NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch. 10. Mesoscopic Nucleation Theory

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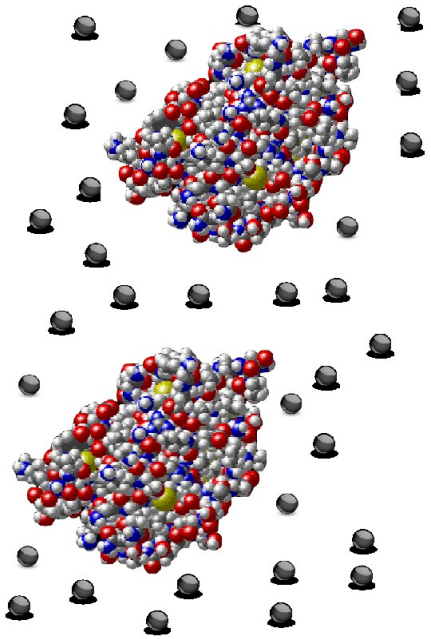
Lecture 12, 2019-2020

Recap: the basic ideas



Fluctuating hydrodynamics + the over-damped limit:

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} = \underbrace{\gamma k_B T \nabla\cdot\rho(\boldsymbol{r},t)\nabla\frac{\delta\beta F}{\delta\rho(\boldsymbol{r},t)}}_{\text{deterministic}} - \underbrace{\nabla\cdot\sqrt{2\gamma k_B T \rho(\boldsymbol{r},t)}\,\xi}_{\text{fluctuating}}$$

"Dean-Kawasaki model"

$F[\rho] \Leftrightarrow$ Microscopic DFT model

Path probability in weak noise limit is given by:

$$P(x(0),x(T)) = \exp\left(-\frac{1}{2}\epsilon^{-2}\int_0^T \left(\frac{dx^i}{dt} + g^{ij}\frac{\partial F}{\partial x^j}\right) g_{jk}\left(\frac{dx^k}{dt} + g^{kl}\frac{\partial F}{\partial x^l}\right) dt\right)$$

… and we use this to determine the ***Most Likely Path*** (MLP) for nucleation

- We can easily prove that

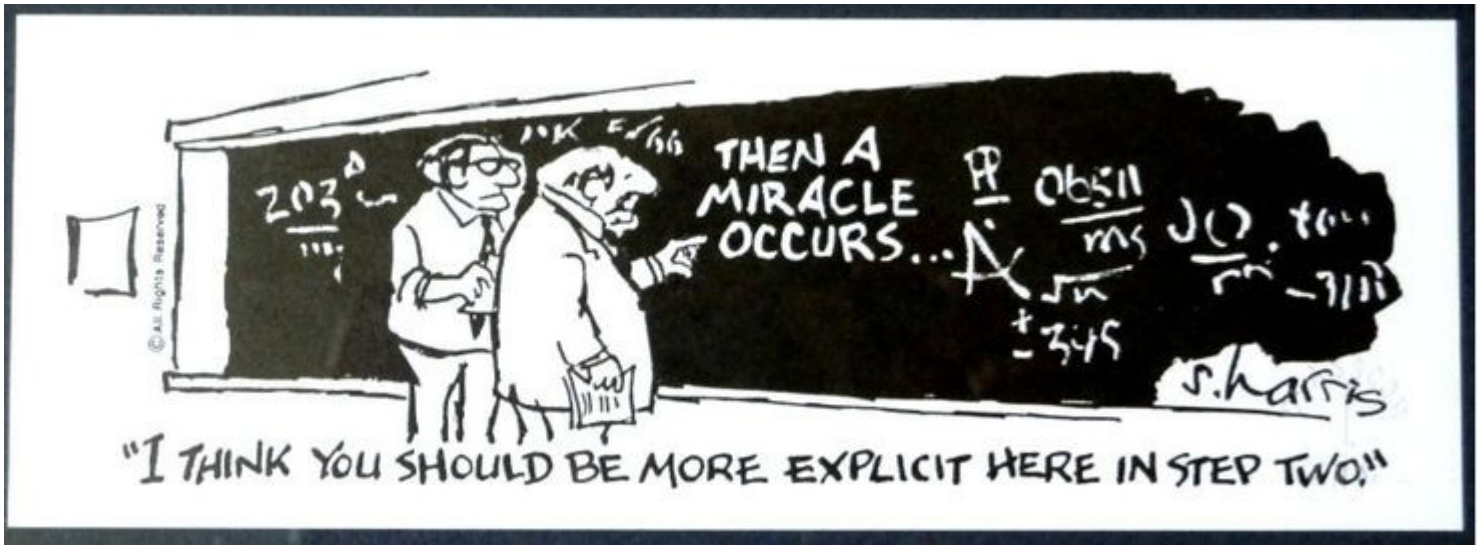
  1) the MLP passes through the saddle point <==> (critical cluster)

  2) the MLP is determined by gradient descent from critical point

  with specific ***metric***: $\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} = \pm\gamma k_B T \nabla\cdot\rho(\boldsymbol{r},t)\nabla\frac{\delta\beta F}{\delta\rho(\boldsymbol{r},t)}$

<u>These tools allow us to investigate nucleation pathways and to therefore access non-classical nucleation.</u>

Microscale to macroscale: recovering CNT



Bridging length scales: Order Parameters

Reduced description in terms of one or more order parameters

$$\rho(r,t)=\rho(r;x^1(t),x^2(t),\ldots)=\rho(r;\boldsymbol{x}(t))$$

$$\frac{dx^i}{dt}=-D\sum_j g^{ij}(\boldsymbol{x}(t))\frac{\partial \beta F(\boldsymbol{x}(t))}{\partial x^j(t)}+\frac{1}{\sqrt{det\, g}}\frac{\partial g^{ij}\sqrt{det\, g}}{\partial x^j}+\sqrt{2D}\sum_a \underbrace{q^{ia}(\boldsymbol{x}(t))}_{\boldsymbol{q}\boldsymbol{q}=\boldsymbol{g}}\ \underbrace{\xi_a(t)}_{\text{white noise}}$$

"Kinetic coefficients"

State-dependent noise
(Stratonovich interpretation)

with

$$F[\rho]\rightarrow F(\boldsymbol{x}) \qquad m(r;x)=\int_0^r 4\pi r'^2\rho(r';\boldsymbol{x})\,dr'$$

$$g_{ij}(\boldsymbol{x})=\int \frac{1}{4\pi r^2\rho(r;\boldsymbol{x})}\frac{\partial m(r;\boldsymbol{x})}{\partial x^i}\frac{\partial m(r;\boldsymbol{x})}{\partial x^j}dr$$

$$g^{ij}g_{jk}=\delta^i_k$$

Bridging length scales: Order Parameters

$$\frac{dx_i}{dt} = -D\sum_j g_{ij}^{-1}(\boldsymbol{x}(t))\frac{\partial \beta F(\boldsymbol{x}(t))}{\partial x_j(t)} + \frac{1}{\sqrt{det\, g}}\frac{\partial\, g_{ij}^{-1}\sqrt{det\, g}}{\partial x_j}$$

$$+\sqrt{2D}\sum_j \underbrace{q_{ij}^{-1}(\boldsymbol{x}(t))}_{\boldsymbol{qq=g}}\ \underbrace{\xi_j(t)}_{\text{white noise}}$$

Fokker-Planck Equation

$$\frac{\partial}{\partial t}P(\boldsymbol{x},t) = -D\frac{\partial}{\partial x^i}\left(-g^{ij}(\boldsymbol{x})\frac{\partial \beta F}{\partial x^j} - g^{ij}\sqrt{det\, g}\,\frac{\partial}{\partial x^j}\frac{1}{\sqrt{det\, g}}\right)P(\boldsymbol{x},t)$$

Equilibrium: $P_{eq}(\boldsymbol{x}) = N\sqrt{det\, g(\boldsymbol{x})}\, e^{-\beta F(\boldsymbol{x})}$

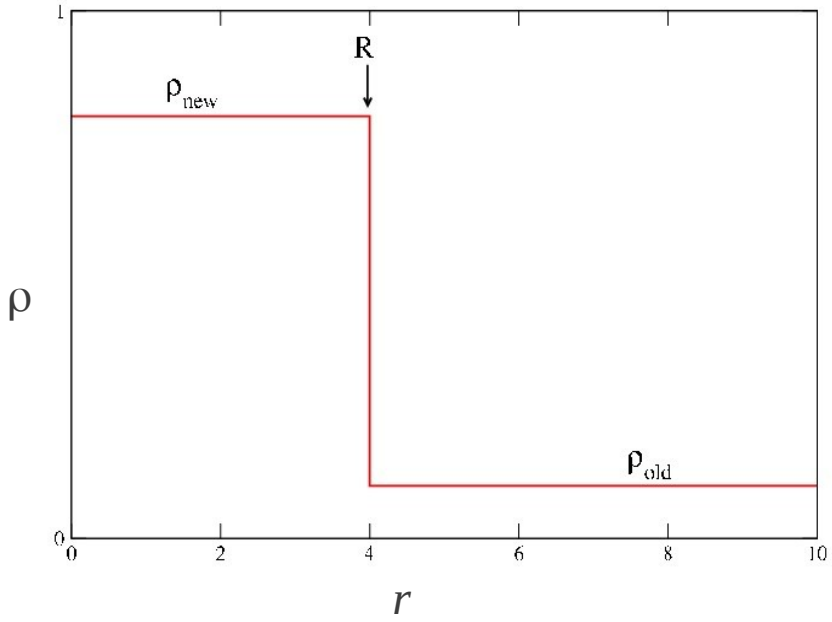
Covariance: $P_{eq}(\boldsymbol{y}) = N\sqrt{det\, g(\boldsymbol{y})}\, e^{-\beta F(\boldsymbol{y})}$

Clarifies ambiguity in CNT: $P_{eq} = Ne^{-\beta F(R)}$ or $P_{eq} = Ne^{-\beta F(N)}$?

