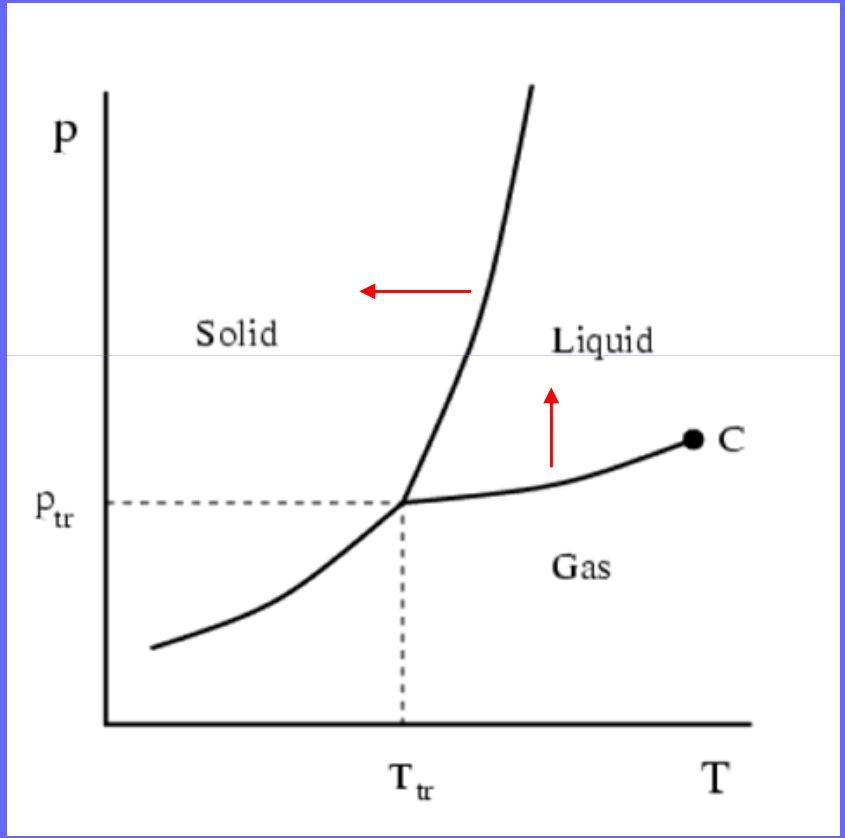
Nucleation, growth and spinodal decomposition

Biman Bagchi

Indian Institute of Science, Bangalore

Gas-liquid phase diagram

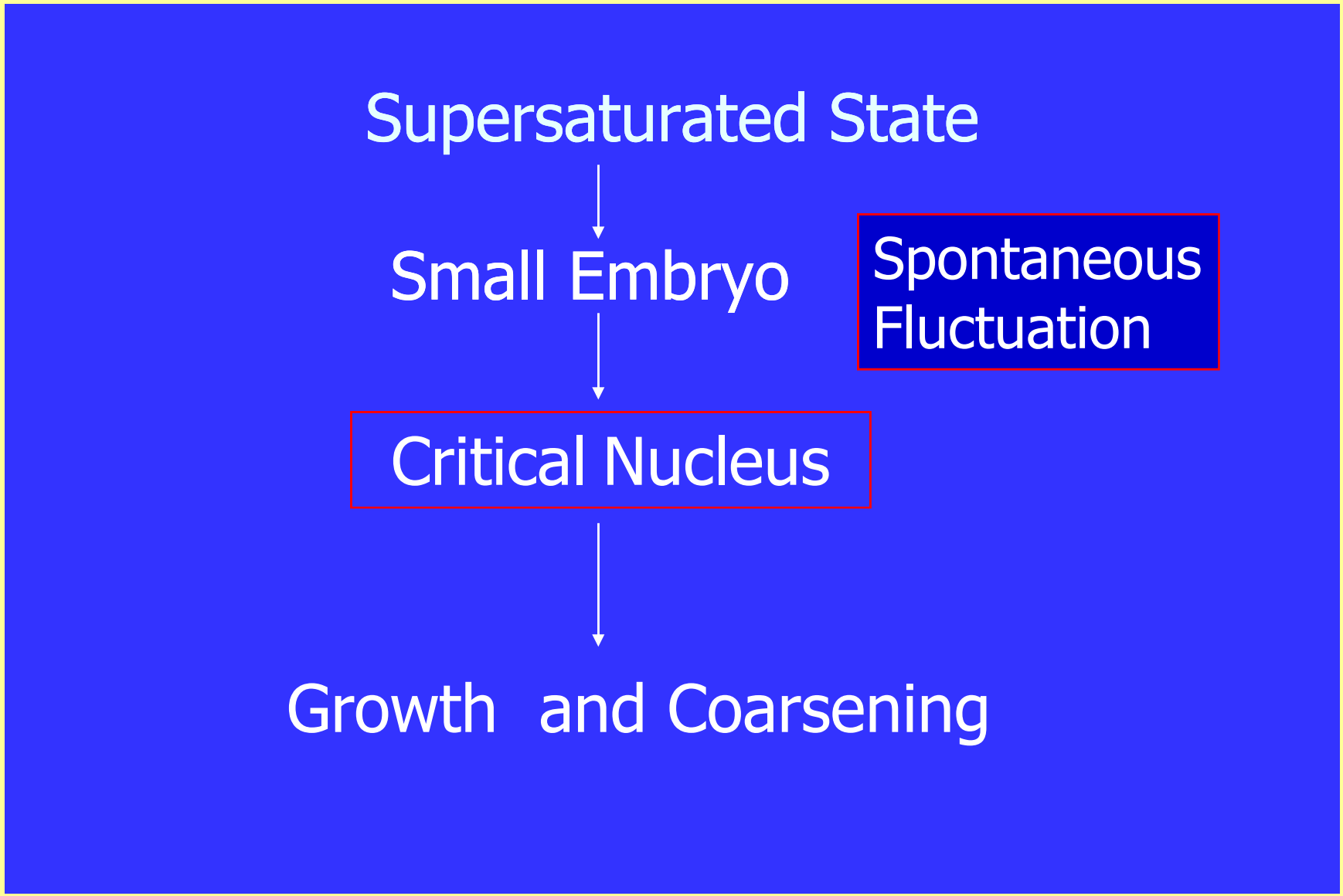


- First-order phase transitions occur through an activated process: **nucleation**
- Formation of a nucleus of stable phase inside parent metastable phase has two competing factors ...

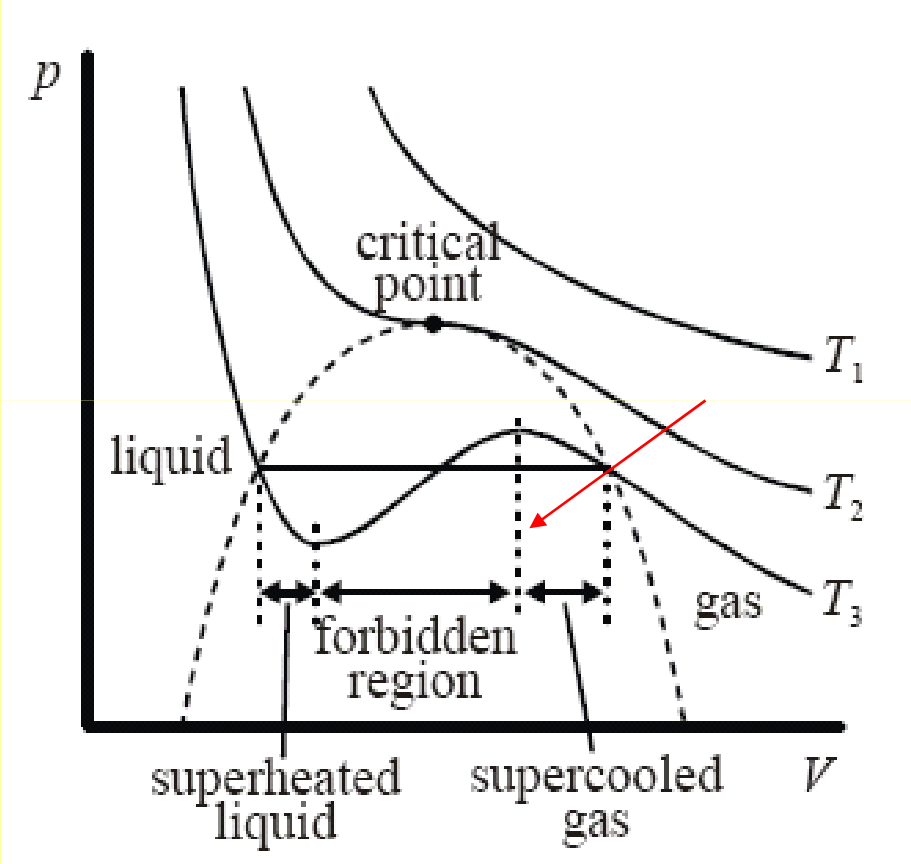
  Profit: Bulk free energy

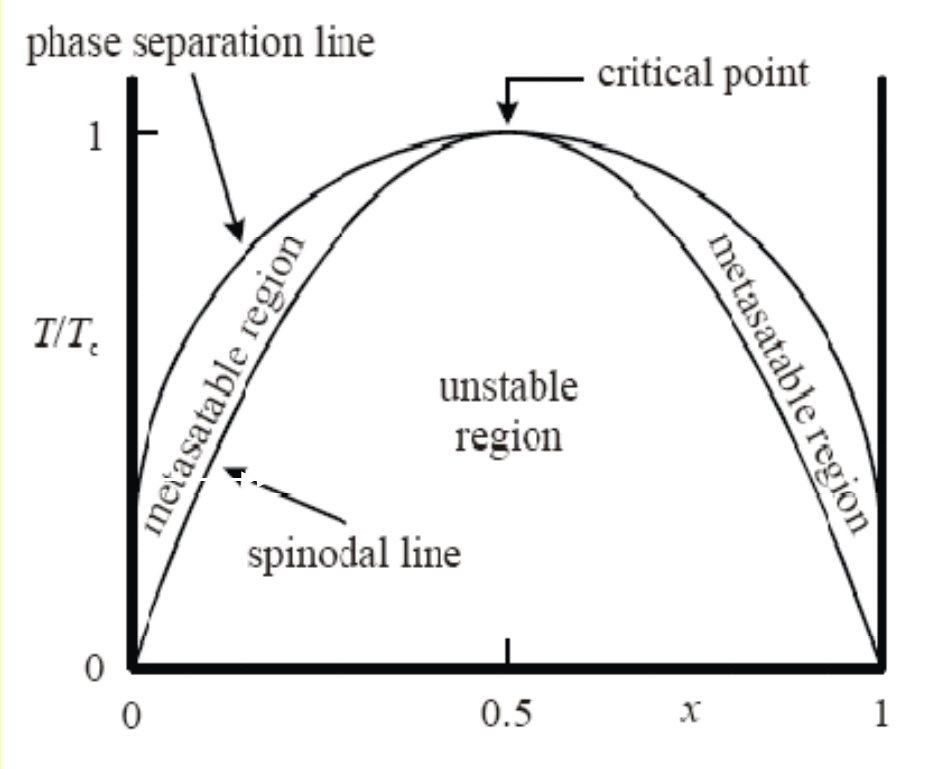
  Loss: Surface free energy
- Nuclei larger than a critical size grow spontaneously, whereas smaller ones dissolve back into the parent phase.
- **This picture of nucleation as a localized and rare fluctuation underlies classical nucleation theory, and is an adequate model at *small supersaturations*.**
- Under these conditions, the nucleation time is long relative to the structural relaxation time, and the nucleation process can be treated by equilibrium (thermodynamic) considerations involving the work needed to form the critical nucleus.

Homogeneous Nucleation



Stability, metastability and instability

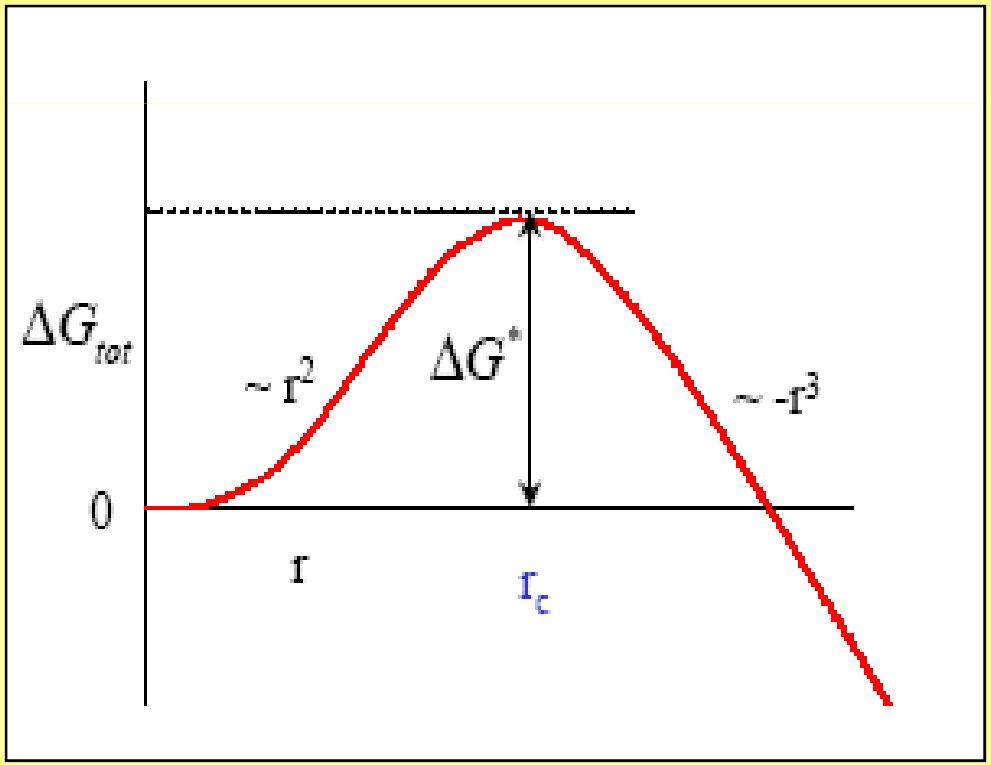




Mean-field theory picture (van der Waals) : Diverging compressibility at MF spinodal

Classical nucleation theory (CNT)

3D: $$\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma$$



γ=Surfac tension

$$R^* = \frac{2\gamma}{\Delta G_V}$$

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta G_V)^2}$$

❑ 2D: $\Delta G(r) = -\pi r^2 \Delta G_A + 2\pi r \gamma_L$

$$R^* = \frac{\gamma_L}{\Delta G_A}$$

$$\Delta G^* = \frac{\pi \gamma_L^2}{\Delta G_A}$$

❑ Rate (BD) = $\Gamma \exp(-\beta \Delta G^*)$

Γ : Kinetic prefactor (usually weak function of T)

Zeldovich Correction : Dynamic Effects on Γ

- **Allows for evaporation of molecules from growing droplet**
- **Similar to Smoluchowski expression of effects of viscosity on rate of a reaction**
- **Non-EQM multiplying factor Z is proportional to the 2nd derivative of free energy, that is barrier frequency (ω_b).**
- **The Zeldovich factor (Z) is typically between 0.01 and 0.001.**

Zeldovich Correction Contd…

$$A_n + A \square \quad A_{n+1}$$

Clusters are developed by addition or removal of single particle

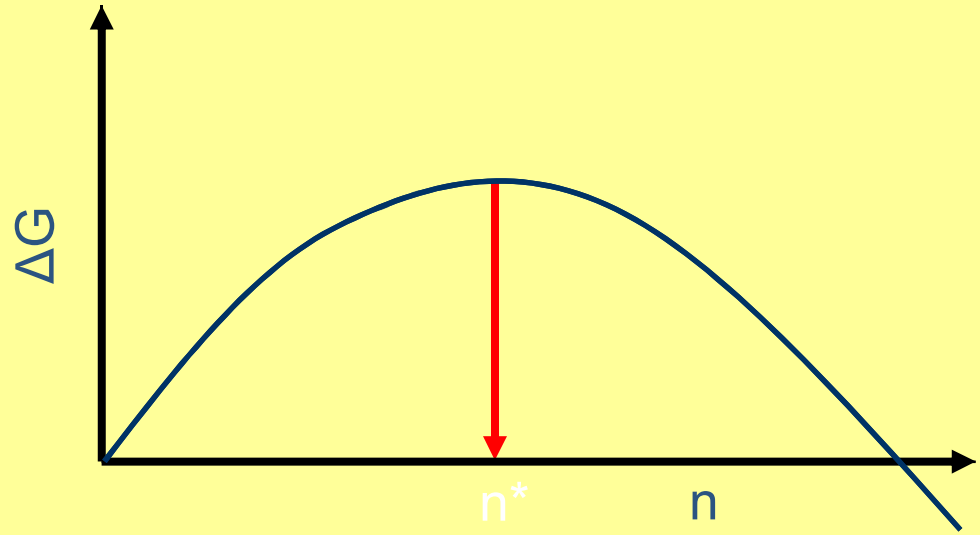
$$C(n) = C(1)\exp(-\frac{\Delta G(n)}{k_B T})$$

C(n) = Equilibrium concentration of embryos of '*n*' particles

$$\Delta G(n) = -n\Delta G_n + \gamma n^{2/3}$$

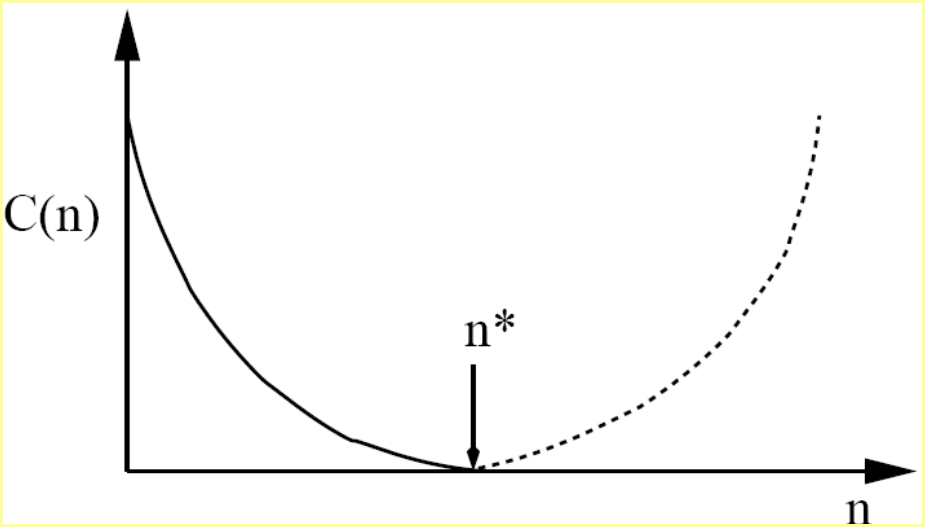
Free energy of formation of cluster of size '*n*'

