Nucleation at extreme supersaturations

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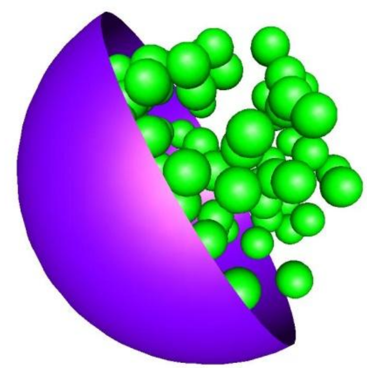
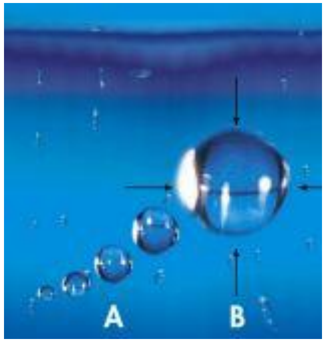
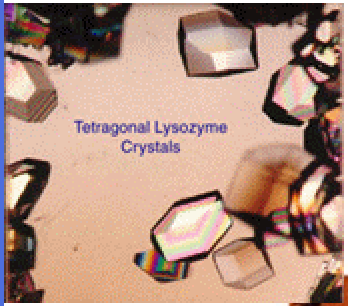
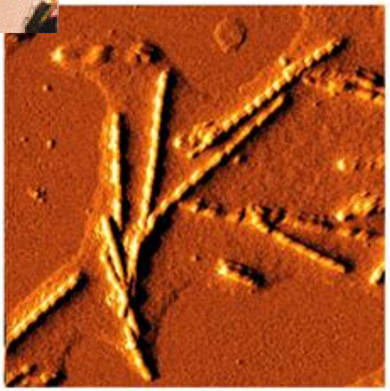


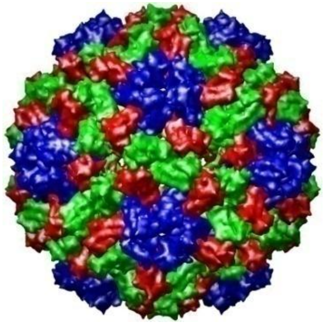
Why is nucleation important?

Nucleation is the first and crucial step in many phase transitions



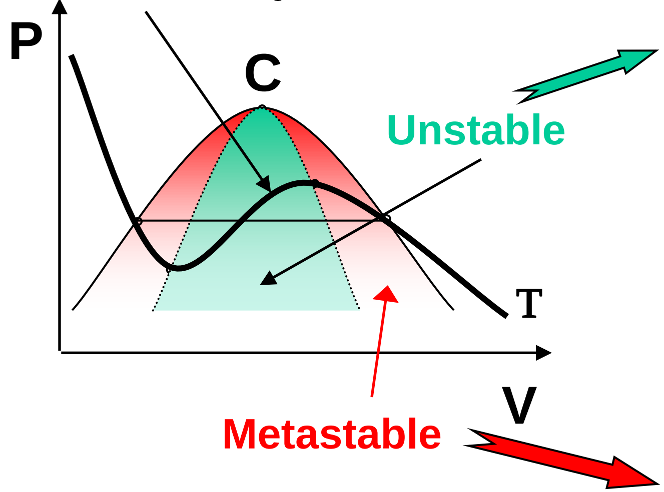




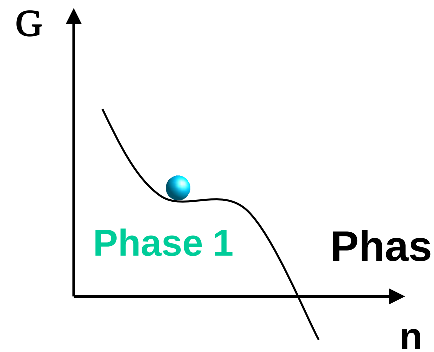


Introduction

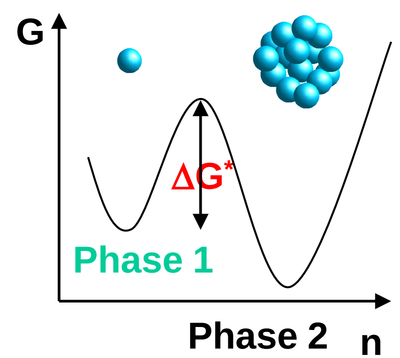
$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T < 0$$



Spinodal Decomposition



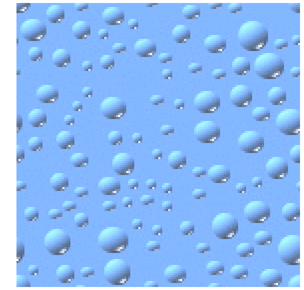
Nucleation



- Supersaturation: $S = p/p_{eq}$
- Nucleation Barrier: ΔG^*
- Critical size: n^*
- Nucleatíon Rate: **J**

Simplest example of a nucleation process: condensation of a vapor

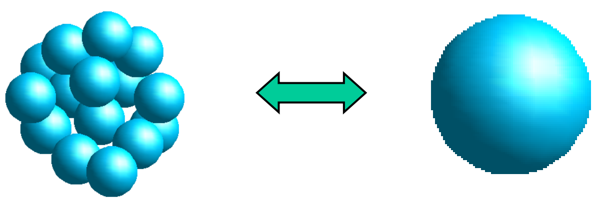
- Nucleation: Initial mechanism that explains the formation of the first embryos of the new phase

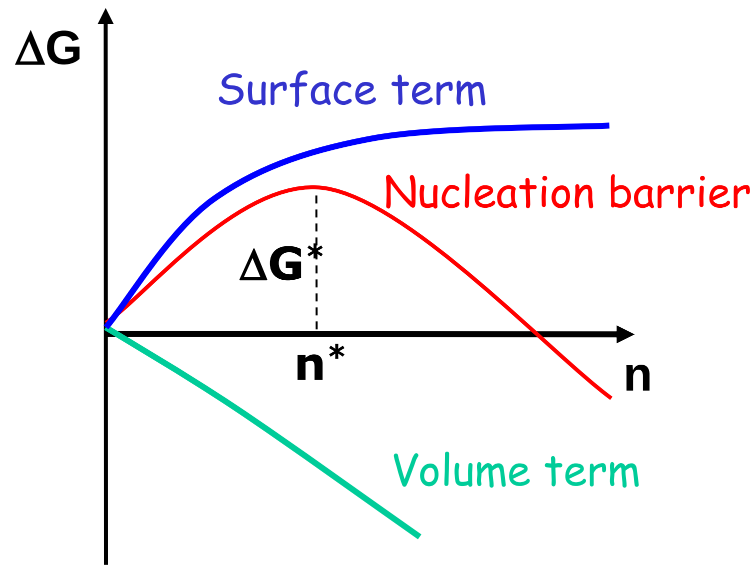


- Classical Nucleation Theory

$$\Delta G_{CNT}(n) = -\Delta\mu\, n + \gamma A(n)$$

n

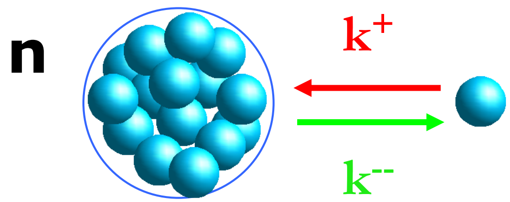




$$\Delta G^* = \frac{16\pi}{3}\frac{v_l^2\gamma^3}{(kT\ln S)^2}$$

$$n^* = \frac{32\pi}{3}\frac{v_l^2\gamma^3}{(kT\ln S)^3}$$

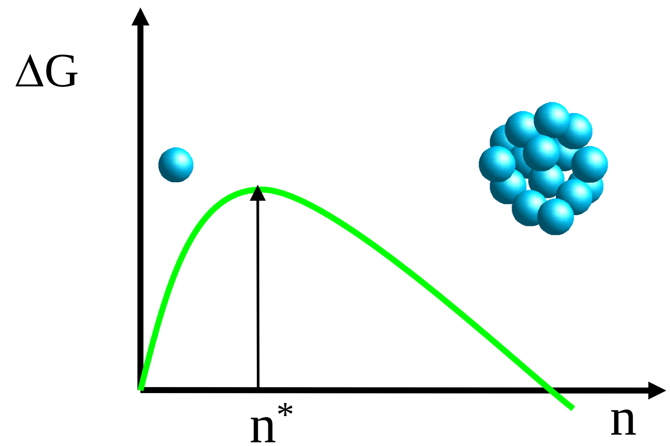
Nucleation Kinetics



Nucleation kinetics:

$$\frac{df(n,t)}{dt} = k^+(n-1)\,f(n-1,t) - k^-(n)\,f(n,t) - k^+(n)\,f(n,t) + k^-(n+1)\,f(n+1,t)$$

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial n}\left(k^+(n)\frac{\partial f}{\partial n} + \frac{k^+(n)}{k_BT}\frac{\partial \Delta G(n)}{\partial n}\,f\right)$$



Boundary conditions

$$\left.\frac{f}{f_{eq}}\right|_{n\to 0} = 1 \qquad \left.\frac{f}{f_{eq}}\right|_{n>>n^*} = 0$$

$$\frac{\Delta G^*}{kT} >> 1$$

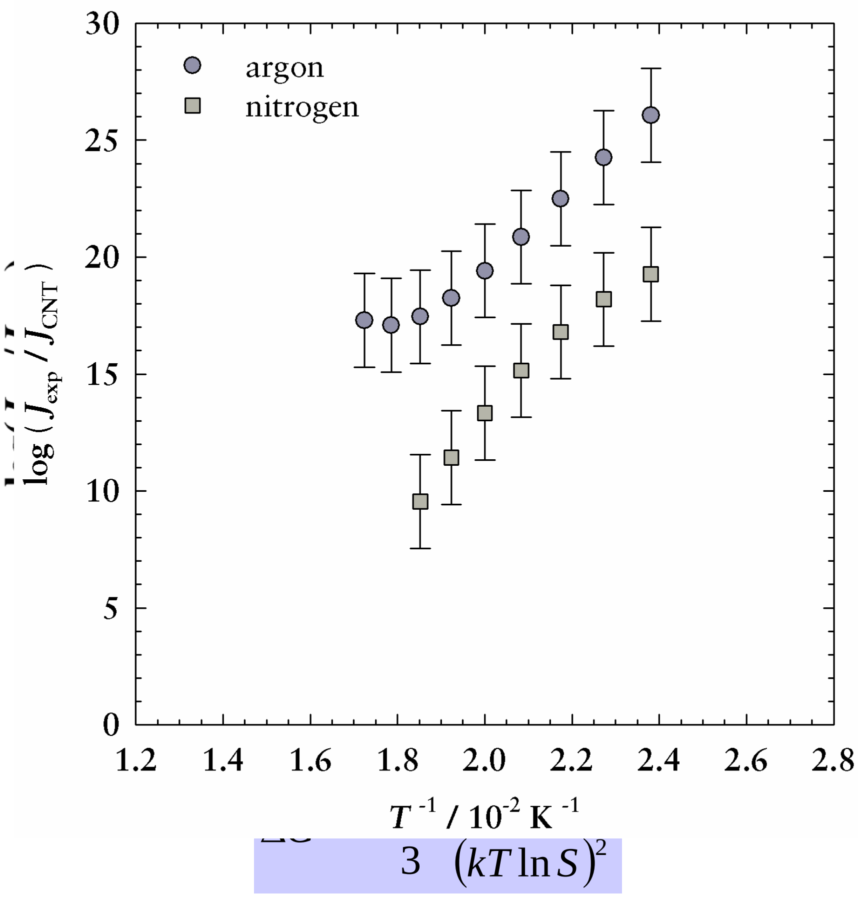
Nucleation rate

$$J_S = N_{tot}\,k^+(n^*)\,Z\,e^{-\frac{\Delta G^*}{k_BT}}$$

How good is CNT?