Mesoscopic Nucleation Theory

- Motivation
- CNT
- Improving CNT: The energy
- Improving CNT: Dynamics
  - Fluctuating Hydrodynamics & overdamped approx.
  - Transition Paths
- Droplet nucleation
- Crystallization

One order parameter: Classical Nucleation Theory



$$\rho(r;R)=\rho_{new}\Theta(R-r)+\rho_{old}\Theta(r-R)$$

$$F(R)=V(R)f(\rho_{new})+S(R)\gamma_{coex}$$

$$V(R)\equiv\frac{4\pi}{3}R^3$$

$$S(R)\equiv 4\pi R^2$$

$$g_{RR}=\frac{(\rho_{new}-\rho_{old})^2}{\rho_{old}}4\pi R^3$$

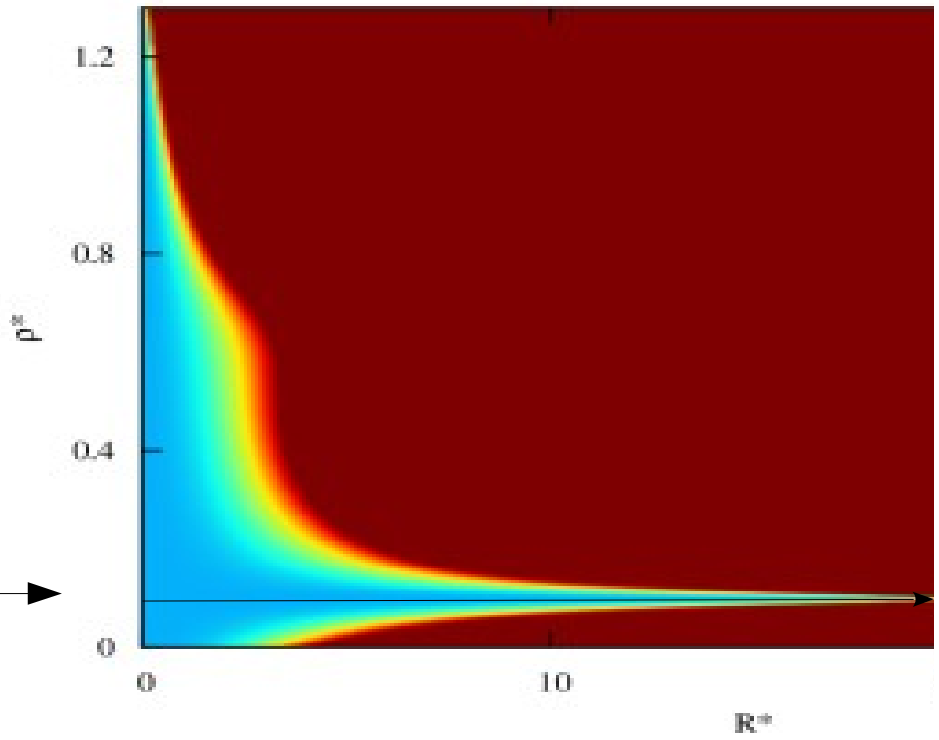
Fokker-Planck Equation

$$\frac{\partial}{\partial t}P(R,t)=D\frac{\partial}{\partial R}\left(g_{RR}^{-1}\frac{\partial\beta F}{\partial R}+g_{RR}^{-1/2}\frac{\partial}{\partial R}g_{RR}^{-1/2}\right)P(R,t)$$

$R\to\infty$ ⟶ Zeldovich equation ⟹ CNT

Two order parameters: density and size of cluster

Free energy landscape



Vapor density

Most probable: $|\rho_0 - \rho_{old}| \ll \rho_{old}$

$R \ll R_{max}$

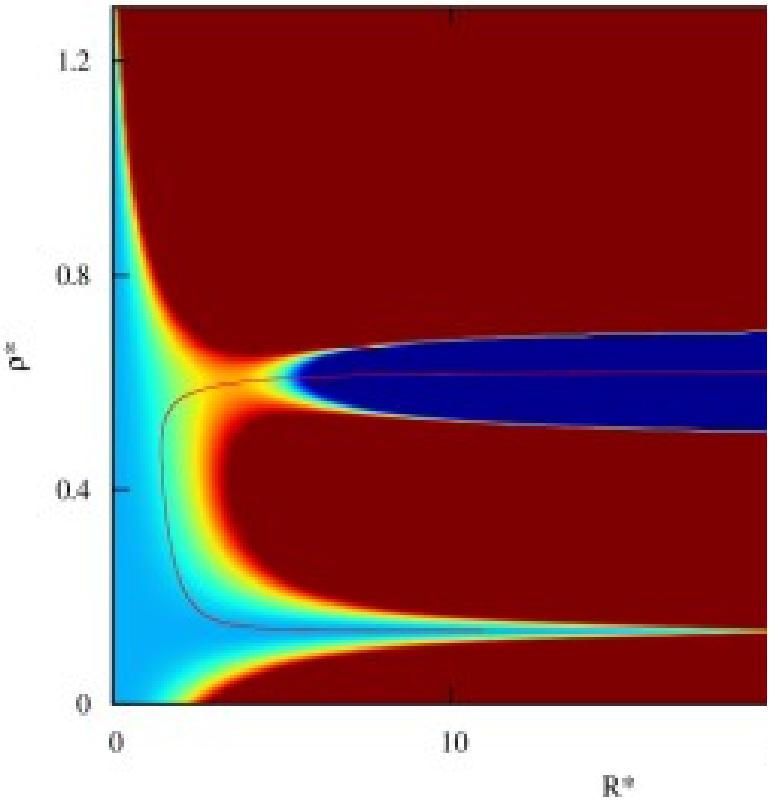
Nucleation in weak noise limit

Most likely path

$$\frac{dx^i}{dt} = -D \sum_j g^{ij}(\boldsymbol{x}(t)) \frac{\partial \beta F(\boldsymbol{x}(t))}{\partial x^j(t)}$$

Mean first passage time

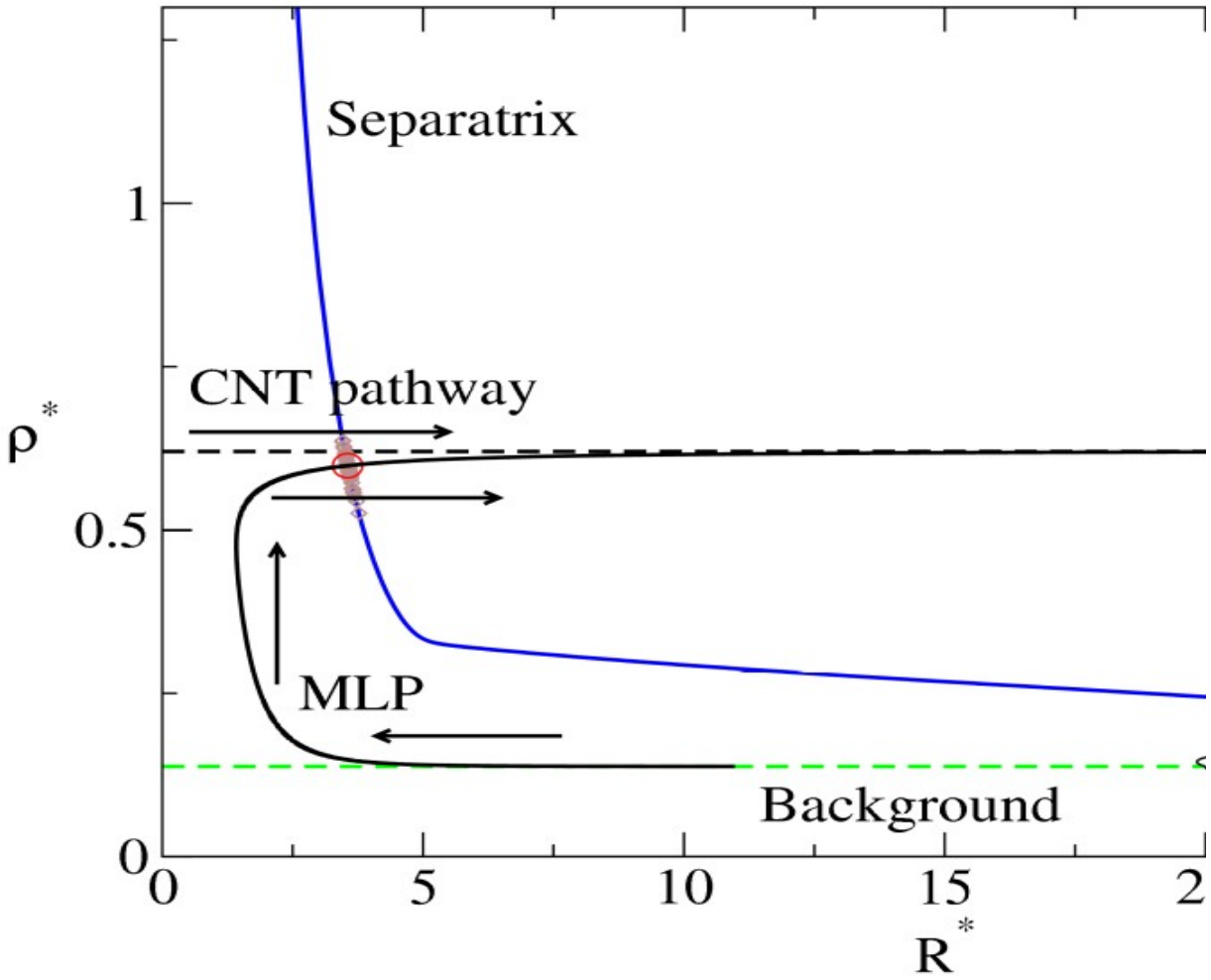
$$T_{MFP} \sim \frac{1}{2D\lambda_-} \frac{\sqrt{\det \beta \Delta F_{ij}(\boldsymbol{x}_c)}}{\sqrt{\det g(\boldsymbol{x}_c)}} \left(\int_{\text{meta}} e^{-\beta F(\boldsymbol{x})} d\boldsymbol{x} \right) \exp^{\beta F(\boldsymbol{x}_c)}$$



Free energy landscape

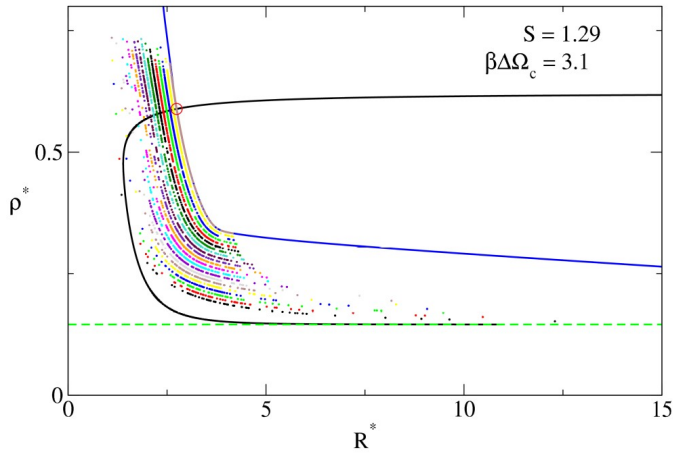
Mass fluctuation → Densification → Nucleation