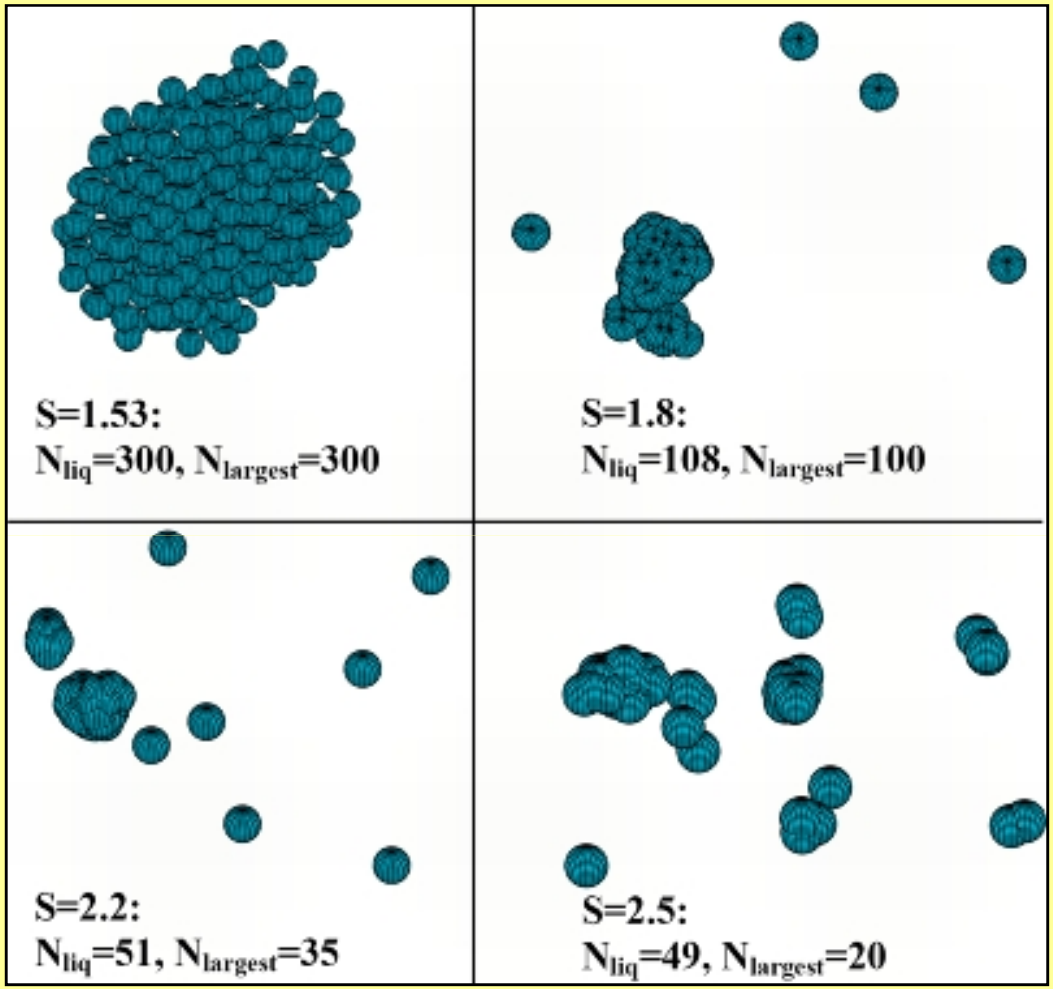
Zeldovich Correction Contd…



equilibrium free energy as a function of cluster size

Number density profile of clusters





As spinodal is approached the separation between the size of the largest cluster and total number of liquid particles in the system increases dramatically.

The growth attains more spinodal character => growth occurs throughout the system.

Nucleus grows in a more continuous and collective manner and clusters becomes spatially more diffuse.

Bhimalapuram, Chakrabarty and Bagchi, Phys. Rev. Lett. **98**, 206104 (2007)

Zeldovich Correction Contd…

The rate of cluster formation by single molecule condensation and/or single molecule evaporation

$$J_n = \beta s(n) f(n,t) - w(n+1)s(n+1) f(n+1,t)$$

principle of detailed balance

$$ws(n+1)c(n+1) = \beta s(n)c(n)$$

Therefore rate

$$J_n = -\left[\beta s(n)\frac{\partial f(n,t)}{\partial n} + \frac{\beta s(n) f(n,t)}{c(n)}\frac{\partial c(n)}{\partial n}\right]$$

Zeldovich Correction Contd…

Again

$$\frac{\partial \ln c(n)}{\partial n} = -\frac{\Delta G(n)}{k_B T}$$

Therefore the rate

$$J_n = -\left[\beta s(n)\frac{\partial f(n,t)}{\partial n} + \frac{\beta s(n) f(n,t)}{k_B T}\frac{\partial \Delta G(n)}{\partial n}\right]$$

Diffusion coefficient in a discrete process is

$$D = \frac{1}{2}\Gamma\left\langle (\Delta x)^2 \right\rangle \quad \text{where } \Gamma = 2\beta s(n)$$

Zeldovich Correction Contd…

After putting the boundary conditions

$$J = \beta \left[\int_0^{\infty} \frac{dn}{s(n)c(n)} \right]^{-1}$$

$c(n)$ goes through a pronounced minimum at the critical size n^*. One can remove the surface area from the integral.

$$J = \beta s(n^*) \Big/ \int_0^{\infty} \frac{dn}{c(n)}$$

Zeldovich Correction Contd…

Taylor series expansion of $\Delta G(n)$ around $\Delta G(n^*)$

$$\Delta G(n) = \Delta G(n^*) + \frac{1}{2}\left(\frac{\partial^2 \Delta G(n)}{\partial n^2}\right)_{n=n^*} (n - n^*)^2$$

goes through a maximum at n^*

$$\left(\frac{\partial^2 \Delta G(n)}{\partial n^2}\right)_{n^*} < 0$$

Zeldovich Correction Contd…

Thus

$$\int_0^\infty \frac{dn}{c(n)} = \left[c(1) \exp\left(- \Delta G(n^*) \Big/ k_B T \right) \right]^{-1} \int_0^\infty dn \exp\left(\frac{\alpha}{2 k_B T} \left(n - n^* \right)^2 \right)$$

With $\alpha < 0$, where α is given by

$$\alpha = \left(\frac{\partial^2 \Delta G(n)}{\partial n^2} \right)_{n=n^*}$$

Zeldovich Correction Contd…

Thus

$$J = \beta s(n^*) c(1) \exp\left(-\Delta G(n^*) / k_B T \right) \left(\frac{|\alpha|}{2\pi k_B T} \right)^{1/2}$$

Zeldovich factor Z is given by

$$Z = \left(\frac{|\alpha|}{2\pi k_B T} \right)^{1/2}$$

$$\alpha = \left(\frac{\partial^2 \Delta G(n)}{\partial n^2} \right)_{n=n^*} = \left(\frac{2\Delta G(n^*)}{3n^*} \right)$$

Zeldovich Correction Contd…

After putting the value of α

$$Z = \left(\frac{\Delta G(n^*)}{3\pi k_B T n^{*2}} \right)^{1/2}$$

The final rate of nucleation becomes,

$$J = Z\beta s(n^*)c(n^*)$$

Zeldovich Correction Contd…

Zeldovich factor Z is given by

$$Z = \left(\frac{|\alpha|}{2\pi k_B T} \right)^{1/2}$$

$$\alpha = \left(\frac{\partial^2 \Delta G(n)}{\partial n^2} \right)_{n=n^*} = \left(\frac{2\Delta G(n^*)}{3n^*} \right)$$

$$Z = \left(\frac{\Delta G(n^*)}{3\pi k_B T n^{*2}} \right)^{1/2}$$

The rate of nucleation

$$J = Z\beta s(n^*)c(n^*)$$

Surface tension and spinodal

- At deep supercooling/large supersaturation, R^* becomes small.
- Curvature dependent surface tension:

$$\gamma(R) = \gamma^{\dagger}[1 - 2\delta / R]$$

Tolman's length $\delta = 0.38\sigma$ for $T = 0.8\varepsilon/k_B$

- **How does surface tension change with supersaturation ?**

Non-classical nucleation theories

- At large supercooling, size of the nucleus becomes small. Thermodynamics may not be applicable.
- Cluster becomes ramified and non-spherical. Concept of surface tension?
- Square-gradient (Cahn-Hillard), Landau-Ginzburg, density functional theory .....

Fundamental Issues and Controversies …

- **Is there a spinodal at all? All MFT, SG theories predict so.**
- **What happens to nucleation barrier? Does it ever go to zero? At the spinodal? Or, beyond?**
- **What happens to the critical nucleus? Its size and shape? … and it's neighbourhood?**
- **What happens in 2D ?**
- **Shape fluctuations ? Nucleation time vs shape relaxation time ?**

Many important theories and conjectures

- Unger and Klein (1984) predicts that the critical radius of nucleation diverges as

$$R^* \sim L\,(h_S - h)^{-1/4}$$

Where L is the range of interaction potential and h is the external magnetic field, h_S is the value of the field at spinodal.

- **Nucleation near the spinodal: Limitations of mean field density functional theory**
  - Gerald Wilemski and Jin-Song Li (JCP, 2002)
  - **"GT predicts that *at the spinodal the free energy barrier to nucleation vanishes while the radius of the critical fluctuation diverges. We show numerically that the scaling behavior found by Cahn and Hilliard for these quantities holds quantitatively* for both GT and MFDFT."**
- **The *divergence of R* is due to the divergence of the mean field isothermal compressibility of the fluid at the spinodal*.**

** Binder Analysis (1986)**

- No divergence of cluster size at the spinodal unless the range of interaction is also very large. Transition from metastable to unstable state is characterized by a transition from activated to continuous growth.

- Curvature-Dependent Surface Tension of a Growing Droplet
  - **Michael P. Moody and Phil Attard (PRL, 2004)**
- ***Surface tension decreases approximately linearly with the supersaturation ratio and that it vanishes at the spinodal.***
- The theory gives a smaller critical radius and reduces the free energy barrier to nucleation compared to classical homogeneous nucleation theory, which have important implications for the kinetics of droplet and bubble formation.

- **Reconstruction of the free energy in the metastable region computer simulations**
- Armando Ticona Bustillos, Dieter W. Heermann, and Claudette E. Cordeiro (JCP, 2004)

- . Although mean-field theory predicts a sharp transition between the metastable and the unstable region where the free-energy barrier is zero, **the results for the nearest-neighbor Ising model show that the free-energy barrier does not go to zero.**

Problems of simple MC

- The convergence is rather slow. Cannot treat high barrier.
  Poor sampling of configurations near phase transitions.
- Traditional MC is good for computing expectation values for internal energy and derivatives but not for free energy or entropy.
- Assigning non-Boltzmann weights become necessary to overcome loss of *ergodicity* in systems with phase transitions or complex energy landscape. Time needed to pass through the low-probability states connecting high-probability states of interest is reduced. Desired Boltzmann distribution is recovered by reweighting.

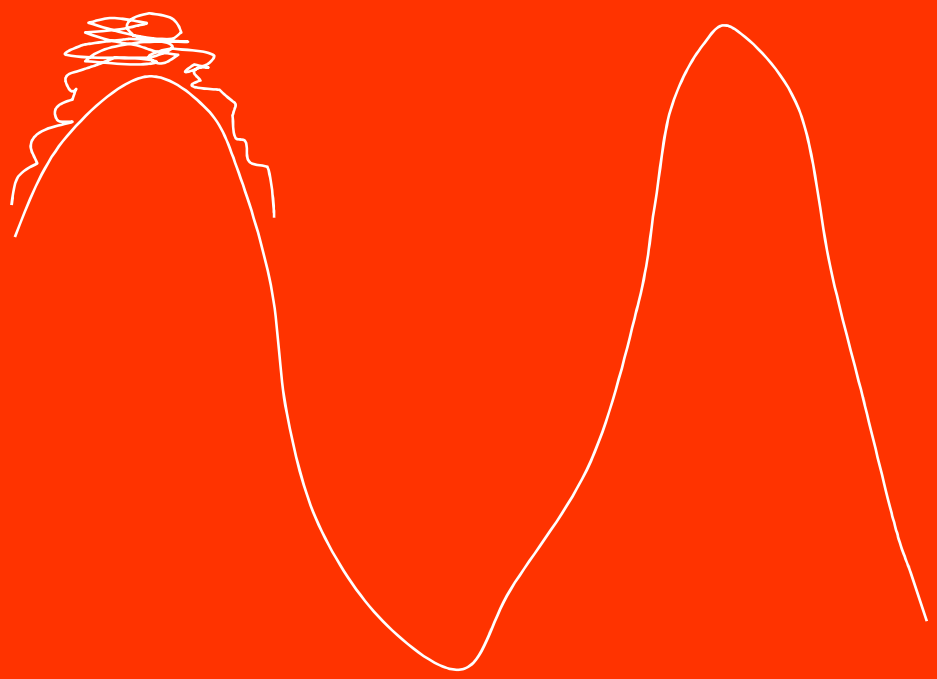
Simple Monte Carlo:

Markov chain visits the microstates at a frequency

$$\pi_s \propto \exp(-\beta H_s)$$

Problems:

- 'Equilibrium configurations' are sampled 'sufficiently' well, but not the barrier top
- Near phase transition
- Simple Monte Carlo is never 'sufficiently' long to cross large barriers



Umbrella sampling: Forcing the system to climb mountain

Suppose original Hamiltonian (H_0) samples order parameter range (x_{min}, x_{max}), but we are interested in (X_{min}, X_{max})

Modified Hamiltonian:

$H_n = H_0 + W$

Simple MC with H_n samples in (X_{min}, X_{max})

W: Weight function to be chosen

Unweighted probability distribution for H_0 can be recovered from the distribution obtained by Boltzmann distribution of H_n

For simple MC with H_n probability of finding order parameter x_i:

$$P^n(x_i) = < \delta(x(\tau) - x_i) >_n$$

Simple math gives back the same distribution had it been sampled with H_0:

$$P^0(x_i) = \frac{\left\langle \delta(x - x_i) \exp(W) \right\rangle_n}{\left\langle \exp(W) \right\rangle_n}$$

But the system has been forced to visit the order parameter range of interest. Averaging is done over the Markov chain generated by H_n.

❑ Choice of W ?

Most popular choice: QUADRATIC

$$W(\tau) = \begin{cases} k(x(\tau)-x_0)^2 \\ -\infty \end{cases} \qquad x(\tau) \in (X_{\min}, X_{\max})$$

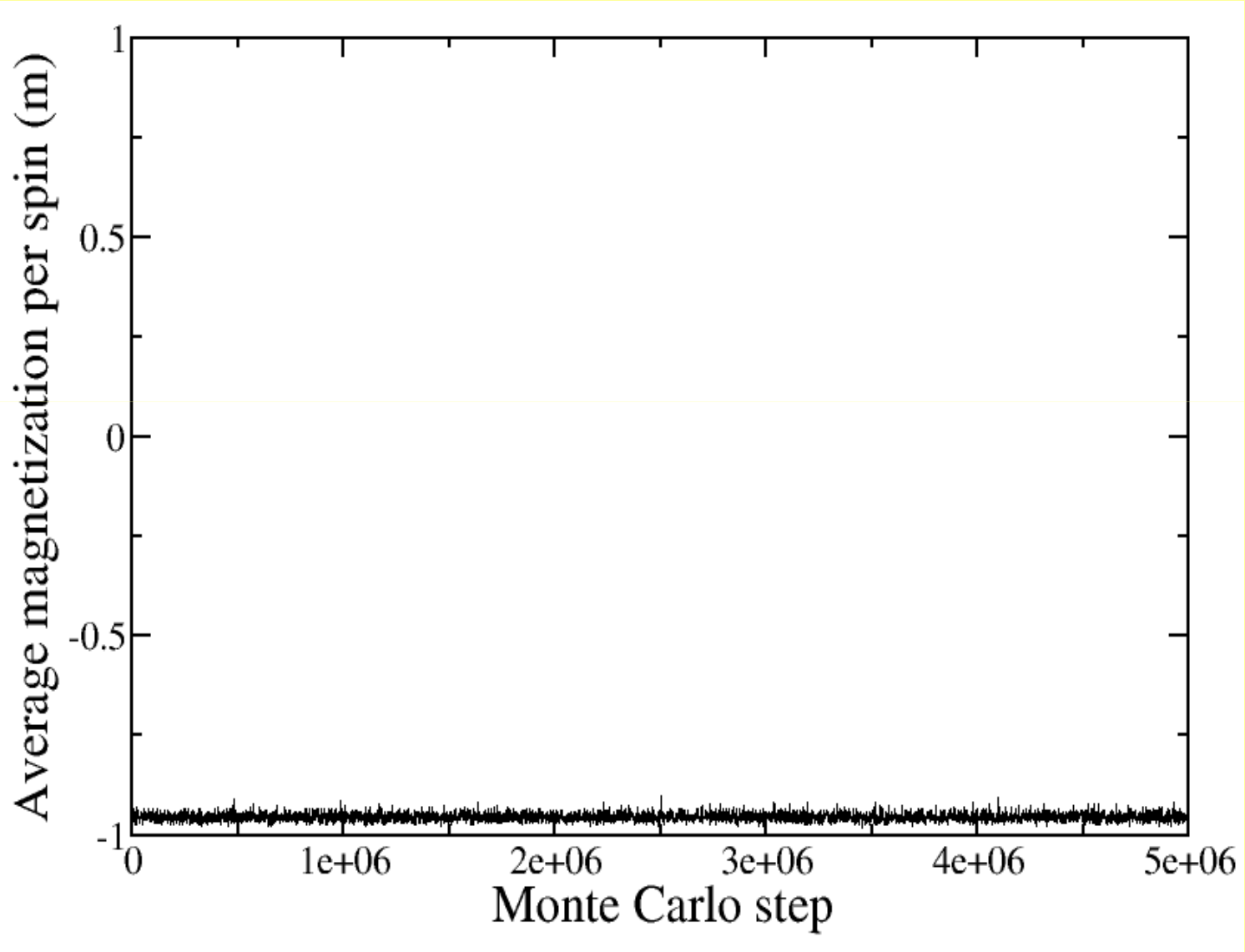
Our choice: TMMC (Transition Matrix Monte Carlo) method

