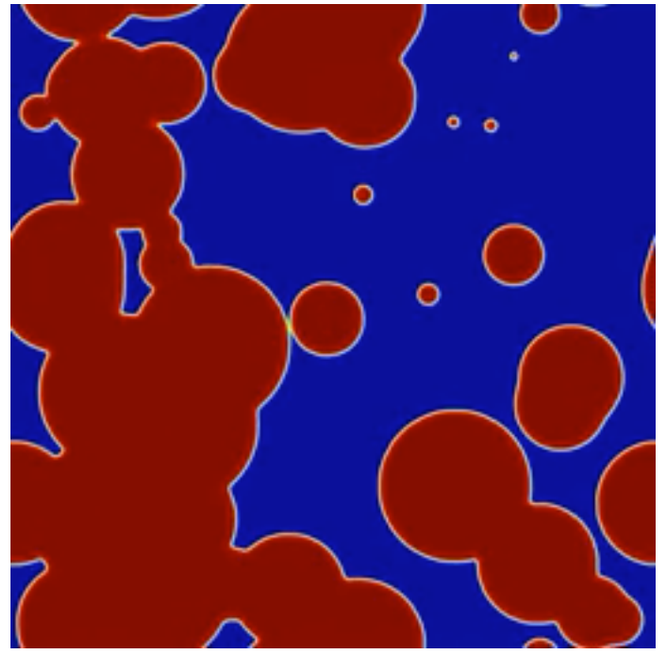
1. Nucleation seen on large scales (“distant” view)

New particles appearing at random places and times (and grow further)

↓

Put solid seeds at random places and times and let them go

Random numbers are needed to generate the nucleation times and coordinates



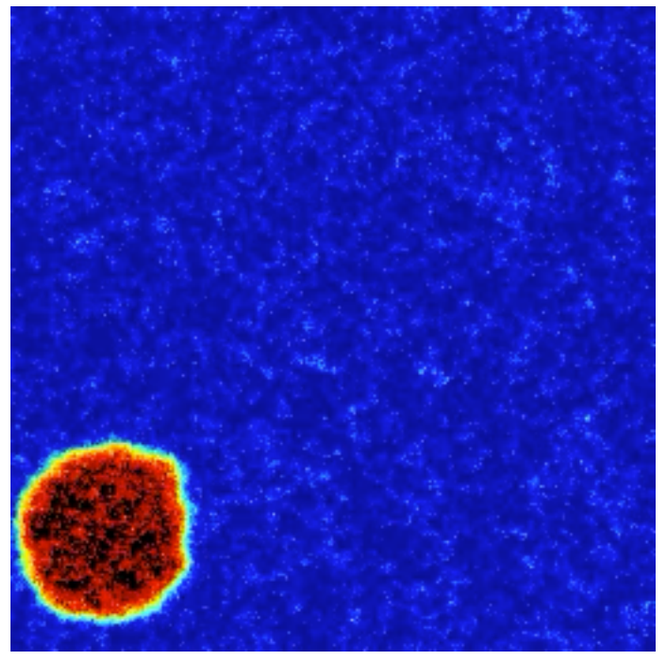
2. Nucleation seen on small scales (“close” view)

Due to the continuous fluctuations in the liquid, solid-like “blobs” appear and disappear. Only the blobs that happen to get big enough can go further.

↓

Add fluctuations to the system and wait

Random numbers are needed to generate the fluctuations



The 2D "toy model" used for illustrations

Simple phase-field model for a pure substance

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

$$g(\phi) = \phi^2 (1-\phi)^2$$
$$p(\phi) = \phi^3 (10 - 15\phi + 6\phi^2)$$

Equilibrium solid-liquid interface:

$$T = T_m, \quad \Delta f = 0$$

$$\phi(x) = \frac{1 - \tanh\left(\frac{x}{\sqrt{2}\delta}\right)}{2} \qquad \delta = \sqrt{\frac{\epsilon^2}{w}}, \quad \gamma = \frac{\sqrt{\epsilon^2 w}}{3\sqrt{2}}$$

$$\phi'(x) = \sqrt{\frac{2w}{\epsilon^2}} \phi(1-\phi)$$

Nucleation and growth in 2D:

$$T < T_m, \quad \Delta f > 0$$

$$r^*_{2D} = \frac{\gamma}{\Delta f} = \frac{\sqrt{\epsilon^2 w}}{3\sqrt{2}\Delta f}$$

$$\dot{\phi} = -M \frac{\delta F}{\delta \phi} = M\left(\epsilon^2 \nabla^2 \phi - w g'(\phi) + \Delta f\, p'(\phi)\right) + \sqrt{\frac{MkT}{\Delta x^2 \Delta t}} \xi$$

Thoughts on Random Number Generators (RNGs)

- Use good quality RNG
  - *"If all scientific papers whose results are in doubt because of bad rand()s were to disappear from library shelves, there would be a gap on each shelf about as big as your fist."* (Numerical Recipes)
  - With factory RNGs, hopefully not an issue any more

- True RNG vs. pseudo RNG
  - HW vs. SW random generators
  - PRNGs require a seed → reproducibility → can be a big advantage in setting up benchmark problems
  - In some cases, reproducibility raises more complicated requirements than simply using the same seed (see later)

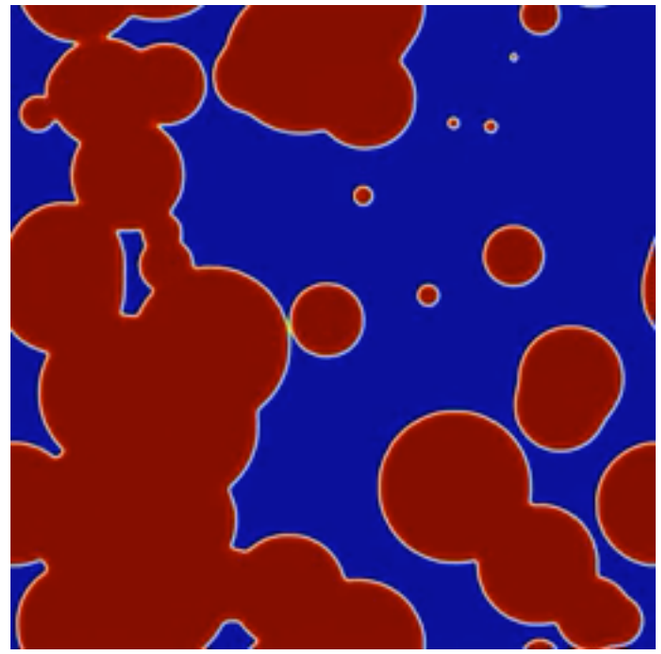
- Cross-platform pseudo RNG where the same sequence of random numbers is guaranteed?
  - Is using the same library (e.g. GSL) enough?

Nucleation in large-scale PF simulations (by hand)

Proposal for the simplest benchmark problem:

isothermal, homogeneous nucleation

Input parameter: nucleation rate, J $\quad [J] = \dfrac{1}{\text{volume} \times \text{time}}$



Generate random coordinates and times for nucleation events, then insert small supercritical seeds respectively

Number of nucleation events N (successful + unsuccessful) in a simulation of volume V and length t:

$$< N > = JVt, \quad \text{Poisson distribution with } \lambda = < N > , \quad P(N = k) = e^{-\lambda}\frac{\lambda^k}{k!}$$

- Simulations with the same RNG seed:
  Not too interesting, not really a nucleation, rather a growth benchmark.
  Works with small samples
- Simulations with different RNG seeds:
  Just statistical similarity, large enough samples required

Comparison to the JMAK theory

Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory:

Assumptions:

- homogeneous nucleation
- constant growth rate
- convex particles with the same orientation
- infinite system (both in space and time)

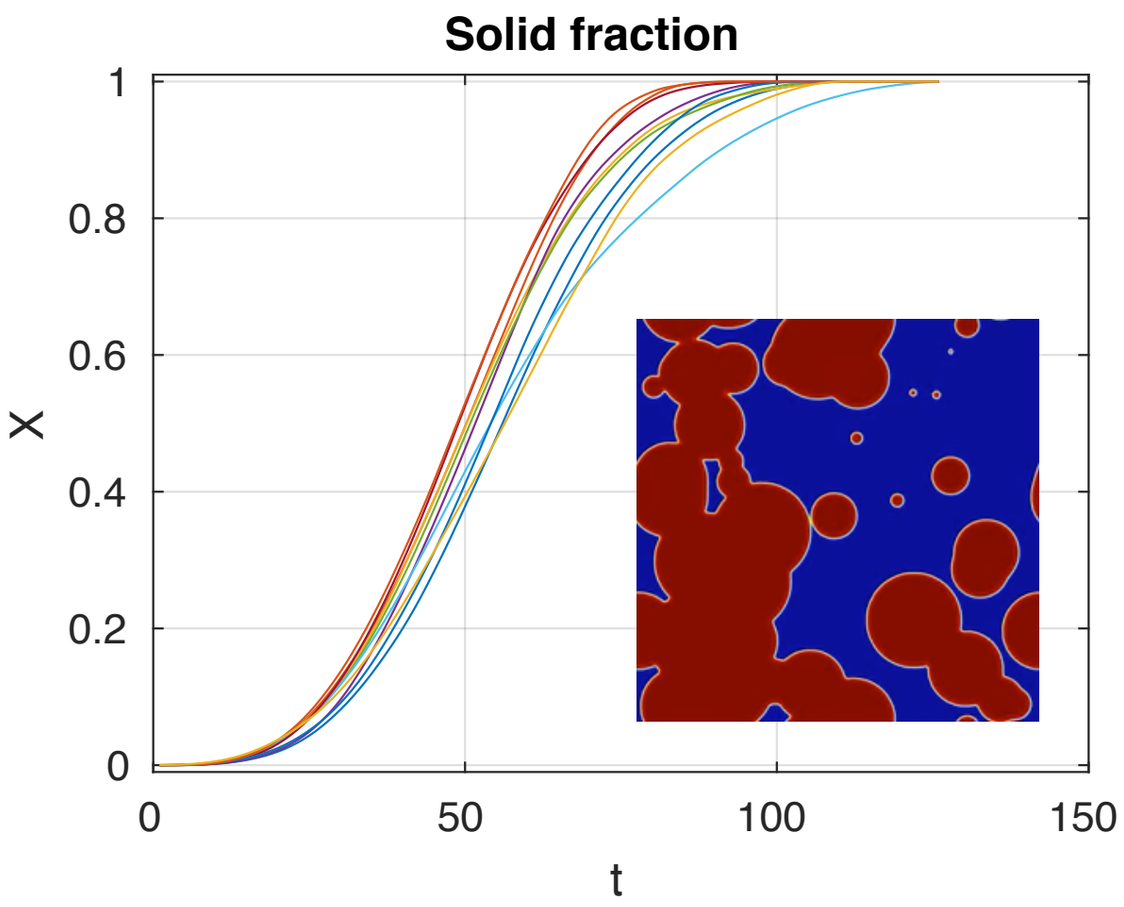
$X(t) = 1 - \exp(-Kt^n)$ exact!!!

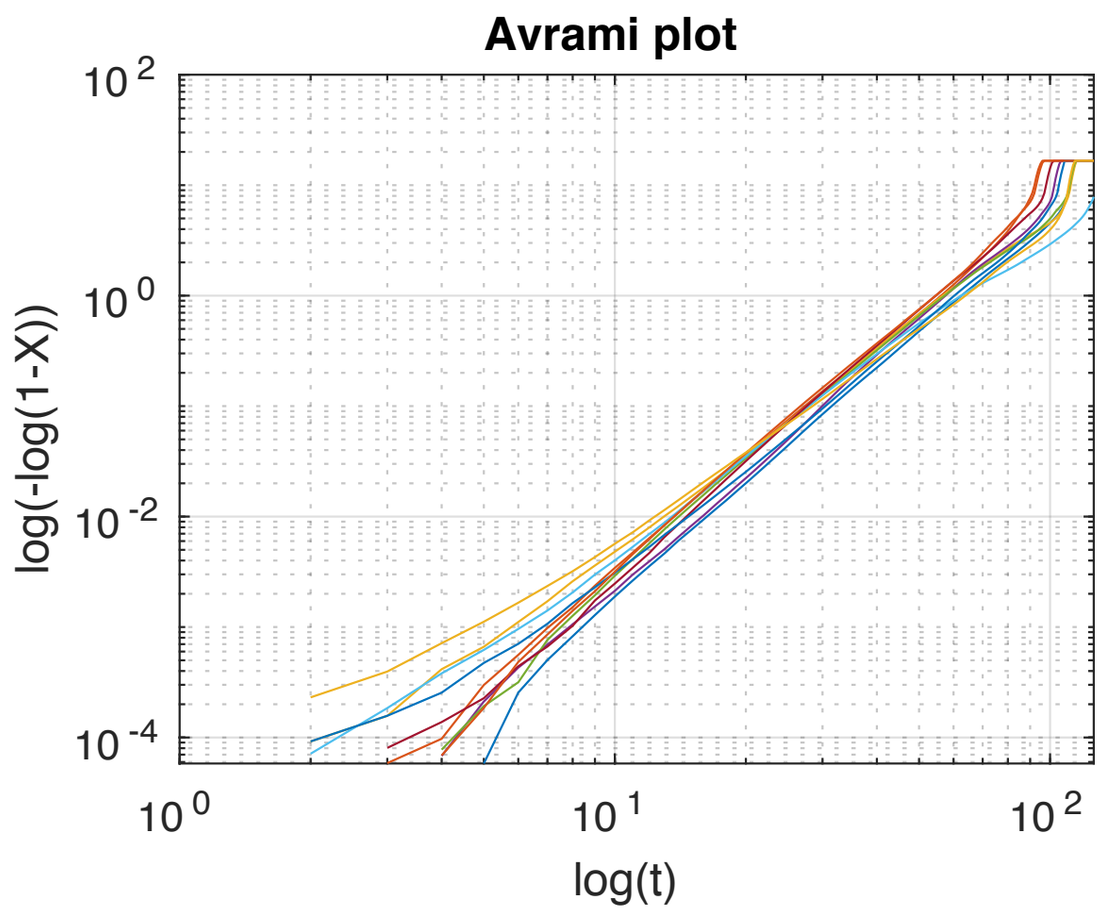
constant nucleation rate: $n = d + 1$

initial nuclei only: $n = d$

Avrami plot: straight line with slope n

10 simulations with different RNG seeds:



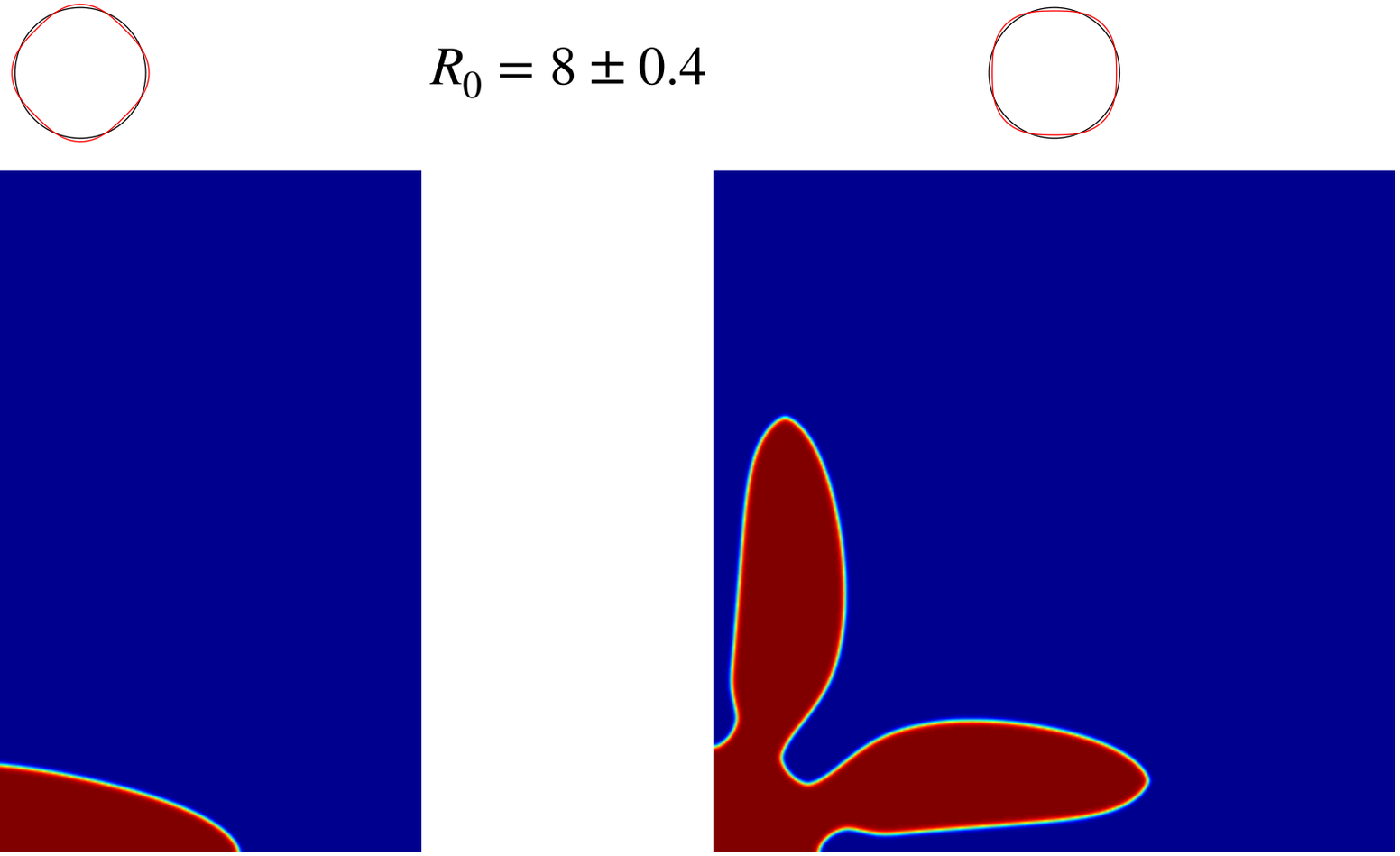


Problem when the growing particles are really small

Results can be very sensitive to the small differences in the initial conditions. It may have physical reasons (e.g. MS instability), but it can be triggered by non-physical effects, e.g. grid anisotropy

Additionally, PF models assume $R > \delta > \Delta x$, which is clearly not the case here

Illustration: PF Benchmark Problem #3 with slightly modified initial conditions:



Possible variants

1. Nucleation events only at $t = 0$ ($n = d + 1 \rightarrow n = d$ in the Avrami exponent)
2. Non-constant nucleation rate
    1. Temperature gradient
    2. Cooling
3. Heterogeneous nucleation
    1. Nucleation events only on the surfaces
4. Athermal nucleation by Greer
    1. Virtual inoculant particles at random places, free growth starts if driving force is supercritical

Nucleation in small-scale PF simulations (by noise)

With the noise term added, the equation of motion becomes a stochastic PDE, the amplitude of the Gaussian noise is determined by the fluctuation-dissipation theorem

Hohenberg-Halperin classification:
(P. C. Hohenberg and B. I. Halperin, Theory of dynamic critical phenomena. Reviews of Modern Physics, 49, 435–479, 1977)

Model A (Non-conserved field):

$$\frac{\partial \phi}{\partial t} = -M\frac{\delta F}{\delta \phi} + \xi(\vec{r},t) \quad \text{with} \quad \begin{aligned} <\xi(\vec{r},t)> &= 0 \\ <\xi(\vec{r},t)\xi(\vec{r}',t')> &= 2MkT\,\delta(\vec{r}-\vec{r}')\delta(t-t') \end{aligned}$$

Model C (Non-conserved field coupled to a conserved field):

$$\frac{\partial \phi}{\partial t} = -M_\phi\frac{\delta F}{\delta \phi} + \xi(\vec{r},t) \quad \text{with} \quad <\xi(\vec{r},t)\xi(\vec{r}',t')> = 2M_\phi kT\,\delta(\vec{r}-\vec{r}')\delta(t-t')$$

$$\frac{\partial c}{\partial t} = \nabla\left[M_c\nabla\frac{\delta F}{\delta c} + \vec{\zeta}(\vec{r},t)\right] \quad \text{with} \quad <\zeta_m(\vec{r},t)\zeta_n(\vec{r}',t')> = 2M_c kT\,\delta_{m,n}\delta(\vec{r}-\vec{r}')\delta(t-t')$$

Nucleation in small-scale PF simulations (by noise)

Discretization:

$$< \xi(r)\,\xi(\vec{r}') > = 2MkT\,\delta(\vec{r}-\vec{r}')\delta(t-t') = \frac{2MkT}{\Delta x^d \Delta t}\delta_{n,n'}\,\delta_{t,t'}$$

where d is the number of spatial dimensions

Complete equation of motion with finite difference and forward Euler:

$$\phi_x^{t+1} = \phi_x^t + \Delta t\, M\left(\epsilon^2 \frac{\phi_{x+1}^t + \phi_{x-1}^t - 2\phi_x^t}{\Delta x^2} - g'(\phi_x^t) + p'(\phi_x^t)\right) + \Delta t\sqrt{\frac{MkT}{\Delta x^d \Delta t}}\xi \qquad \begin{aligned} < \xi > &= 0 \\ < \xi^2 > &= 1 \end{aligned}$$

deterministic part — stochastic part

Mind the dimensionality!!!

In 2D or 1D simulation we still use 3D materials parameters → some thickness is always implicitly assumed.
This is not a problem in the deterministic part, but results in a different scaling of the stochastic part!

Nucleation in small-scale PF simulations (by noise)

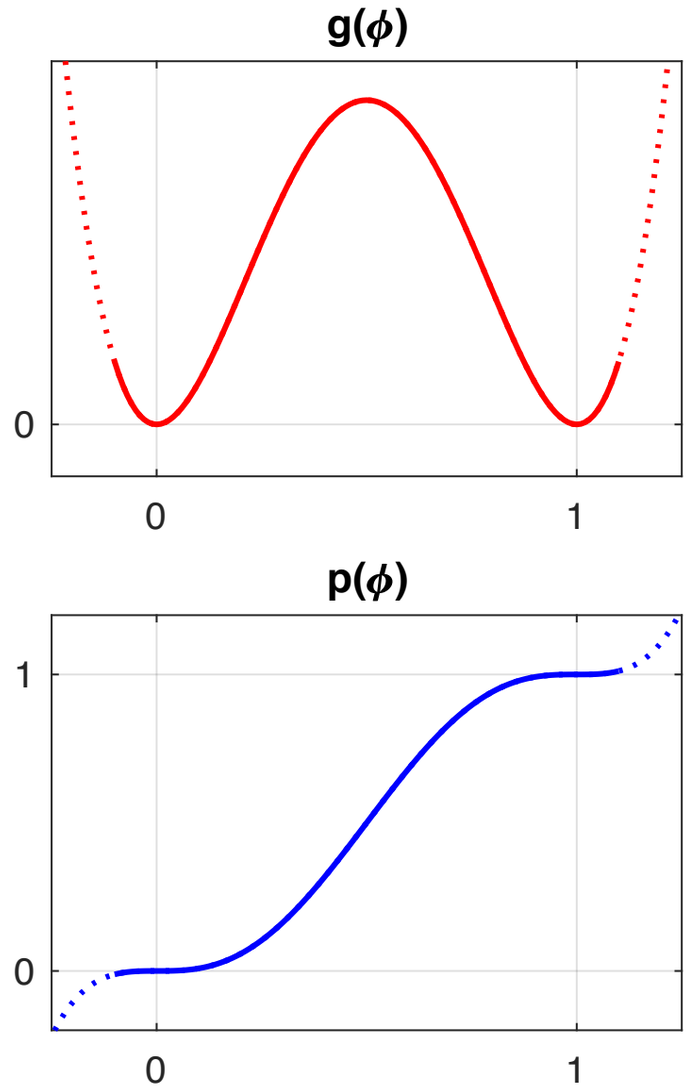
- What do we have to do? Add fluctuations (noise) and wait

$$\frac{\partial \phi}{\partial t} = -M\frac{\delta F}{\delta \phi} + \xi$$

$$\frac{\partial \phi}{\partial c} = \nabla\left[M\nabla\frac{\delta F}{\delta c} + \vec{\zeta}\right]$$

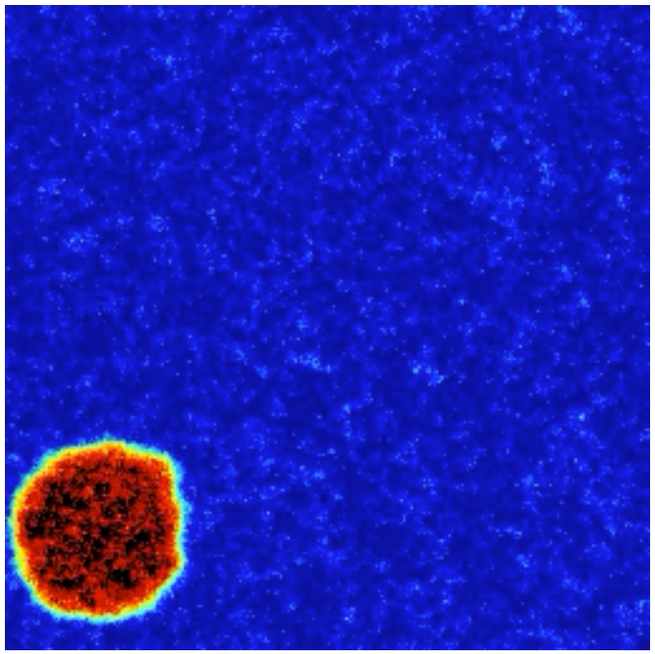
where ξ and $\vec{\zeta}$ are gaussian random variables with zero mean that put the "right amount" of fluctuations into the system

- Problems / issues in actual simulations:
  - What if the amplitude of noise is not small on the [0 1] scale?
  - Conserved fields: local and global conservation
  - If there are $\log(c)$ terms in F then $0 < c$ must be strictly satisfied! What if the flux noise wants to make c negative?



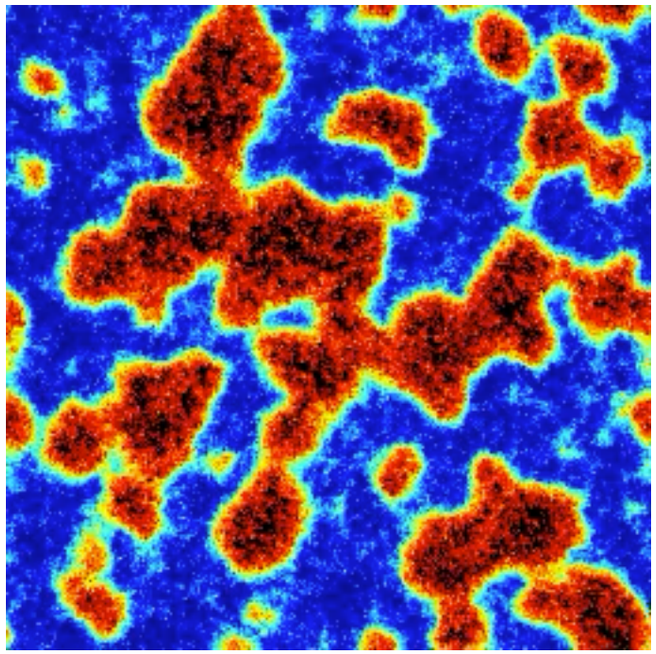
Slow and fast nucleation for benchmarking

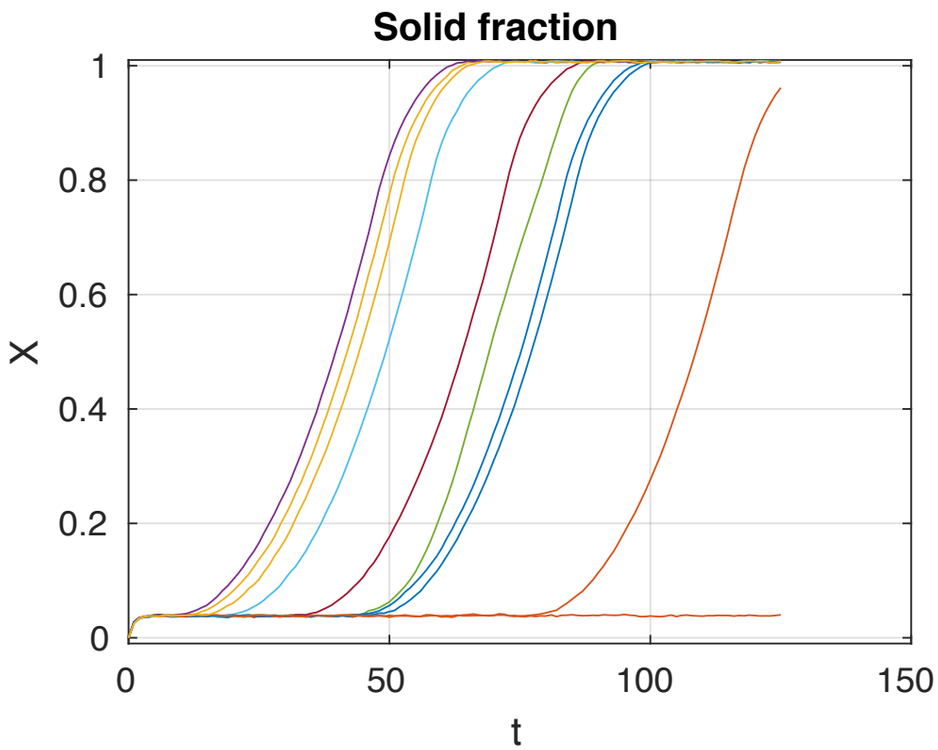
Slow nucleation, only a few isolated nuclei, large samples needed for statistics