- Predominant theory: CNT
  - Only uses bulk (measurable) thermodynamic parameters

- CNT has serious problems:
  - Wrong T dependence of nucleation rates:
    - J_{CNT} too high at high T
    - J_{CNT} too low at low T
  - It does not account for the spinodal



Outline

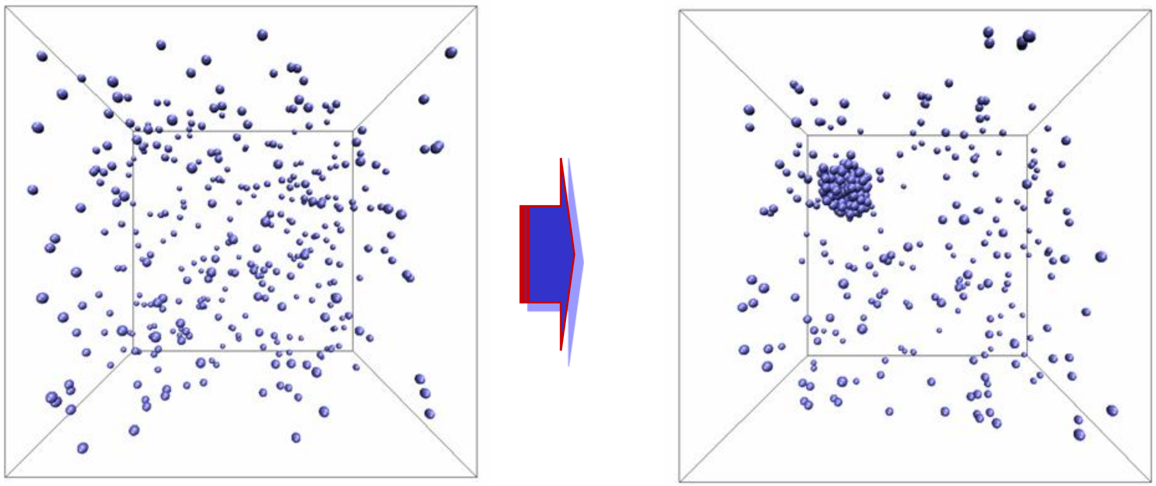
Nucleation at extreme supersaturations

- MD Simulations:
  - Optimization of system size: Finite-size effects
  - A new method to evaluate rates: MFPT
  - Kinetic reconstruction of the free-energy landscape
- MD results:
  - Nucleation Rates, critical cluster sizes and barrier heights
  - Comparison with CNT
  - Transition between nucleation and spinodal decomposition
- Conclusions and outlook

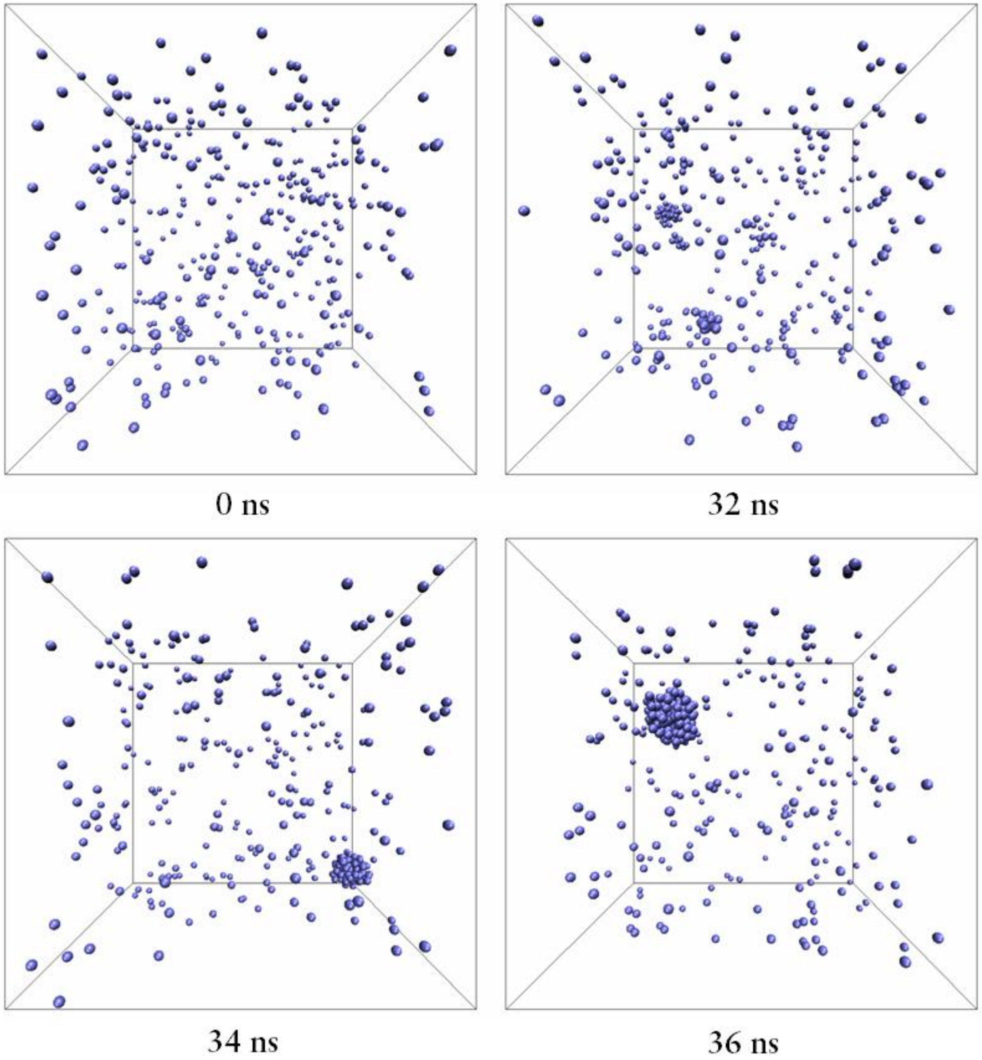
MD Simulations of Lennard-Jones Argon Nucleation:

MD "brute force" simulations
in the canonical (NVT) ensemble

T = 80.7K (T*=0.67)



Molecular Dynamics Simulation[4)]



4) Frenkel and Smit, Understanding Molecular Simulation, 2nd ed. (Academic Press, San Diego, 2002).
5) Wonczak, Ph.D. Thesis, Universität zu Köln, Cologne 2001.

MD Simulations of Argon Nucleation:

Q1: How large should the system be???

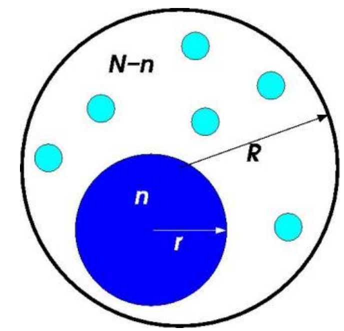
"The bigger, the better"

Optimization of system size
and
finite size effects

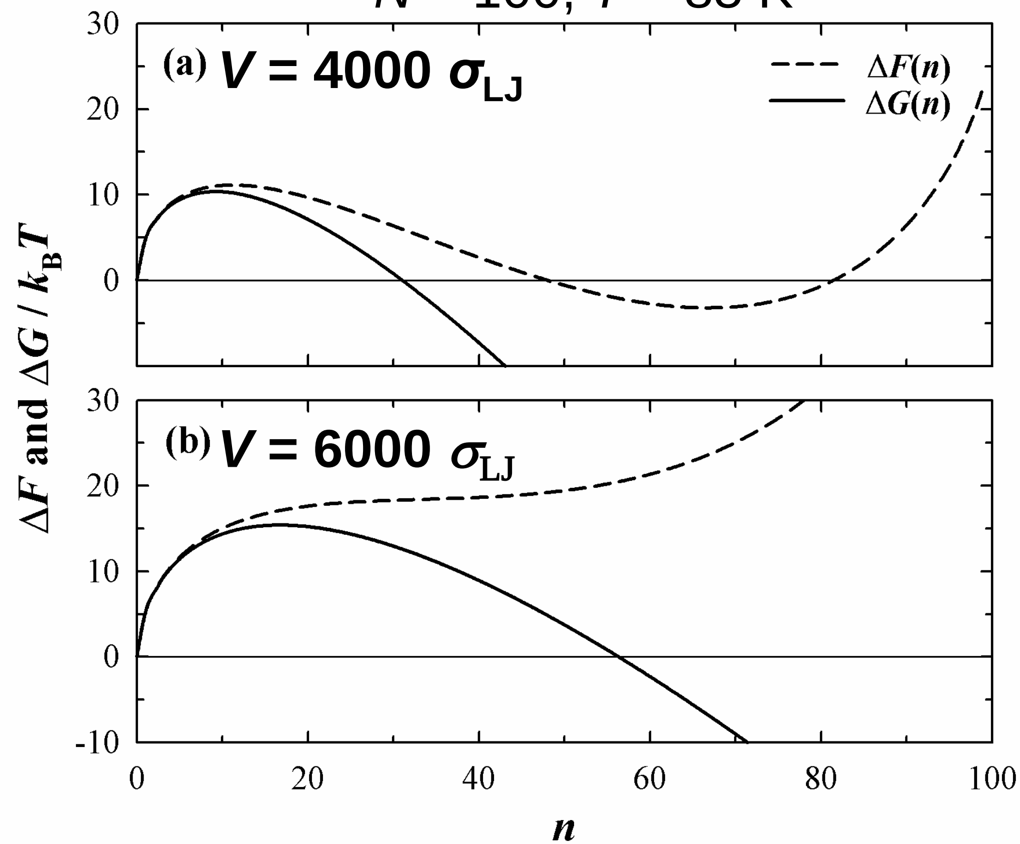
Finite-size effects:
Condensation in a finite (N,V,T) system

Modified Liquid Drop (MLD) Model

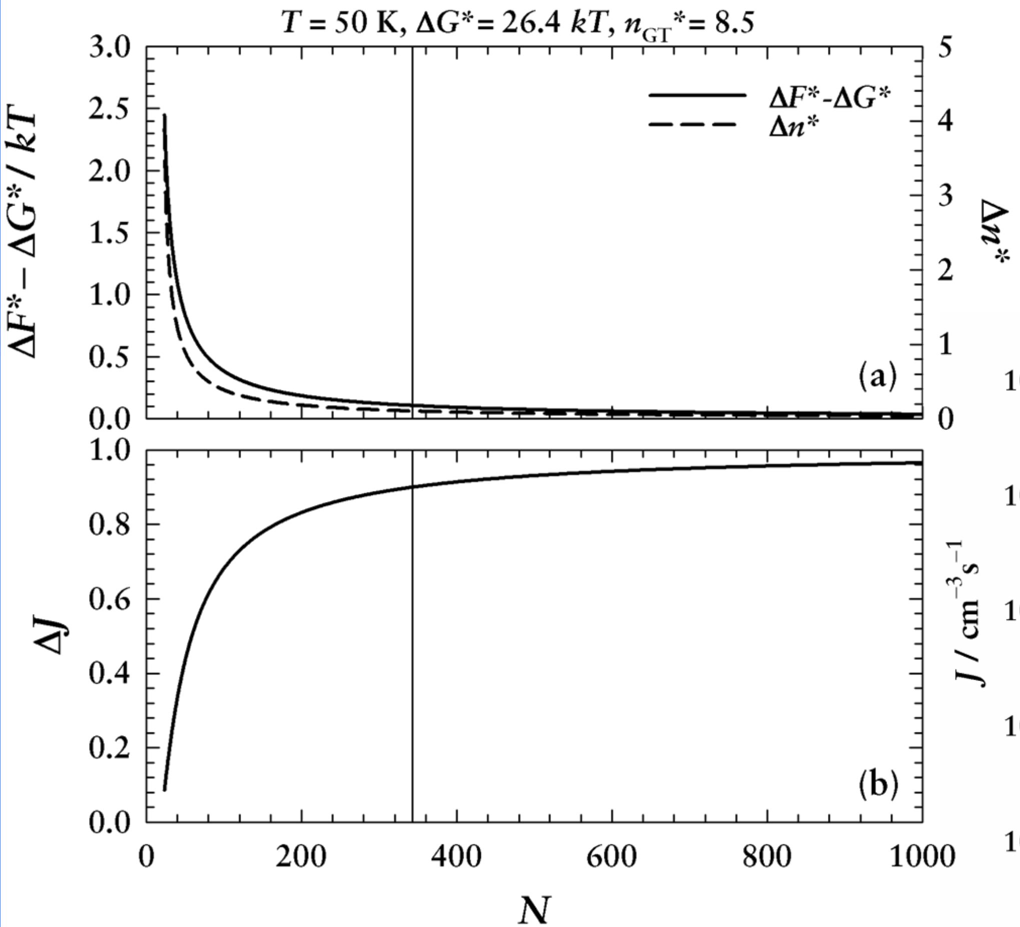
$$\Delta F(n) = -n\,kT\,\ln\frac{p_1}{p_{eq}} + \sigma A + n(kT - v_l p_{eq}) + NkT\,\ln\frac{p_1}{p_0}$$

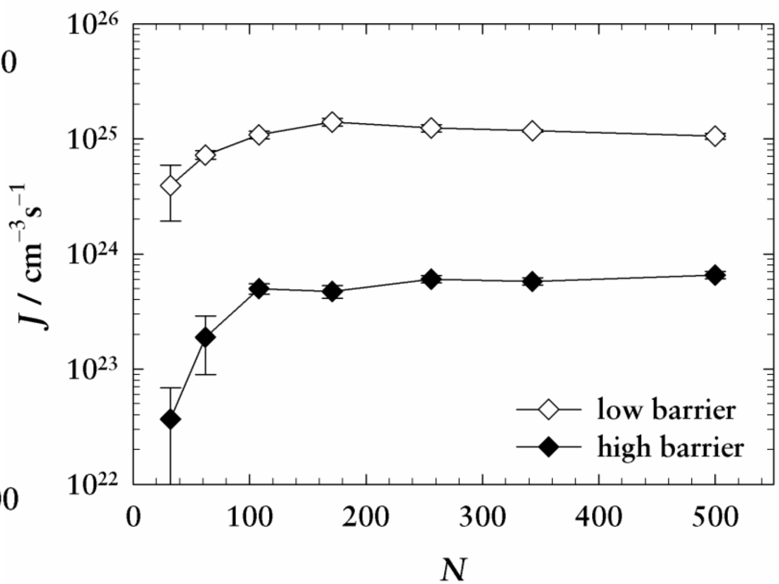


$N = 100$, $T = 85$ K



Optimization of system size





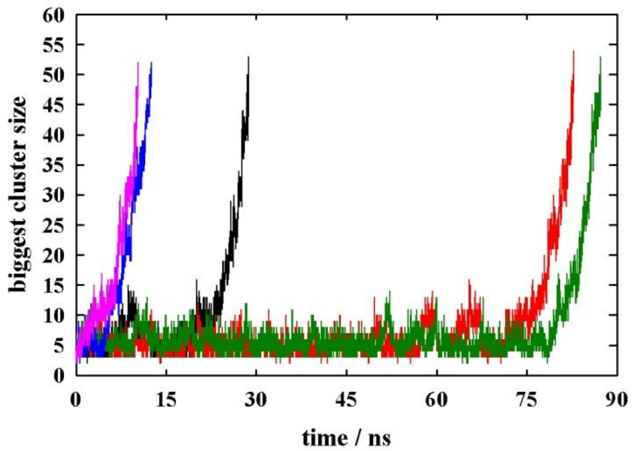
Nucleation at extreme supersaturations

Q2: How can we analyze the rates???