$$W_i(x) = -\log P_{i-1}(x)$$

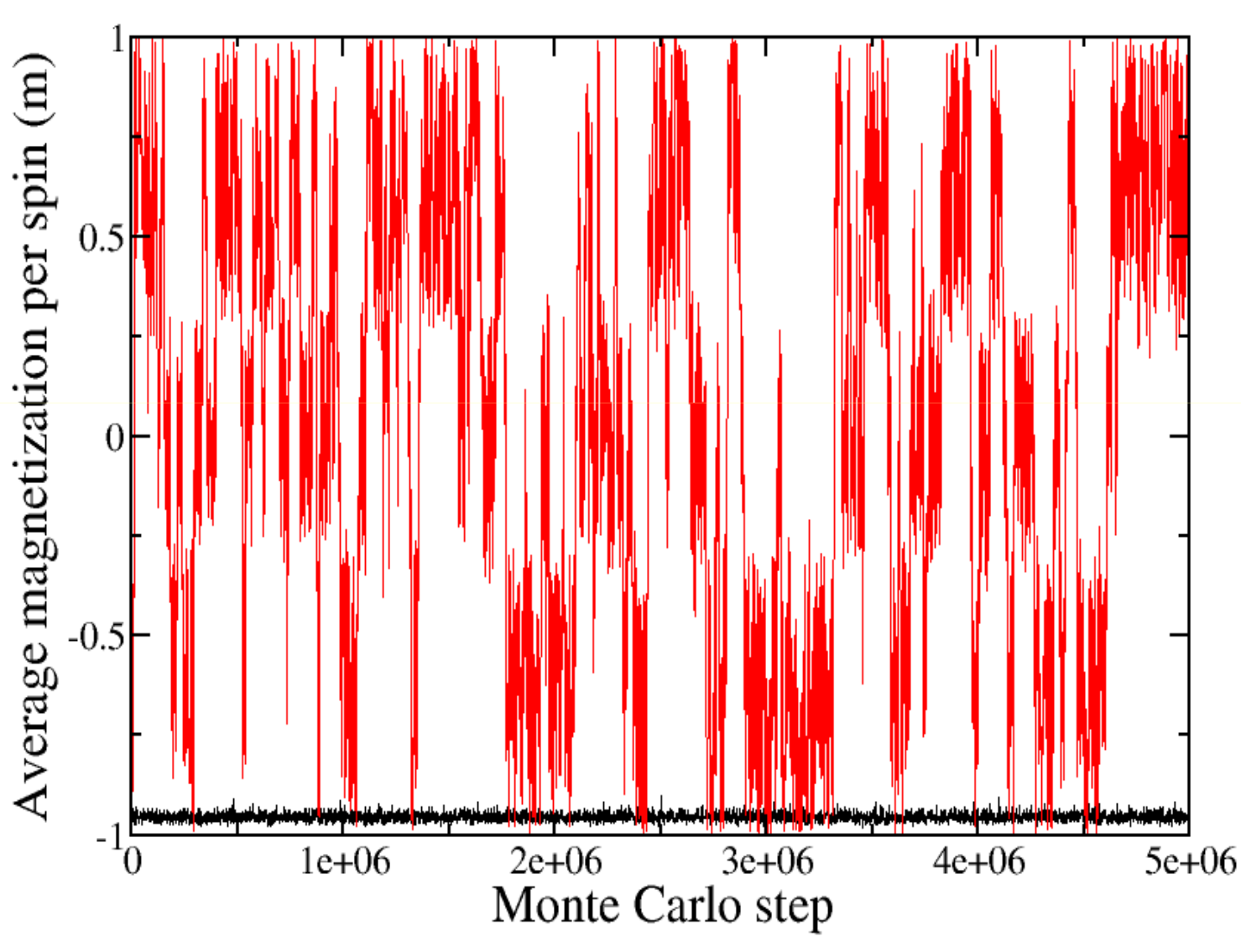
Weight function calculated from the macrostate probability in a feedback process so that system LEARNS TO CROSS THE BARRIER and sampling histogram becomes flat automatically !

M. Fitzgerald, R. R. Picard and R. N. Silver, *Europhys, Lett.* **46**, 282 (1999)

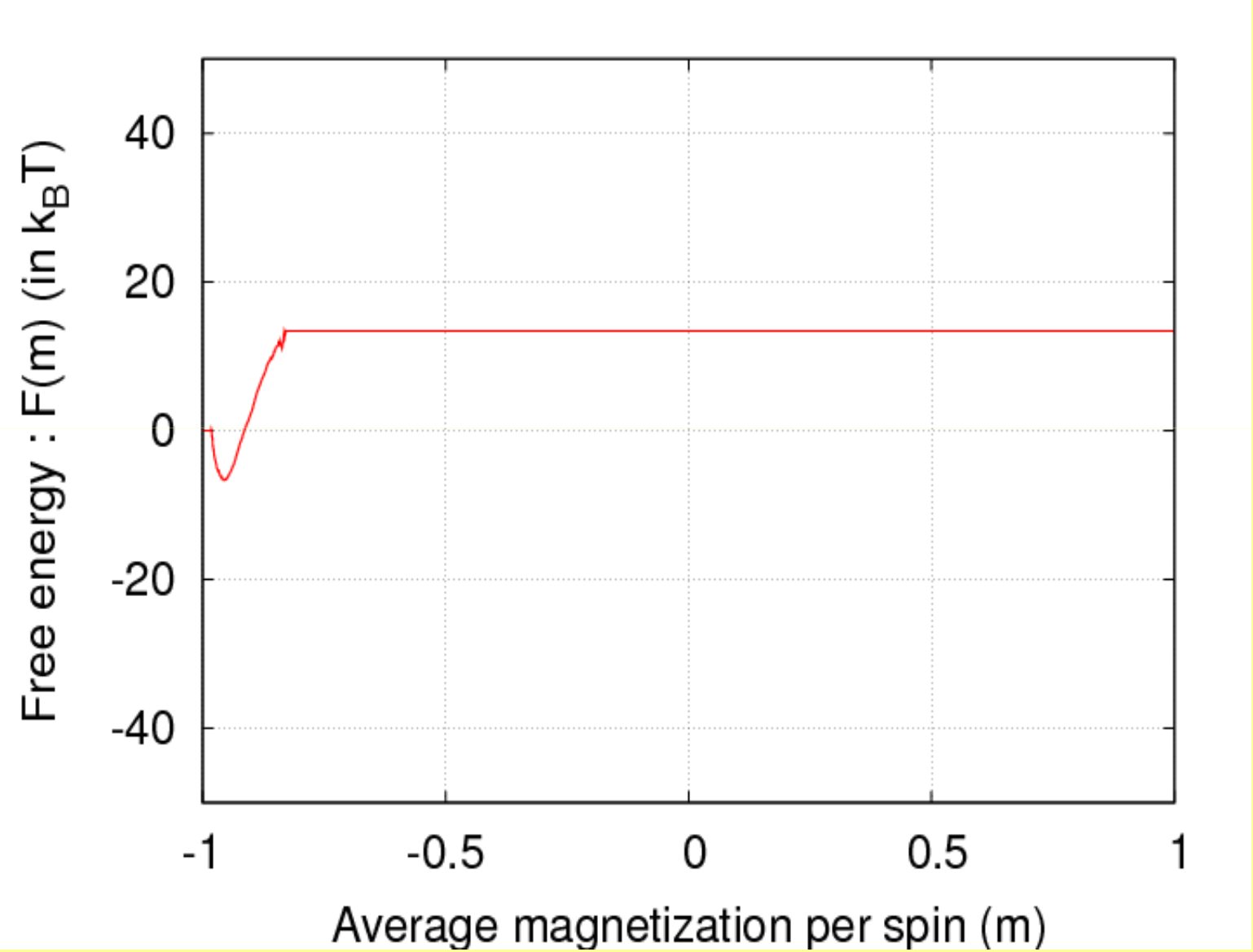
Ising model: Sampling without TMMC



Ising model: Sampling with TMMC

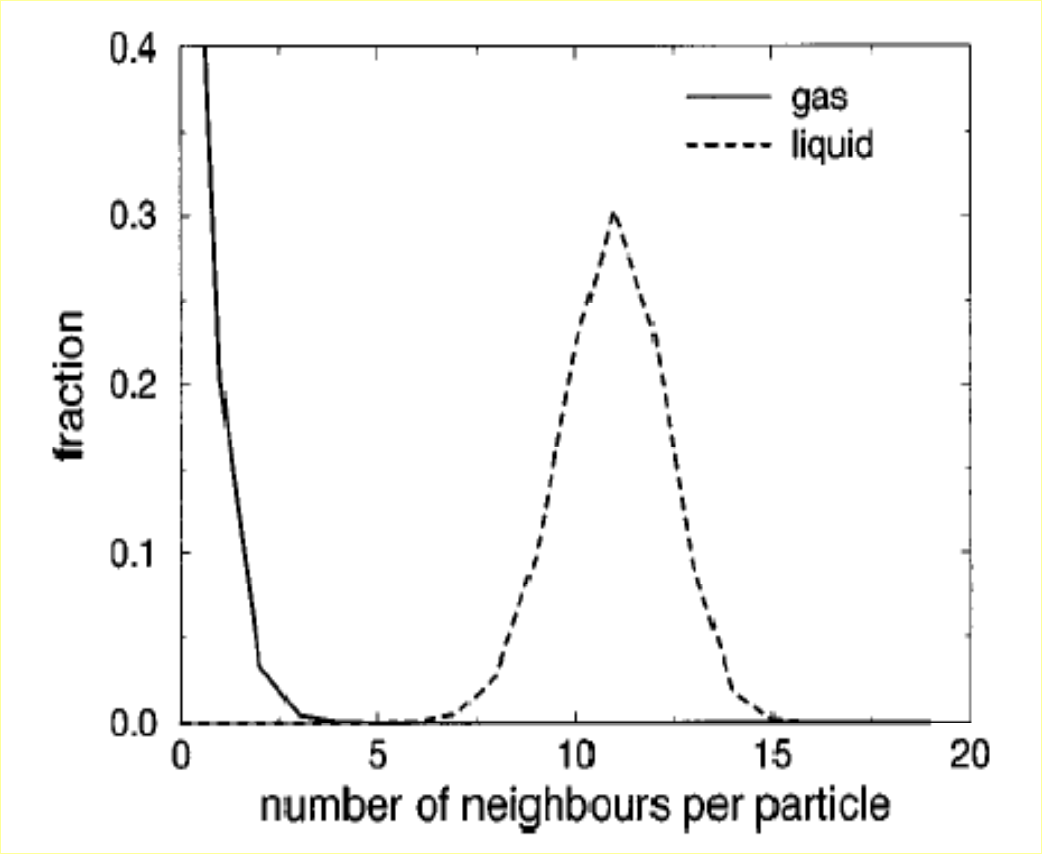


Convergence of FES



Mechanism of nucleation and growth near gas-liquid spinodal

Definition of "liquid-like" clusters



At coexistence: T*=0.741, P*=0.00783

Two particles are considered to be neighbors if they are separated by a distance less than q_c=1.5.

A particle is "liquid-like" if it has more than 4 neighbours within cut-off distance q_c.

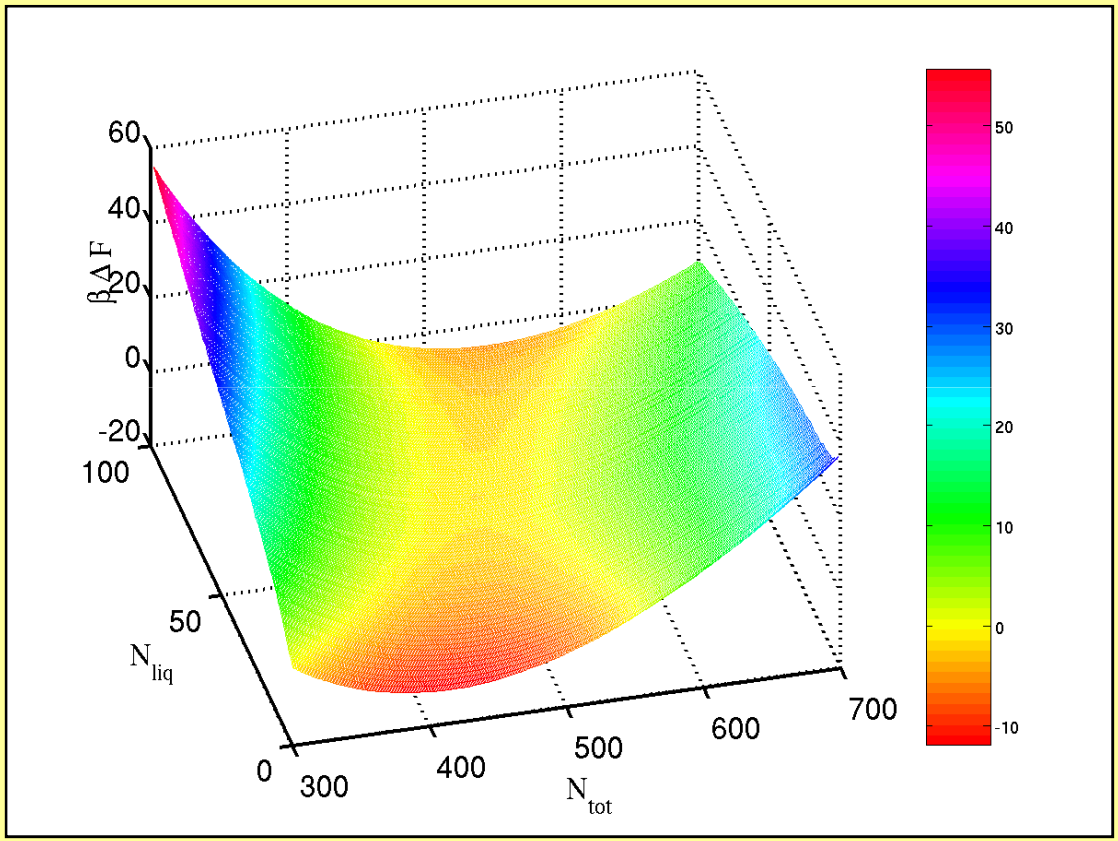
All liquid-like particles connected by same "neighborhood" belong to same "liquid-like" cluster.

P. R. ten Wolde and D. Frenkel, J. Chem. Phys. 109, 9901 (1998)

Order parameters/Reaction coordinates

- In the Landau theory, it is the density difference between liquid and gas that is the order parameter.
- We need additional, coarse-grained order parameters : Number of liquid-like clusters and Largest liquid-like cluster.
- We use Stillinger's definition of liquid-like cluster.

Free energy surface (S ~ 1.8)



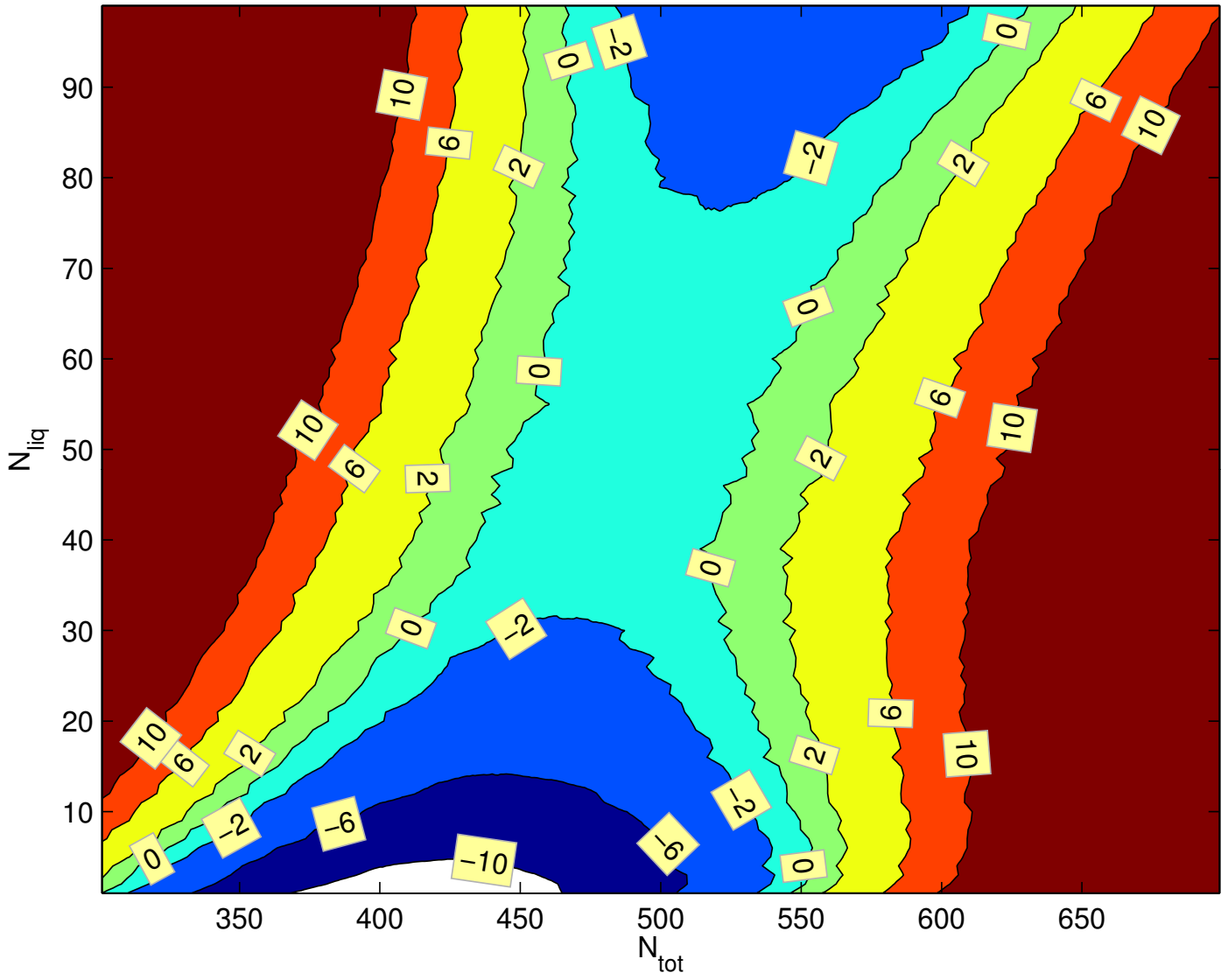
$S = P/P_C$

- Choice of proper order parameter/ reaction coordinate is important.
- Both N and Nliq are coupled.