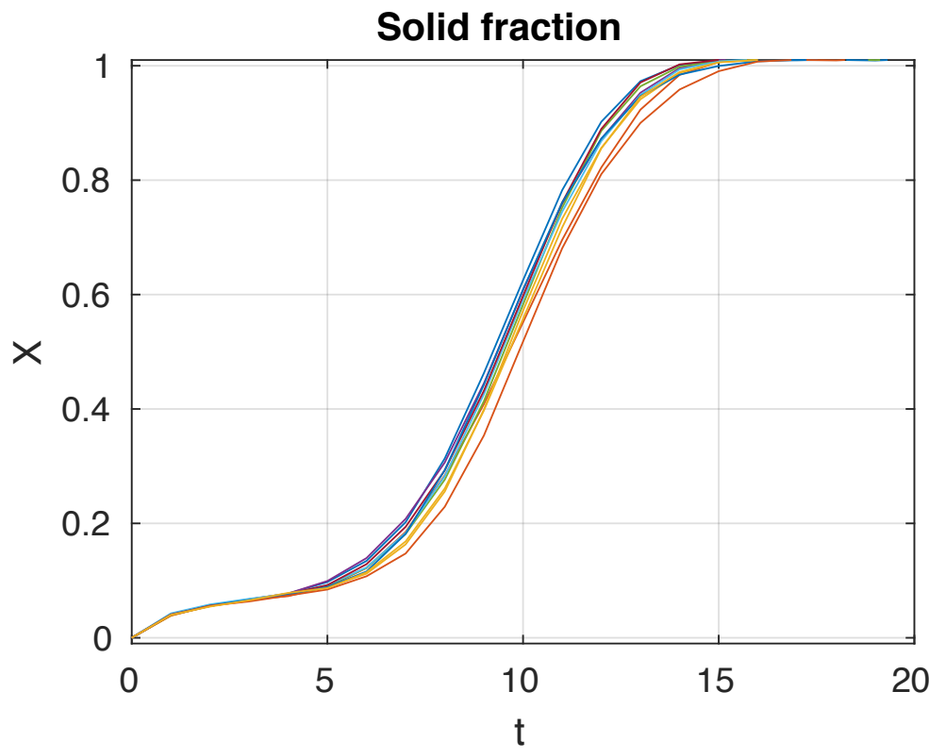


noise amplitude ×1.5

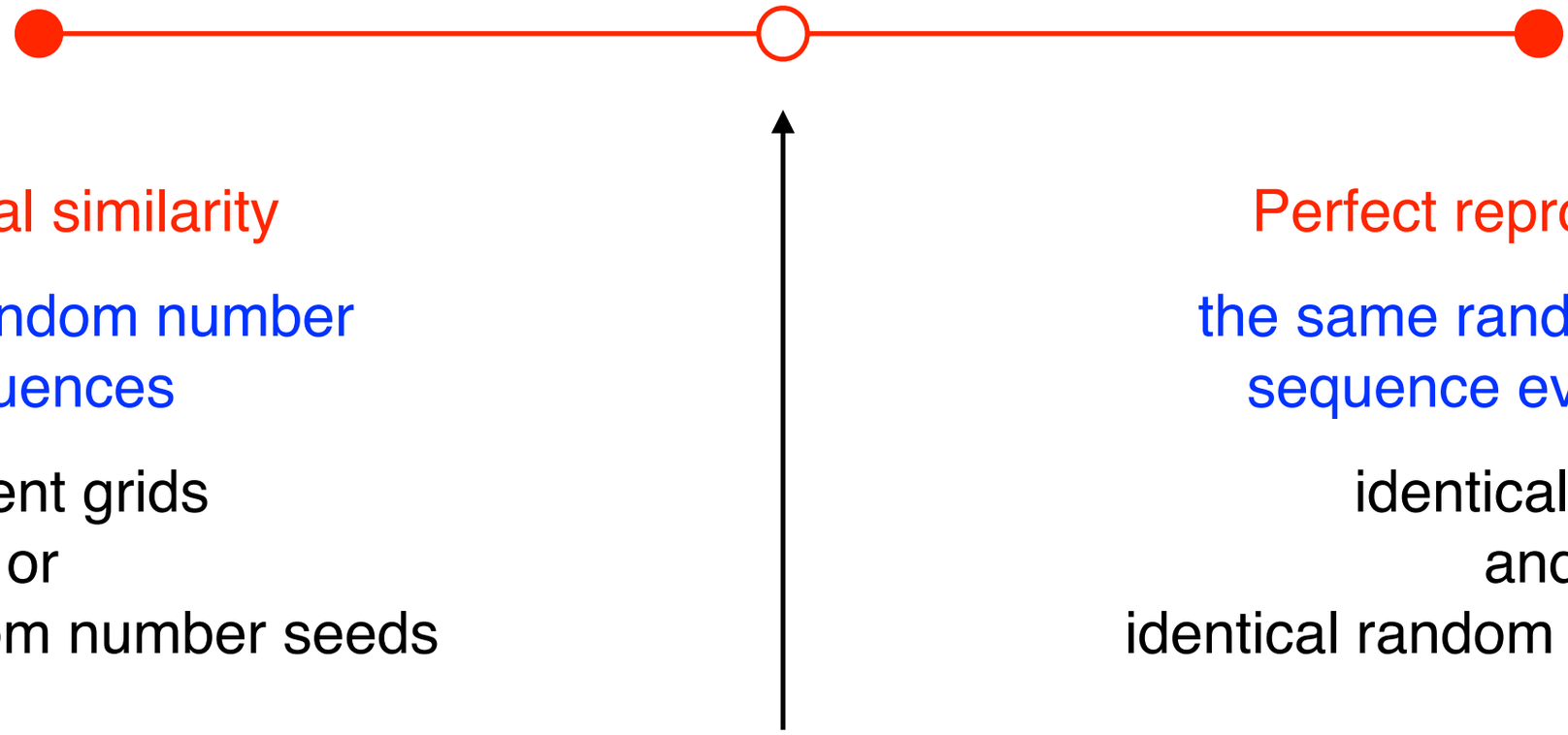
Fast nucleation, seems to happen everywhere, even smaller samples can provide enough statistics







Reproducibility of the results with noise



Statistical similarity

different random number sequences

different grids
or
different random number seeds

Perfect reproducibility

the same random number sequence everywhere

identical grids
and
identical random number seeds

Can we do something in between?

Generate noise patterns that are similar across different grids or meshes

Similar noise patterns → nucleation is expected to happen at the same places

Quick reminder on Gaussian random variables

Normal distribution

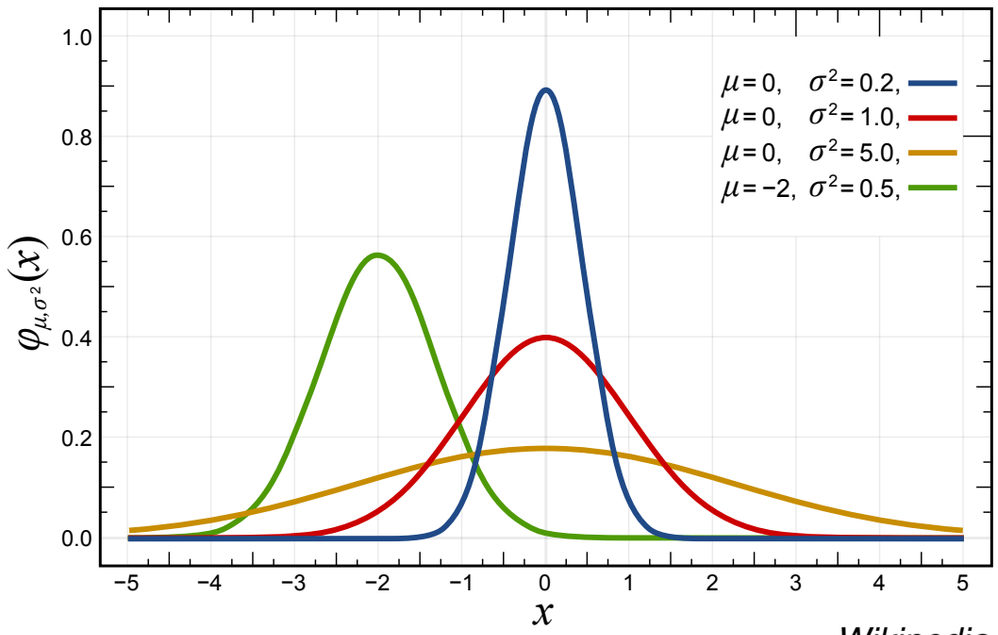
Probability density function:

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

Mean or expected value: μ

Standard deviation: σ

Variance: σ^2



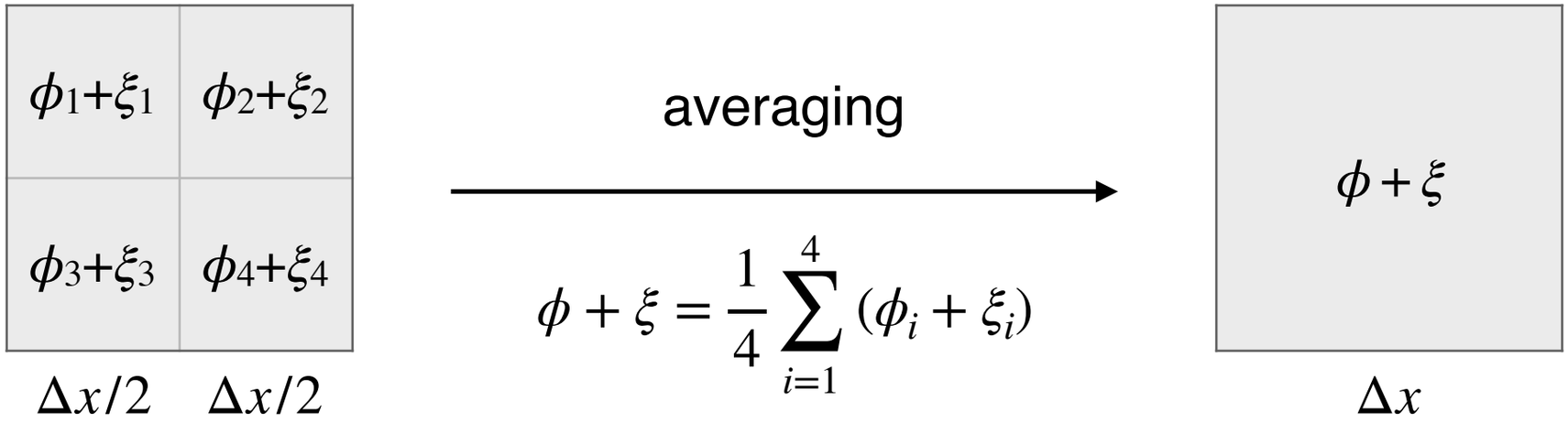
Wikipedia

The sum of $i = 1 \ldots N$ independent Gaussian random variables are also Gaussian random variables with

$$\mu = \sum_{i=1}^{N} \mu_i, \quad \sigma^2 = \sum_{i=1}^{N} \sigma_i^2$$

Generating Δx and Δt independent noise patterns

2D rectangular grid: ϕ_i: regular variables, ξ_i: stochastic variables, $<\xi_i>=0, <\xi_i^2>=\sigma^2$



mean value: $\overline{\phi+\xi}=\frac{1}{4}\sum_{i=1}^{4}\overline{\phi_i+\xi_i}=\frac{1}{4}\sum_{i=1}^{4}\phi_i=\phi$

variance: $\overline{\left(\phi+\xi-\overline{\phi+\xi}\right)^2}=\overline{\left(\frac{1}{4}\sum_{i=1}^{4}\xi_i\right)^2}=\frac{1}{16}\sum_{i=1}^{4}\overline{\xi_i^2}=\frac{1}{4}\sigma^2$

Coarsening in 2D: $\Delta x/2 \rightarrow \Delta x \quad \Rightarrow \quad$ standard deviation: $\sigma \rightarrow \frac{1}{2}\sigma$

This is in agreement with the scaling required by the fluctuation-dissipation theorem!

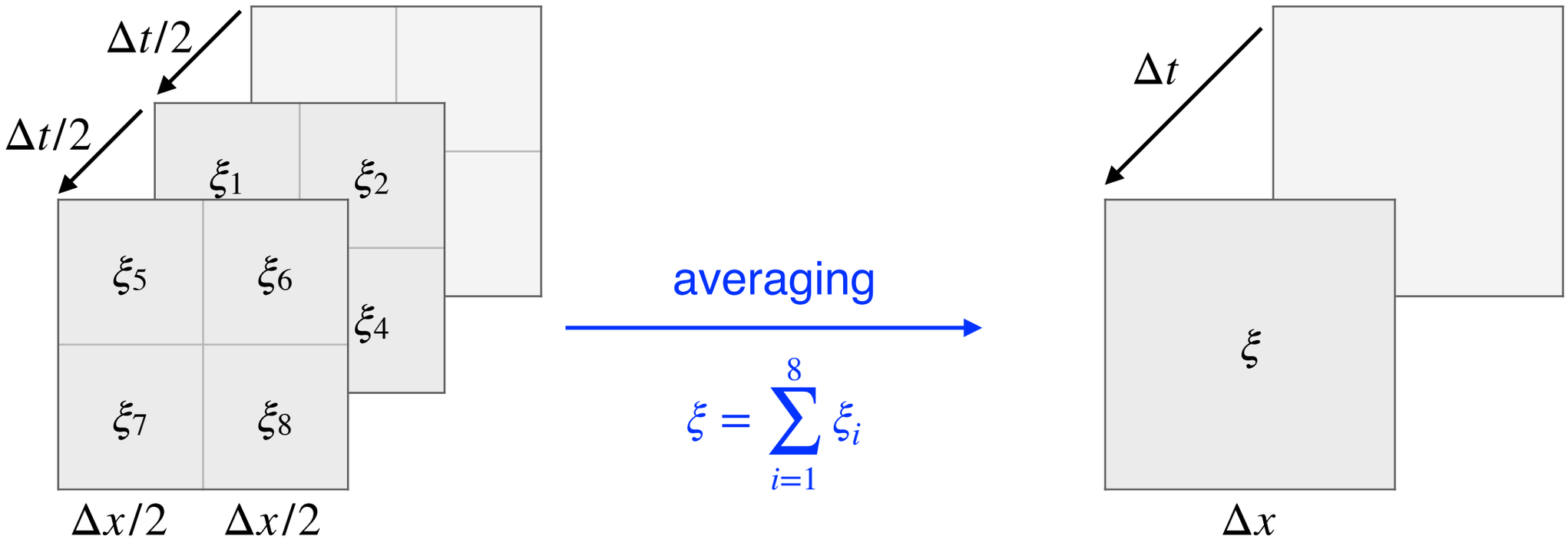
$\sigma \propto \sqrt{\frac{1}{(\Delta x/2)^2}}$ vs. $\sigma \propto \sqrt{\frac{1}{\Delta x^2}}$

Generating Δx and Δt independent noise patterns

This averaging works not only in 2D, and it works with Δt, too

The proposed technique for generating random numbers that provide similar noise patterns independent of Δt and Δx:

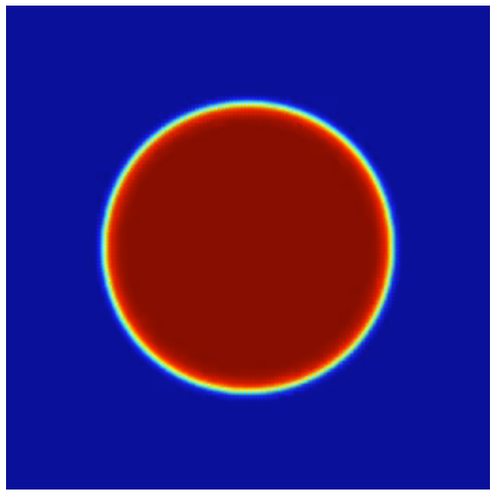
- For reproducibility, fix the RNG seed
- Generate the random numbers for the finest temporal and spatial resolutions
- Obtain the random numbers for the coarser simulations by averaging the random numbers for the finer simulations. They will automatically have the required scaling properties



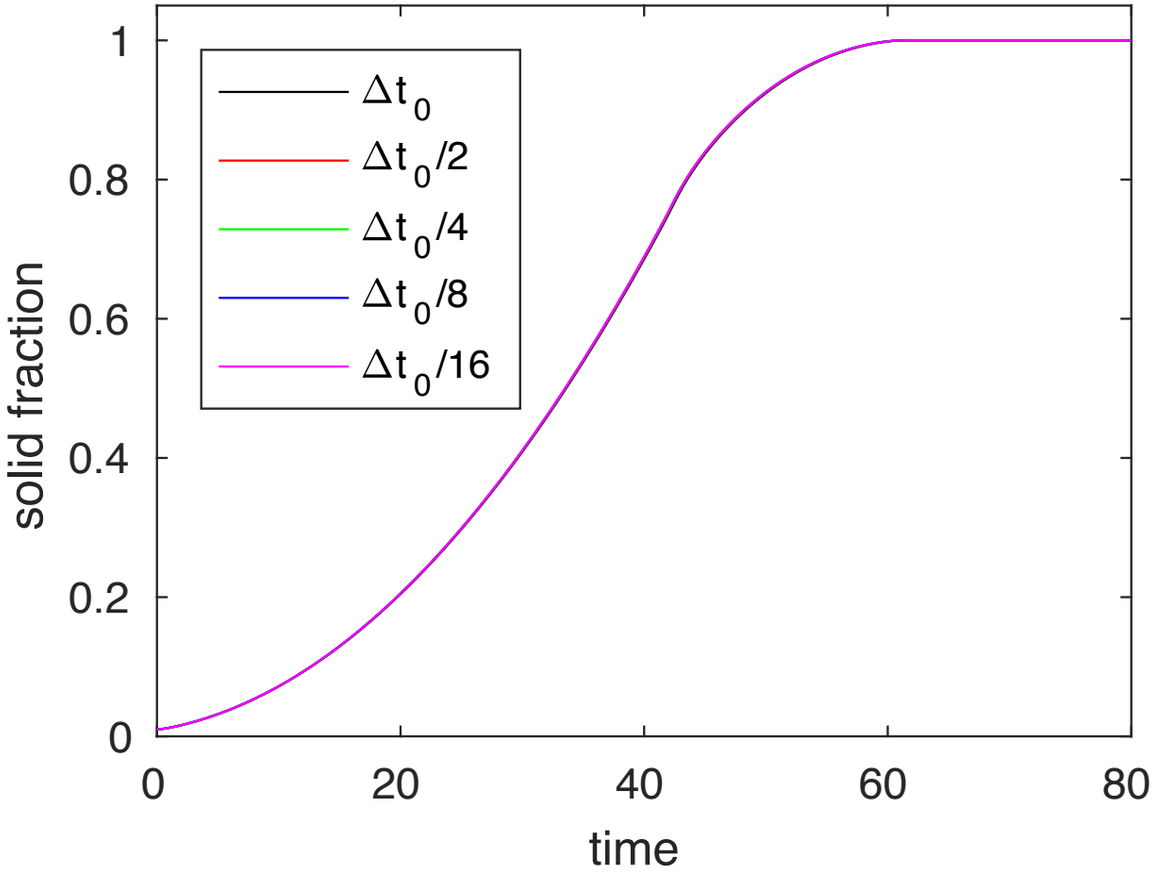
Solid seed growing without noise, convergence