A new method to analyze rates
in simulations of activated processes

How to analyze the rates?

- General problems:
  - Nucleation is a stochastic process: one realization is not enough
  - n* is not known a priori



- Different methods:
  - Time required to have a cluster of a particular size

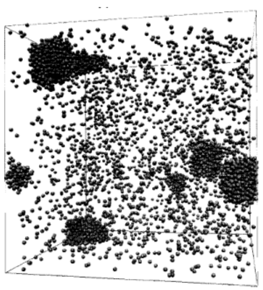
$$rate = \frac{1}{Vt}$$

Problems:

- arbitrary size
- more than 1 cluster can be formed

- Number of large drops formed per unit time and V

$$J = \frac{1}{V}\frac{dN(t)}{dt}$$



Problems:

- Nucleation/ growth are coupled
- Depletion effects
- Nonstationary rates

New method to analyze rates in MD simulations

- Based on evaluation of Mean First Passage Times
- Advantages:
  - Efficient and easy to implement
  - Allows an accurate evaluation of nucleation rates
  - One can easily see if nucleation and growth are coupled
  - Allows to extract additional useful information:

    - evaluation of the critical cluster size from pure kinetic considerations!

    - estimates of the height of the nucleation barrier, the Zeldovich factor and the time lag

Nucleation (Activation) Rates and MFPT

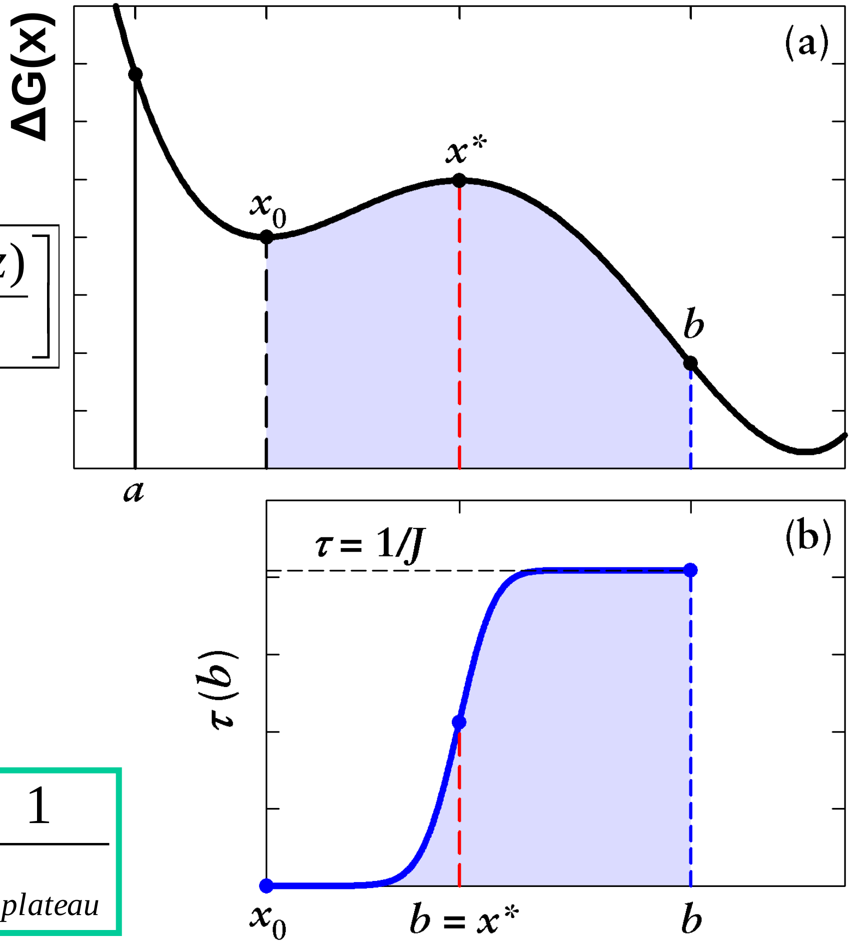
Fokker-Planck equation

$$\frac{\partial f(n,t)}{\partial t} = \frac{\partial}{\partial n}\left(D(n)e^{-\beta\Delta G(n)}\frac{\partial}{\partial n}\left(f(n,t)e^{\beta\Delta G(n)}\right)\right)$$

Diffusion over the free energy landscape

Mean First Passage Time to leave the domain (a,b)

$$\tau(b;x_0) = \int_{x_0}^{b} dy \frac{1}{D}\exp\left[\frac{\Delta G(y)}{kT}\right]\int_a^y dz \exp\left[\frac{-\Delta G(z)}{kT}\right]$$



$$\left.\frac{\partial^2\tau}{\partial b^2}\right|_{b=n^*} = \frac{1}{D} \approx 0$$

Locates the critical cluster!

$$J_{st} = \frac{1}{2\tau(n^*)}$$

For $\frac{\Delta G^*}{kT} >> 1$

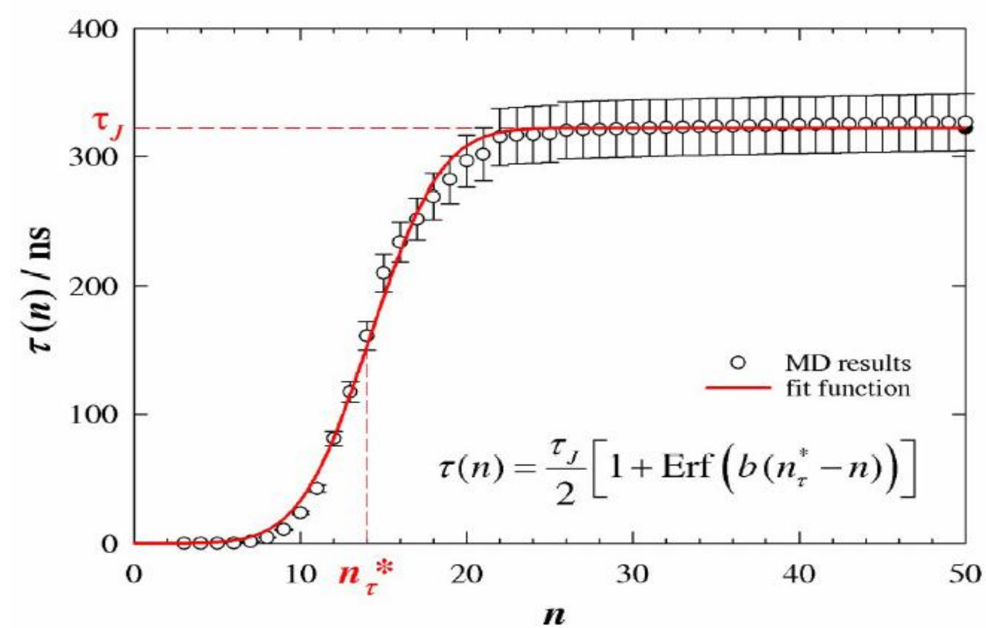
$$J_{st} = \frac{1}{\tau_{plateau}}$$

Extracting thermodynamic information from the kinetics

For $\frac{\Delta G^*}{kT} >> 1$

Fitting function:

$$\tau(n) = \frac{\tau_J}{2}\left[1 + Erf\left(b(n - n^*)\right)\right]$$



where:

$$J_{st} = \frac{1}{\tau_J}$$

Steady state nucleation rate

$$n^*$$

Critical cluster size

$$b = \sqrt{\pi} Z$$

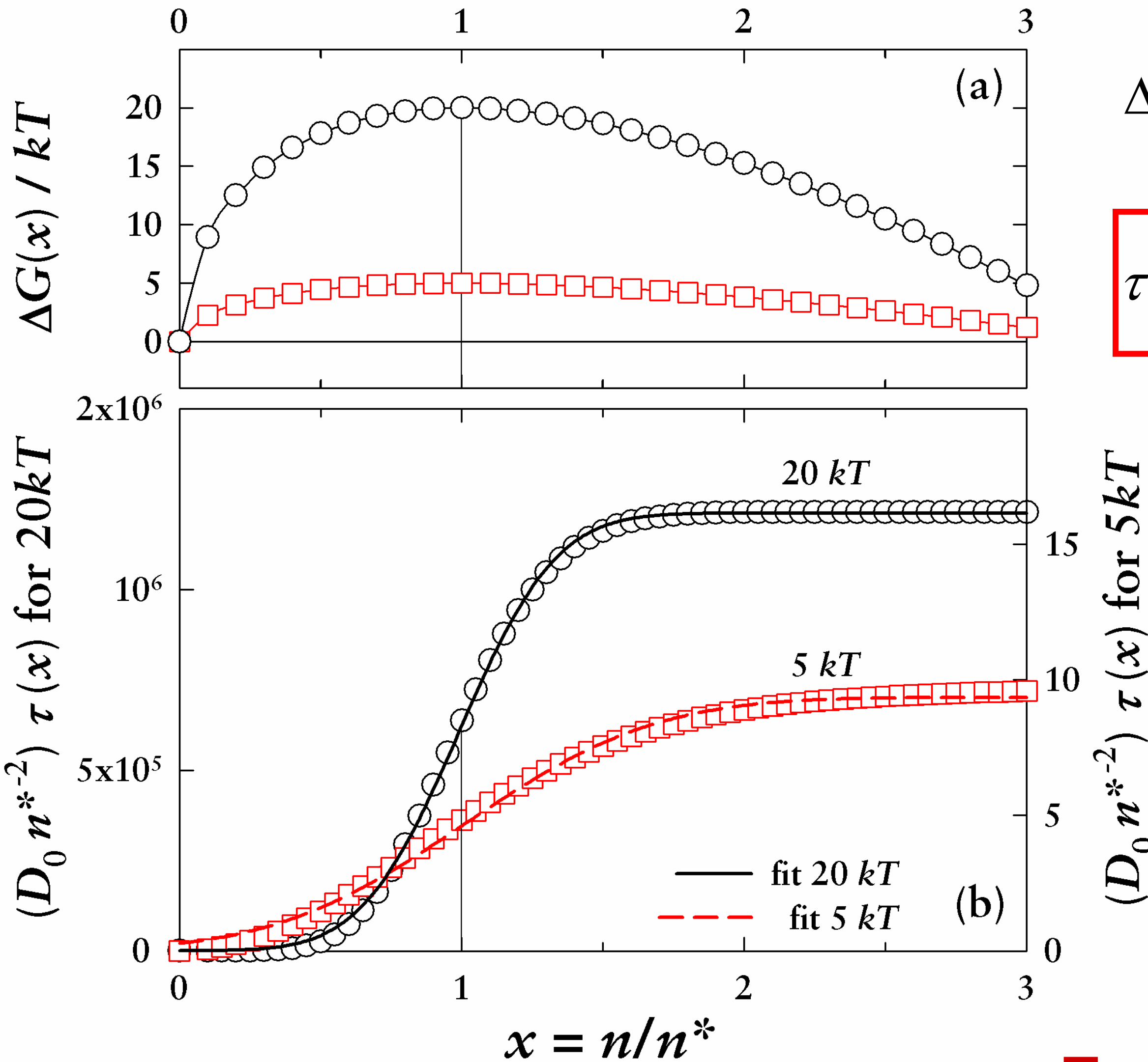
Zeldovich factor

$$t_{lag} \sim \frac{1}{D(n^*)b^2}$$

Time lag

J. Wedekind, R. Strey, D.R., J. Chem. Phys.(subm)

Comparison: Analytical Result and Fit



$$\Delta G(x) = 2\Delta G^* \left(-x + \frac{3}{2} x^{2/3} \right)$$

$$\tau(n) = \frac{\tau_J}{2} \left[1 + Erf\left(b(n - n^*) \right) \right]$$

ΔG*=20 KT

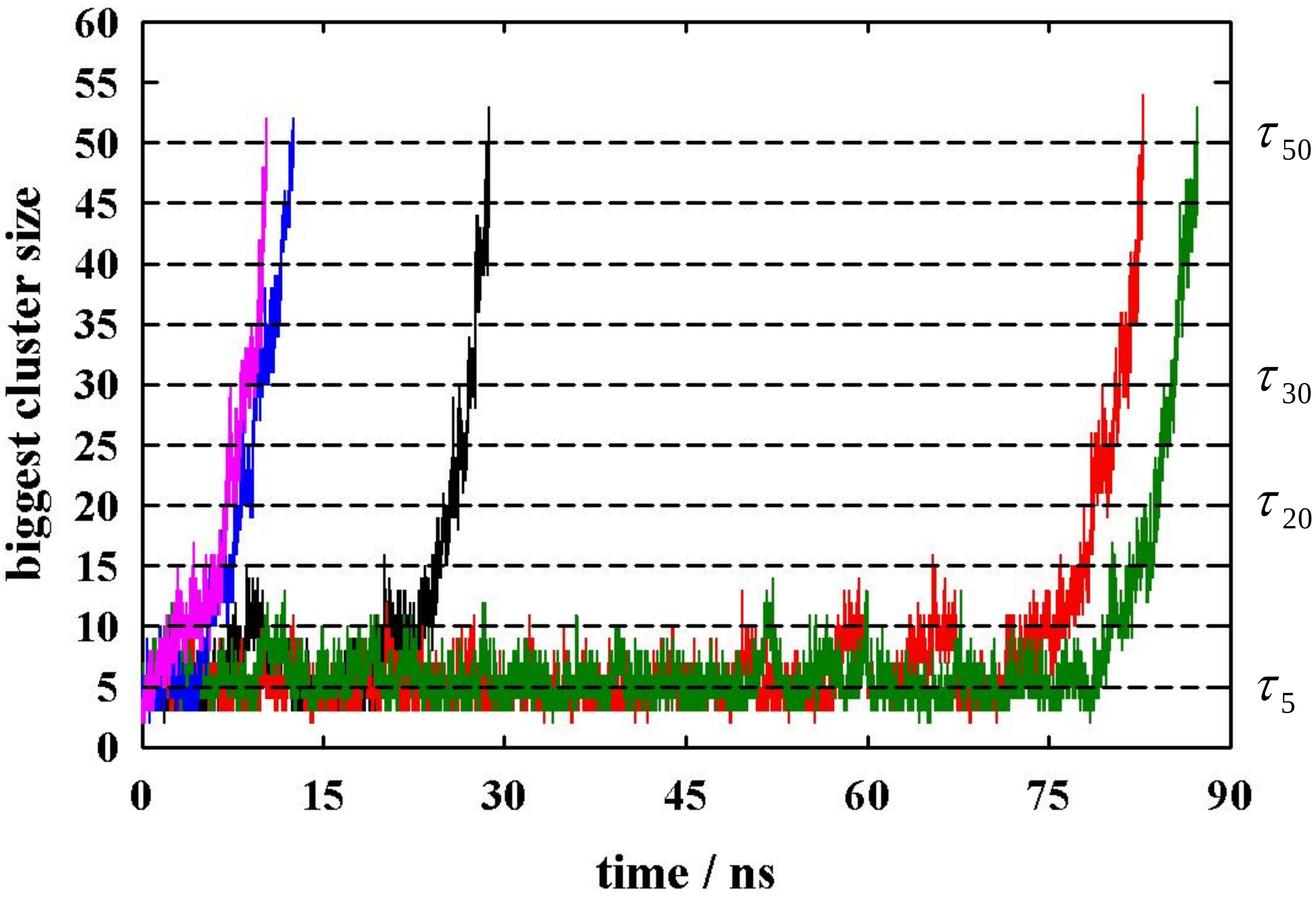
	Exact	Fit	%
*x**	1.00	0.99	1
J	$8.24\ 10^{-7}$	$8.30\ 10^{-7}$	1
Z	1.46	1.47	1

ΔG*=5 KT

	Exact	Fit	%
*x**	1.00	1.03	3
J	0.104	0.104	1
Z	.73	.72	2

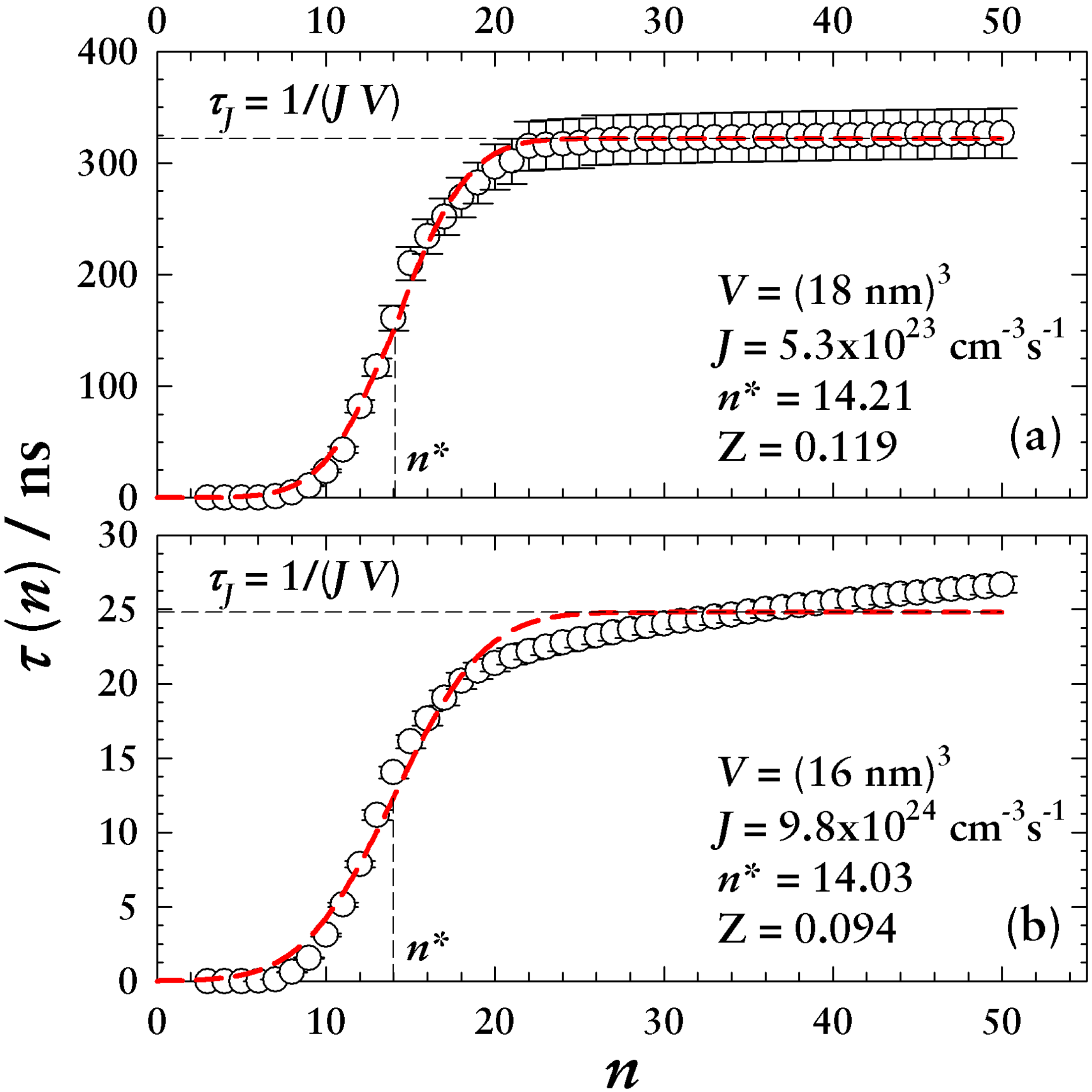
Excellent agreement!!

Practical implementation



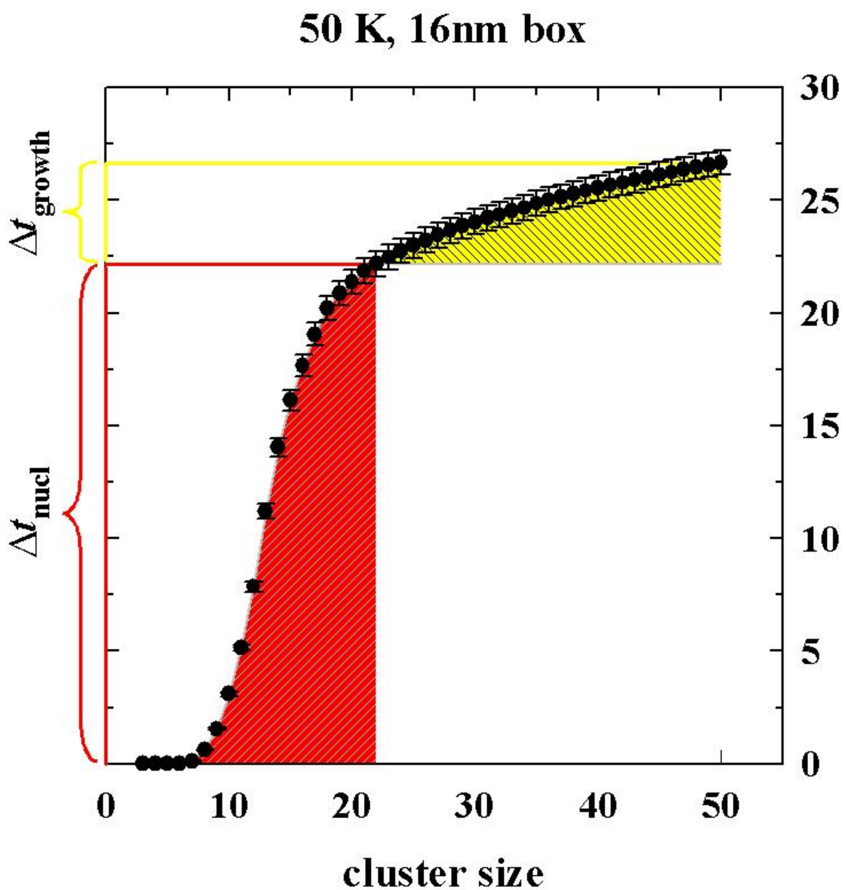
$$\tau(n) = \frac{\sum_{i=1}^{M} t_i(n)}{M}$$

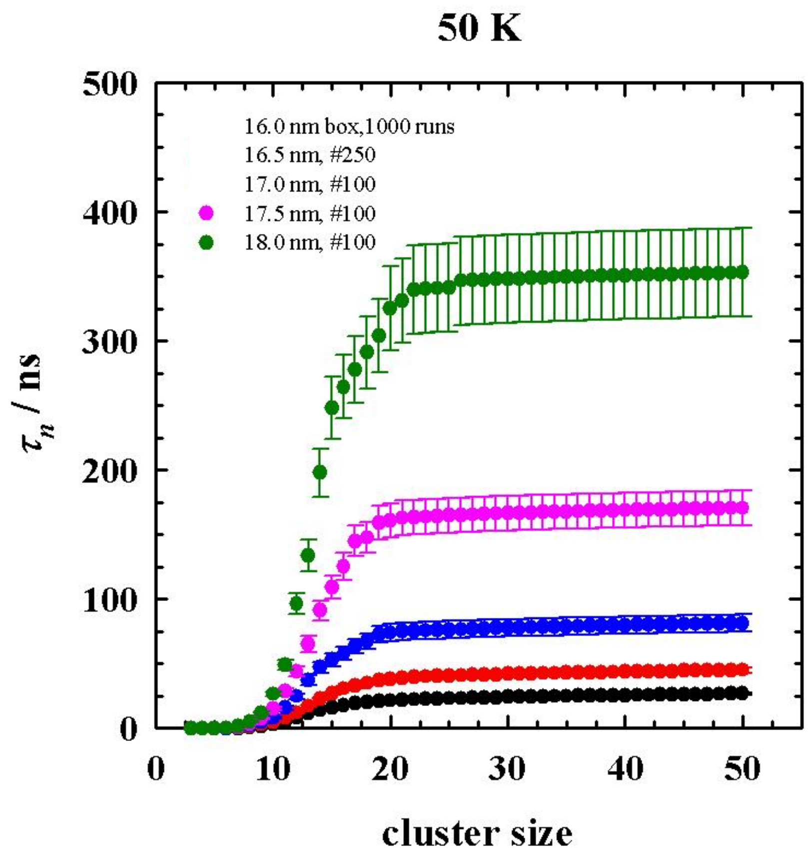
MD results and fits



$$\tau(n) = \frac{\tau_J}{2}\left[1 + Erf\left(b(n - n^*)\right)\right]$$

Coupling of nucleation and growth





low barrier:

➔ Dt_{nucl} ~ Dt_{growth}

➔no plateau: Nucleation and growth are coupled!

high barrier:

➔ $\Delta t_{nucl} >> \Delta t_{growth}$

➔ plateau

Nucleation at extreme supersaturations

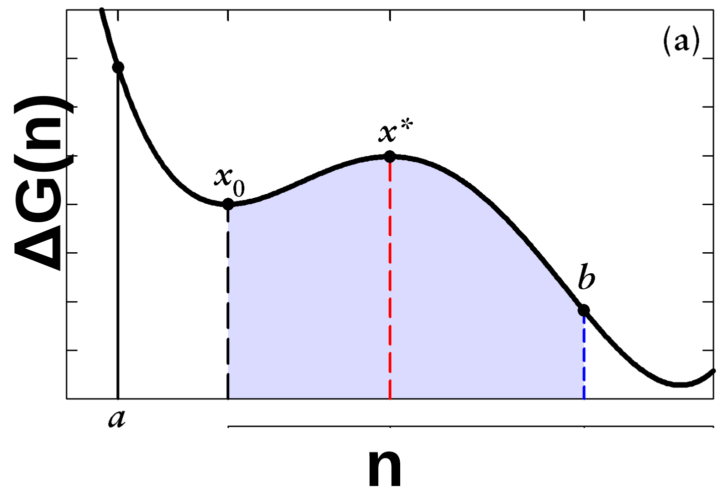
Kinetic Reconstruction of the free energy landscape

Kinetic Reconstruction of the free energy landscape

- Dynamics of an activated process

$$\frac{\partial f(n,t)}{\partial t} = \frac{\partial}{\partial n}\left(D(n) e^{-\beta \Delta G(n)} \frac{\partial}{\partial n}\left(f(n,t) e^{\beta \Delta G(n)} \right)\right)$$

- Ingredients:
  - Steady-state Probability: $P^{st}(n)$
  - MFPT: $\tau(n)$



Free energy landscape

$$\beta \Delta G(n) = \ln B(n) - \int \frac{1}{B(n')} dn' + C$$

$$B(n) = \frac{1}{P^{st}(n)}\left[\int_0^n P^{st}(n') dn' - \frac{\tau(n)}{\tau(b)} \right]$$