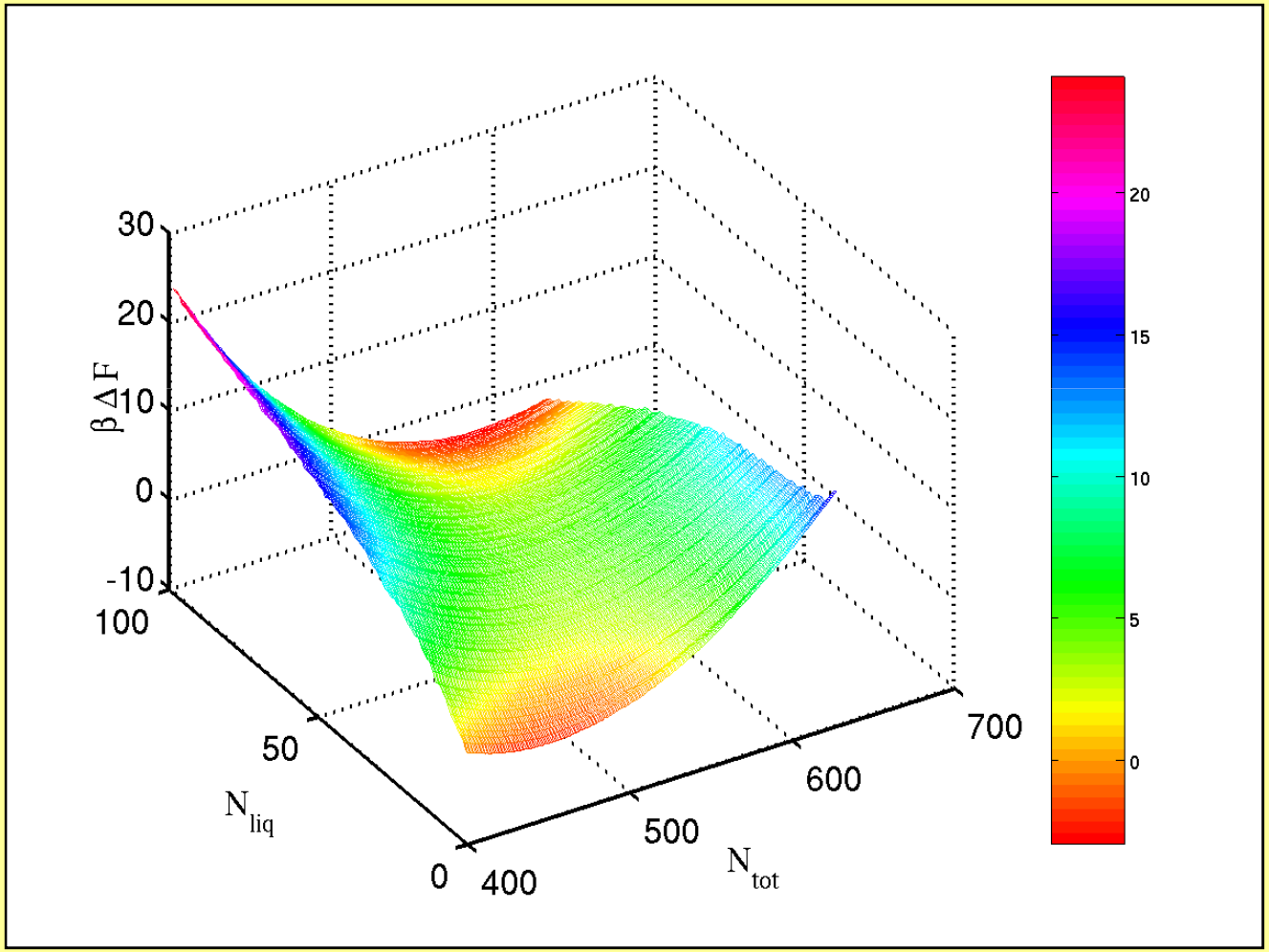
$S=P/P_C$

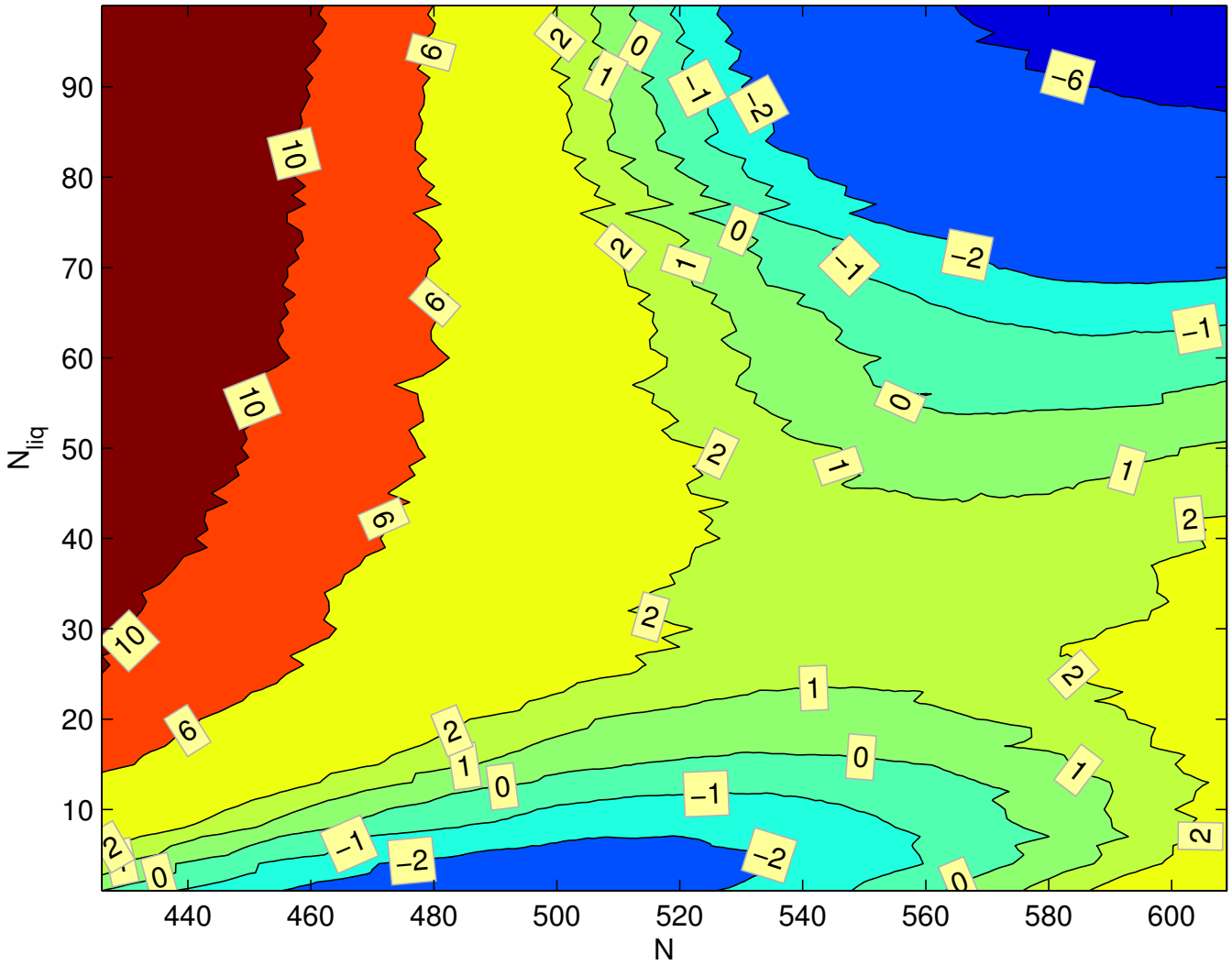
PRL (2007)

FREE ENERGY CONTOUR



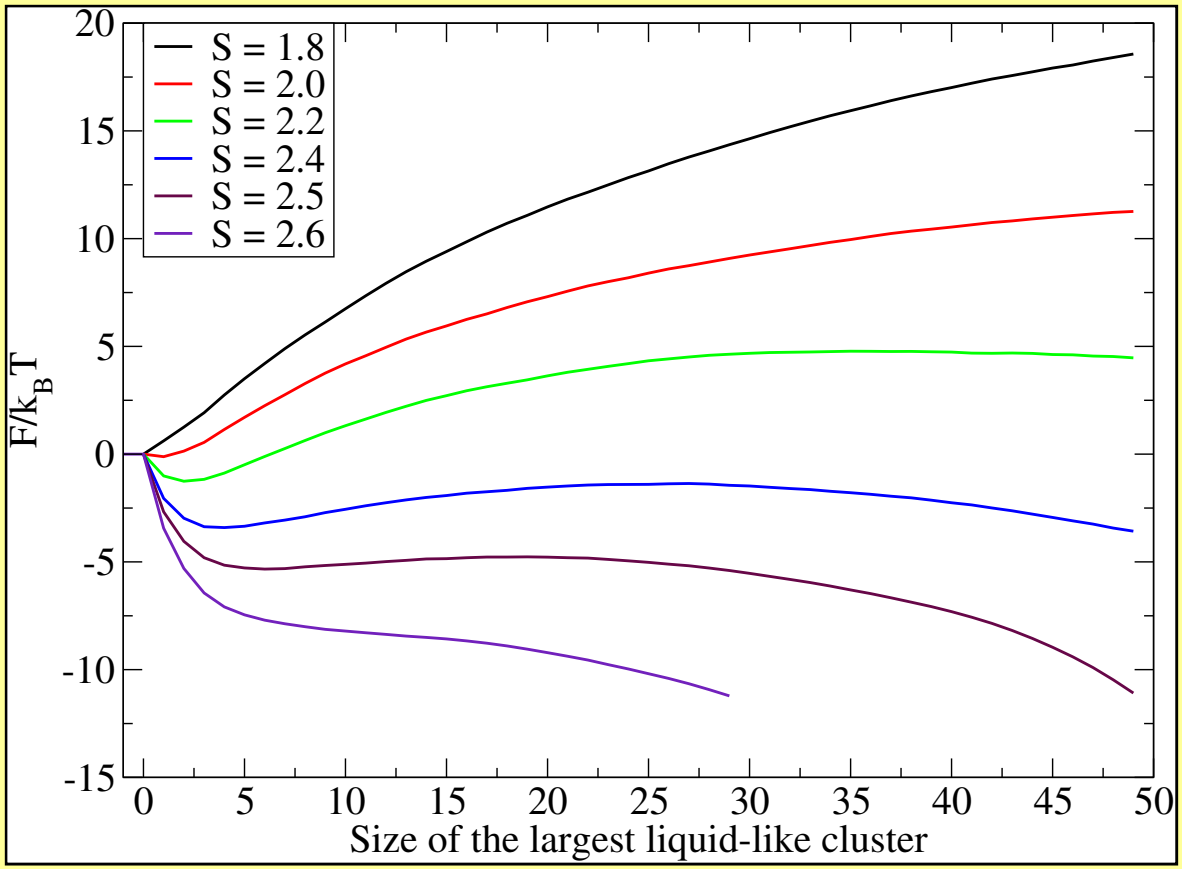
Free energy surface (S ~ 2.4)





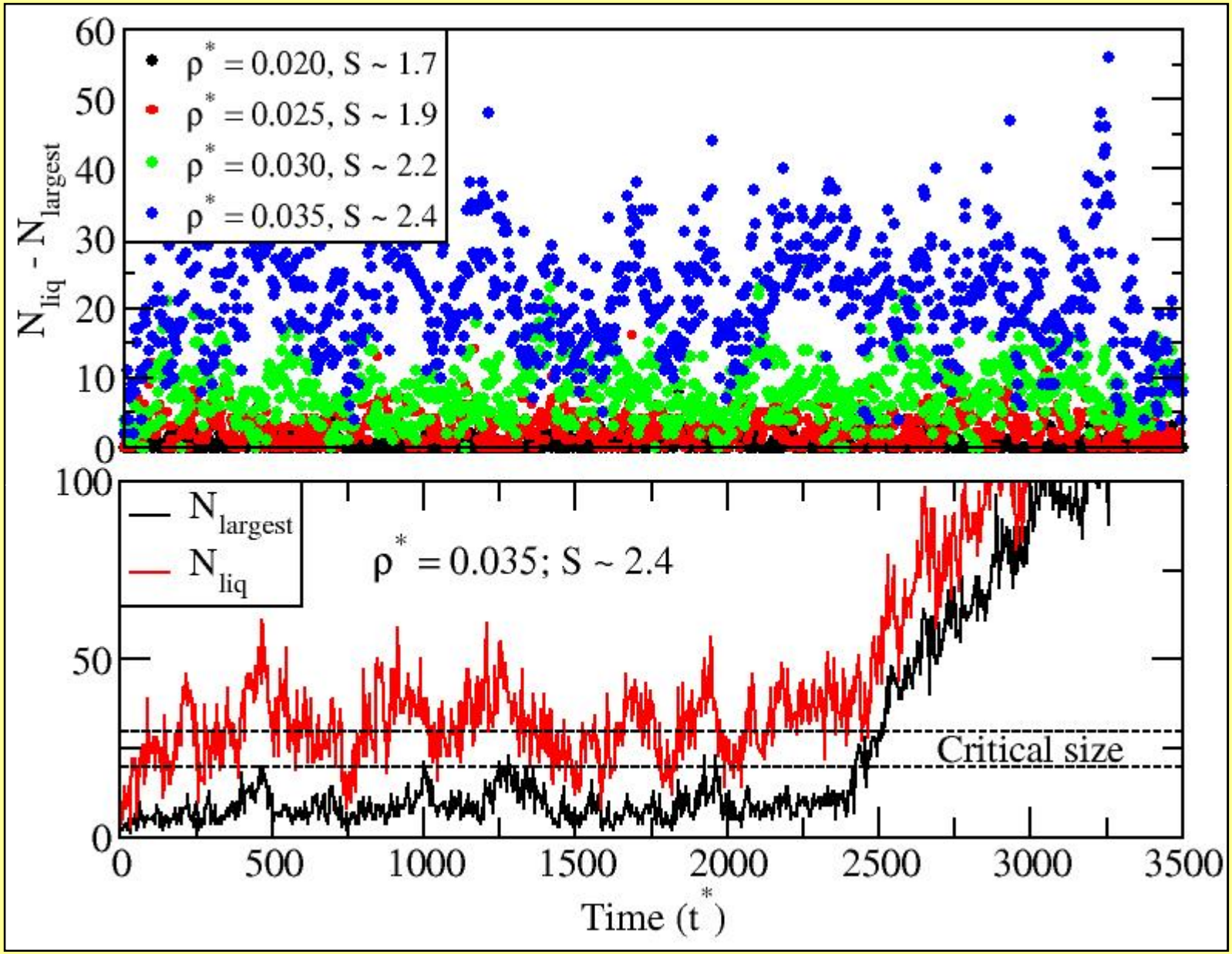
Bhimalapuram, Chakrabarty and Bagchi, Phys. Rev. Lett. **98**, 206104 (2007)

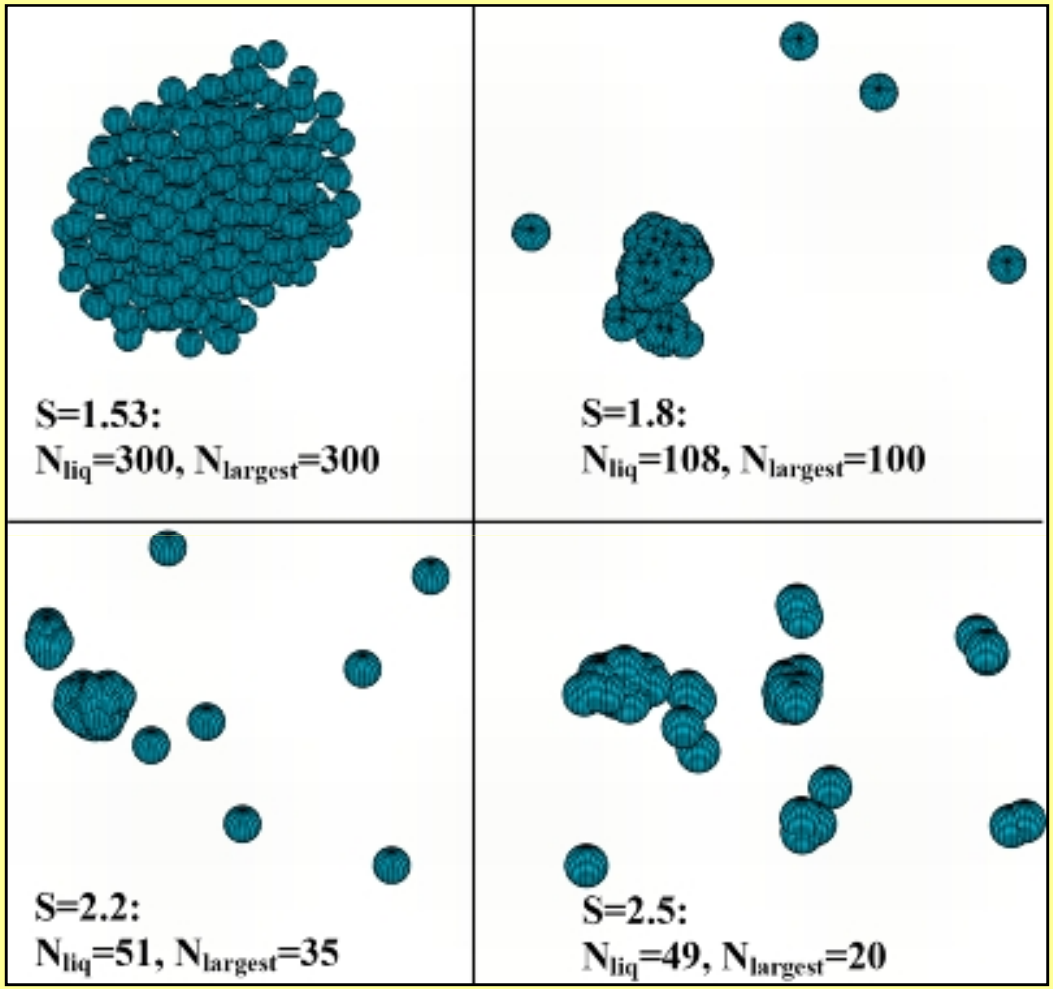
Nucleation barrier and supersaturation



With increasing supersaturation ($S=P/P_c$) barrier height and critical size are lowered.