Growth of a spherical seed:

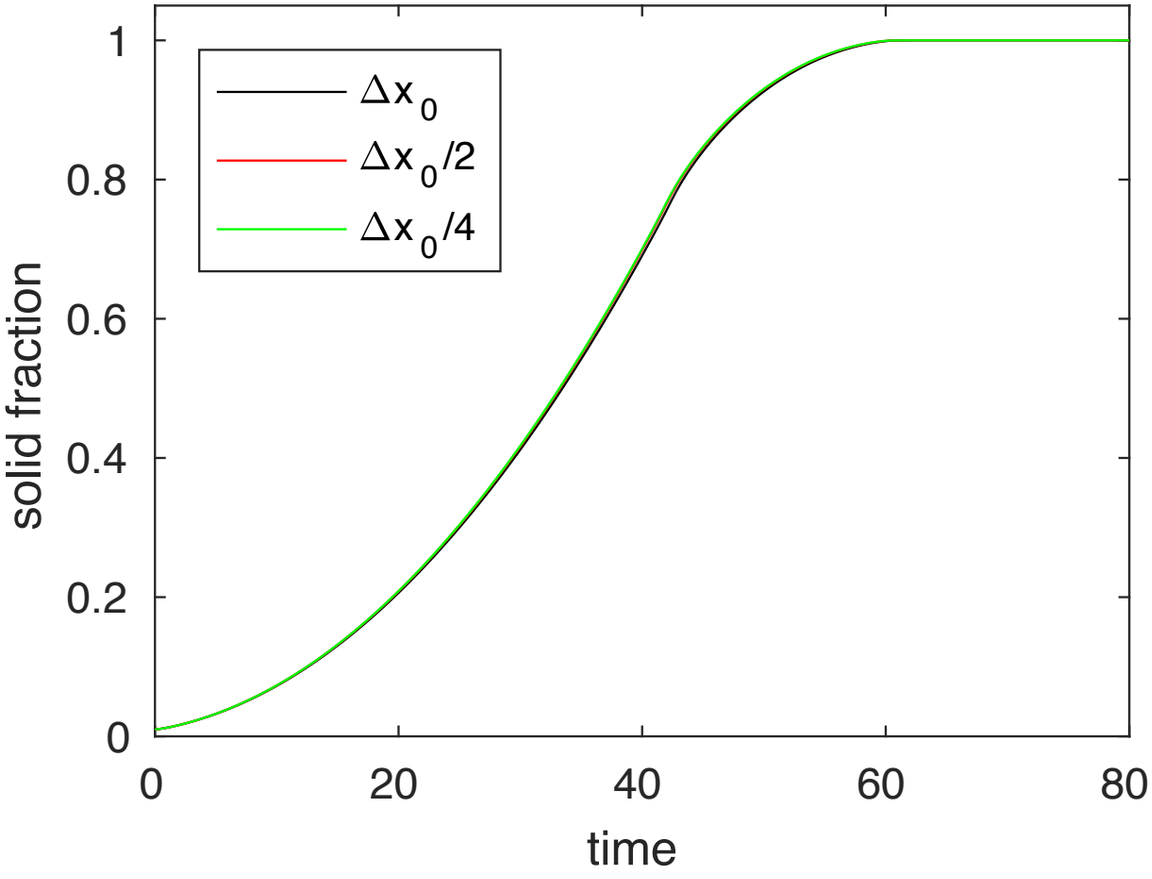
$$\epsilon^2 = W = M = 1$$
$$\Delta f = 0.3,\ r^*_{2D} = 0.79$$



$\Delta x_0 = 0.4,\ \Delta t_0 = 0.01$

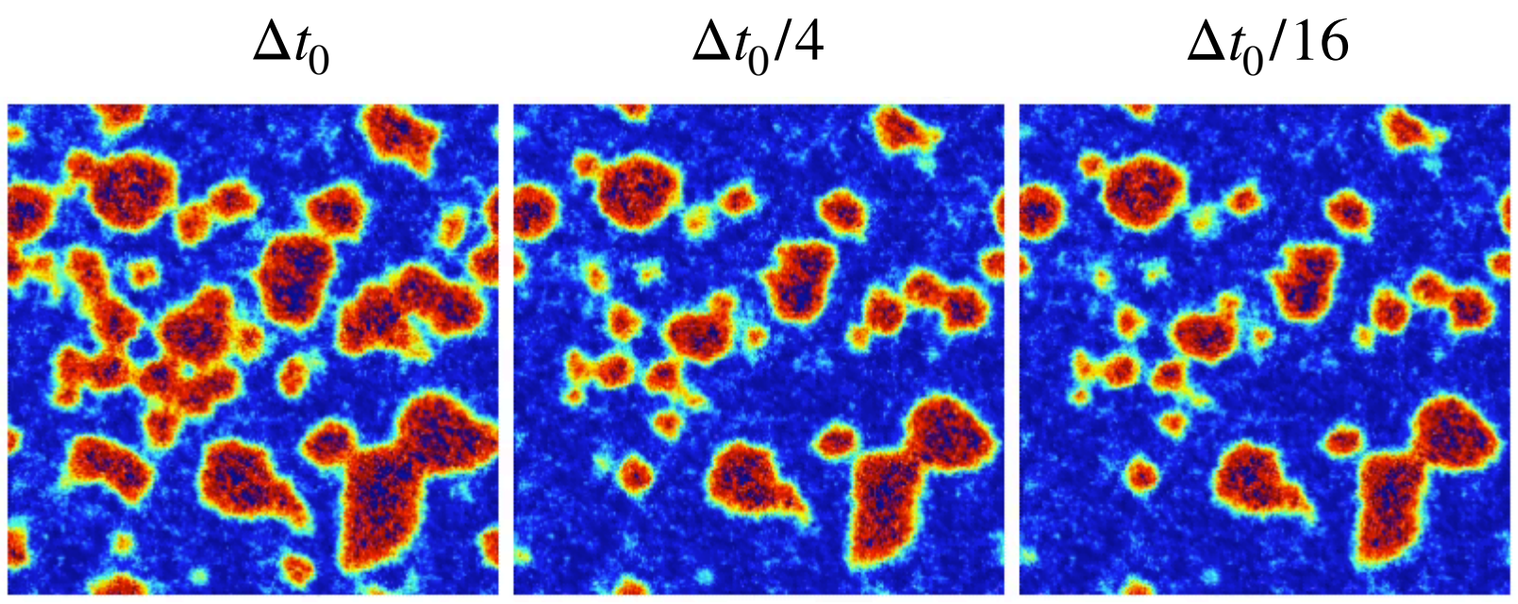


$\Delta x_0 = 0.4,\ \Delta t_0 = 0.01/16$



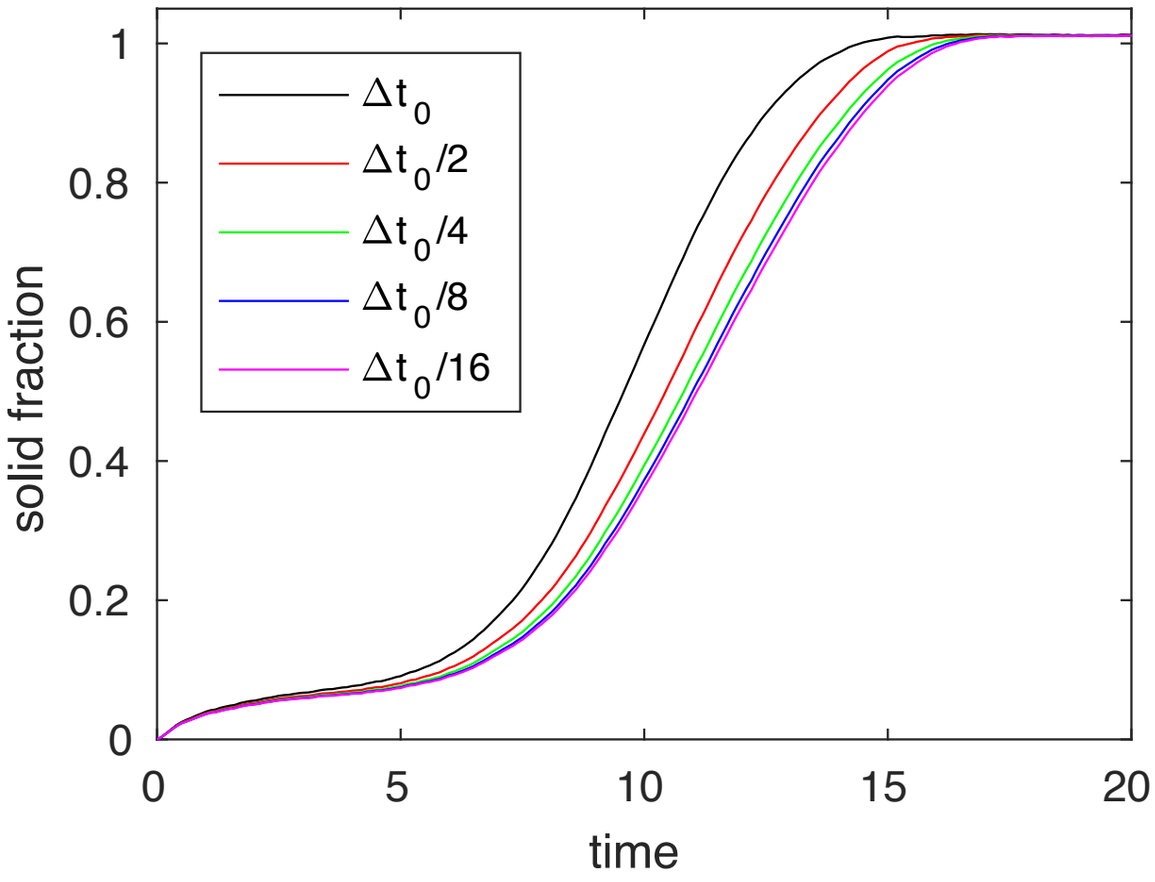
Results are well converged!

Nucleation with noise, convergence with Δt

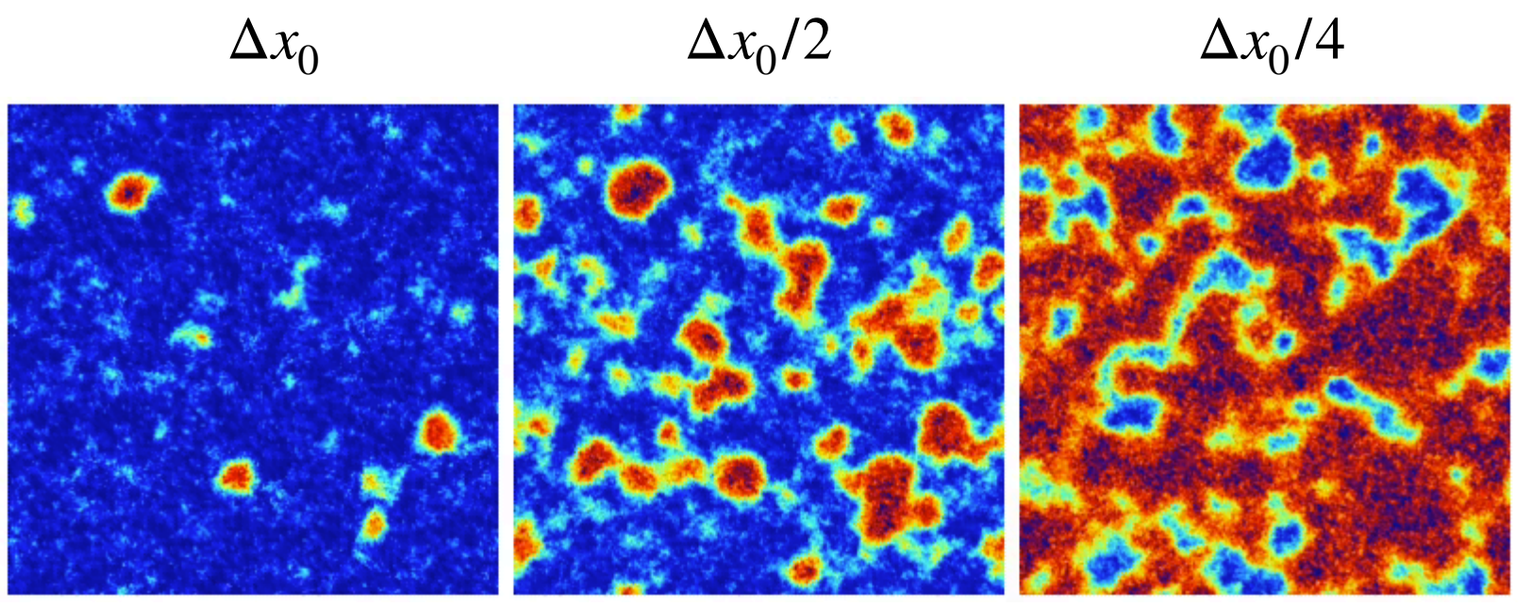


Snapshots from the same simulation time

$$\epsilon^2 = W = M = 1$$
$$\Delta f = 0.3$$
$$\Delta x_0 = 0.4,\ \Delta t_0 = 0.01$$
$$< \xi_0^2 > \ = \frac{0.015}{\Delta x_0^2 \Delta t_0}$$