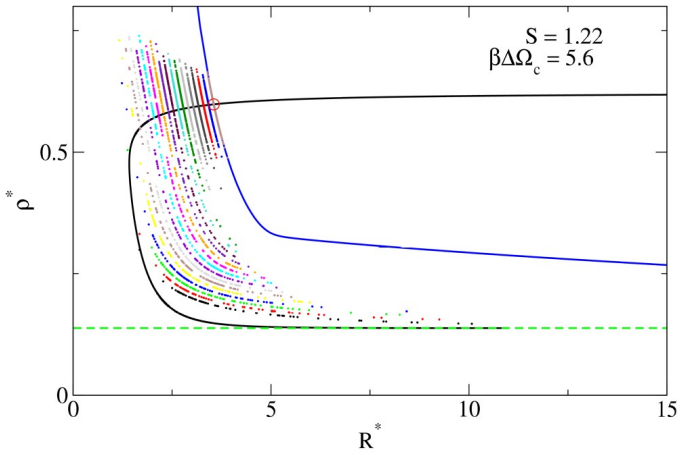
Nucleation pathway

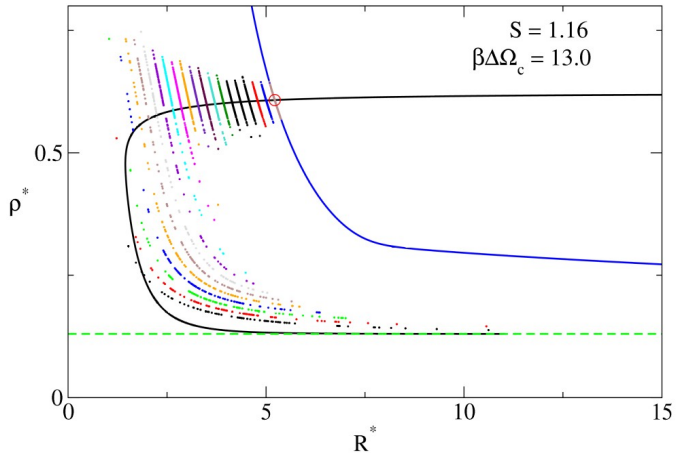


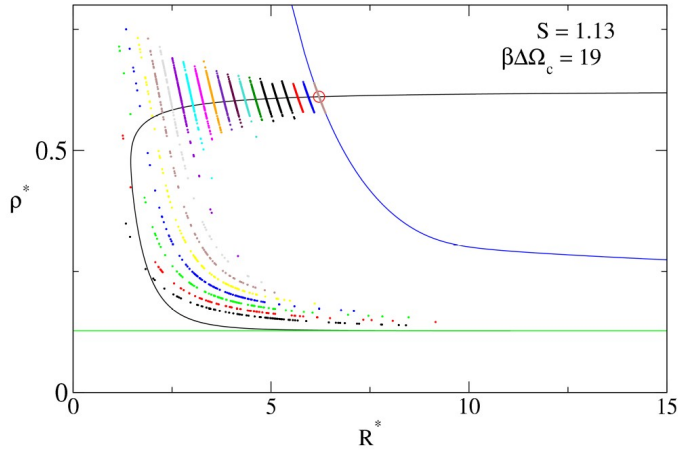
- 3-step nucleation pathway
- Pathway is same as in full field theory
- Clusters are never very small in radius