Attachment rate

$$D(n) = \frac{B(n)}{\left(\frac{\partial \tau(n)}{\partial n} \right)}$$

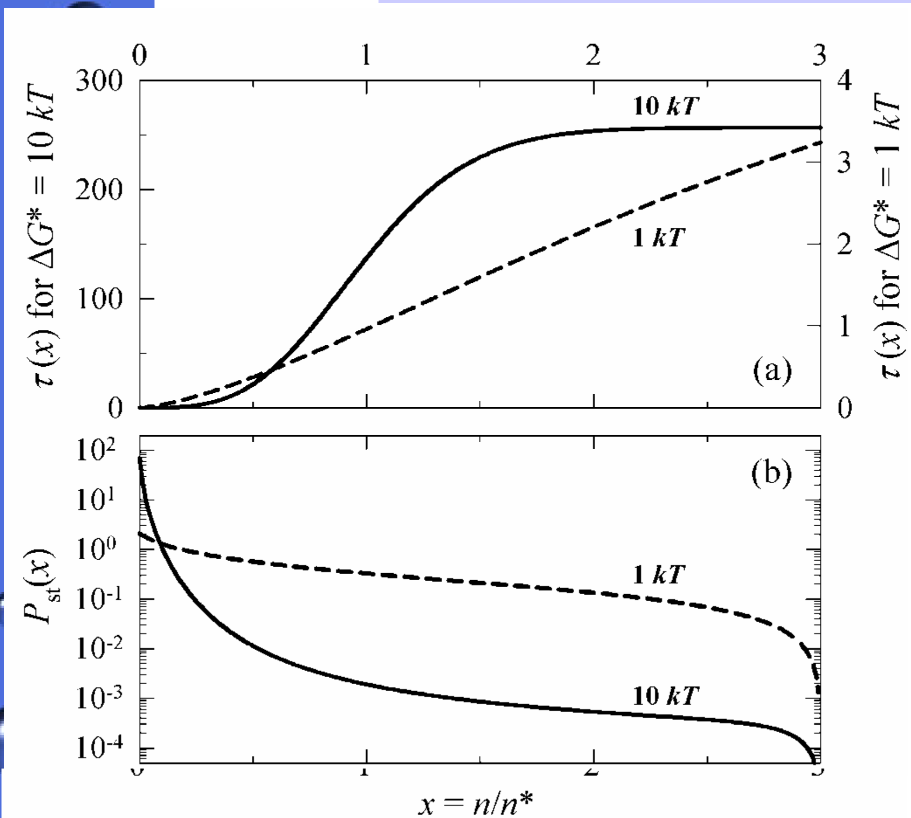
J. Wedekind, D.R., J. Phys. Chem. B, 2008, 112, 11060

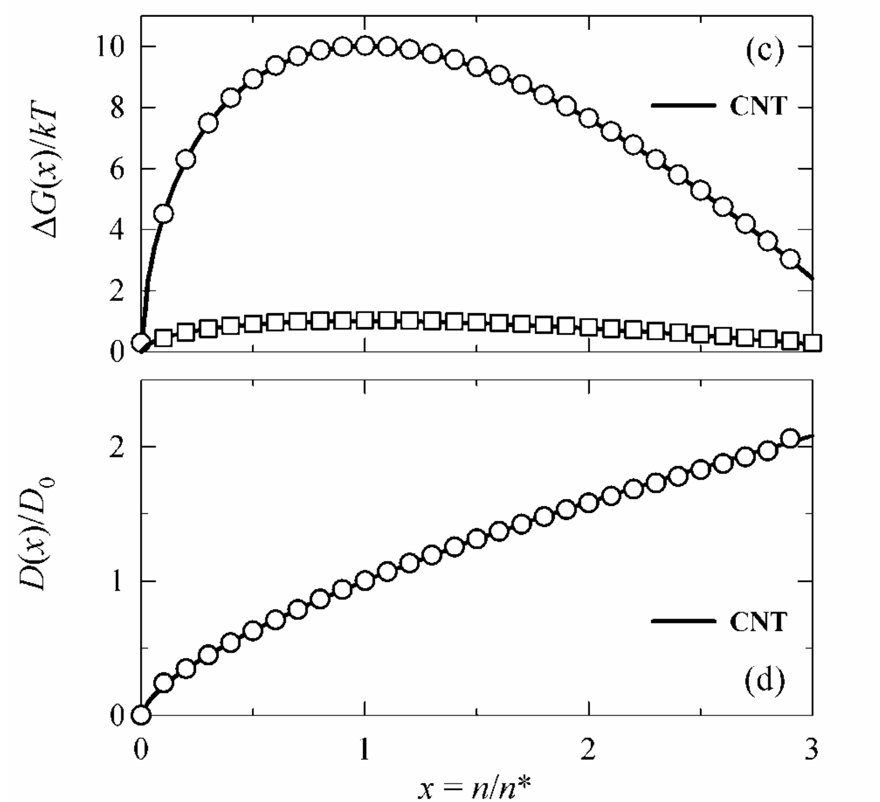
Comparison: Analitic results vs Reconstruction

$$\Delta G(x) = 2\Delta G^*\left(-x + \frac{3}{2}x^{2/3}\right)$$

$$D(x) = D_0 x^{2/3}$$

$$x = n/n^*$$





$$\beta\Delta G(x) = \ln B(x) - \int \frac{1}{B(x')}dx' + C$$

$$B(x) = \frac{1}{P^{st}(x)}\left[\int_0^x P^{st}(x')dx' - \frac{\tau(x)}{\tau(b)}\right]$$

$$D(x) = \frac{B(x)}{\left(\frac{\partial \tau(x)}{\partial x}\right)}$$

Perfect Reconstruction!

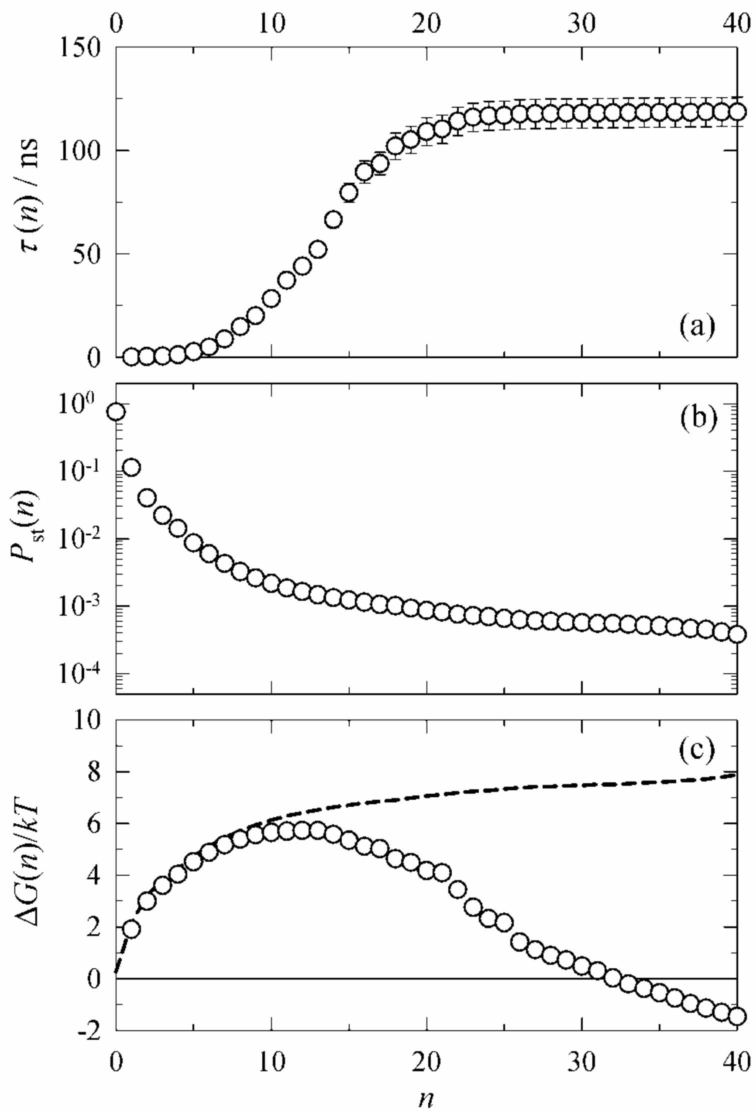
Kinetic reconstruction in a simulation

- Example:
  - MD simulation of argon nucleation at T=70K; V=(11nm)^3

$$\beta\Delta G(n) = \ln B(n) - \int \frac{1}{B(n')} dn' + C$$

$$B(n) = \frac{1}{P^{st}(n)}\left[\int_0^n P^{st}(n')dn' - \frac{\tau(n)}{\tau(b)}\right]$$

$$\beta\Delta G(n) \neq -\ln P^{st}(n)$$



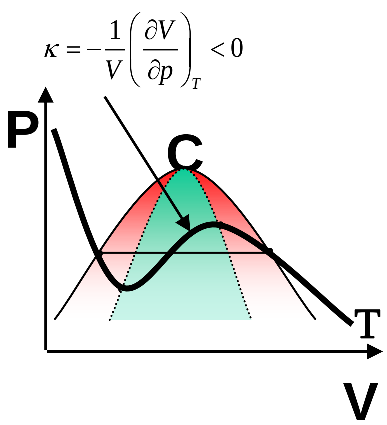
MD Simulations of Lennard-Jones Argon Nucleation at extreme supersaturations