Nucleation with noise, convergence with Δx



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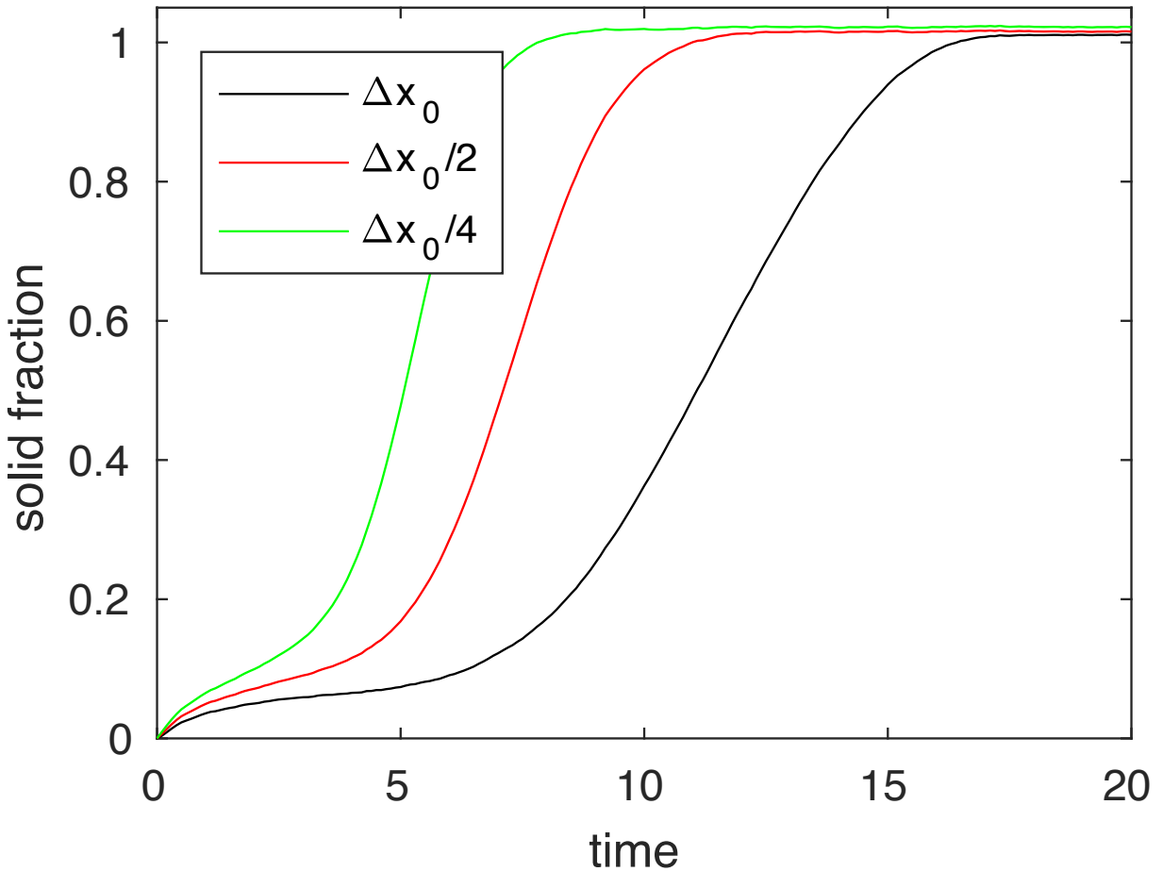
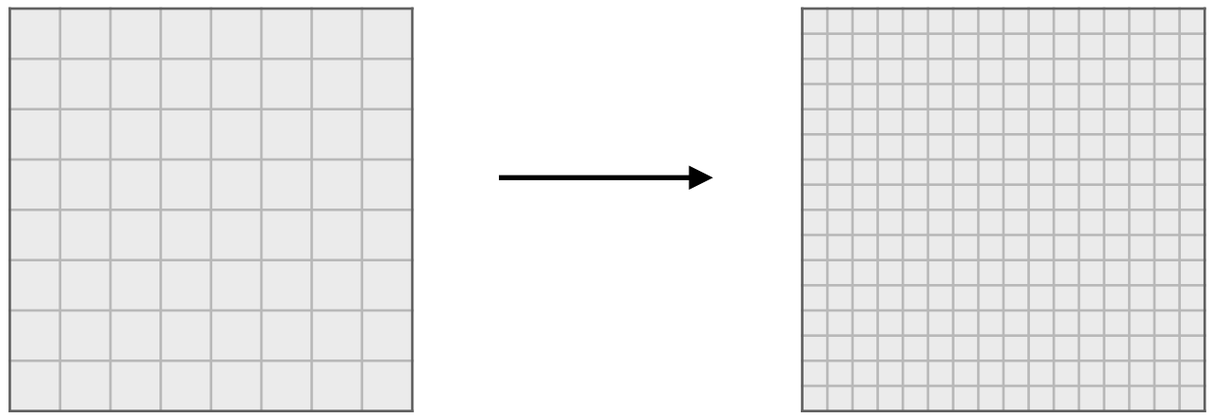


Why no convergence with Δx?

Increasing the spatial resolution when using white noise → new, higher frequencies are added to the system → the energy of the system is changed (increased) → nucleation is highly affected



$L, N, \Delta x_0$ $\qquad$ $L, 2N, \Delta x_0/2$

In fact, for $d \geq 2$ the total energy diverges as $\Delta x \to 0$: ultraviolet divergence

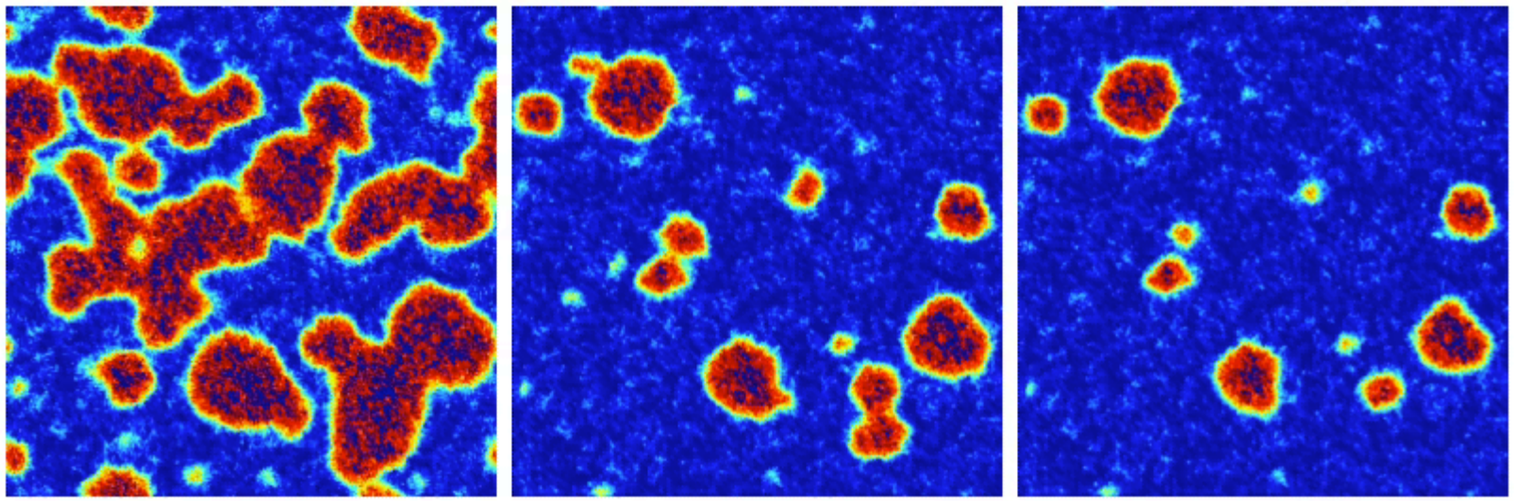
Solution: use a filtered noise with cutoff $\lambda_c > 2\Delta x_0$ before refining the grid

Justification:

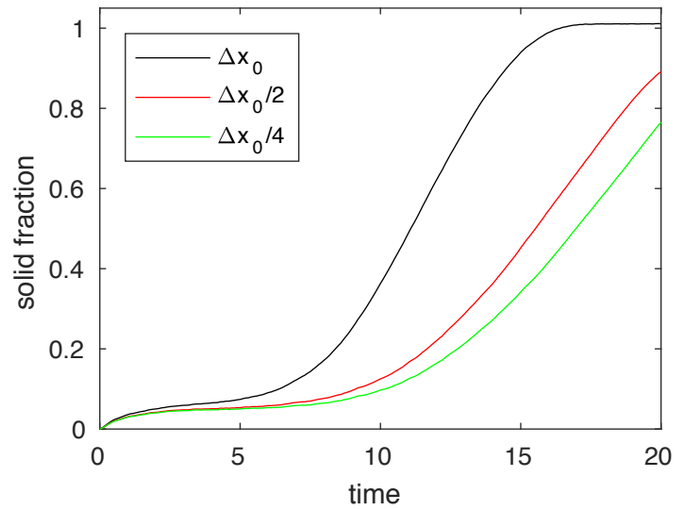
- "Top down" approach: it is just a necessity to have converged solutions, or even just to avoid the ultraviolet divergence
- "Bottom up" approach: coarse graining with length λ → fluctuations below λ are already included in the system → they should not be added again.

Convergence, Δx, filtered noise

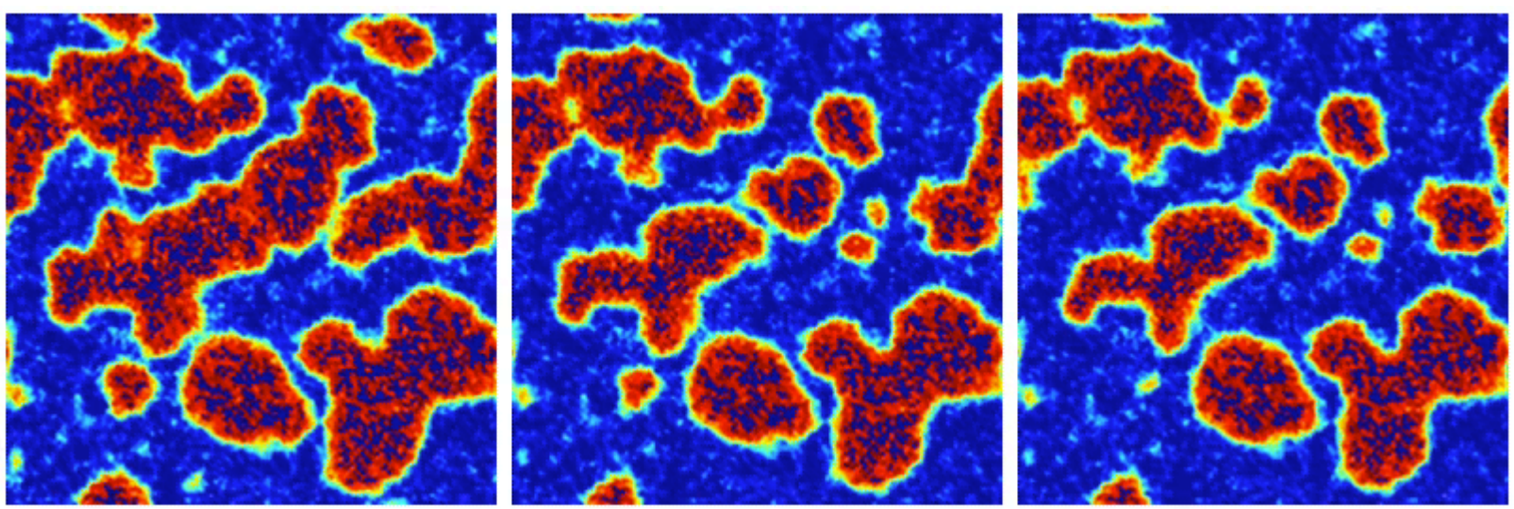
$\lambda_c = 2\Delta x_0$



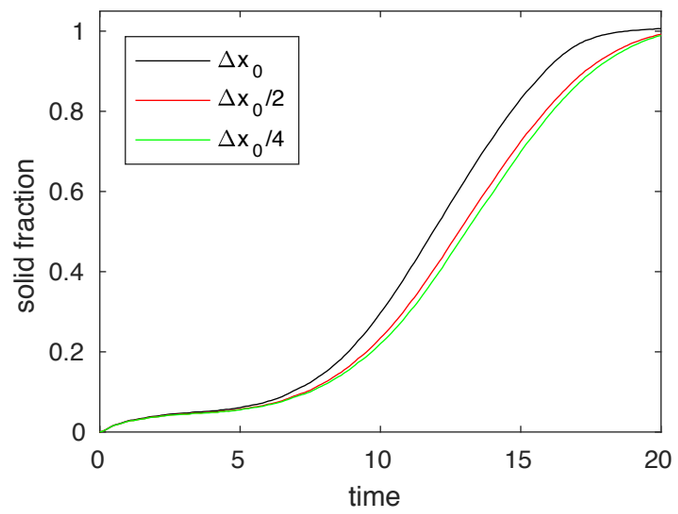
Δx_0 $\Delta x_0/2$ $\Delta x_0/4$



$\lambda_c = 4\Delta x_0$

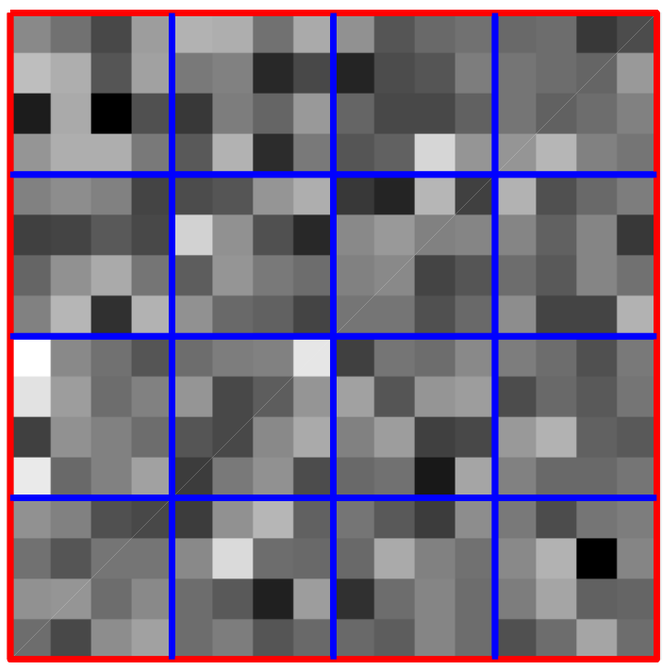


Δx_0 $\Delta x_0/2$ $\Delta x_0/4$

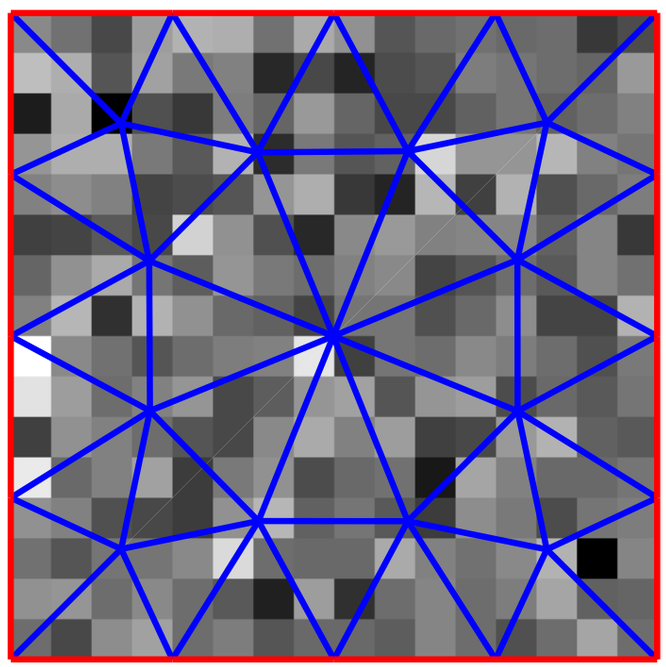


Similar noise patterns in different methods?