Simulation of 2 variable model: FFS



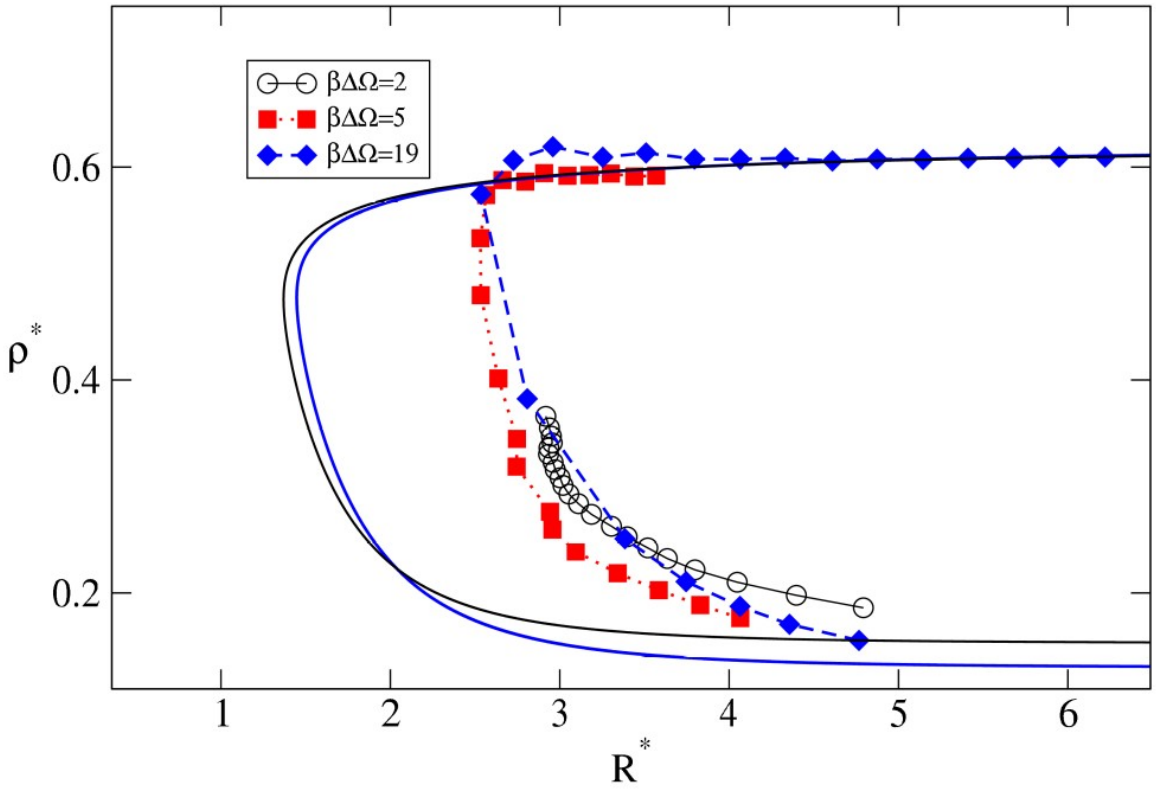






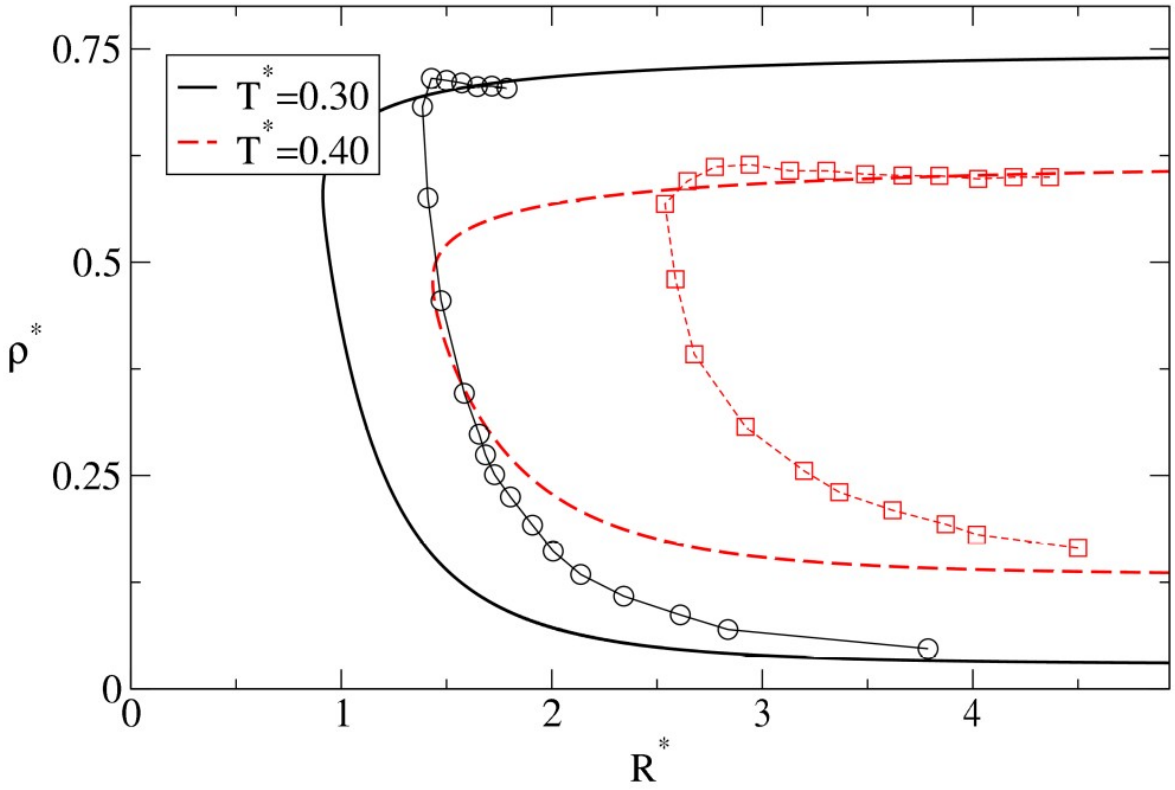
Simulation of Nucleation: FFS

Average pathway: Independent of barrier

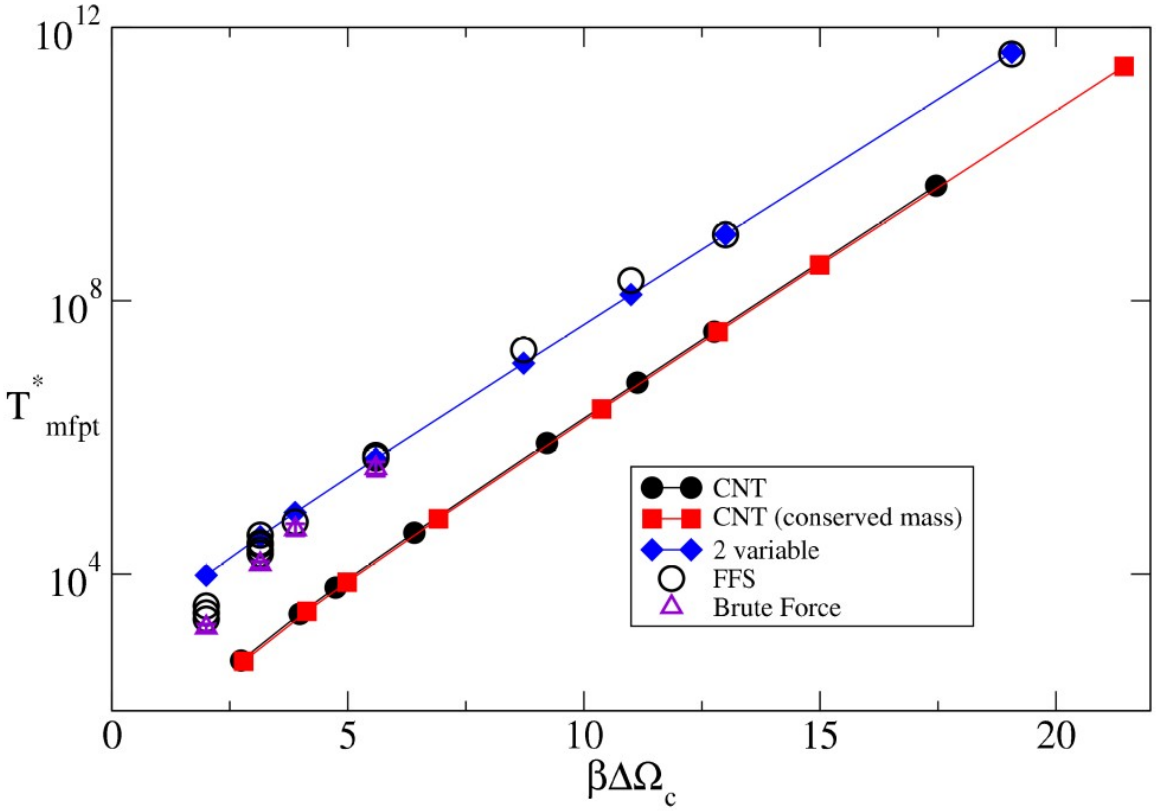


Simulation of Nucleation: FFS

Average pathway depends on temperature
“weak noise” <==> low temperature



Simulation of Nucleation: Nucleation times



- Correcting the free energy moves the prediction along the CNT curve.

- Dynamics produces further order(s) of magnitude differences in nucleation time.

Mesoscopic Nucleation Theory

- Motivation
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  - Fluctuating Hydrodynamics & overdamped approx.
  - Transition Paths
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- Crystallization

Crystallization: Challenges

- No spherical symmetry ==> all calculations performed in 3D
- Boundary Conditions:
  - closed system ==> big, big systems
  - How do study open systems with conservative dynamics?
    - Fixed density boundary conditions …
- What is end state? (Not uniform crystal!)
  - Use canonical/grand canonical duality to isolate stationary clusters
- Equations are very stiff
  - Use integration factor for diffusive term and implicit scheme for the rest

$$\frac{\partial \rho}{\partial t} = D \nabla \rho \nabla \frac{\delta F}{\delta \rho}$$

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho + D \nabla \rho \nabla \frac{\delta F_{ex}}{\delta \rho}$$

Crystallization: Challenges

- Multiple free energy minima ==> use “string method”

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{g}(\boldsymbol{x}) \cdot \frac{\partial F(\boldsymbol{x})}{\partial \boldsymbol{x}} + \boldsymbol{q}(\boldsymbol{x}) \cdot \boldsymbol{\eta}(t)$$

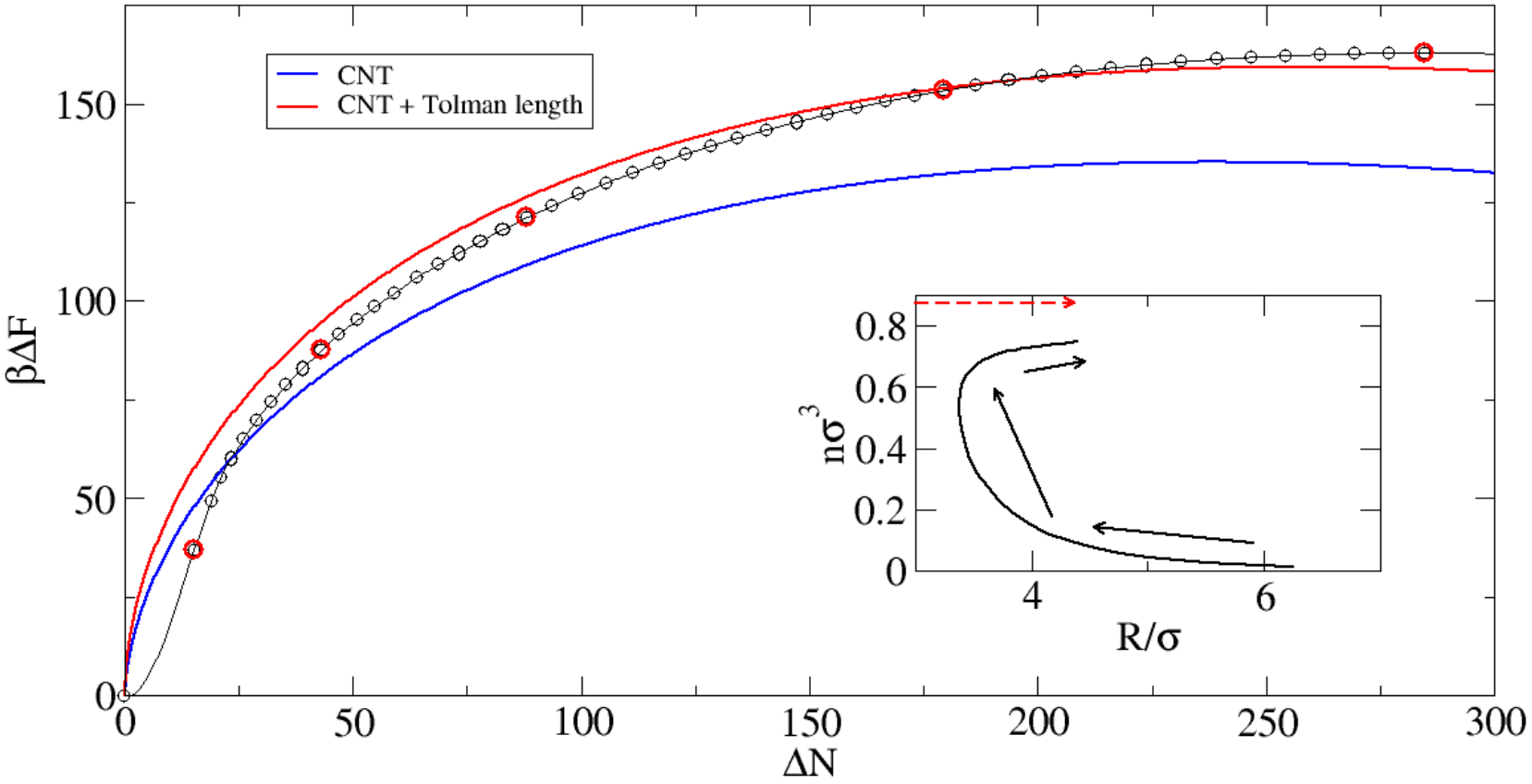
1. Guess a path from the starting point **x**(0) to the end point **x**(T)
2. Create N points on the path= $\mathbf{x}_0$= **x**(0) … $\mathbf{x}_N$=**x**(T)
3. Iterate:
   a. Move one time step according to deterministic dynamics:
   b. calculate distances along path:

$$s_1 = |\boldsymbol{x}^1 - \boldsymbol{x}^0|$$

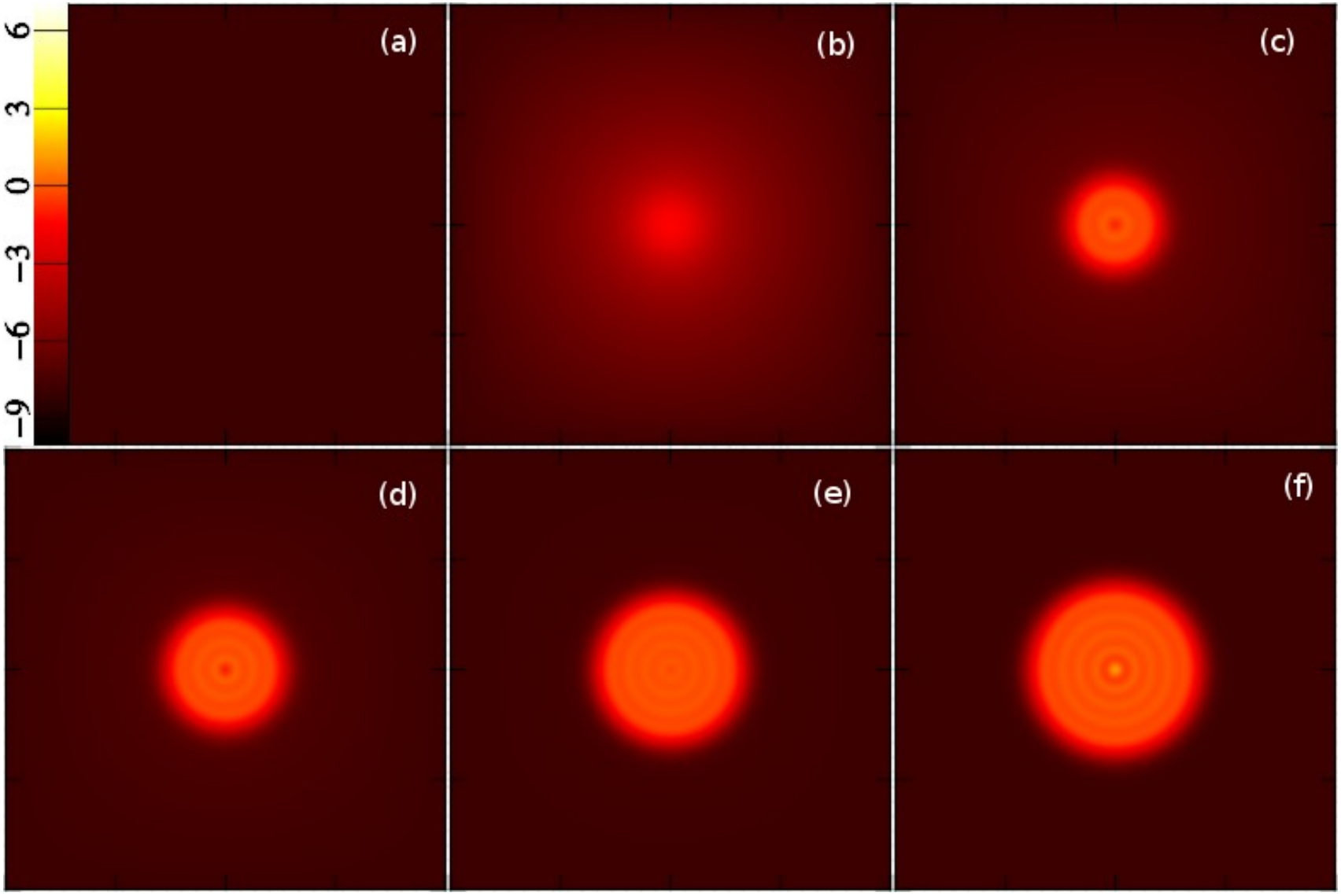
$$s_2 = s_1 + |\boldsymbol{x}^2 - \boldsymbol{x}^1|$$