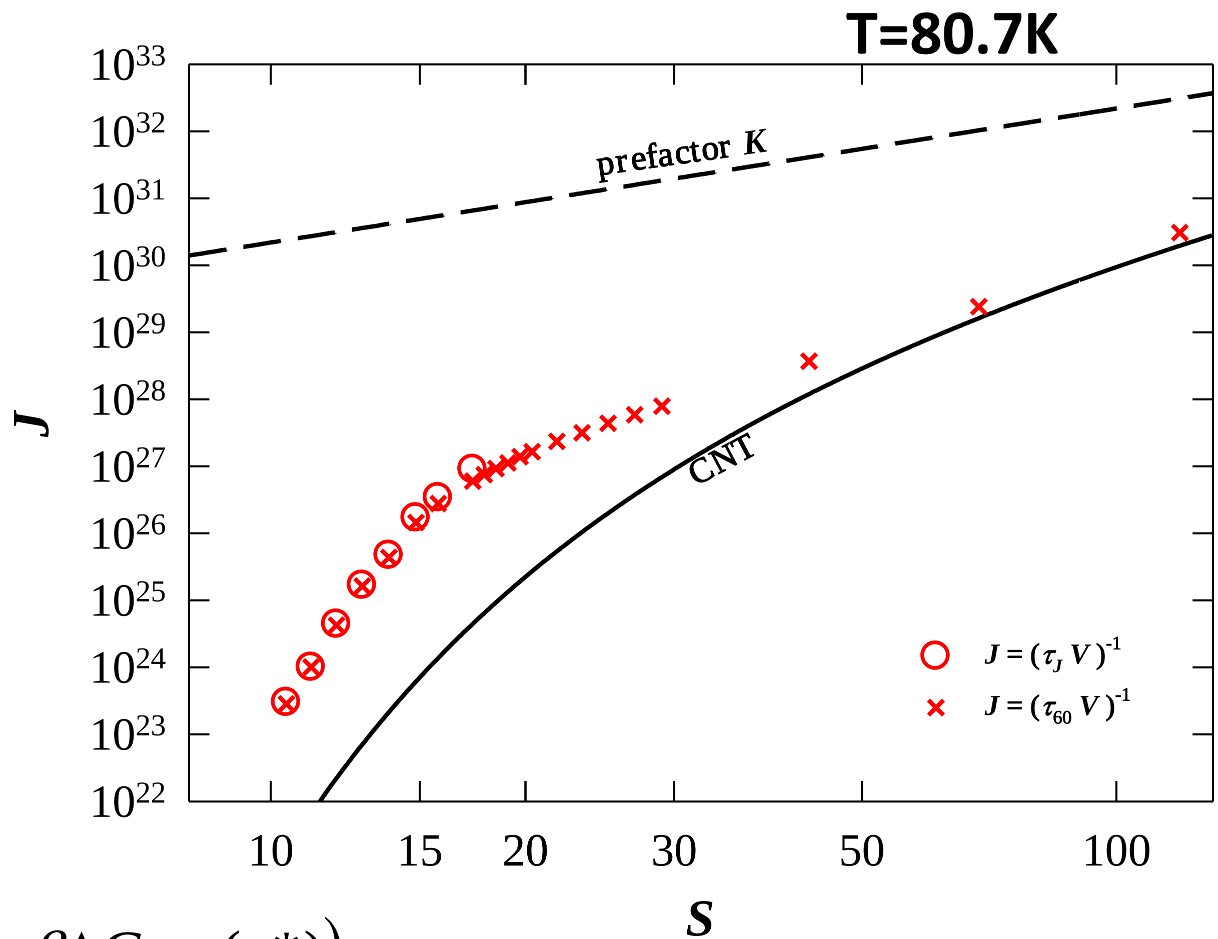
RESULTS

T = 80.7 K

Nucleation Rates

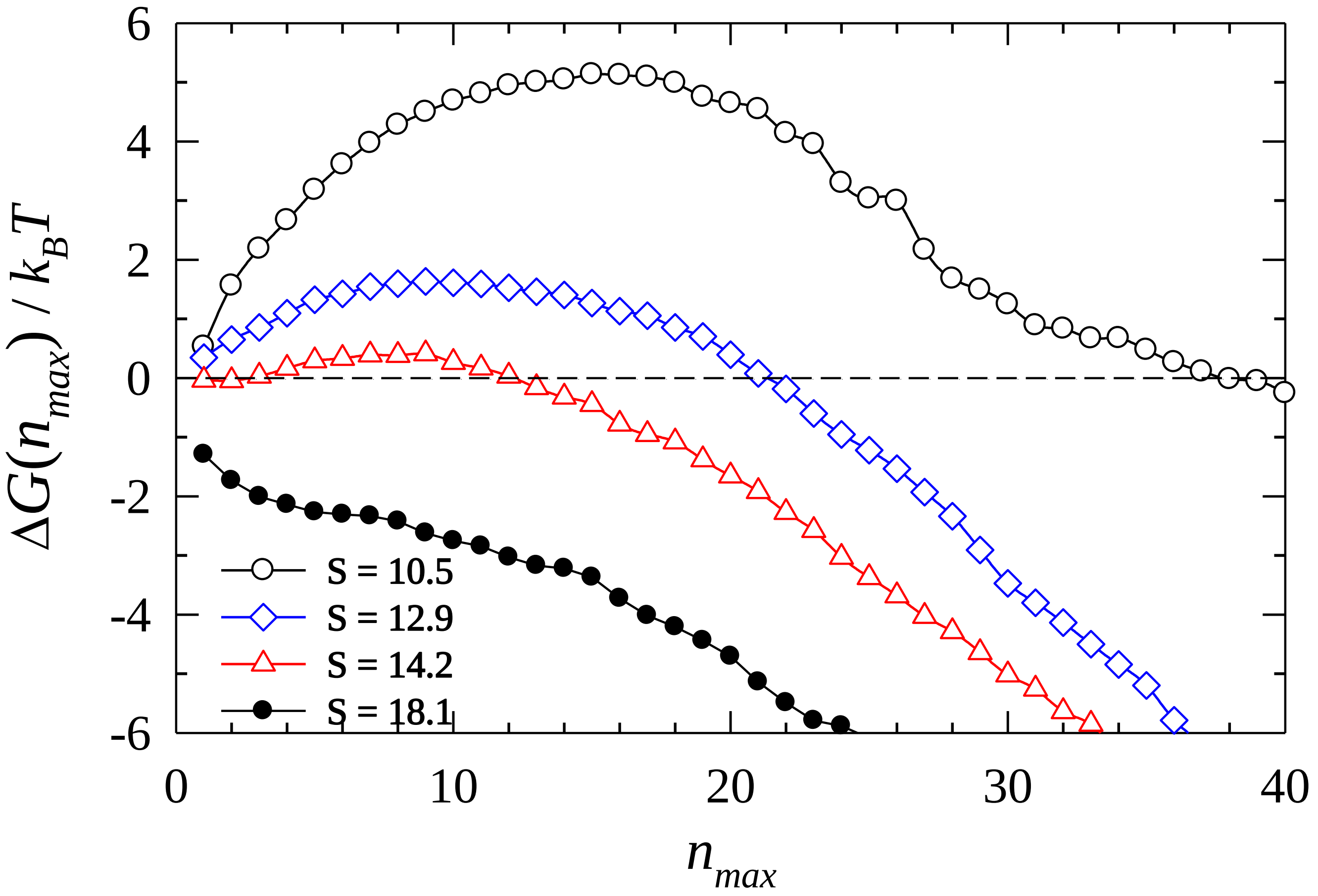
- Condensation at extreme supersaturations



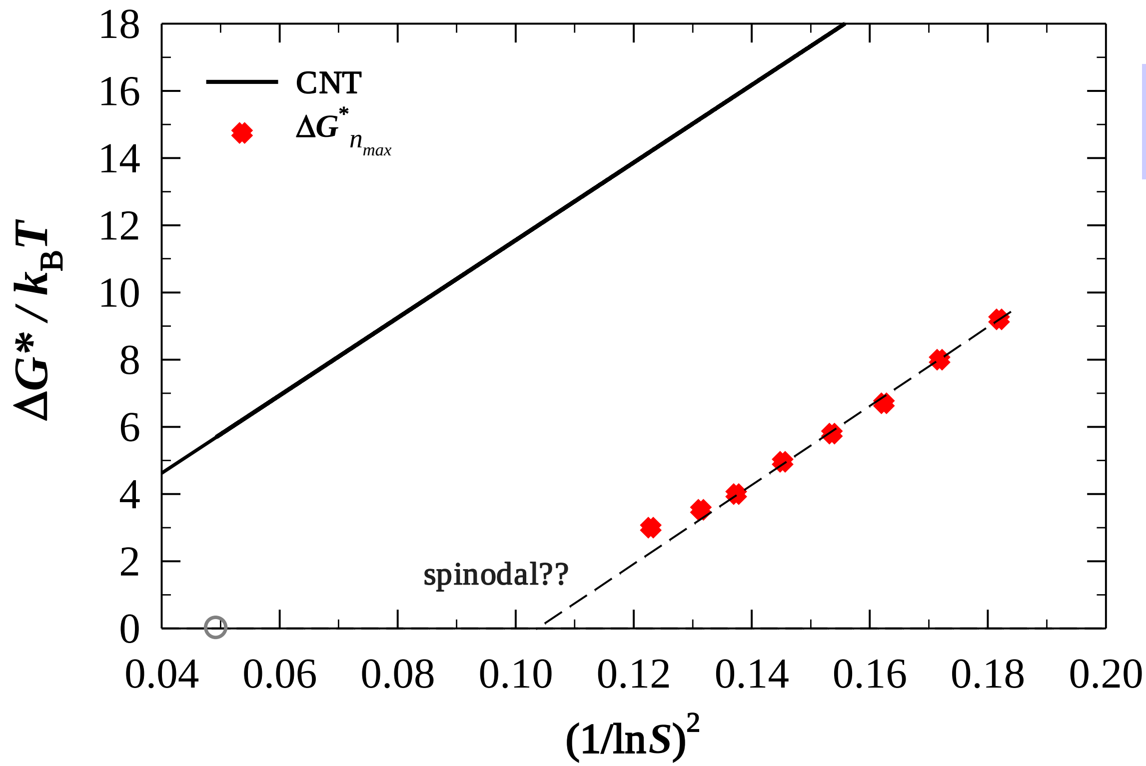


$$J_{CNT} = K_{CNT} \exp\left(-\beta \Delta G_{CNT}(n^*)\right)$$

Reconstruction of the free energy of cluster formation for the largest cluster



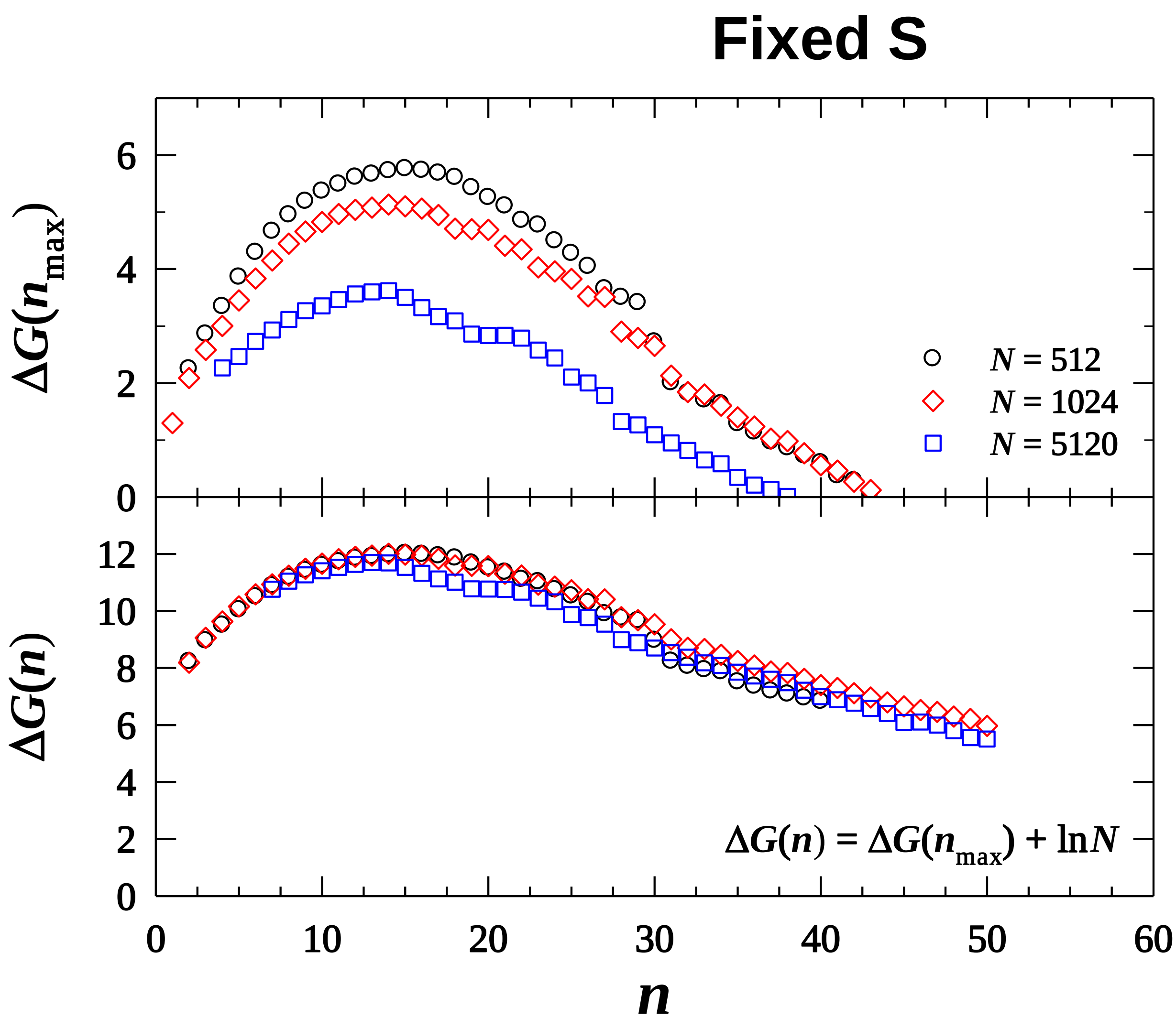
Nucleation Barrier Height: reaction coordinate matters



$$\Delta G^*_{CNT} = \frac{16\pi}{3} \frac{v_l^2 \gamma^3}{(kT \ln S)^2}$$

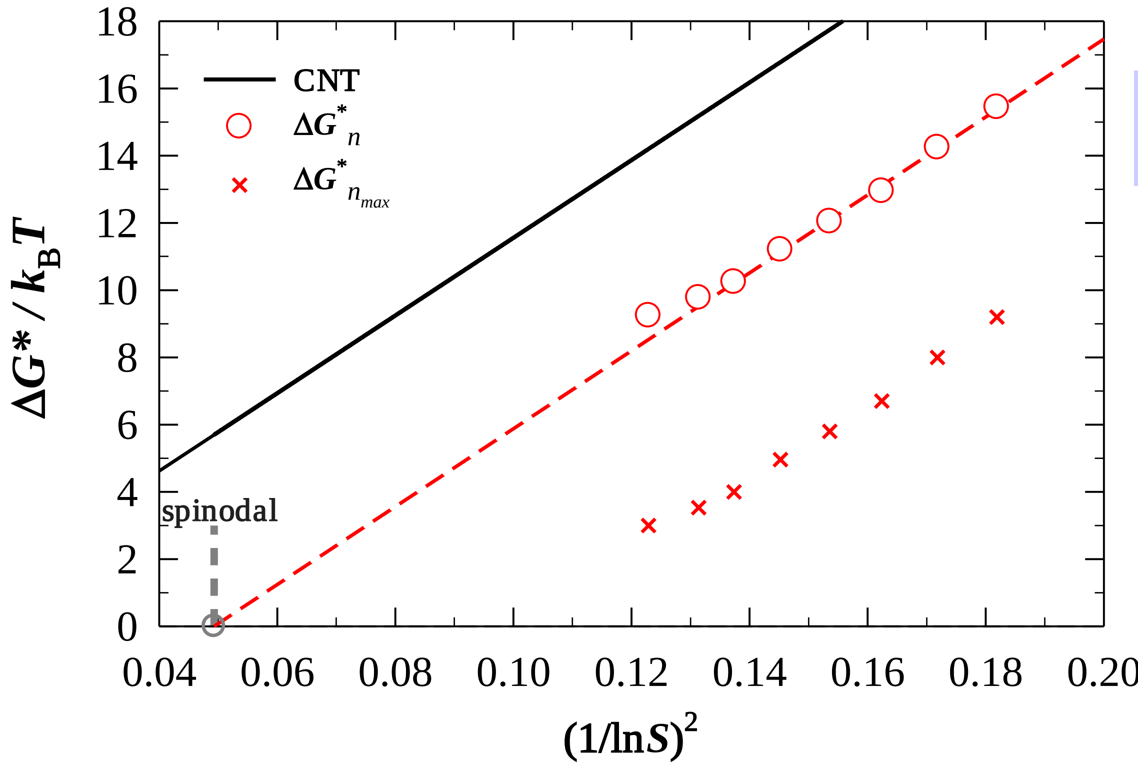
The vanishing of the barrier for the largest is NOT the signature of the spinodal

System size dependence of the free energy landscape for the largest



Nucleation Barrier Height: reaction coordinate matters

$$\beta\Delta G(n) = \beta\Delta G(n_{\max}) + \ln N$$



$$\Delta G^*_{CNT} = \frac{16\pi}{3}\frac{v_l^2\gamma^3}{(kT\ln S)^2}$$

Scaling relations seem to hold

$$\Delta G(n^*) = \Delta G_{CNT}(n^*) + D(T)$$

What does the vanishing of the free energy for the largest mean?