Rectangular grid



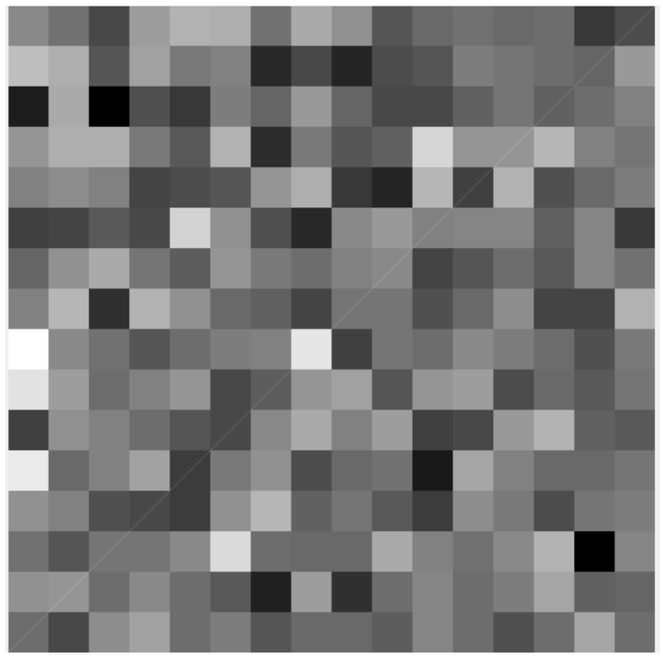
Triangular mesh



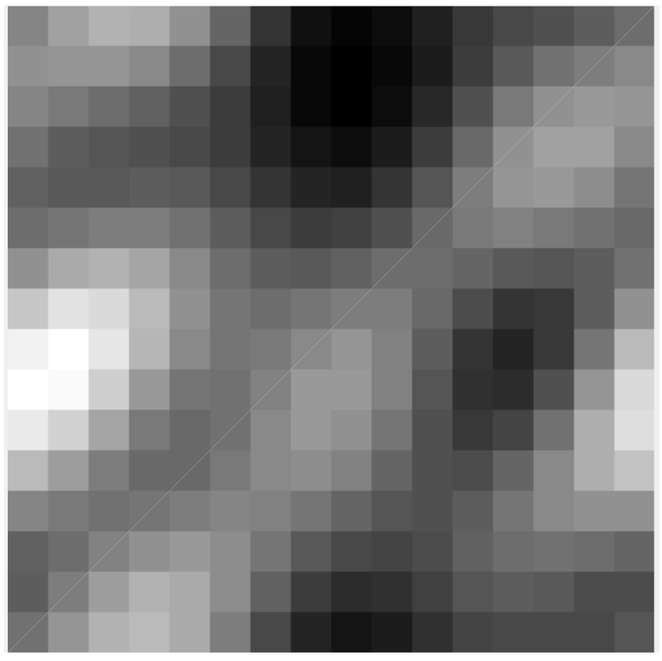
For the correct scaling and similarity, the values corresponding to the centers of the large cells (blue mesh) should be the average of the values corresponding to the underlying noise pattern (gray pixels)

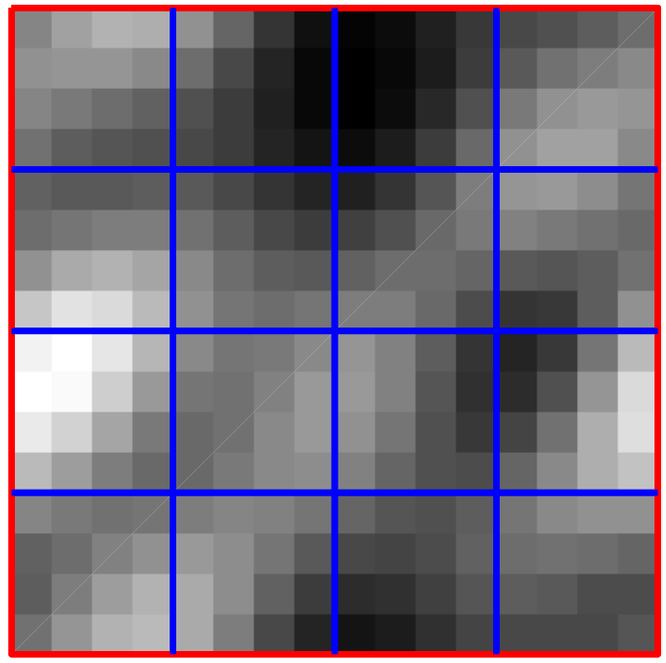
- For rectangular grids: simple mean of the contributing pixel values
- For non-rectangular grids: weighted mean of the contributing pixel values
  - Each pixel must be shared between the larger cells overlapping it according to their overlap area
  - Simplification that may work for fine if the cells are large compared to the noise pixels: each noise pixel is assigned to the cell that contains its center
  - Simple interpolation is not good

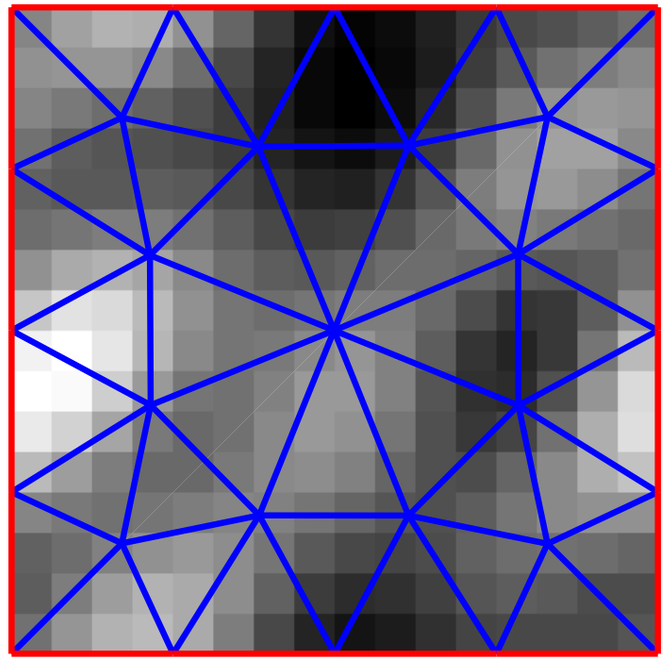
How to use filtered noise with non-regular mesh?



FFT





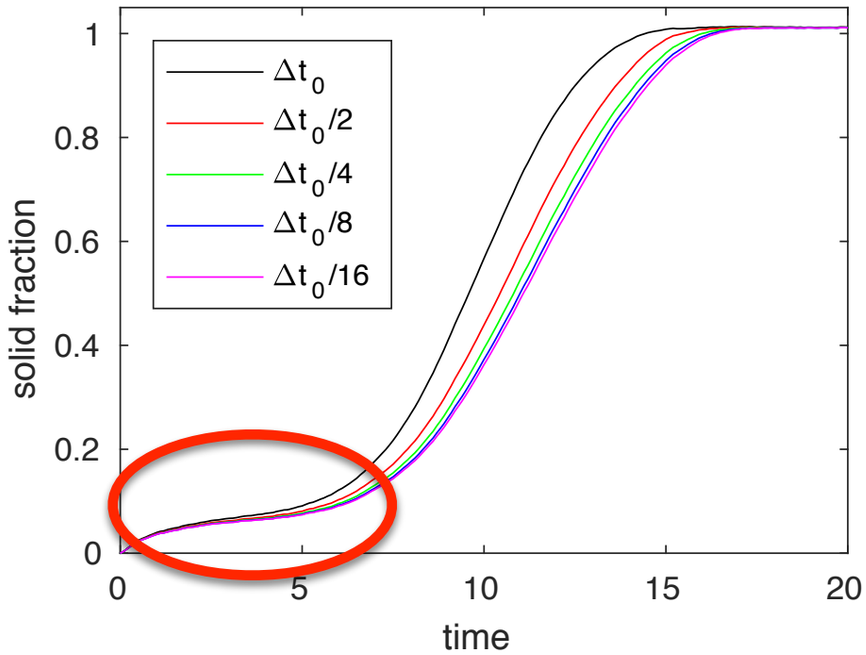


Other issue: the renormalization of F by the noise

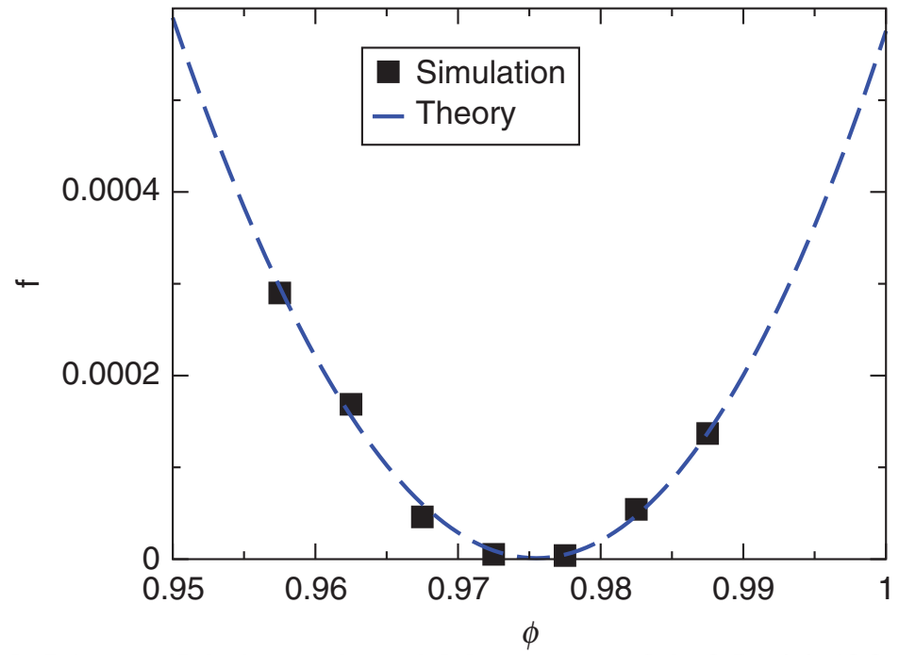
Adding noise renormalizes the phase-field equations.

Consider the double well potential around the minima at ϕ=0,1 → add fluctuations → asymmetric restoring forces → the mean value will be shifted from ϕ=0,1.

Illustration:
my earlier transformation curves



Solution:
Renormalization of the potential



M. Plapp: *Philosophical Magazine*, *91*, 25–44 (2011)

The renormalization is not significant for simulations with large cells (small noise), e.g. in MS instability, dendritic sidebranching, but causes problems with small cells (large noise), e.g. in nucleation:

- The properties of our model are not what we think
- No 1 to 1 correspondence between the two nucleation methods (noise & EL)

Benchmark problems for nucleation by noise

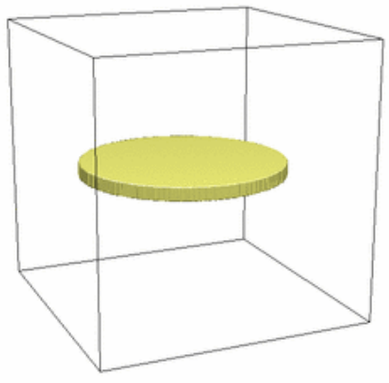
1. Check the model when filtered noise is added (small noise limit)
    1. Obtain the mean value and the standard deviation of ϕ (space and time)
    2. Calculate the free energy of the system, $F[\phi]$, and its standard deviation (time)

        The results should not depend on the mesh

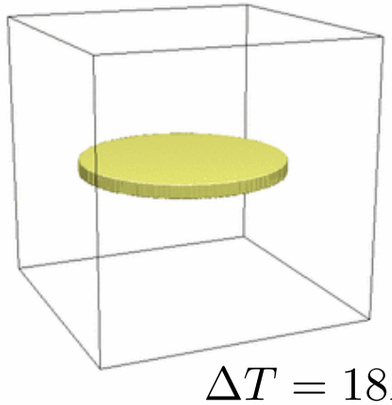
2. Nucletion by noise (increase the noise amplitude)
    1. Calculate the solid fraction, determine the Avrami exponent
    2. Number of particles vs. time? (not easy) → nucleation rate

Possible variants

1. Nucleation events only at $t = 0$ ($n = d + 1 \rightarrow n = d$ in the Avrami exponent)
2. Non-constant nucleation rate
    1. Temperature gradient
    2. Cooling
3. Heterogeneous nucleation
    1. Nucleation events only on the surfaces
    2. Boundary conditions? Suggestion: Model A and B, see later
4. Athermal nucleation by Greer
    1. Virtual inoculant particles at random places, free growth starts if driving force is supercritical
    2. True inoculant particles at random places, nucleation and the formation of dormant embryos happens automatically. Free growth should also be automatic if $\Delta f > \Delta f_{crit}(R)$. Check?



$\Delta T = 17K$



$\Delta T = 18K$

Nucleation by solving the Euler-Lagrange equations

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

Simple binary PF model with no $(\nabla c)^2$ term

The Euler-Lagrange equations:

$$\frac{\delta F}{\delta \phi} = \frac{\partial f}{\partial \phi} - \epsilon^2 \nabla^2 \phi = 0$$

nonlinear elliptic PDE

$$\frac{\delta F}{\delta c} = \nabla M_c \nabla \frac{\partial f}{\partial c} = 0 \quad \rightarrow \quad \frac{\partial f}{\partial c} = \mu(\phi, c) = \text{const} = \mu_0$$

scalar equation

If $\mu(\phi, c)$ is a simple function, then $c(\phi)$ can be obtained and plugged back into the first ELE

The binary problem is reduced to the single phase-field problem

↓

Further simplification: the spatial dimensions of the problem can be reduced if spherical or cylindrical symmetry can be assumed

↓

Solution methods: relaxation methods, shooting methods, etc.

$$\phi(\vec{r}) \rightarrow c(\phi(\vec{r})) \rightarrow W^* = F[\phi(\vec{r}), c(\phi(\vec{r}))]$$

This is also a candidate for a benchmark poroblem: determine $\phi(\boldsymbol{r})$ and W^*

Phase field modeling of surfaces

surface = boundary of the simulation domain → surface properties = boundary conditions

Free energy functional including the $Z(\phi)$ surface function:
(Cahn JCP 1977)

$$F[\phi(\mathbf{r}), c(\mathbf{r})] = \int \left[f(\phi, c) + \frac{\epsilon^2}{2} (\nabla \phi)^2 \right] \mathrm{d}V + \int Z(\phi)\, \mathrm{d}S$$

At the extremum by $\phi(\mathbf{r})$ and $c(\mathbf{r})$, the variation of F should disappear for any infinitesimally $\rho(\mathbf{r})$ and $\chi(\mathbf{r})$ compatible with the boundary conditions:

$$\delta F = F[\phi(\mathbf{r}) + \rho(\mathbf{r}), c(\mathbf{r}) + \chi(\mathbf{r})] - F[\phi(\mathbf{r}), c(\mathbf{r})] = 0$$

This leads to the Euler-Lagrange equations

$$\frac{\partial f(\phi, c)}{\partial \phi} - \epsilon^2 \nabla^2 \phi = 0$$

$$\frac{\partial f(\phi, c)}{\partial c} = \mu$$

in the volume

$$\left[Z'(\phi) - \epsilon^2 \nabla \phi \cdot \mathbf{n} \right] = 0$$

on the surface

Cases:

- $\phi(\mathbf{r})$ is fixed along the boundary:

  $\rho(\mathbf{r}) \equiv 0$ on the surface, so the surface EL eq. holds

- $\phi(\mathbf{r})$ is not fixed along the boundary:

  the first part of the surface EL eq. gives the b.c. to use

J.A. Warren et al. Phase field approach to heterogeneous crystal nucleation in alloys. Physical Review B, 79, 014204 (2009)

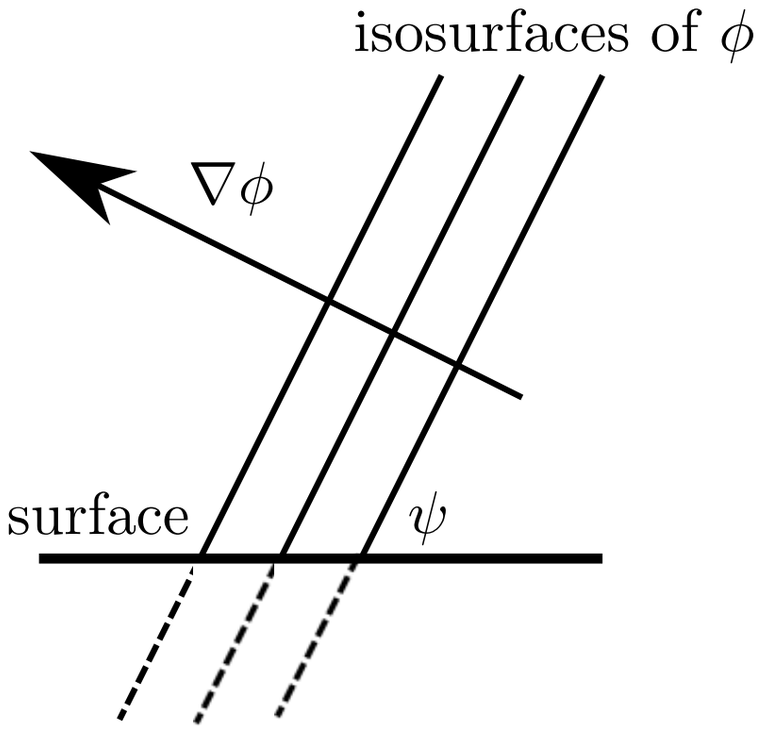
Model A

(not according to the Hohenberg-Halperin classification!!!)