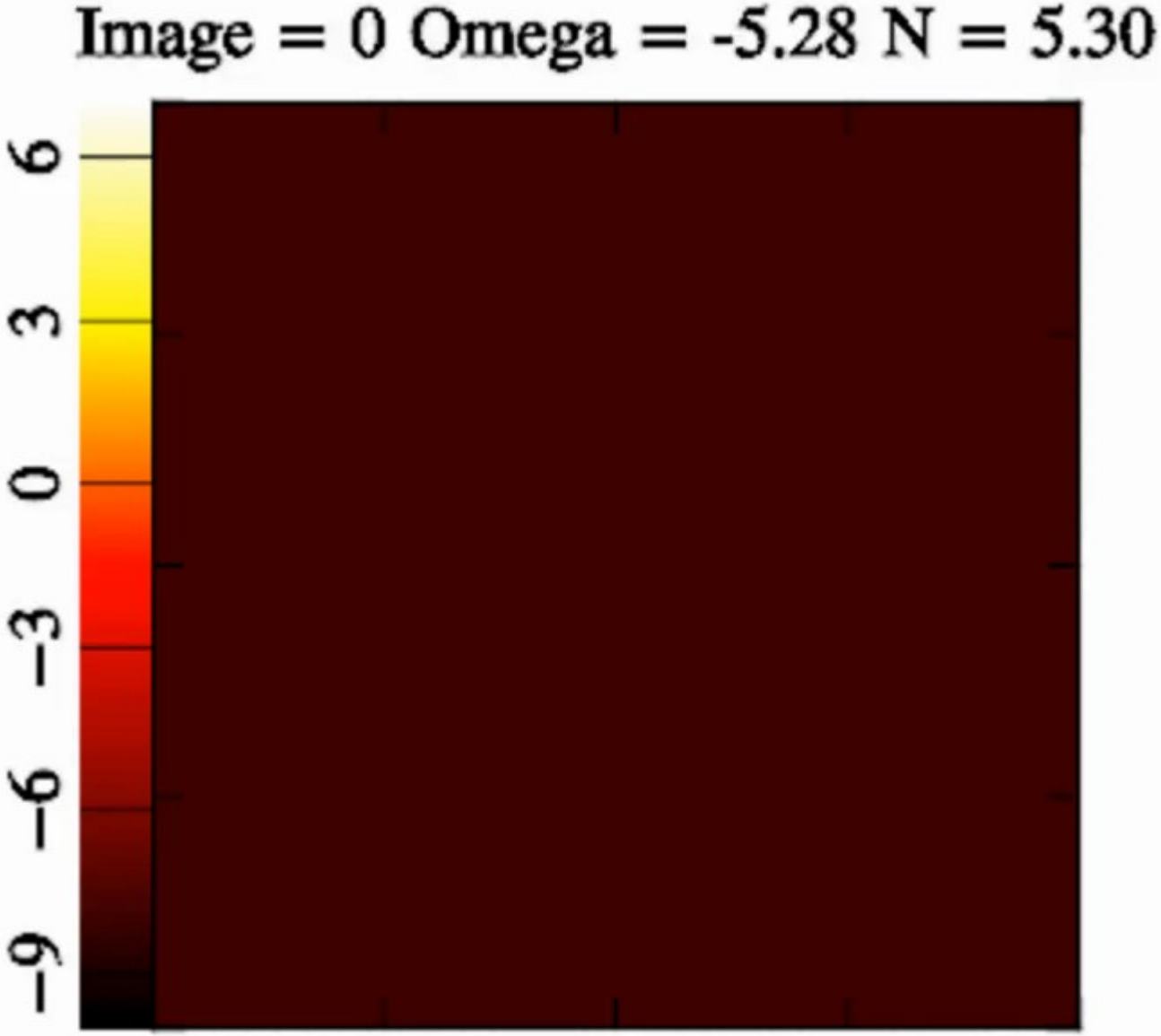
   c. Interpolate to get new points evenly spaced on path

Back to droplets …



Back to droplets …

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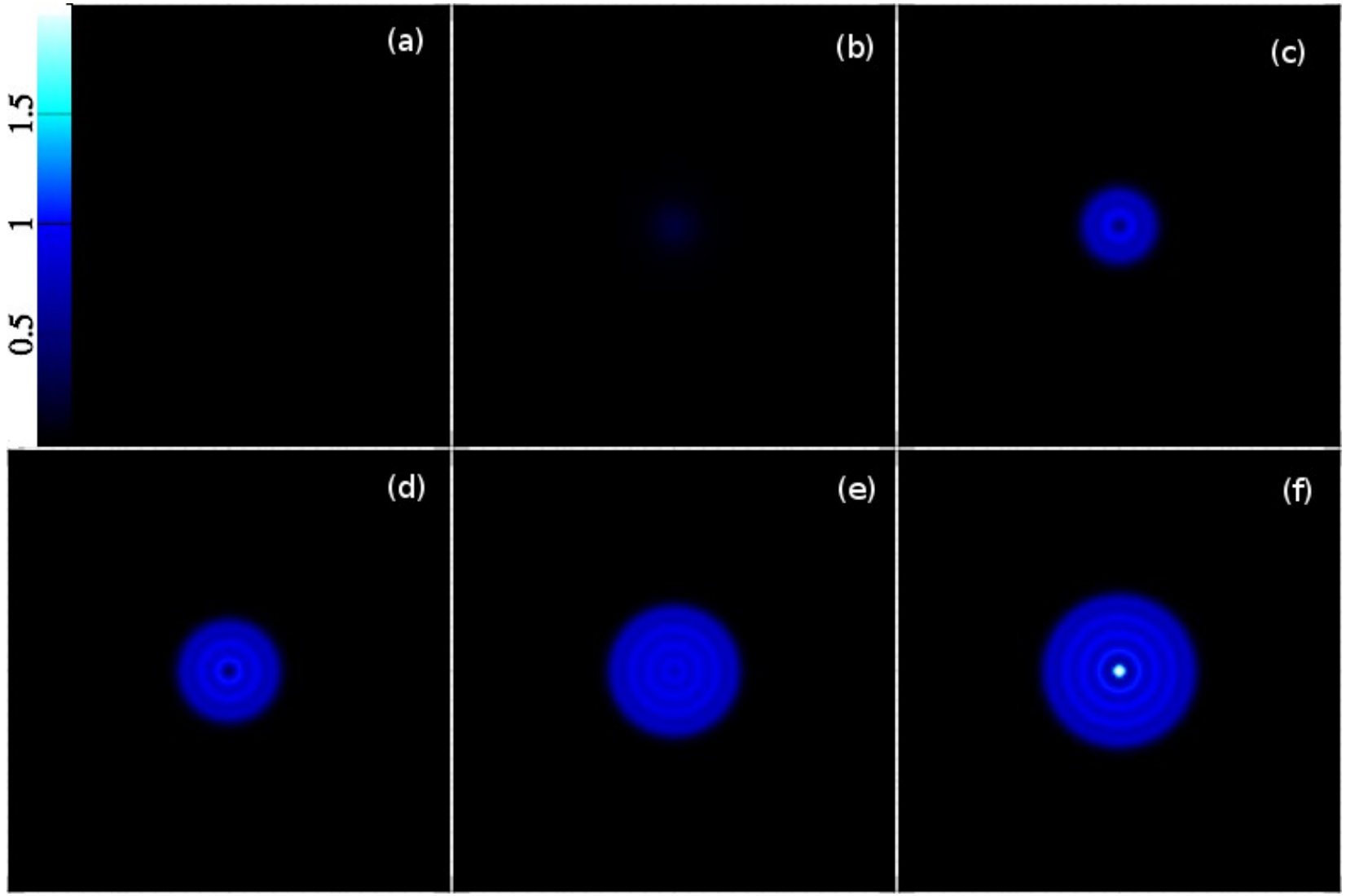
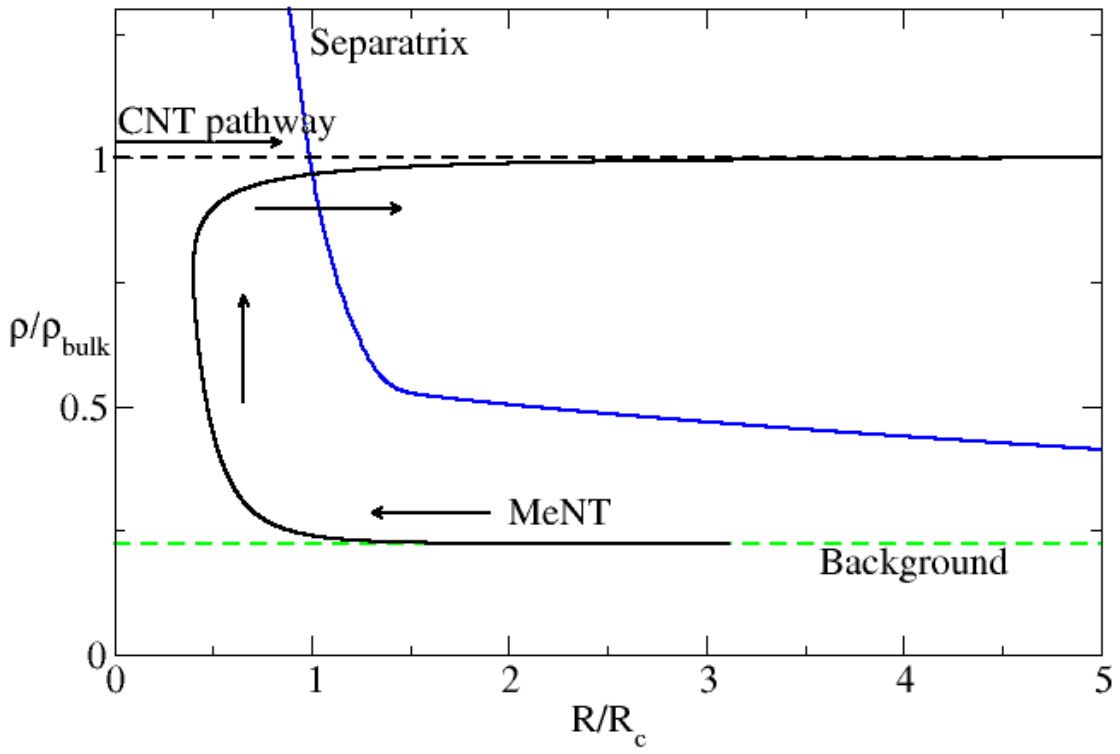
6
3
0
−3
−6
−9