The minimum and the maximum coalesce at a inflection point corresponding to spinodal; continuous growth ensues.


60
50
40
30
20
10
0
N_{liq} - $N_{largest}$
$\rho^* = 0.020$, S ~ 1.7
$\rho^* = 0.025$, S ~ 1.9
$\rho^* = 0.030$, S ~ 2.2
$\rho^* = 0.035$, S ~ 2.4
100
50
0
$N_{largest}$
N_{liq}
$\rho^* = 0.035$; S ~ 2.4
Critical size
0
500
1000
1500
2000
2500
3000
3500
Time (t^*)



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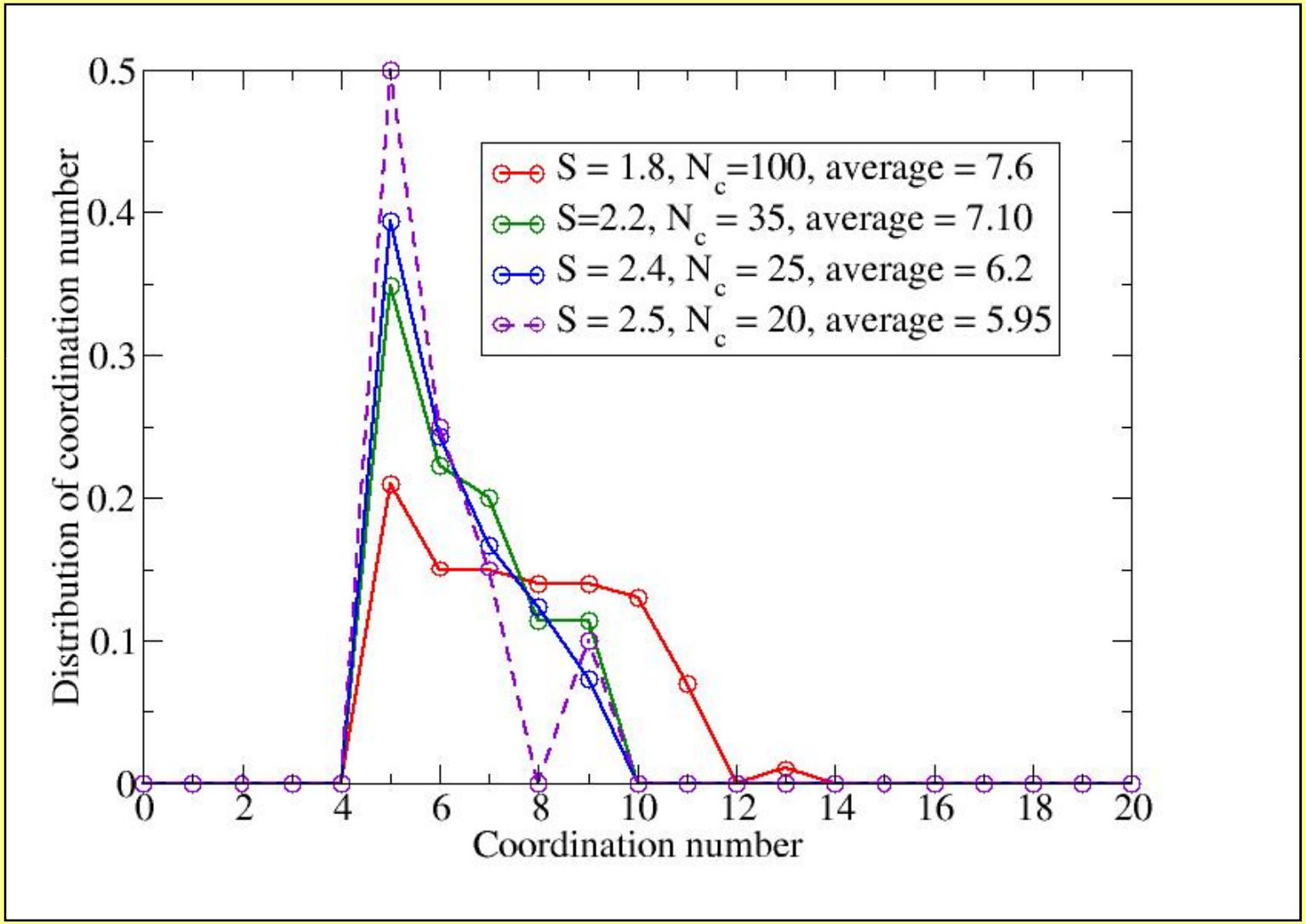
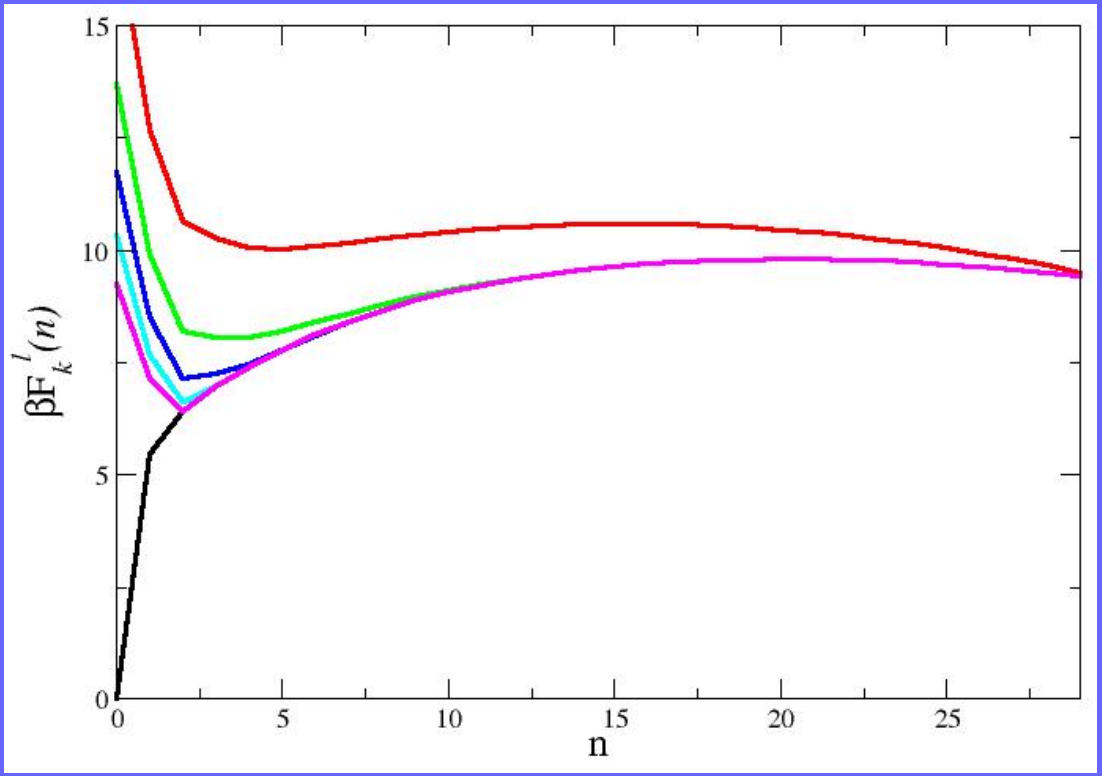
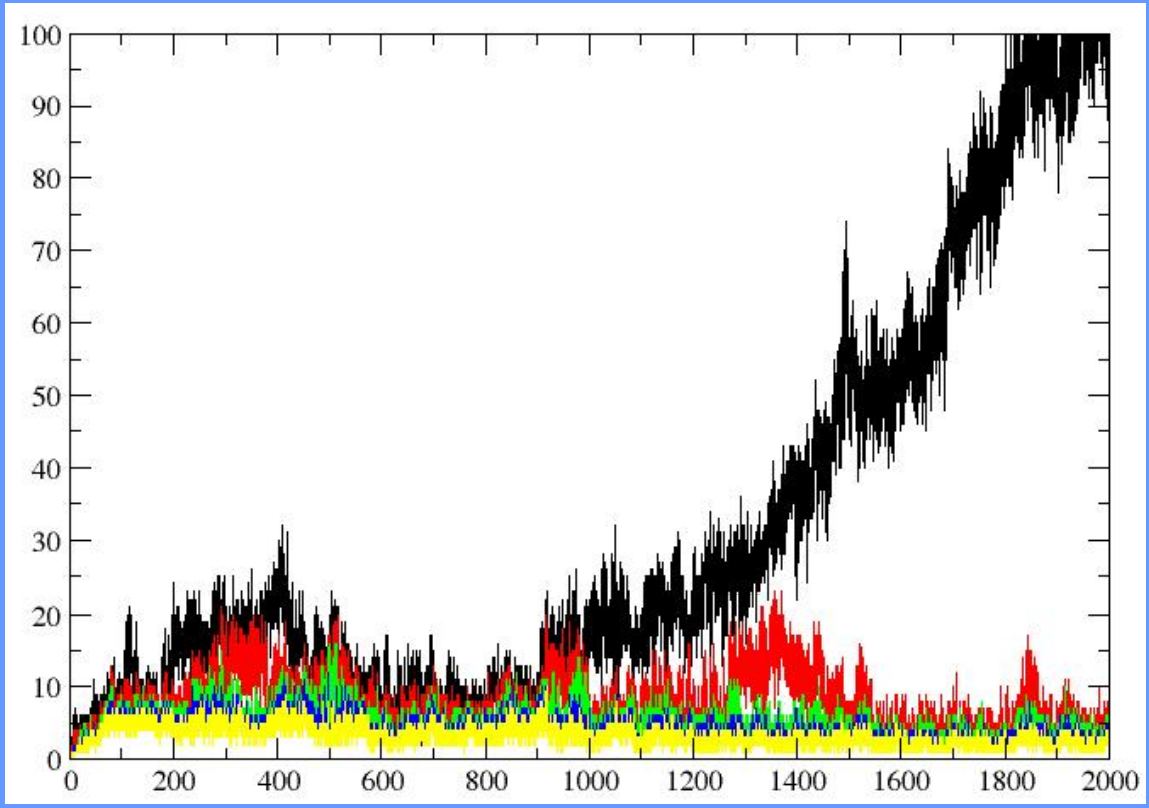
Chakrabarty et al., Phys. Rev. Lett. **98**, 206104 (2007); (2008)

Distribution of coordination number in the critical nucleus

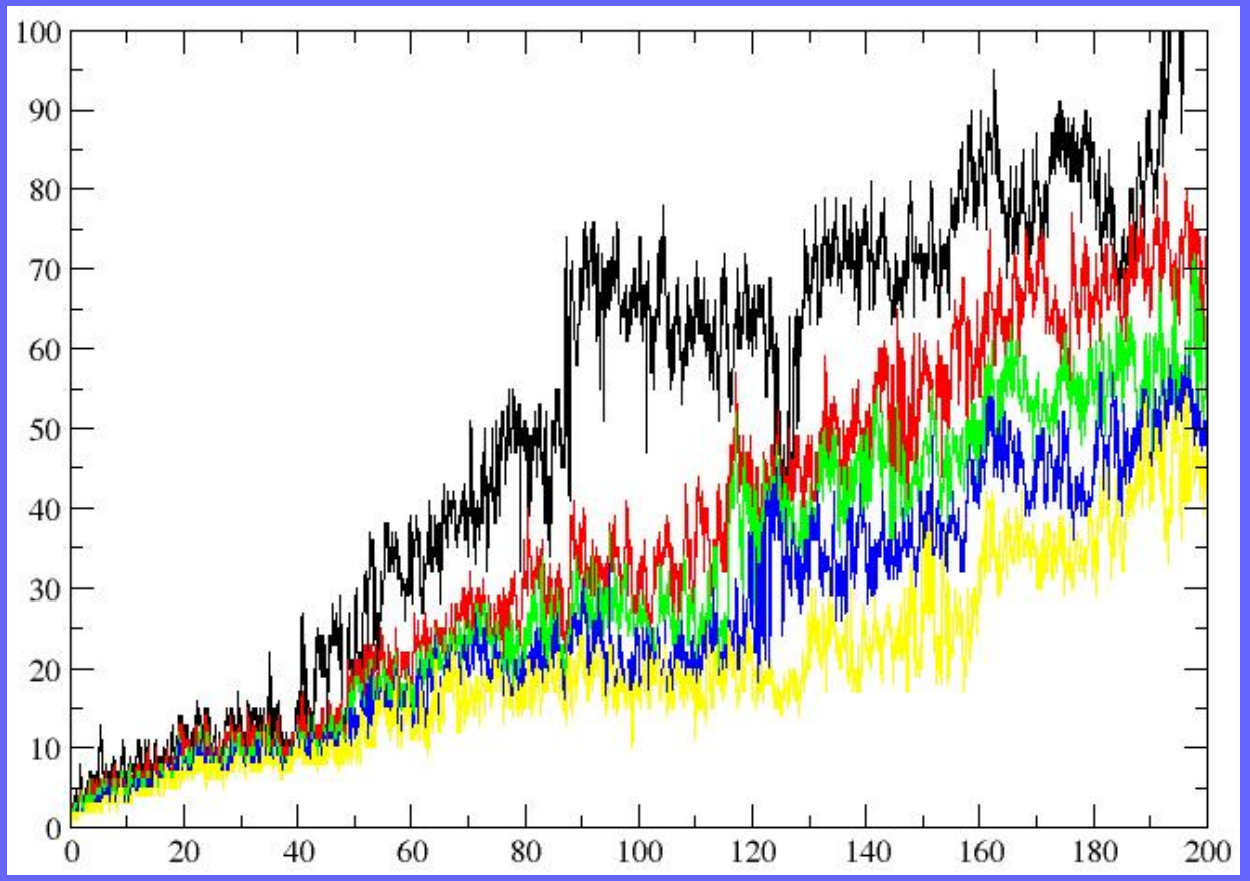




Free energy of the first five largest clusters at $\rho^*=0.04158$ and $T^*=0.741$ for N=1000.
The black line shows the free energy of a cluster obtained from simulation.

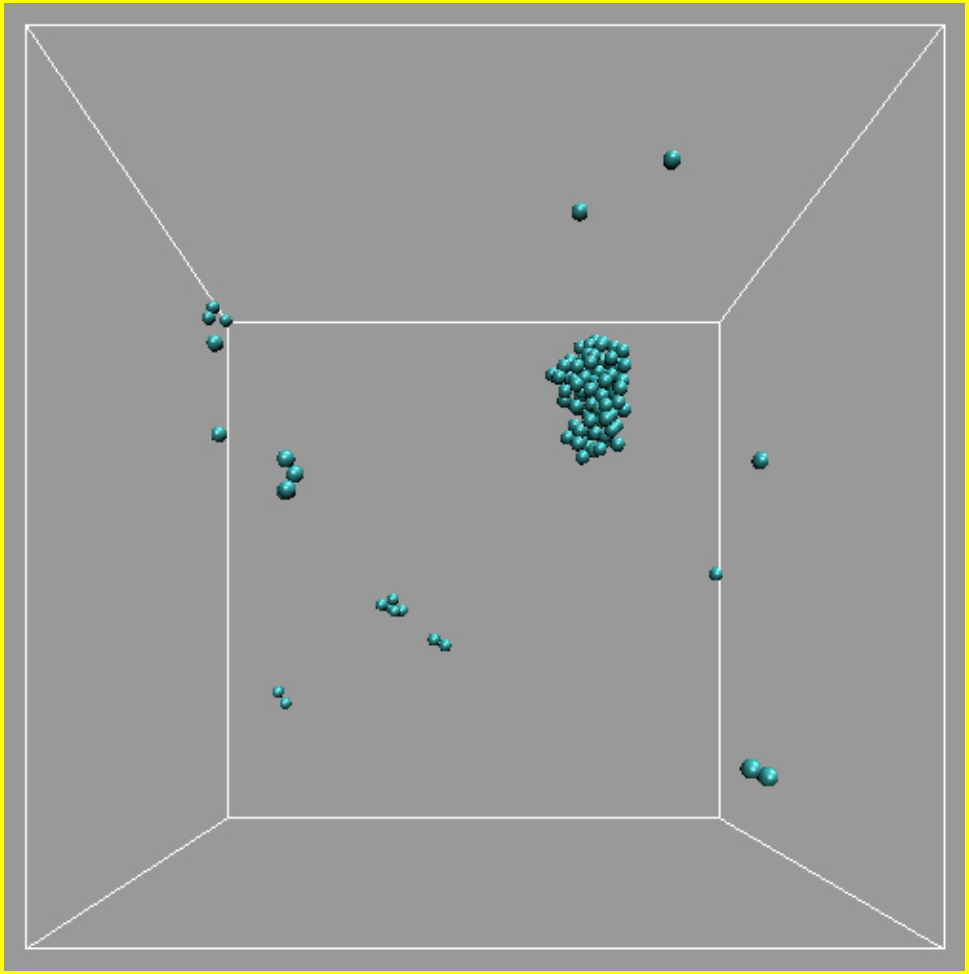


Growth of the 1st five largest clusters at ρ^*=0.0334083 and T*=0.741 for N=4000. Black line is for the largest cluster (k=1), red is for 2nd largest (k=2), The figure shows the barrier crossing of only one cluster (i.e. the largest cluster) through activated process.