- "Equilibrium" probability of having 1 critically-sized cluster:

$$N(n^*) = N\exp(-\beta\Delta G(n^*)) = 1$$

$$\ln N = \beta\Delta G(n^*)$$

$$\beta\Delta G(n^*) = \beta\Delta G(n^*_{\max}) + \ln N$$

$$\beta\Delta G(n^*_{\max}) \approx 0$$

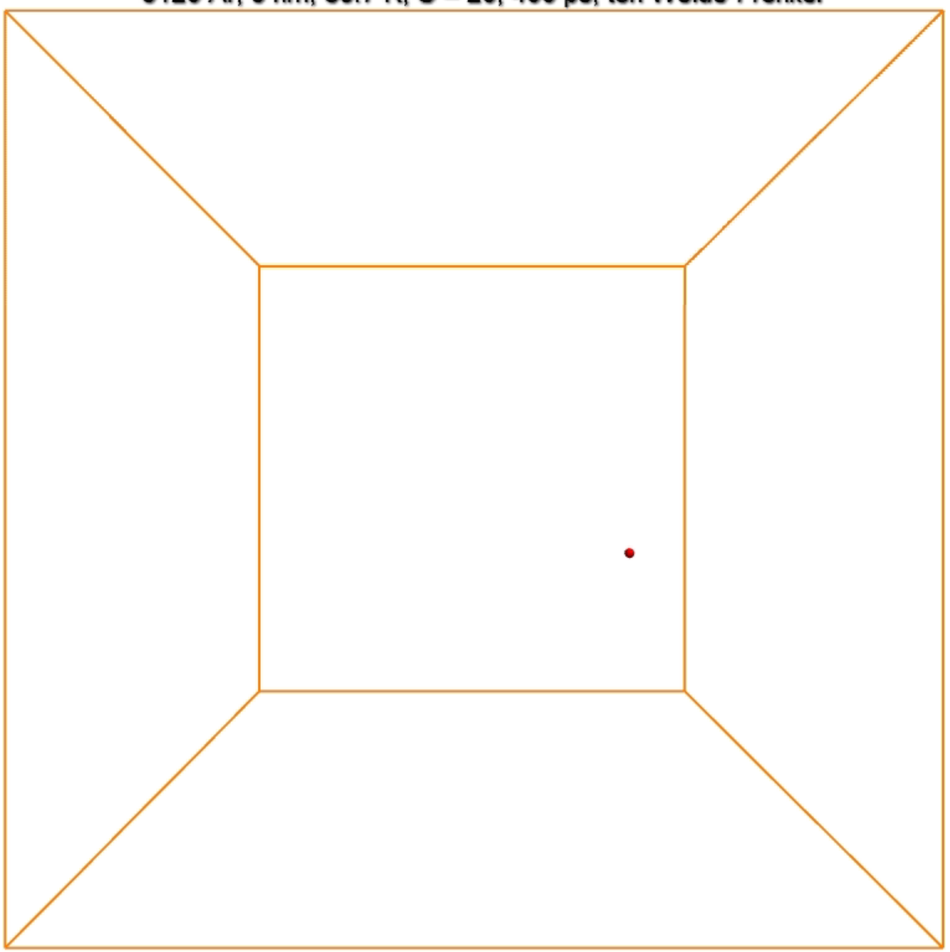
- The vanishing of the barrier for the largest indicates where the system has probably a critical cluster right at the start ⟷ the limit of kinetic metastability , which is NOT the spinodal

- The kinetic limit of stability of a metastable phase is system size dependent!