Goal: direct realization of the ψ contact angle

(L. Gránásy)

$$\nabla\phi \cdot \mathbf{n} = \sqrt{\frac{2w}{\epsilon^2}}\,\phi(1-\phi)\cos(\psi)$$



We need $Z(\phi)$ to calculate the free energy of the system

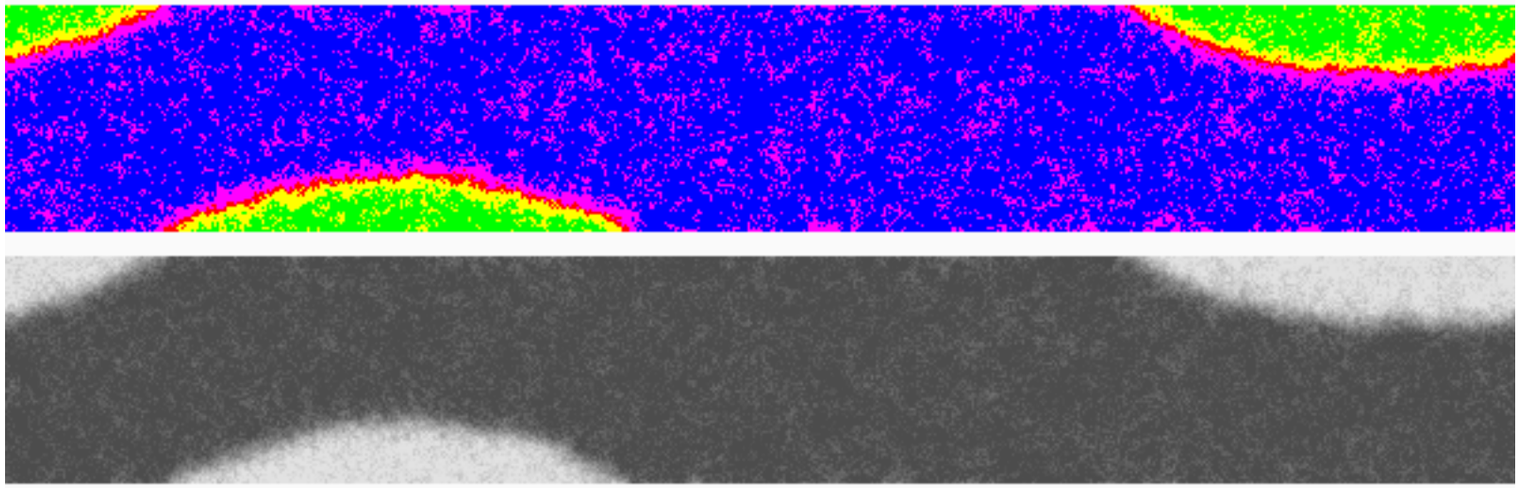
$$Z'(\phi) = -\epsilon^2\nabla\phi \cdot \mathbf{n} = -6\gamma_{SL}\phi(1-\phi)\cos(\psi)$$
$$Z(\phi) = -\gamma_{SL}(3\phi^2 - 2\phi^3)\cos(\psi)$$

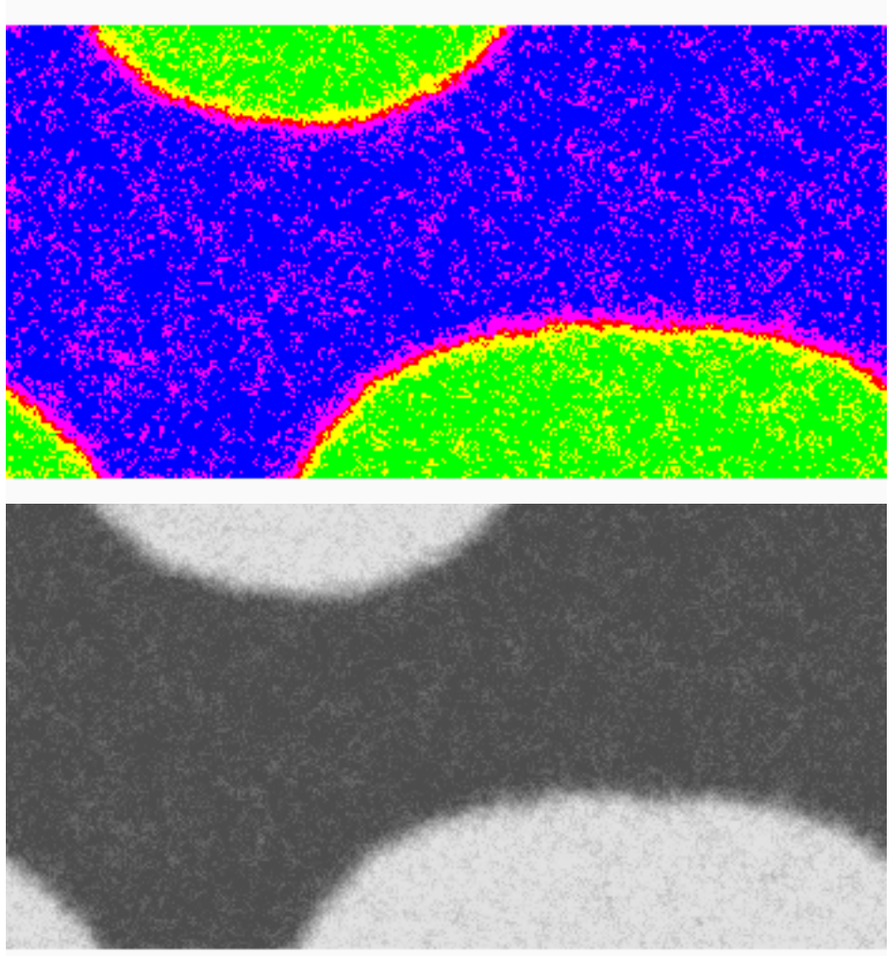
Model A

Ni:

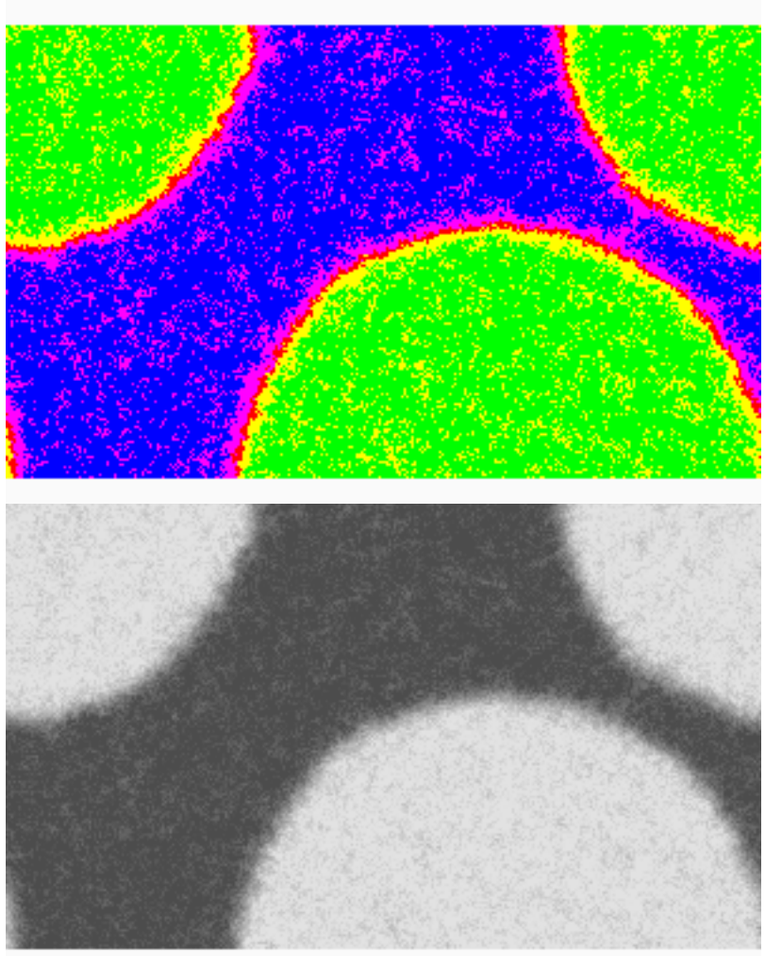
- d10-90% = 2 nm
- γ = 364 mJ/m2
- Δx = 2Å (1 pixel ~ 1 atom)
- fluctuation-dissipation noise
- thermal feedback

$\psi = 45°$

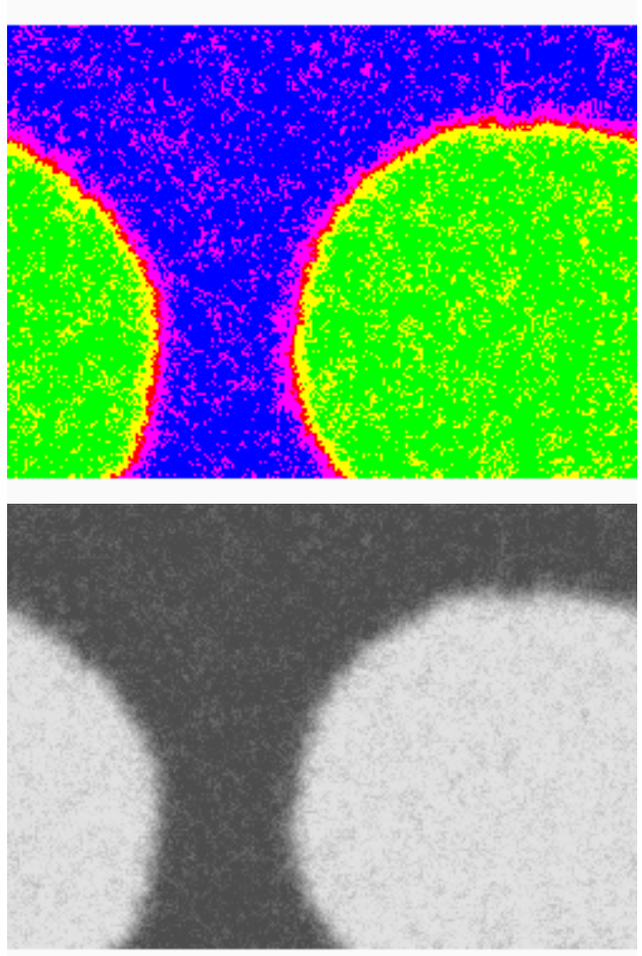




$\psi = 60°$



$\psi = 90°$

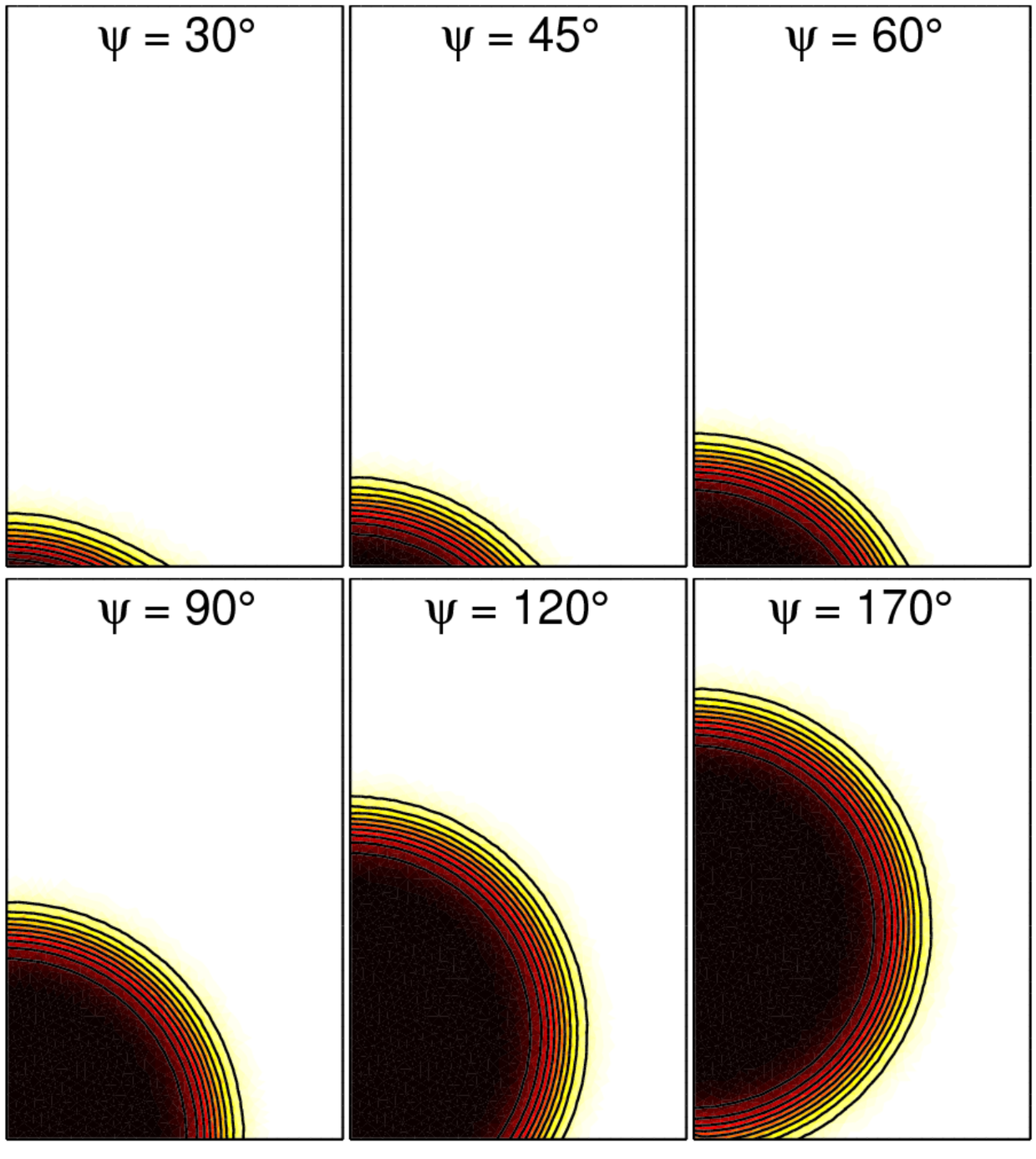


$\psi = 120°$

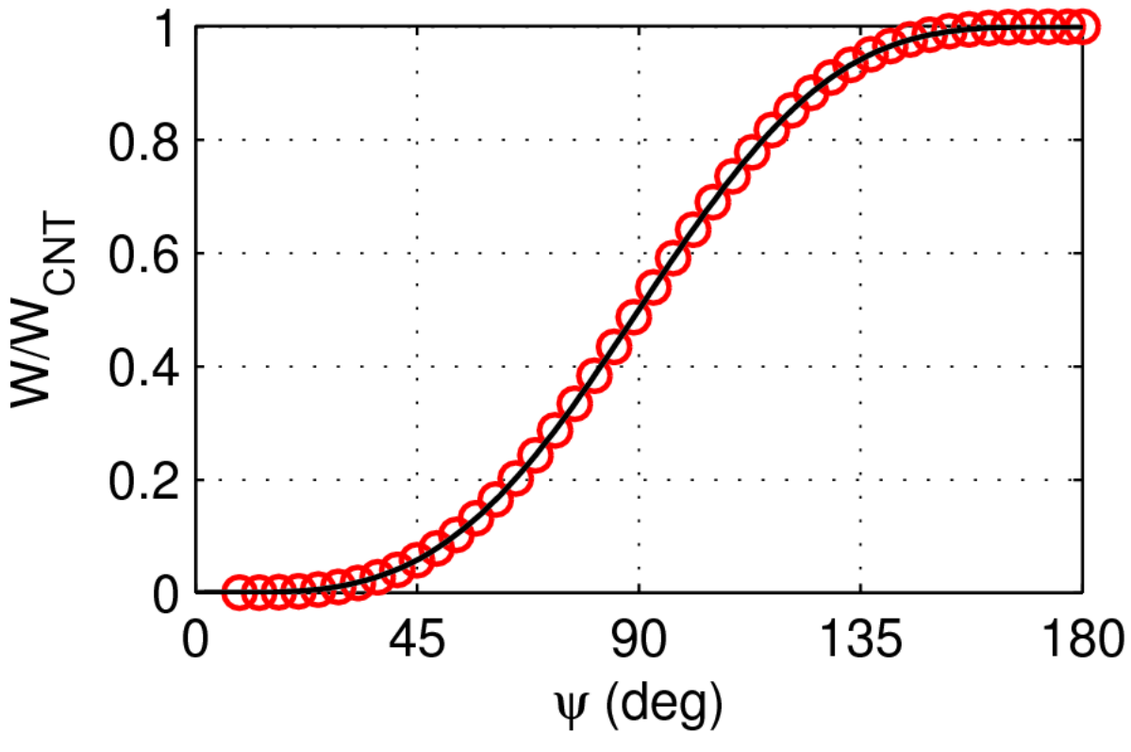
László Gránásy

Model A

Solving the PDEs in cylindrical coordinate system (Matlab PDE toolbox)



The work of formation compared to the classical theory



Model B

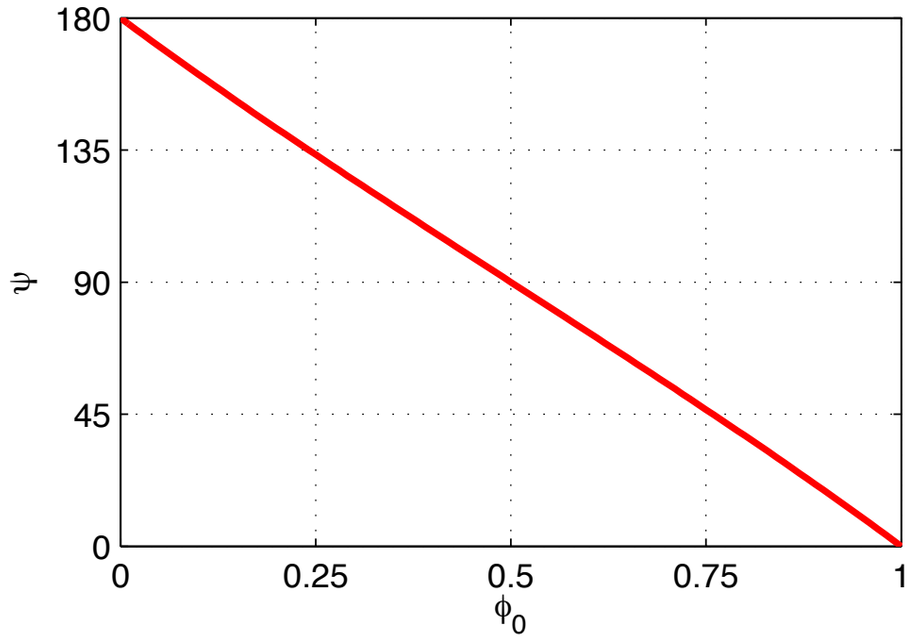
Constant ϕ=ϕ_0 at the interface (Dirichlet b.c.)