Growth of the 1st five largest clusters at ρ^*=0.05545, T*=0.741 for N=4000.

The figure shows growth of more than cluster through barrierless diffusion.



Snapshot of liquid-like particles in the system when the largest cluster crosses the critical size at low supersaturation of ρ^*=0.0334083 for N=4000. The size of the largest cluster in the figure is of 100 liquid-like particles.

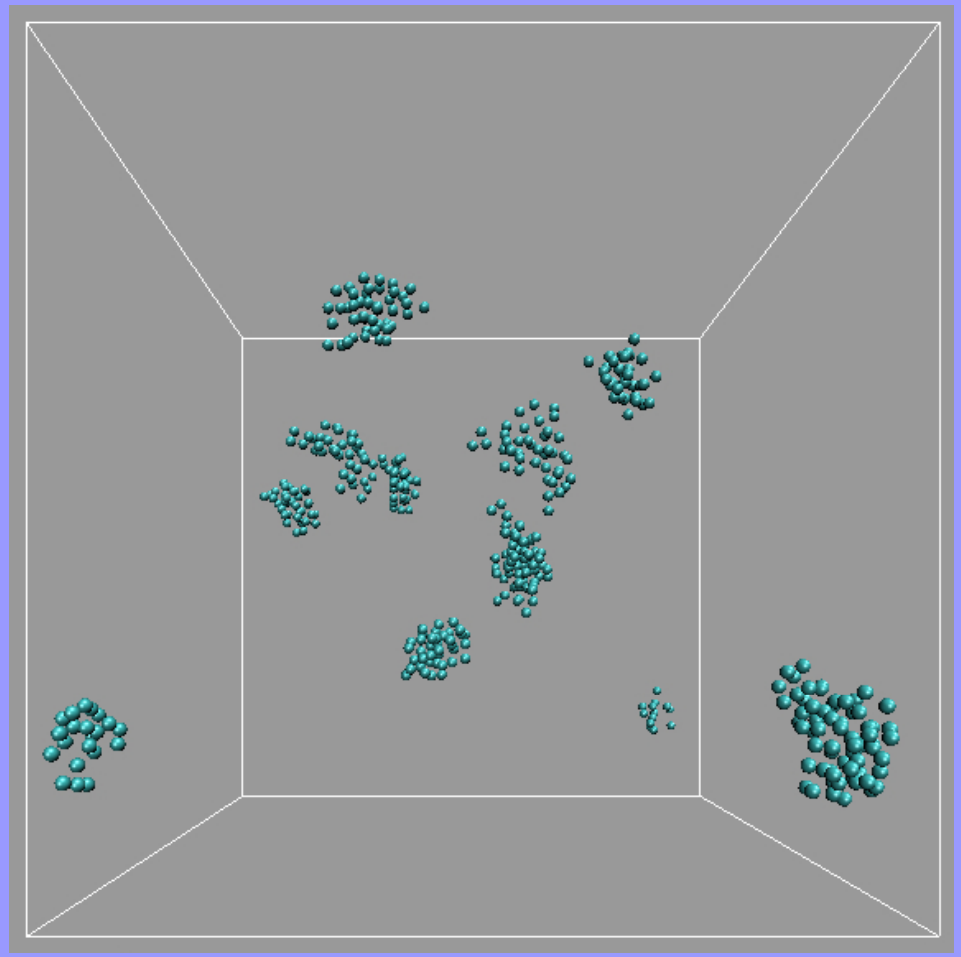
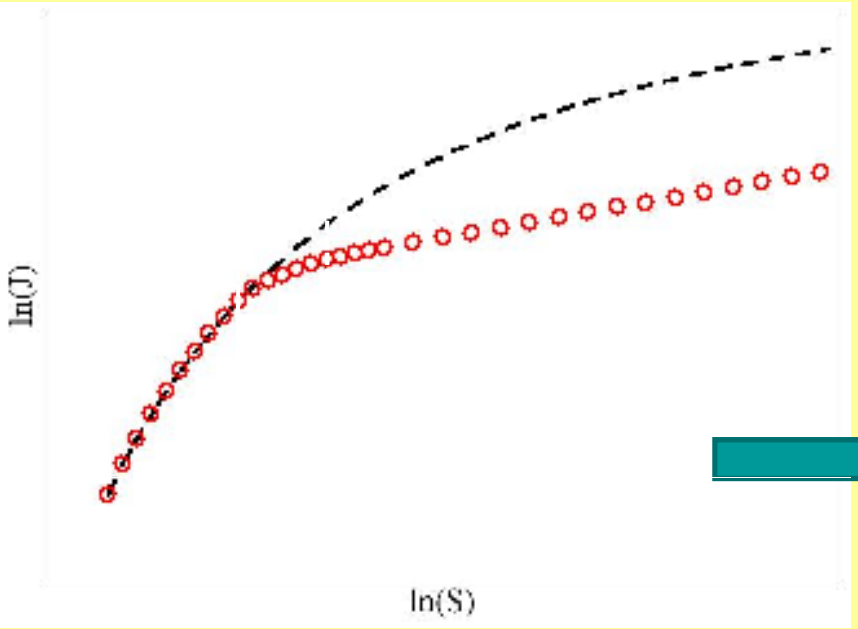
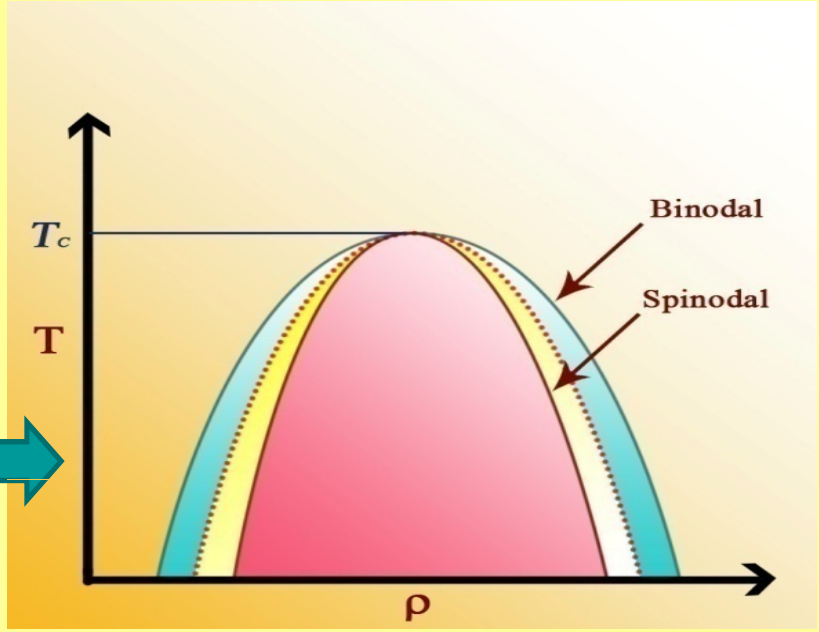


Fig.2(c): The snapshot of clusters in the system that have crossed the critical size at large supersaturation of $\rho^* = 0.05545$ for $N = 4000$. The size of the largest cluster in the figure is of 100 liquid-like particles. The snapshot shows that at high supersaturation more than one cluster start nucleating and they are of comparable size.

Kinetic spinodal





- **At low super saturation rate follows CNT prediction.**
- **There is a cross-over from activated to barrierless diffusion when the free energy barrier of the largest cluster is ~$k_B T$.**
- **Starting pint of the crossover can be called as kinetic spinodal.**

For barrierless crossing: $\tau\left(n_c - n_{eq}^L\right) = A\left(n_c - n_{eq}^L\right)^{4/3}$

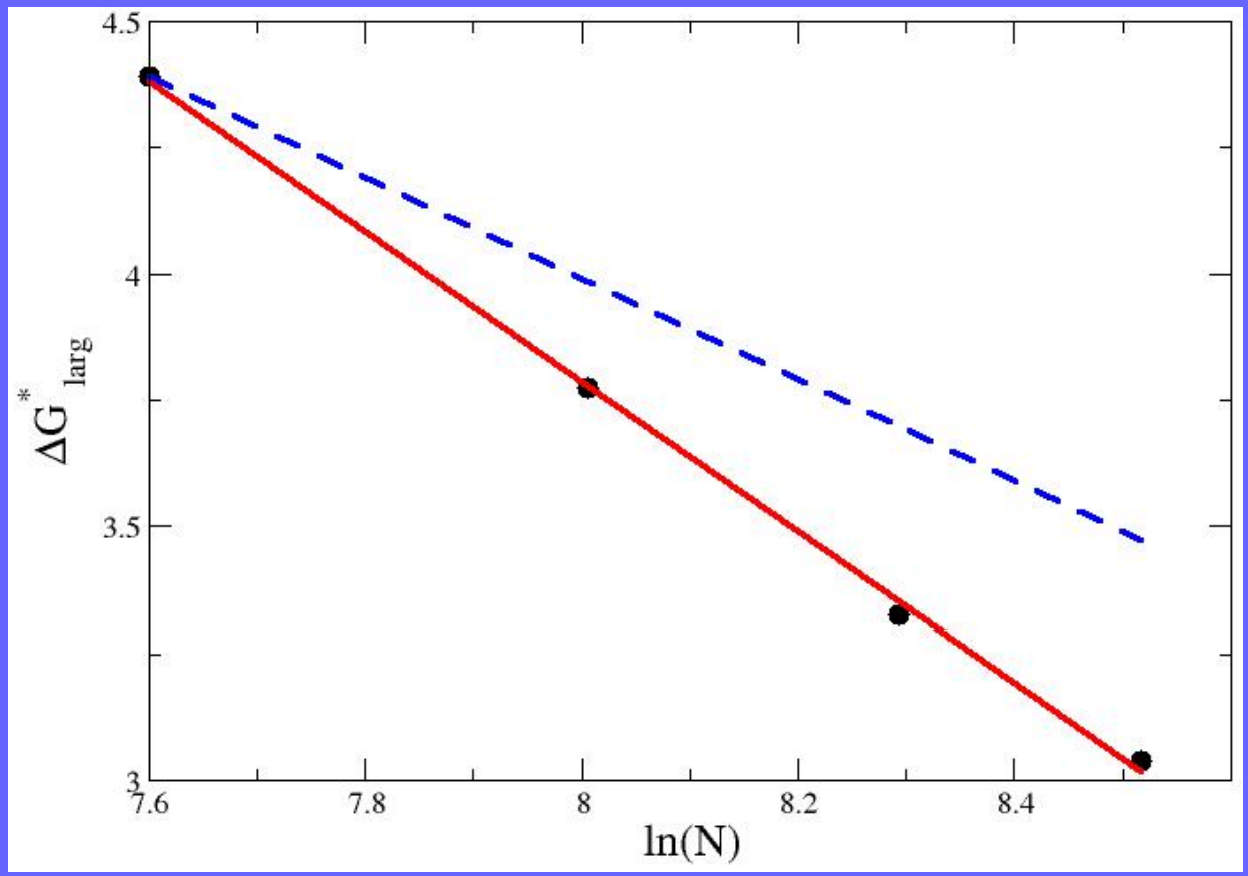
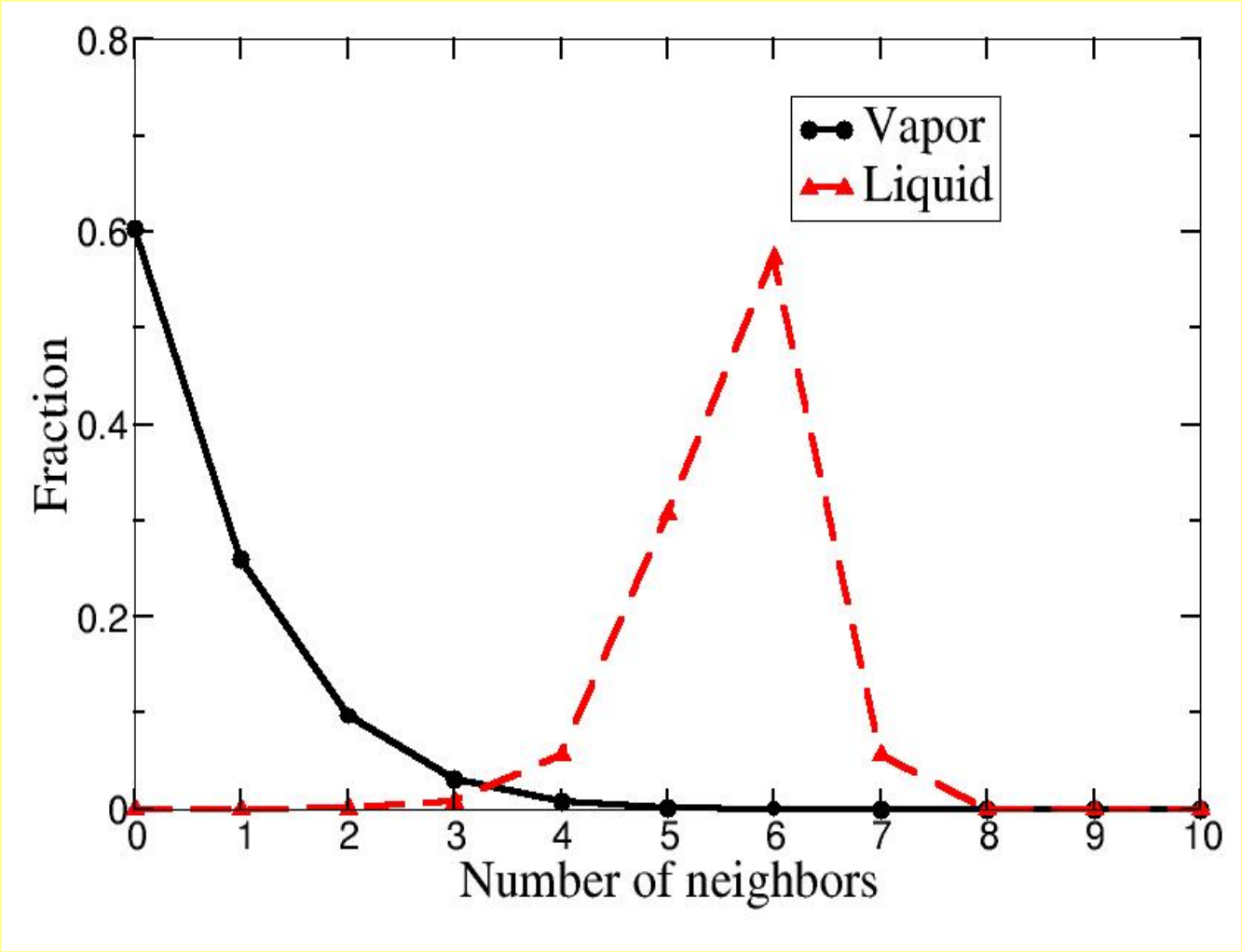


Fig.4: Free energy of the largest cluster vs. *ln*(*N*) at $\rho^* = 0.032162$ and $T^* = 0.741$. The circles are simulation data and the solid line is the corresponding fit with negative slope *1.48*. The dashed line (with slope equal to *-1*) is shown for comparison.