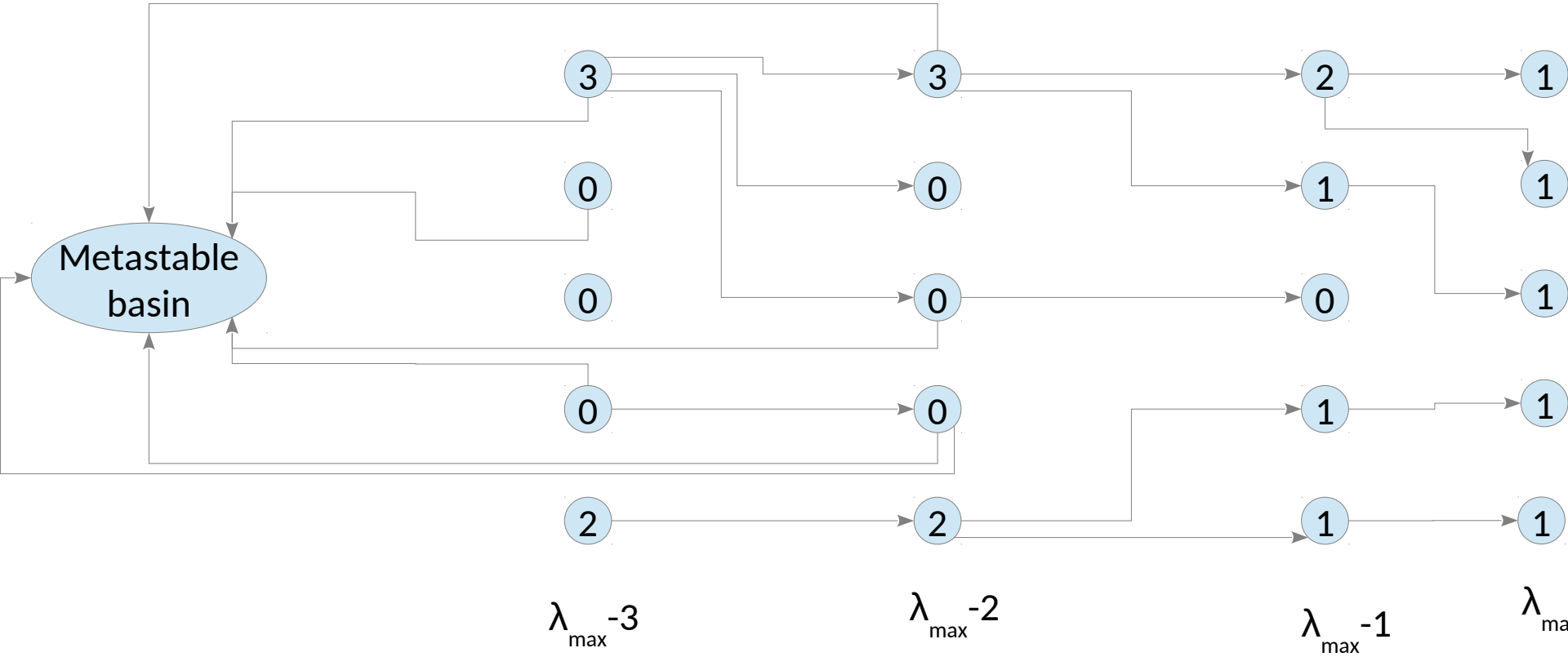
Back to droplets …



Confirming the non-classical initiation of nucleation



Confirming the non-classical initiation of nucleation

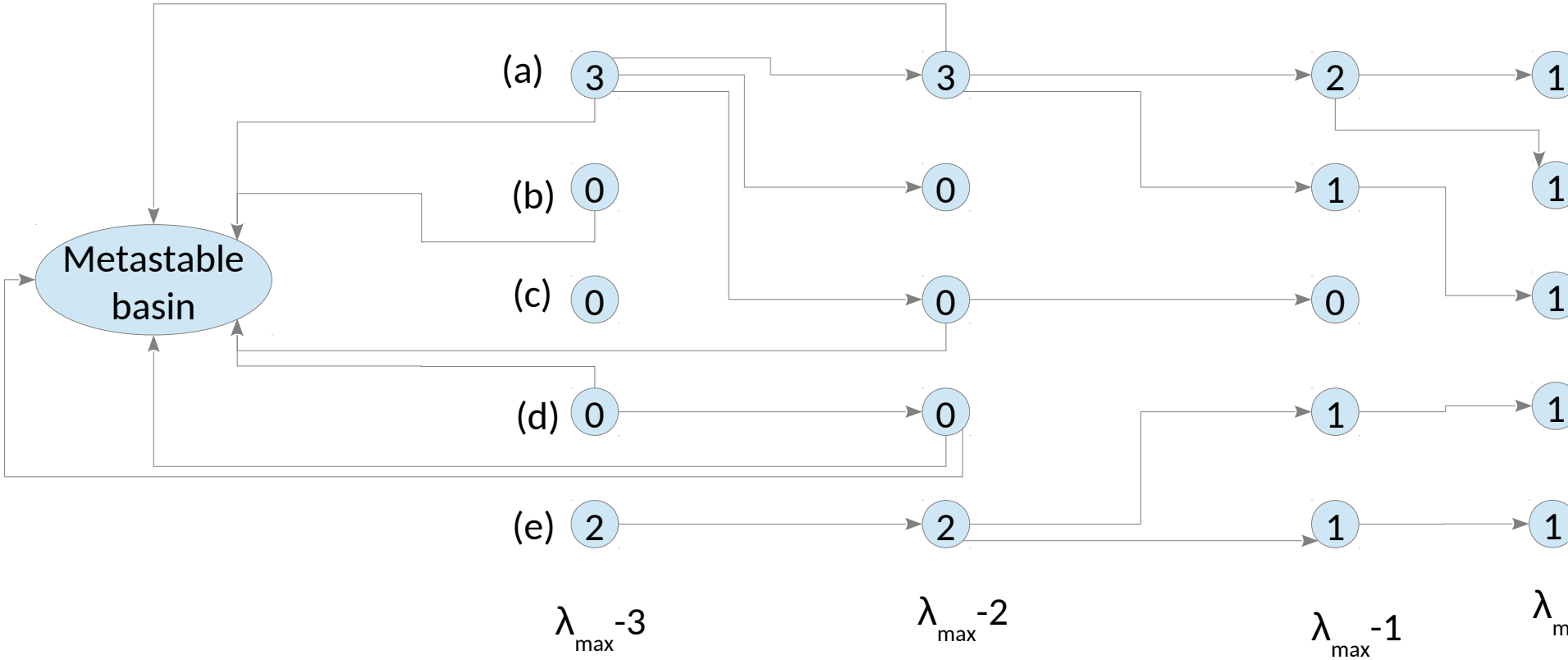


A “successful” trajectory is one that ends in the new phase (λ_{max})

A “failure” is one that does not.

For each node, we can determine the number of successes and of failures.

Confirming the non-classical initiation of nucleation



For fixed lambda, we can determine the average number of molecules in the simulation cell:

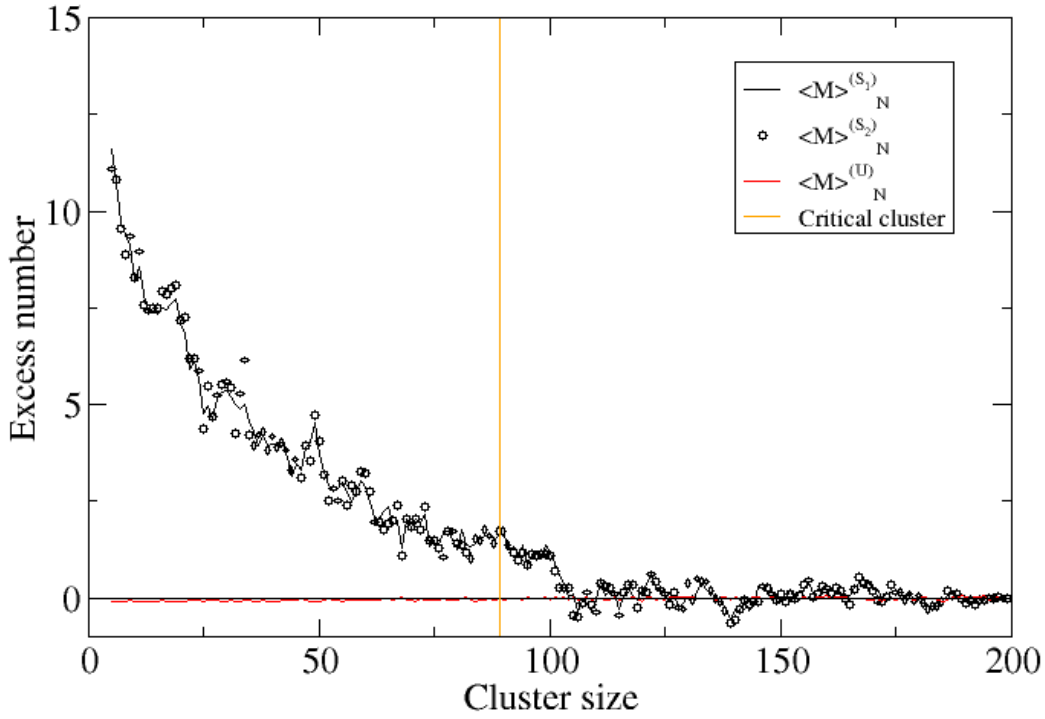
$$\langle N \rangle = (N_a + N_b + N_c + N_d + N_e)/5$$

We can also do this, but weighting each node by the number of successful trajectories:

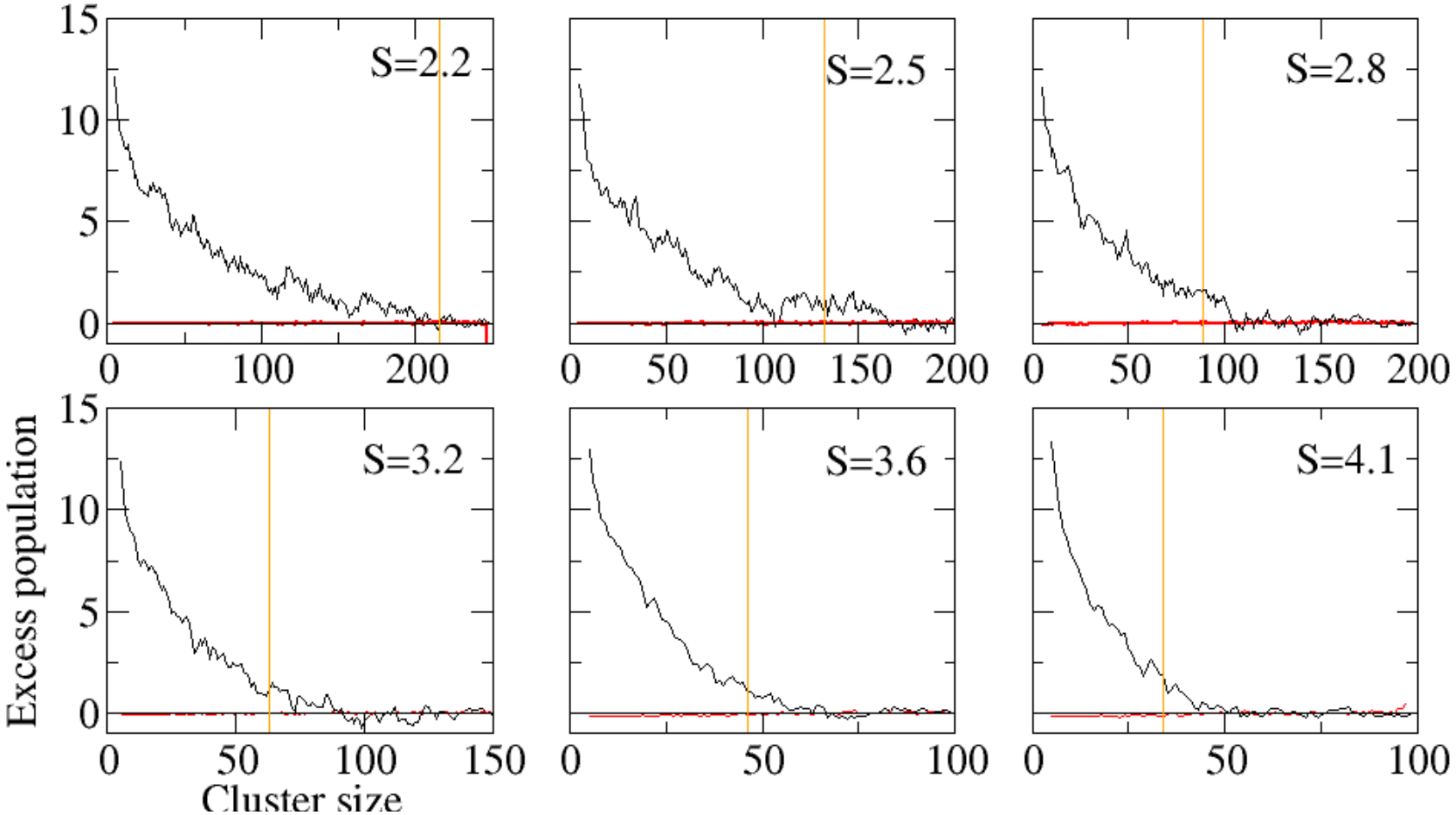
$$\langle N \rangle = (N_a \times 3 + N_b \times 0 + N_d \times 0 + N_e \times 2)/(3+0+0+2)$$

Or the percentage of successful trajectories, etc.

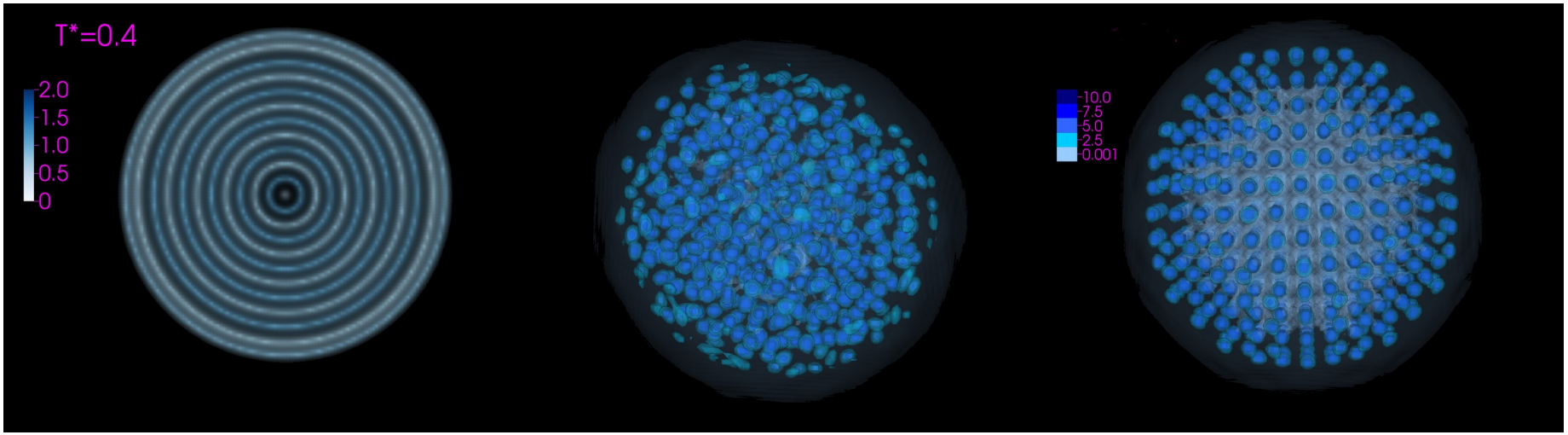
Confirming the non-classical initiation of nucleation



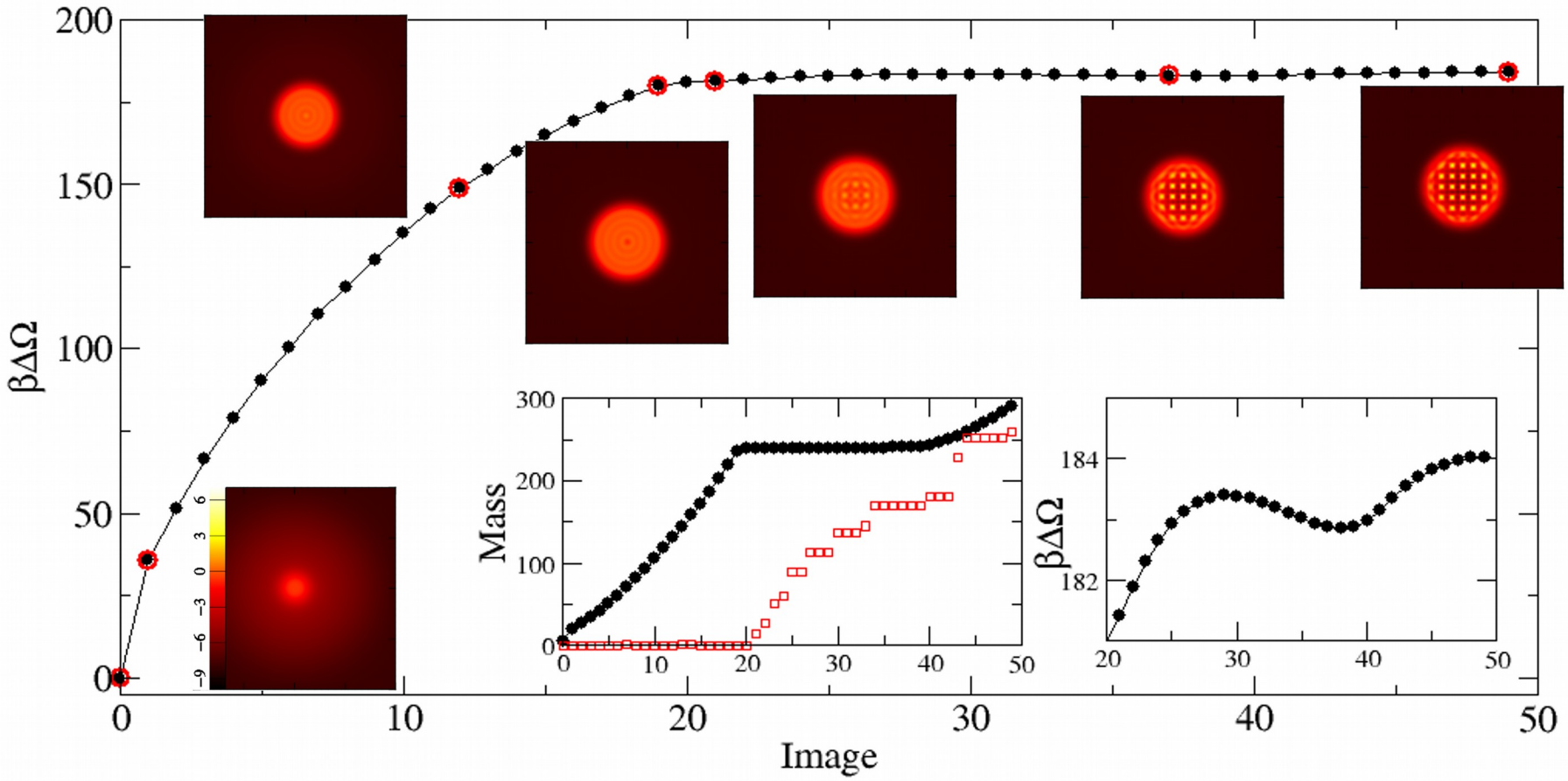
Confirming the non-classical initiation of nucleation