Nucleation vs spinodal decomposition

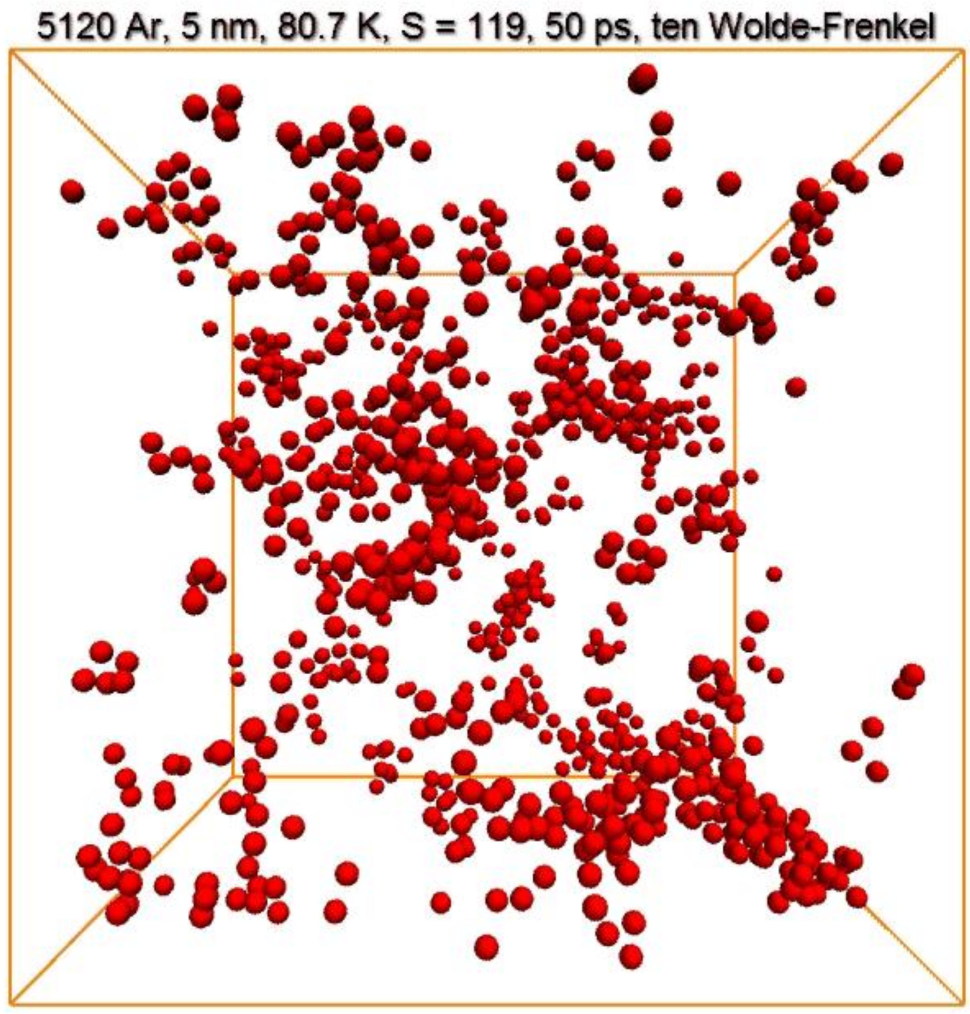
- Nucleation

5120 Ar, 9 nm, 80.7 K, S = 20, 400 ps, ten Wolde-Frenkel

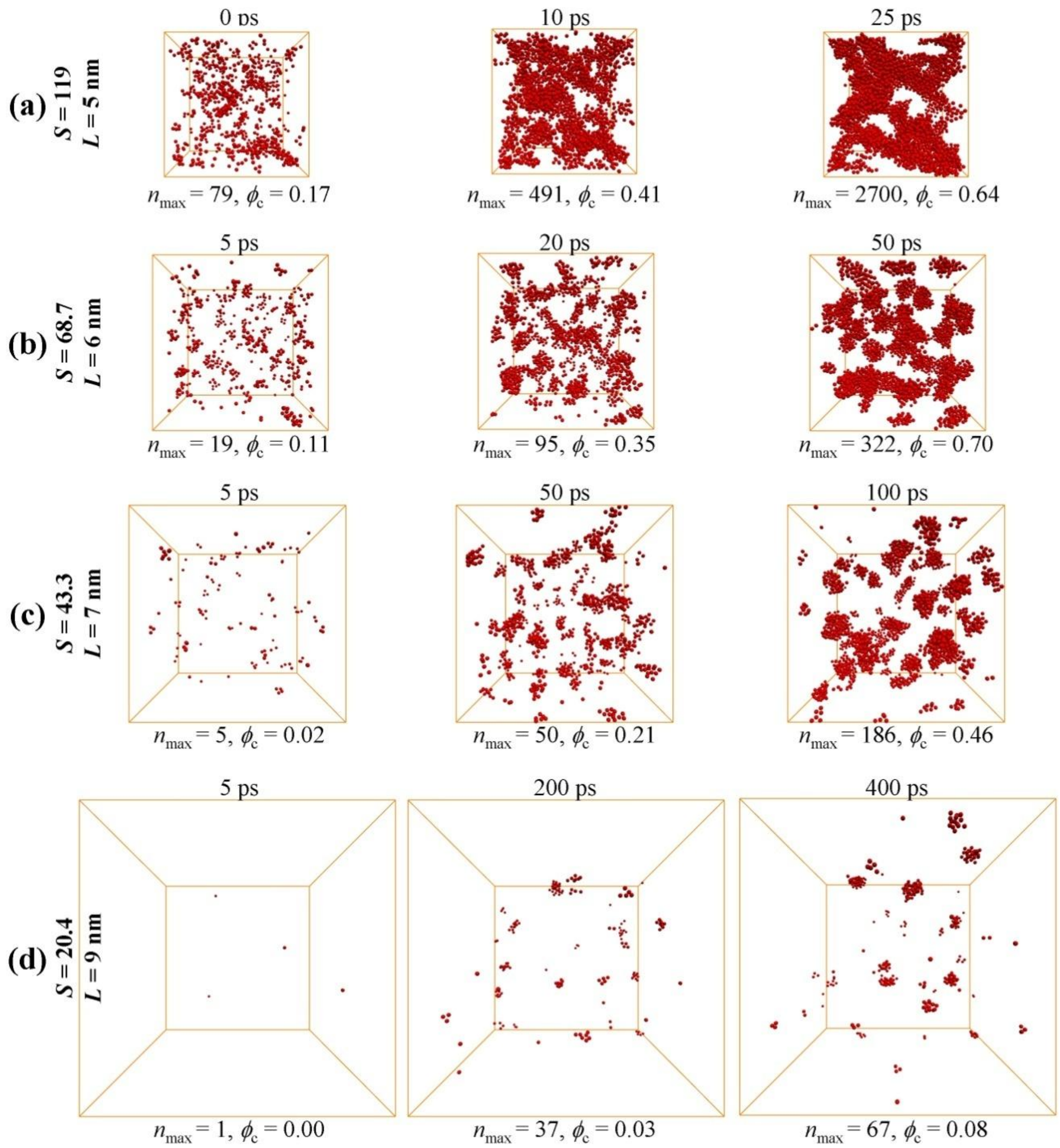


Nucleation vs spinodal decomposition

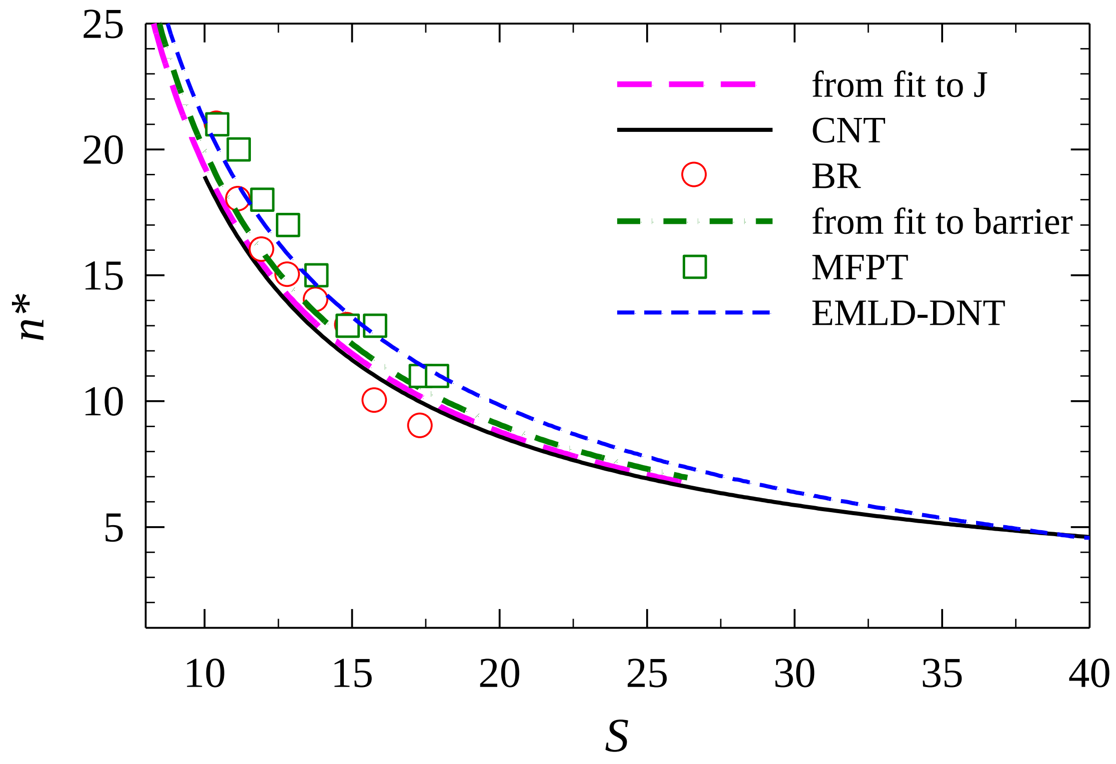
- Spinodal decomposition



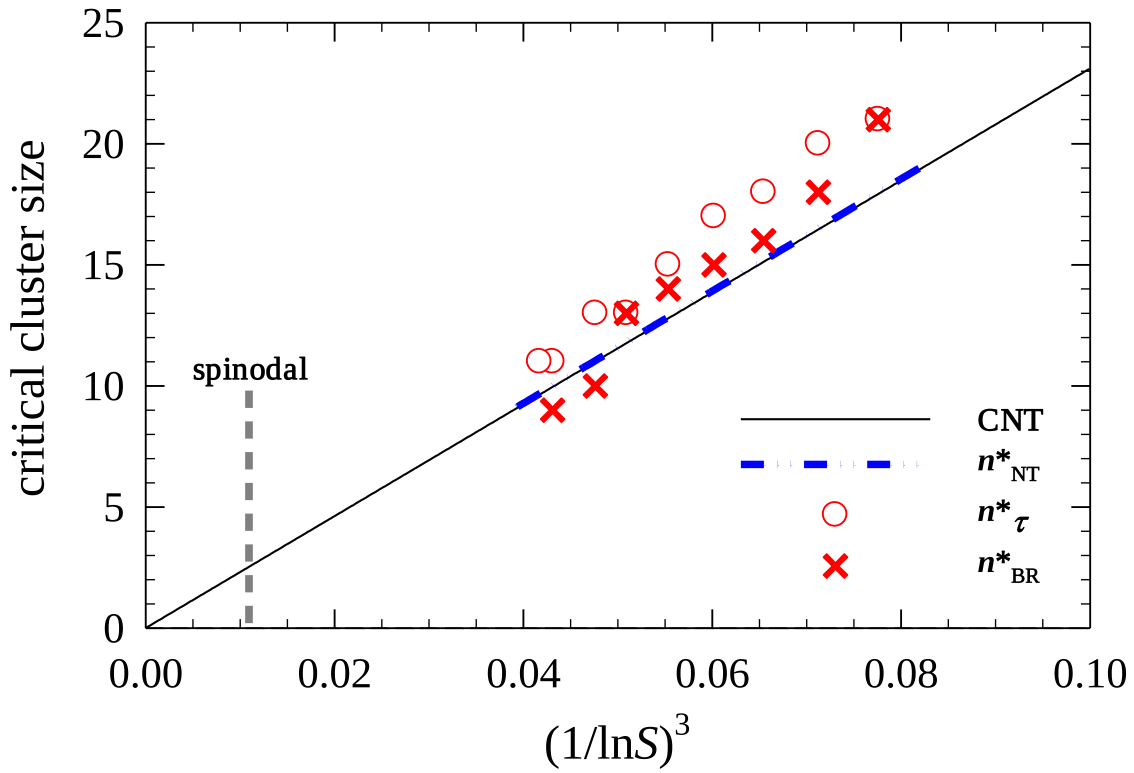
From nucleation to spinodal decomposition



Critical cluster size approaching the spinodal: No evidence of divergency



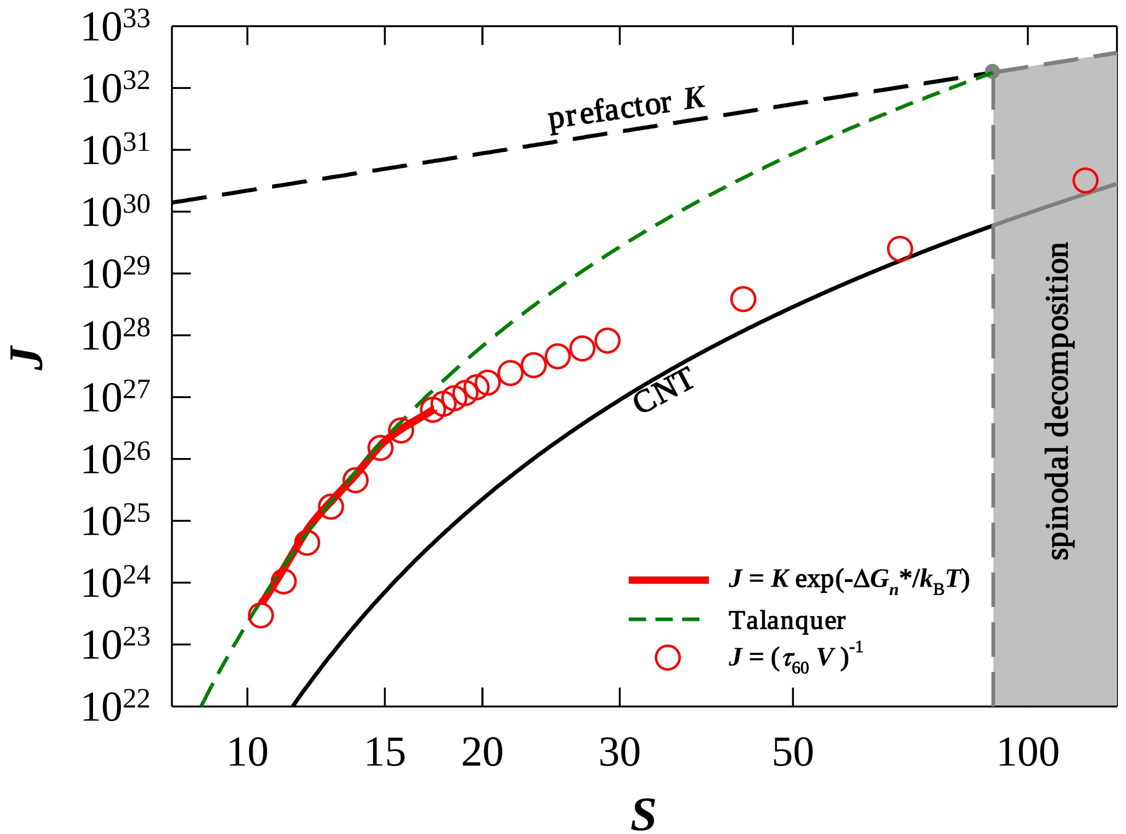
Critical cluster size approaching the spinodal



$$n^* = \frac{32\pi}{3}\frac{v_l^2\gamma^3}{(kT\ln S)^3}$$

CNT prediction is surprinsingly good

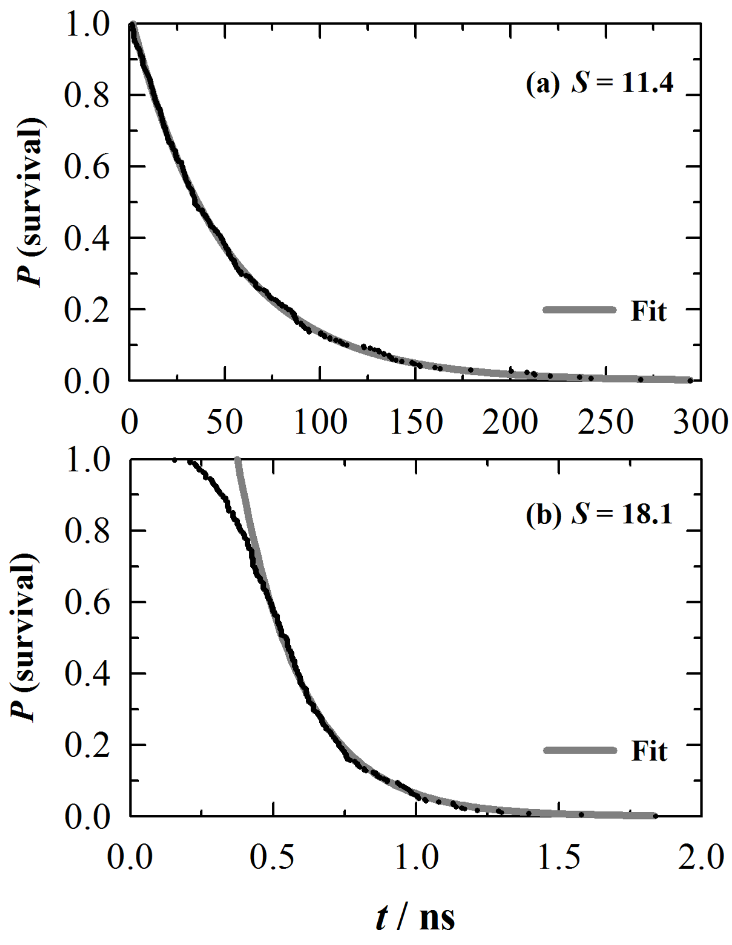
Putting the pieces back together



$$J_{Talanquer} = K_{CNT} \exp\left(-\beta\left(\Delta G_{CNT}(n^*) - \Delta G_{CNT}^{spinodal}\right)\right)$$

Timescales: nucleation vs growth

- Survival probabilities

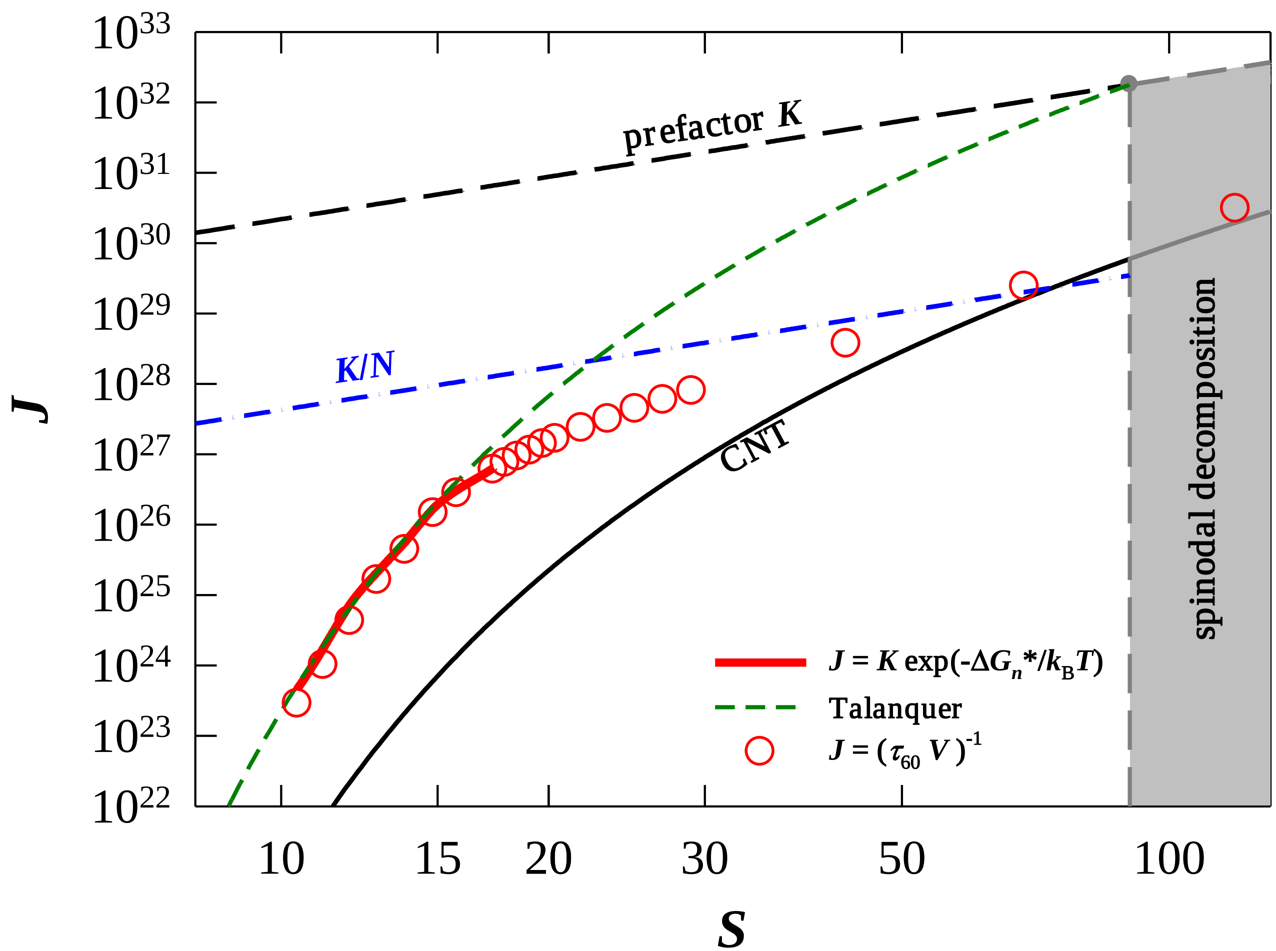


$$P_{surv}(t) = \exp\left(-\frac{t-t_0}{\tau_J}\right)$$

Beyond $\Delta G(n^*_{max})=0$
$\tau_J < t_0$

The speed of phase transformation is controlled by how fast a cluster can grow

Crossover between nucleation and (diffusion-limited) growth



Conclusions

- **Nucleation at extreme supersaturations using MD simulations**
- **New simulation techniques:**
  - **Finite-size effects in simulations of nucleation**
  - **A new method to analyze simulations of activated processes: Mean First-Passage Times**
  - **Kinetic Reconstruction of the free-energy landscape**
- **Main Results:**
  - **Reaction coordinate matters**
  - **The kinetic stability limit of a metastable phase depends on system size and it is different from the spinodal**
  - **Crossover between nucleation and (diffusion-limited) growth of the new phase**
  - **CNT predicts accurately n^* but mispredicts ΔG^* by a temperature dependent constant**

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