Nucleation in Two Dimensional Systems

Mantu Santra
Suman Chakrabarty
JCP (2009)

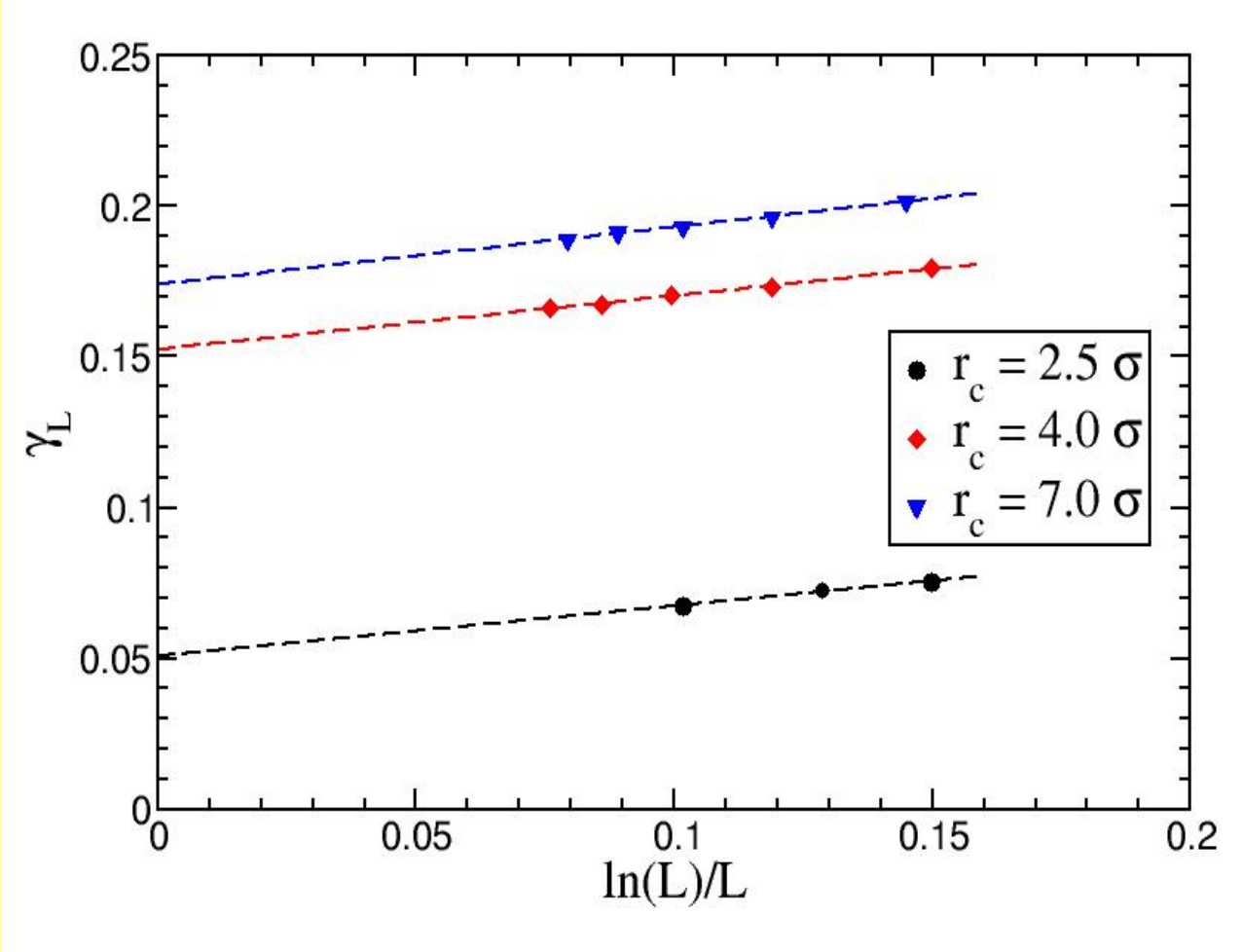
In 2 dimensional system…



T*= 0.427

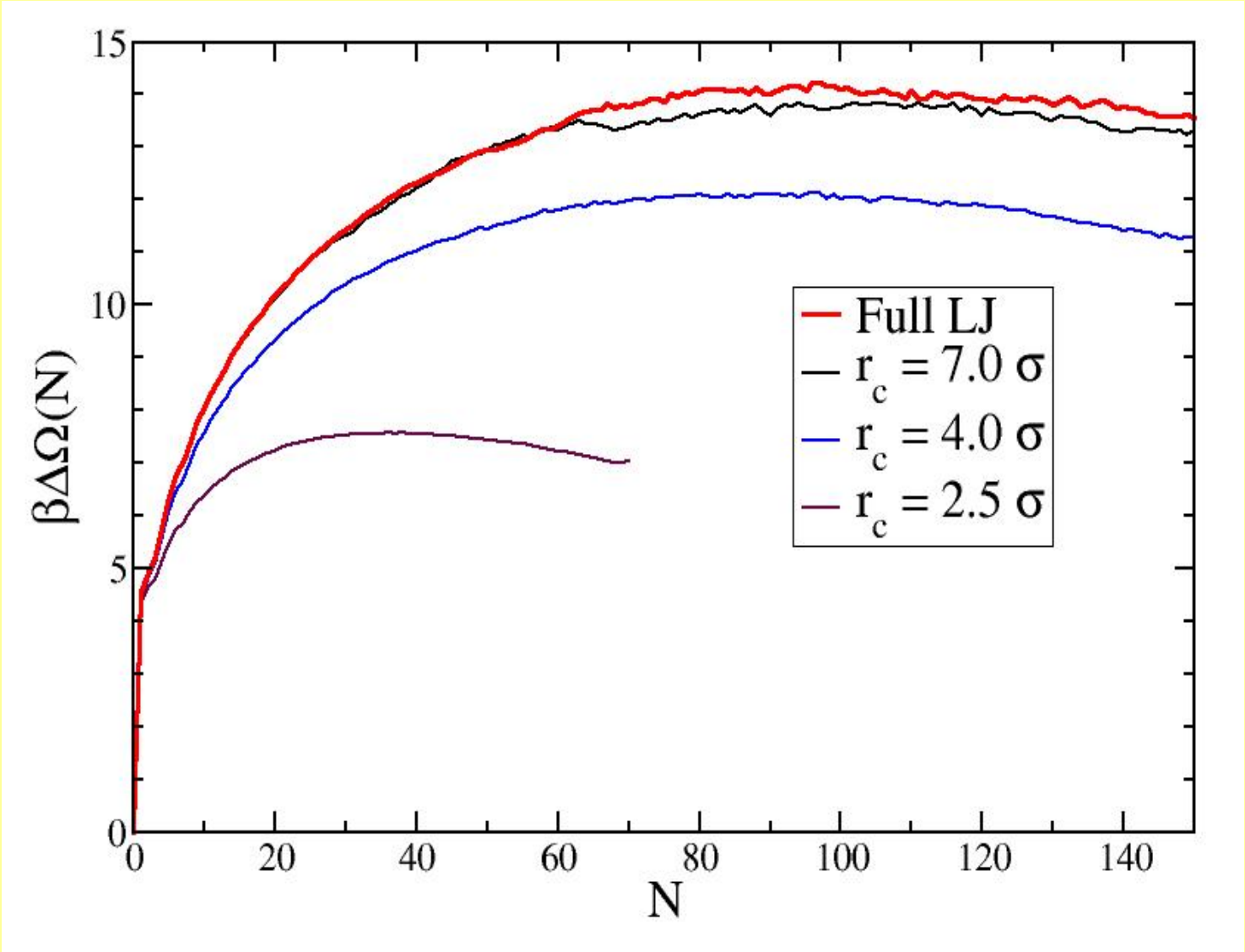
q_c = 1.65

Line tension: Cut-off dependence

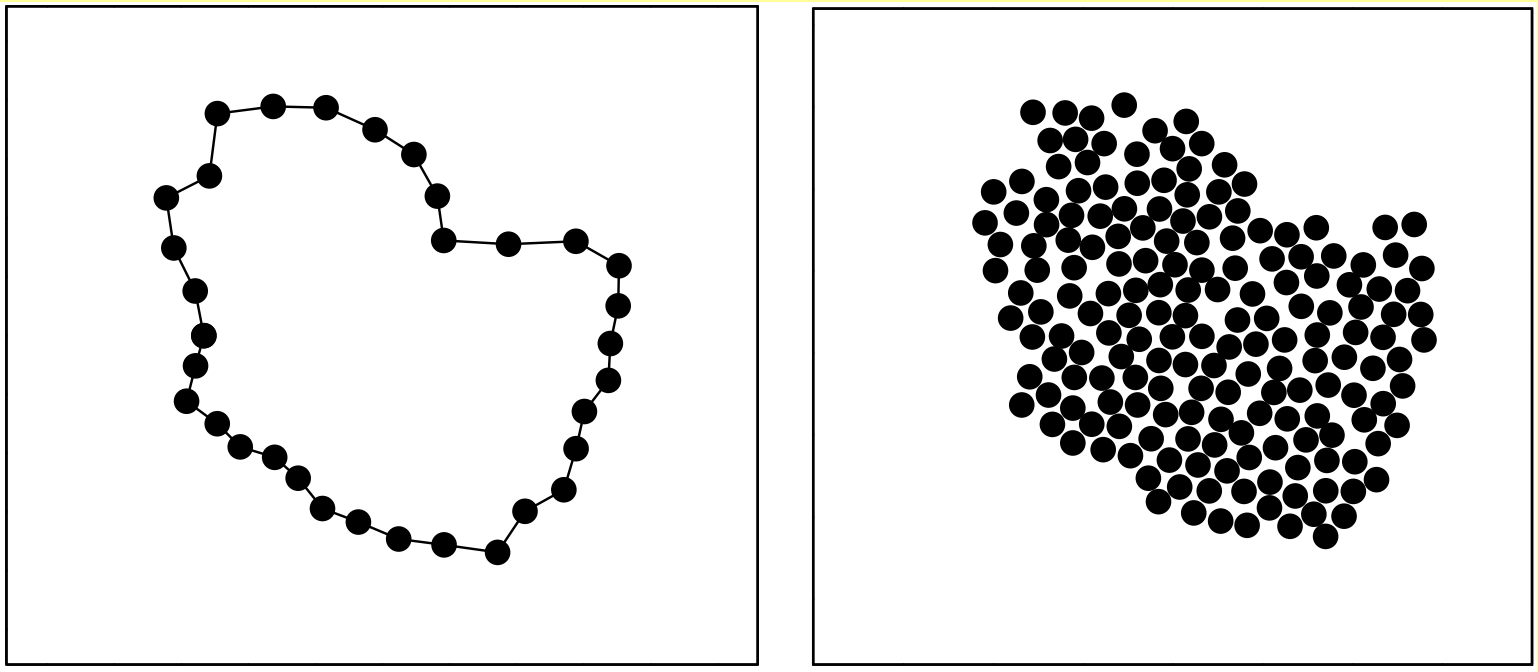


Bulk surface tension at coexistence computed by Binder's method of finite size scaling

F(N): Cut-off dependence

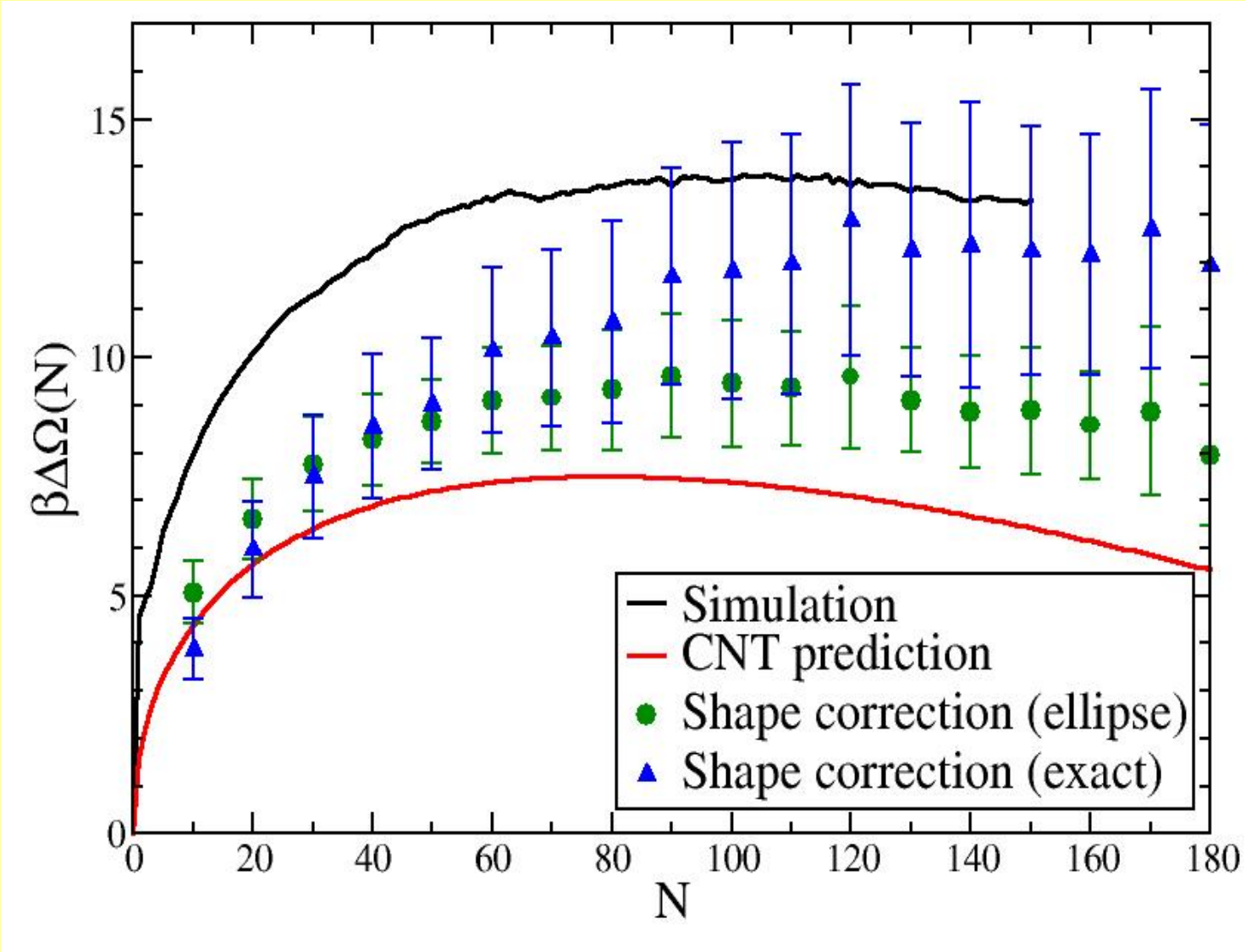


CNT with curved surface

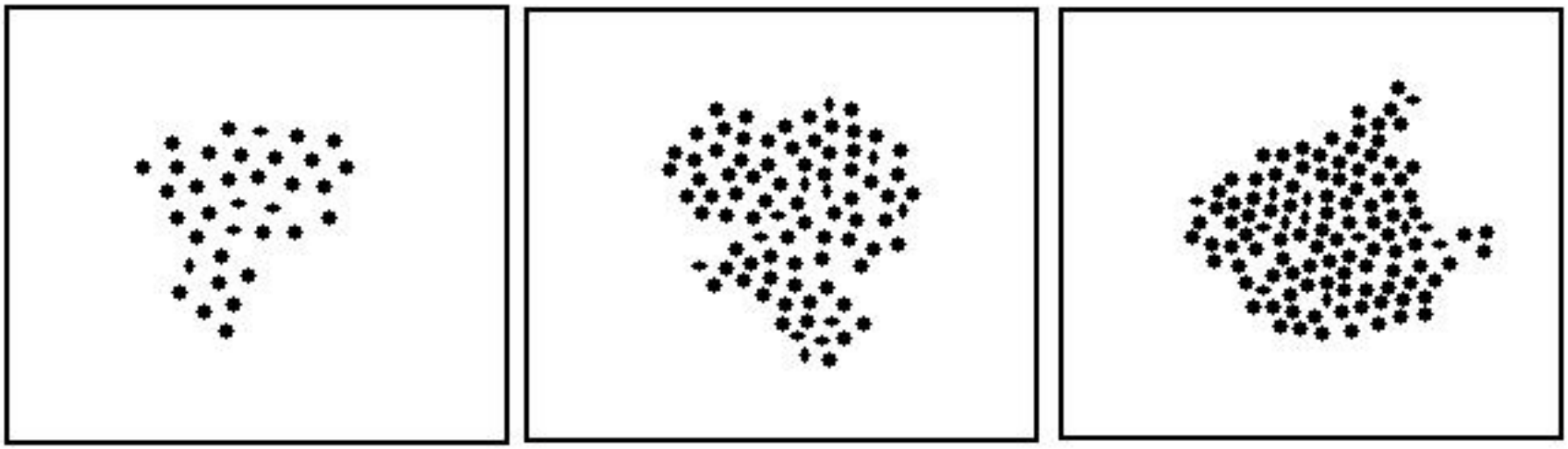


JCP (2009)

F(N): CNT versus simulation

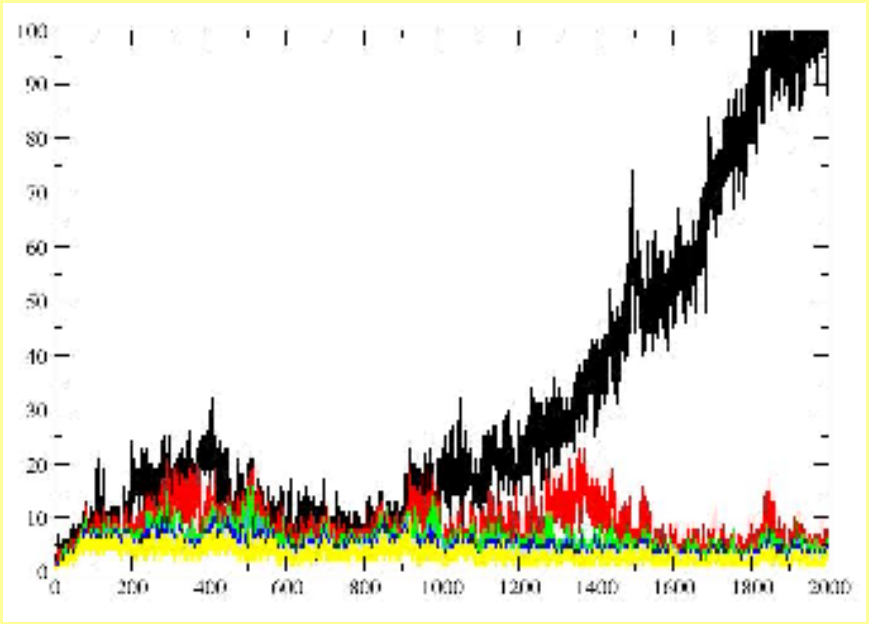


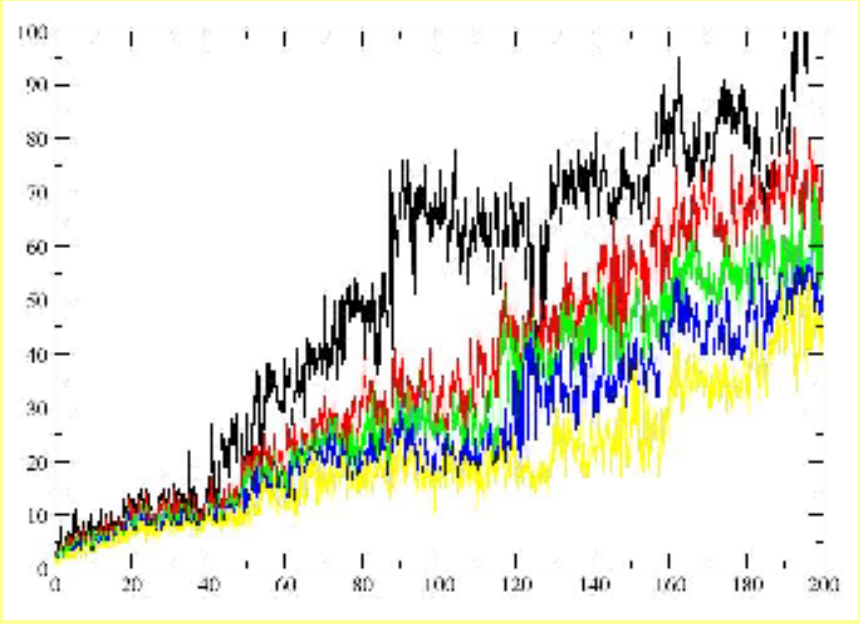
Snapshots



$r_c = 2.5\sigma$, $n^* = 35$ $r_c = 4.0\sigma$, $n^* = 85$ $r_c = 7.0\sigma$, $n^* = 115$