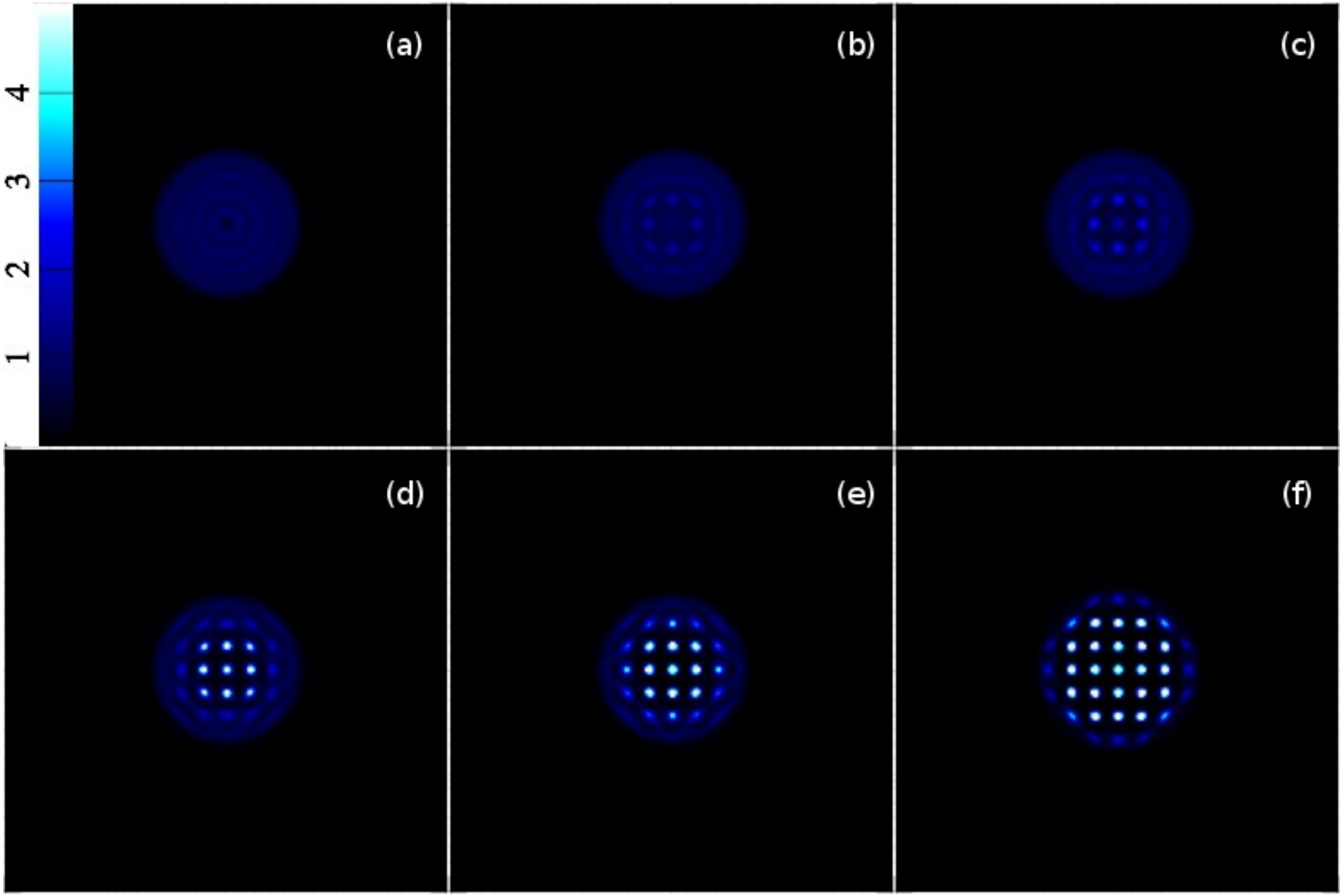
Crystallization: Critical clusters

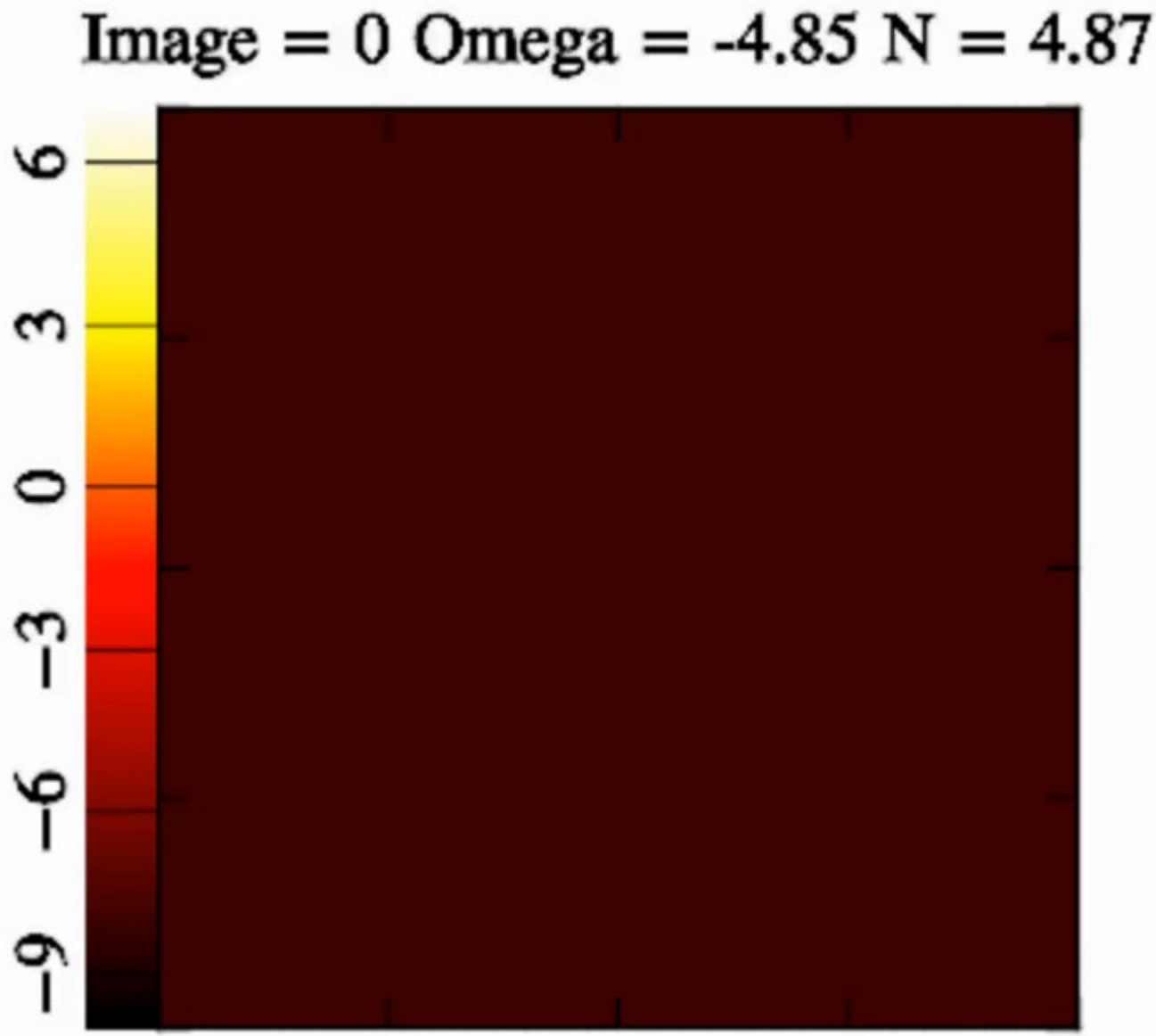


Crystallization: pathways and metastable states



Crystallization: Transition

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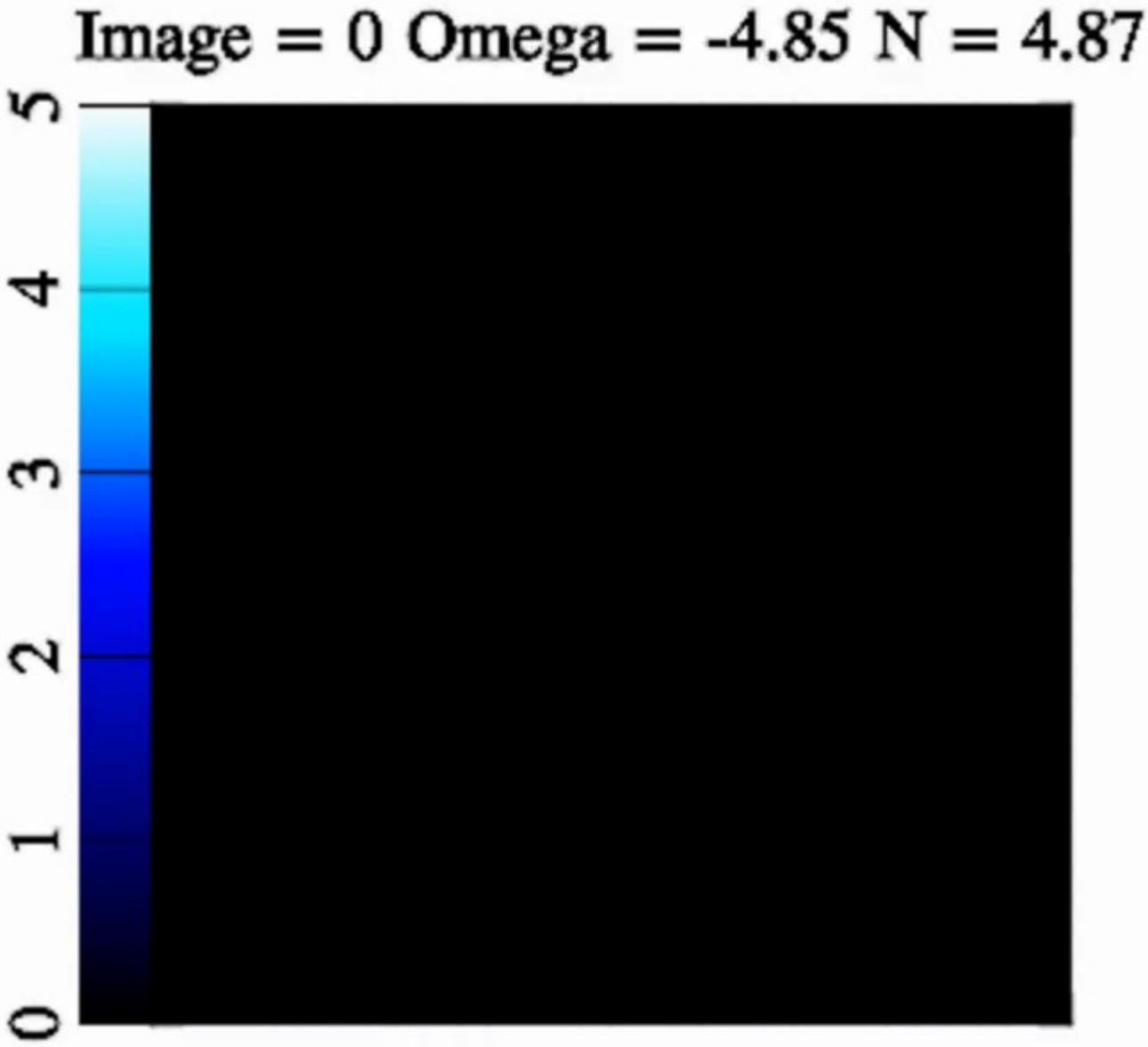
−6
−9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3
2
1
0