(J. Warren)

Obtaining the ψ contact angle via Young's law:

$$\gamma_{\mathrm{wl}} = \sqrt{2\epsilon^2 w} \int_0^{\phi_0} \phi^2(1-\phi)^2 = \gamma_{\mathrm{sl}}(3\phi_0^2 - 2\phi_0^3)$$

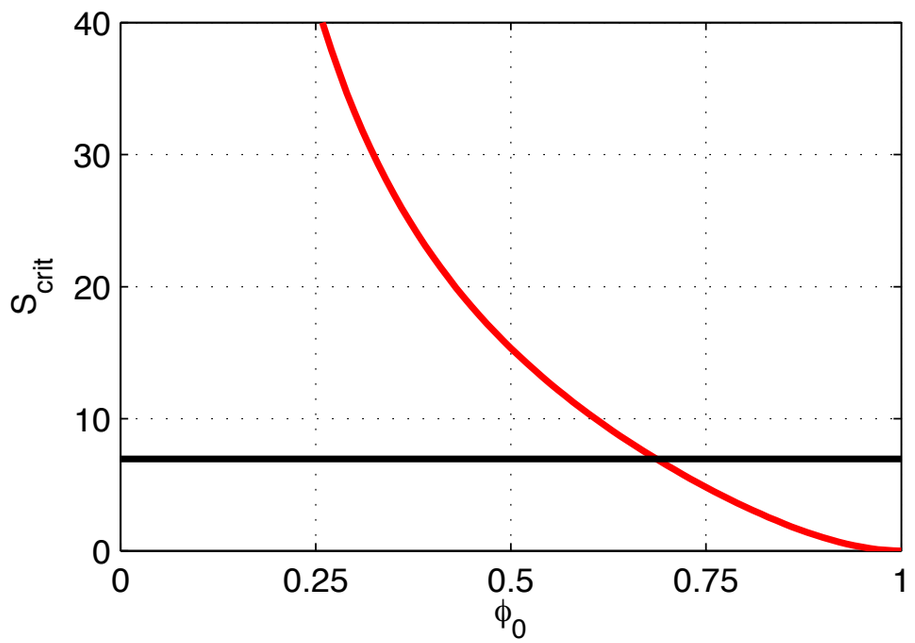
$$\gamma_{\mathrm{ws}} = \sqrt{2\epsilon^2 w} \int_{\phi_0}^{1} \phi^2(1-\phi)^2 = \gamma_{\mathrm{sl}}(1 - 3\phi_0^2 + 2\phi_0^3)$$



$$\cos(\psi) = \frac{\gamma_{wl} - \gamma_{ws}}{\gamma_{sl}} = 2\phi_0^2(3 - 2\phi_0) - 1$$

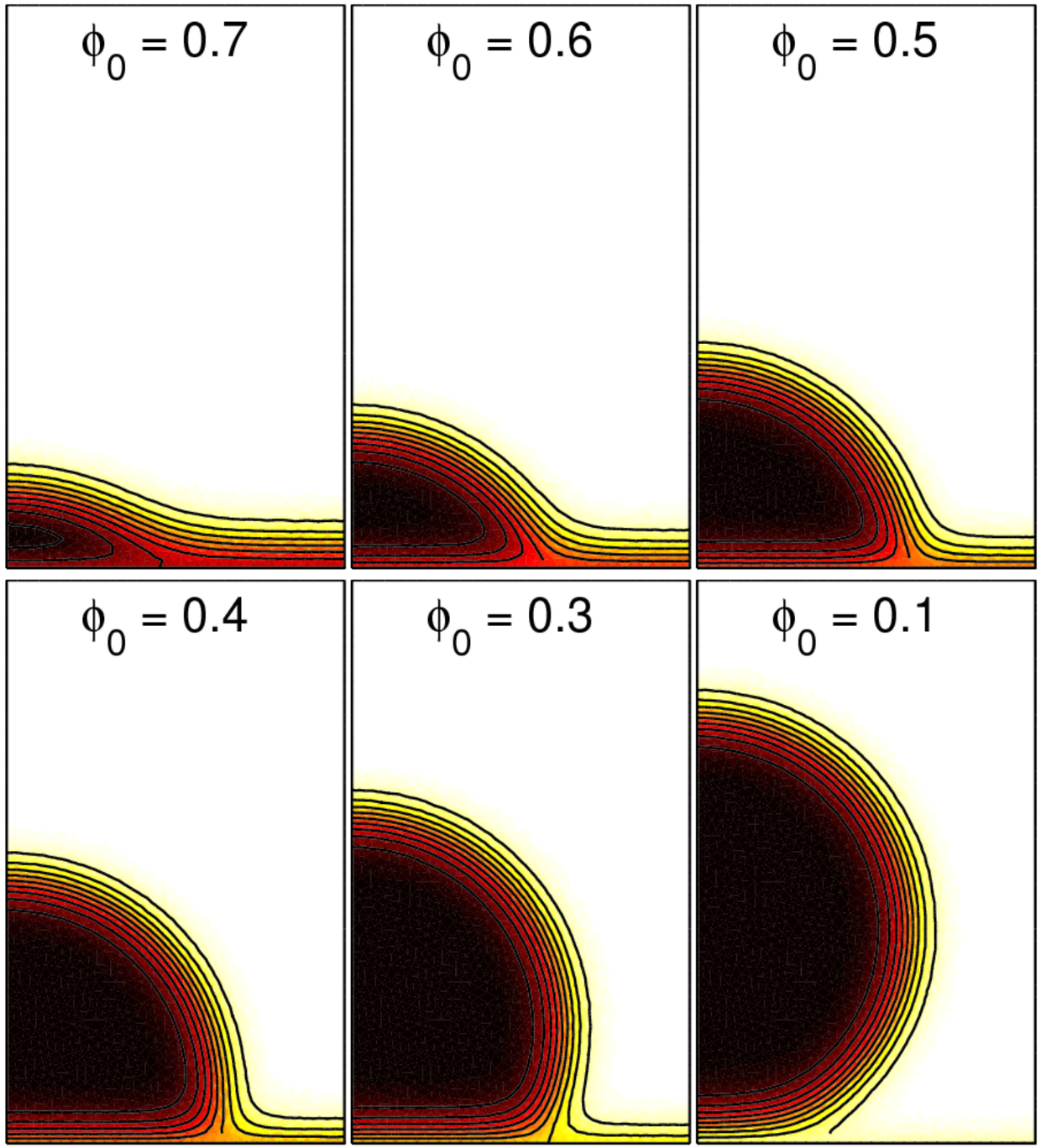
Setting ϕ=ϕ_0 at the interface: wetting layer

There exist a critical value of ϕ, below which the interface can grow freely

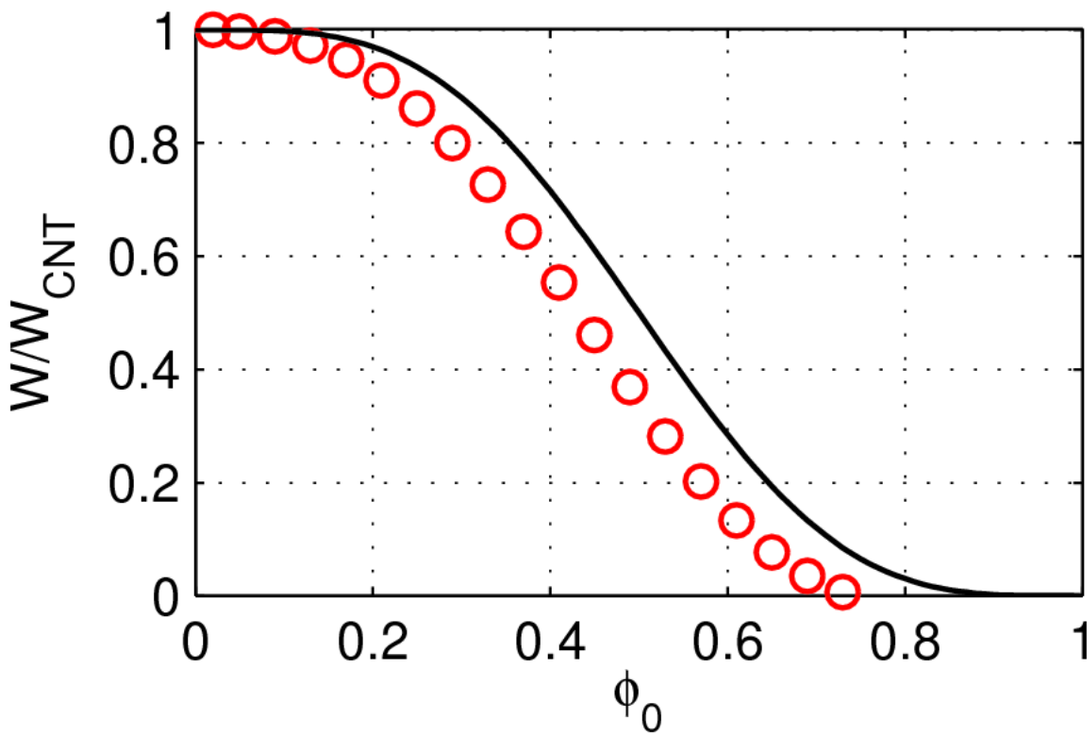


Model B

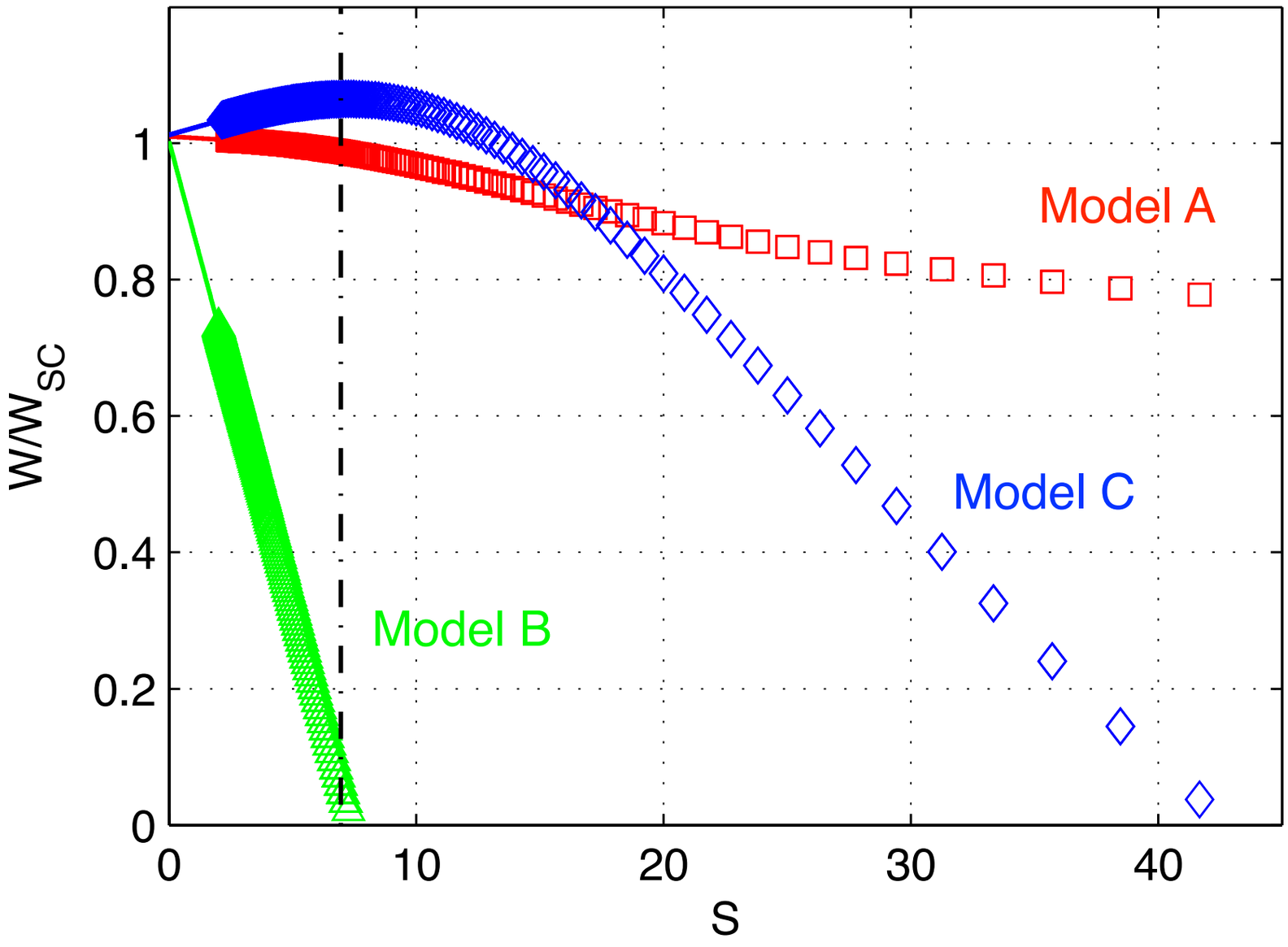
Solving the PDEs in cylindrical coordinate system



The work of formation compared to the classical theory



Comparison of Models A, B and C



All 3 models are in agreement with the classical nucleation theory the in the $R \to \infty$ limit

Summary

Benchmark problems proposed:

Simulating the time evolution of the process

1. Insert nuclei at random places at random times (large scale view)
    1. Homogeneous / heterogeneous
2. Add fluctuations and wait (small scale view)
    1. Homogeneous / heterogeneous (with appropriate boundary conditions)
3. Athermal nucleation by Greer
    1. Use the model to justify a non-stochastic “nucleation”
    2. Simulate the whole process (heterogeneous nucleation + growth barrier)

Determining the equilibrium configuration of the nucleus

1. Solve the respective Euler-Lagrange equations to obtain the saddle point solutions
    1. Homogeneous / heterogeneous / athermal nucleation