Time evolution of clusters



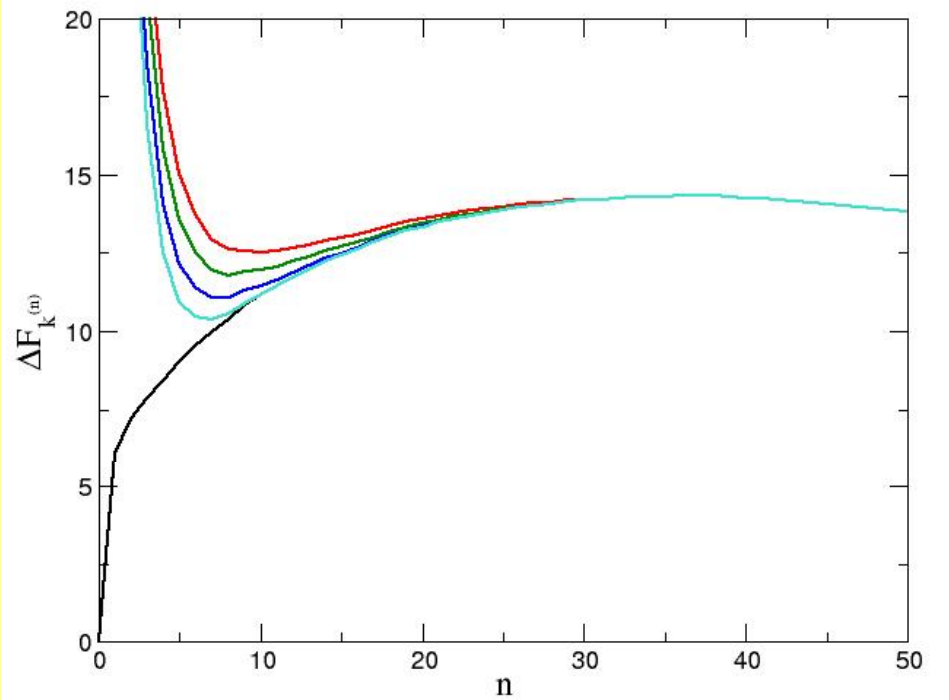


$\rho = 0.030$ $\rho = 0.048$

- **At low super saturation only one cluster grows through activated barrier crossing dynamics.**

- **At high super saturation more than one cluster grow through barrierless diffusion.**

Free energy of k-th cluster

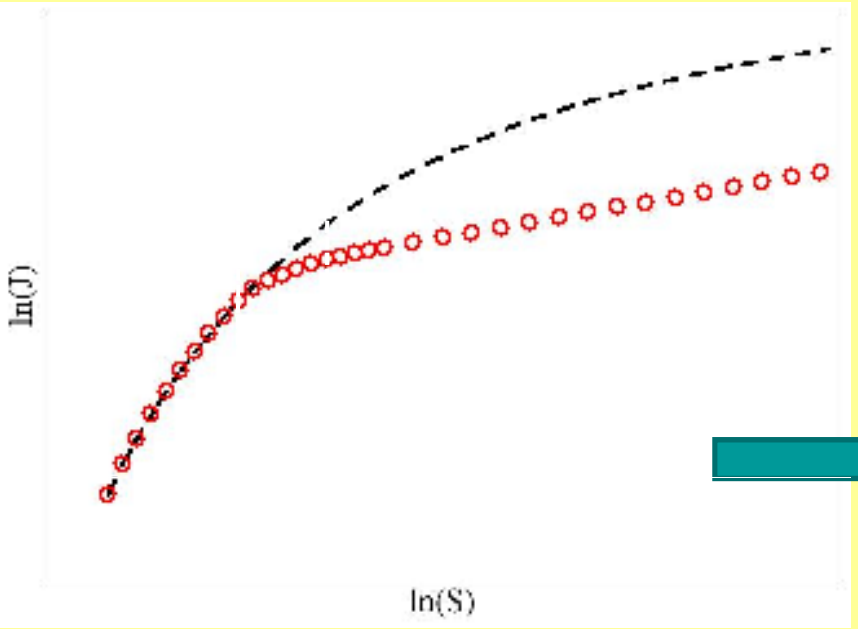


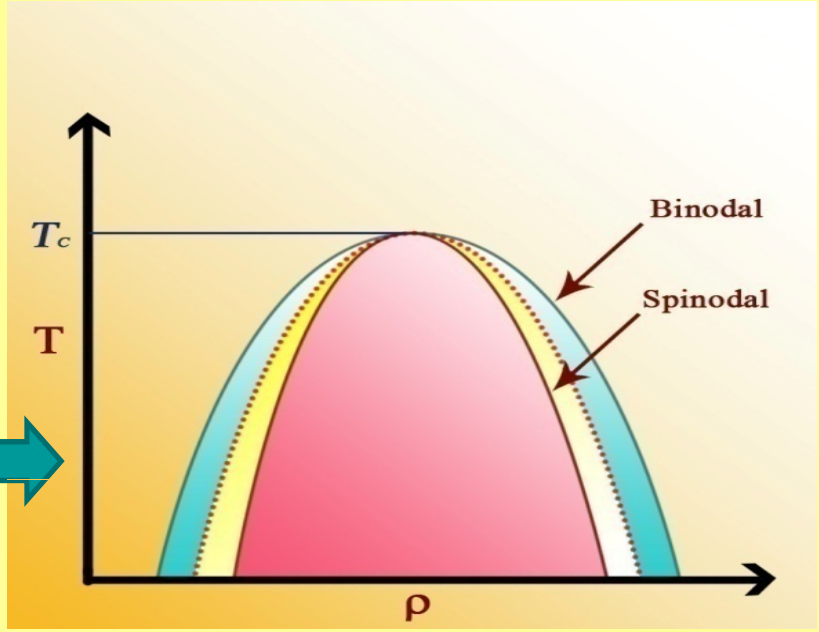
- **Progression of the free energy surface of k-*th* largest cluster towards CNT free energy surface.**
- **Smaller clusters face larger barrier.**

$$\beta F_k^L(n) = \beta F(n) - \ln\left[\frac{(M-k-1)!}{(k-1)!}\right] - (M-k)\ln G(n) - (k-1)\ln\left[1-G(n)\right]$$

M is the total number of clusters. G(n) is the cumulative probability.

Kinetic spinodal





- **At low super saturation rate follows CNT prediction.**
- **There is a cross-over from activated to barrierless diffusion when the free energy barrier of the largest cluster is ~$k_B T$.**
- **Starting pint of the crossover can be called as kinetic spinodal.**

For barrierless crossing: $\tau\left(n_c - n_{eq}^L\right) = A\left(n_c - n_{eq}^L\right)^{4/3}$

Non-classical Crystal Nucleation

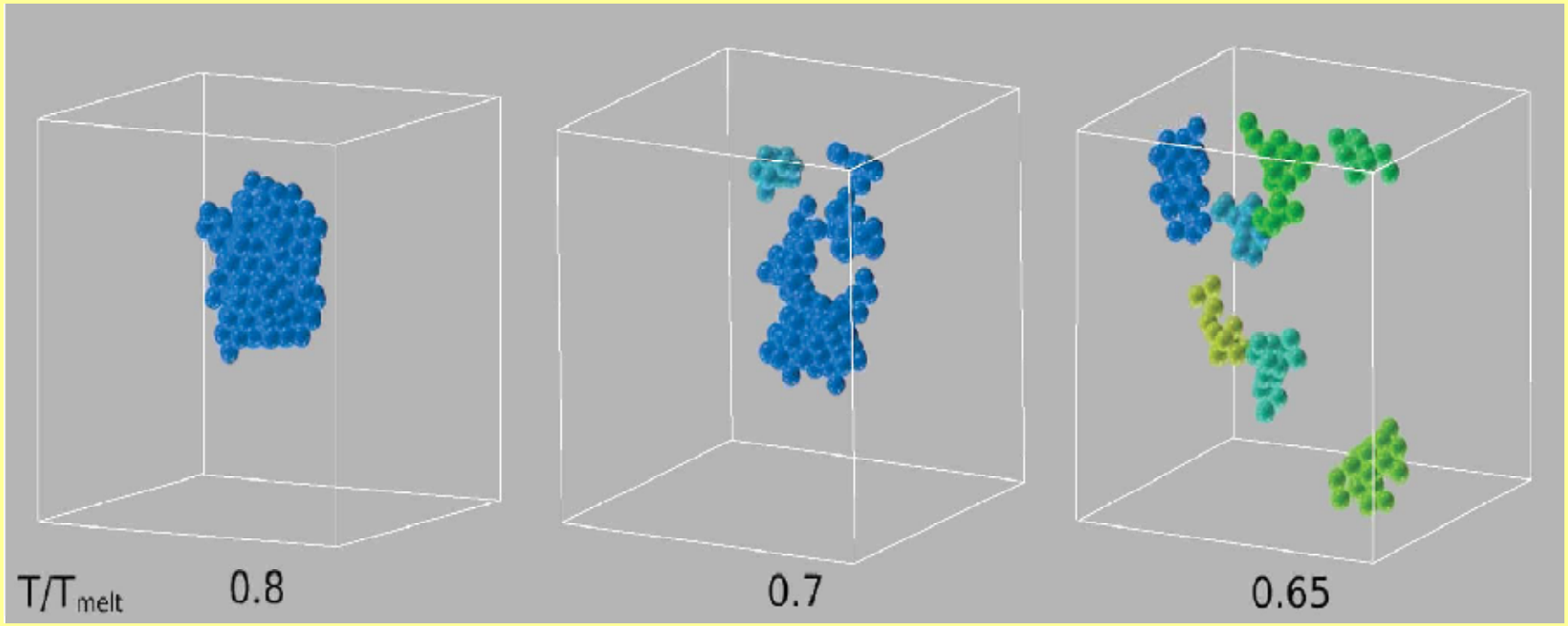


FIG. 4 (color). For T/T_{melt} = 0.8, a snapshot of a critical nucleus is shown. For T/T_{melt}= 0.7 and 0.65. Colored spheres represent particles with a solid-like environment. Different colors indicate different aggregates with solid-like character. For clarity, the liquid-like particles are not shown.

Trudo et al PRL (2006)

Final Scenario (subject to change!)

- Increase in supercooling/supersaturation –
  → slower structural relaxation in clusters
  → metastable tree-like clusters (low N_{coord}.
  → Low surface tension
  → ΔG_V also decreases, but already quite large
  → Nucleation barrier disappears for small clusters
  → But ripening is slow
  → Coalescence mechanism – need to improve upon Zeldovich. Ref. Metiu-Kitahara-Ross.

Summary

- A multidimensional free energy surface of nucleation of the liquid phase from the parent supercooled and supersaturated vapor phase near the gas-liquid spinodal. In particular, removed the Becker-Doring constraint of having only one growing cluster in the system.
- Close to the spinodal, the free energy, as a function of the size of the largest cluster, develops surprisingly a minimum at a subcritical cluster size.
- It is this minimum at intermediate size that is responsible for the barrier towards further growth of the nucleus at large supersaturation.
- An alternative free energy pathway involving the participation of many subcritical clusters is found near the spinodal where the growth of the nucleus is promoted by a coalescence mechanism.

Bhimalapuram, Chakrabarty and Bagchi, Phys. Rev. Lett. **98**, 206104 (2007)

intermediate sized clusters (No Ostwald ripening!).

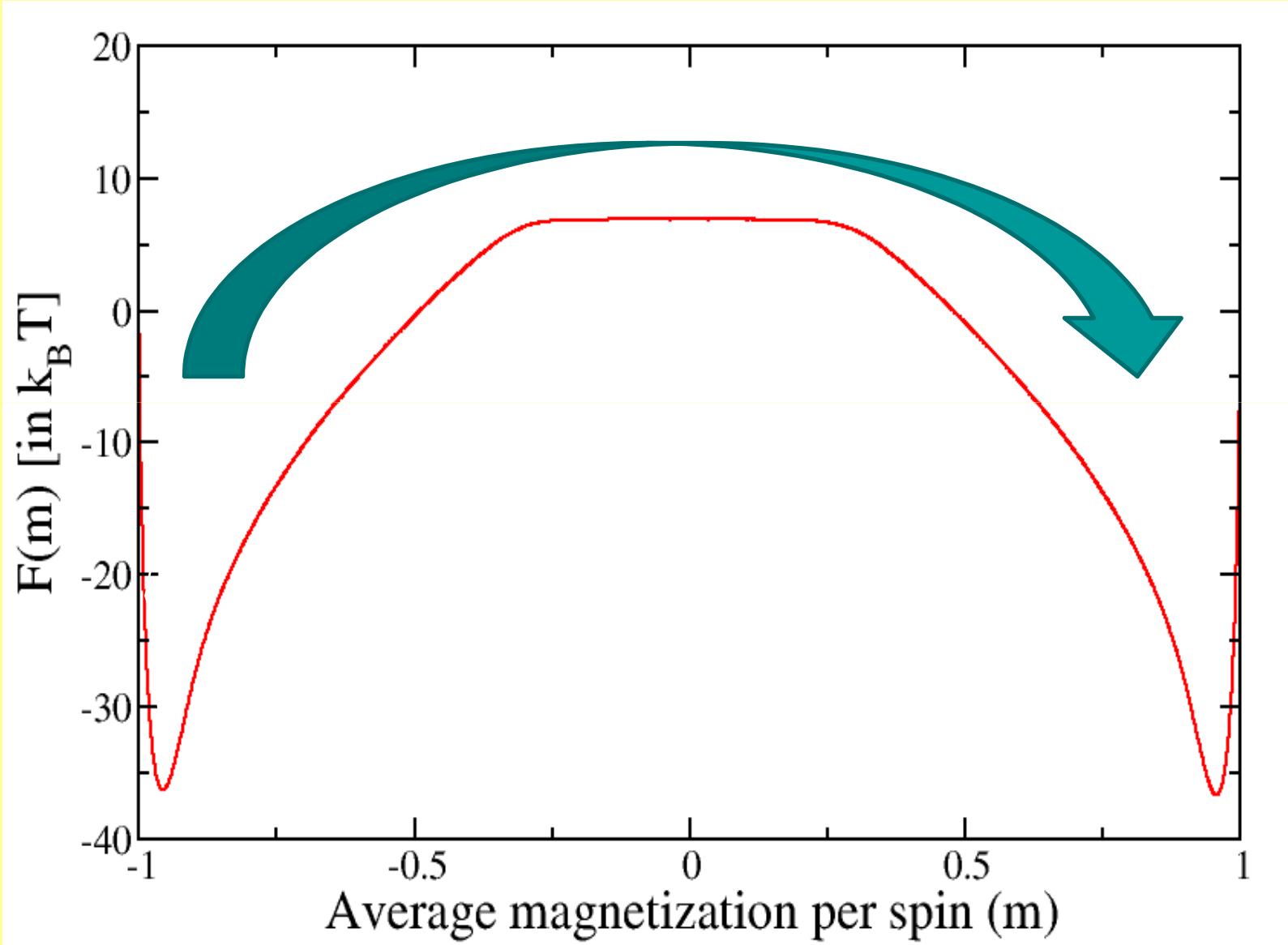
Acknowledgement

- Suman Chakrabarty
- Mantu Santra
- Dr. B. Prabhakar

Thank you !

Bhimalapuram, Chakrabarty and Bagchi, Phys. Rev. Lett. **98**, 206104 (2007); PRL 2008); Jose PRL (2006), JCP (2008, 2009), PRE (2006)

Why non-Boltzmannn sampling?



Non-Boltzmann sampling

For Hamiltonian H_0 system visits microstates with frequency: $\pi(s) = \exp\{-\beta H_0(s)\} / Z(\beta)$

But it samples only a particular minimum in free energy surface, say in the region: $x \subset (x_{min}, x_{max})$.

We introduce a new Hamiltonian $H_n = (H_0 + W(x))$ so that Markov chain visits order parameter in the range of our choice: $x \subset (X_{min}, X_{max})$.

Choice of weight function

- Traditional umbrella sampling:

$W(x) = k(x - x_0)^2$ if $x \subset (X_{min}, X_{max})$

$= -\infty$ Otherwise

- Transition Matrix Monte Carlo (TMMC):

$W(x) = -\ln(P(x))$ = βF(x) : Potential of mean force/free energy

P(x) is generated from initial estimate; on the fly

M. Fitzgerald, R. R. Picard and R. N. Silver, *Europhys. Lett.* **46**, 282 (1999)

TMMC algorithm

- Upon equilibration following bookkeeping step is added:

Given that the system is in state $s \in S$ and state $t \in T$ has been proposed, we store the *unweighted* transition probabilities:

✓ For S ≠ T:

$$C_{S,T}(\beta) = C_{S,T}(\beta) + r_{s,t}(\beta, \vec{0})$$

$$C_{S,S}(\beta) = C_{S,S}(\beta) + [1 - r_{s,t}(\beta, \vec{0})]$$

✓ For S = T:

$$C_{S,S}(\beta) = C_{S,S}(\beta) + 1$$

At any point the canonical transition probability can be estimated by:

$$P_{S,T}(\beta) = \frac{C_{S,T}(\beta)}{\sum_{U} C_{S,U}(\beta)}$$

Macrostate transition probabilities are estimated from the detailed balance equation:

$$\Pi_S(\beta,\vec{0})P_{S,T}(\beta) = \Pi_T(\beta,\vec{0})P_{T,S}(\beta)$$

Once estimated macrostate probabilities (Π_S) are useful in adaptive updates of weights.

- **Free energy:** $F(\beta,\vec{0}) = -k_B T \ln \Pi_S(\beta,\vec{0})$