Approaching and Leaving Metastability

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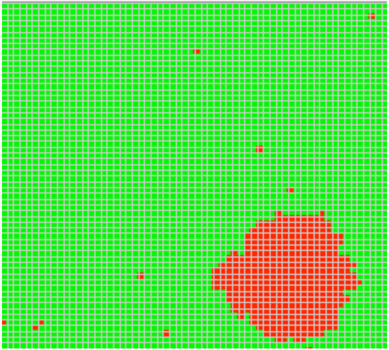
Outline of Talk

- Metastable states. For example, a liquid supercooled several decades below the freezing temperature without crystallizing.
- Nucleation – decay of metastable state to stable phase.
- When is a "metastable" state truly in equilibrium? Ising model example.
- What is the nature of nucleation in a supercooled Lennard-Jones liquid?
- Umbrella sampling.
- Classical nucleation theory.
- Spinodal nucleation theory.
- Heterogeneous nucleation in Lennard-Jones liquids.

What is nucleation?

Consider a 64×64 Ising model on a square lattice at temperature $T = 1 \, (< T_c = 2.29)$ and magnetic field $H = 0.72$.

What happens when we flip the field, $H \to -H$?

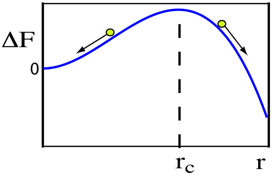


Assumptions of classical nucleation theory

- Key assumption is that a nucleating droplet can be considered to be an equilibrium fluctuation. That is, the system is in metastable equilibrium before nucleation. The probability of a thermal fluctuation $\propto e^{-\beta \Delta F}$.
- Nucleating droplets are rare and non-interacting.
- Nucleating droplets have a well defined interior and surface. Free energy of forming a droplet:

$$\Delta F = F_{\mathrm{bulk}} + F_{\mathrm{surf}} = -|\Delta f| r^d + \sigma r^{d-1}.$$

droplet radius r, spatial dimension d, free energy (density) difference between metastable and stable states Δf, surface tension σ.



Probability of nucleation

- What is the probability of nucleation occurring at time t after the change of field?
- Divide time t into intervals Δt. The probability that system nucleates in the time interval Δt is $\lambda\,\Delta t$; the nucleation rate λ is a constant.
- Probability that nucleation occurs in the time interval $(n+1)$:

$$P_n = (1-\lambda\Delta t)^n \lambda\,\Delta t.$$

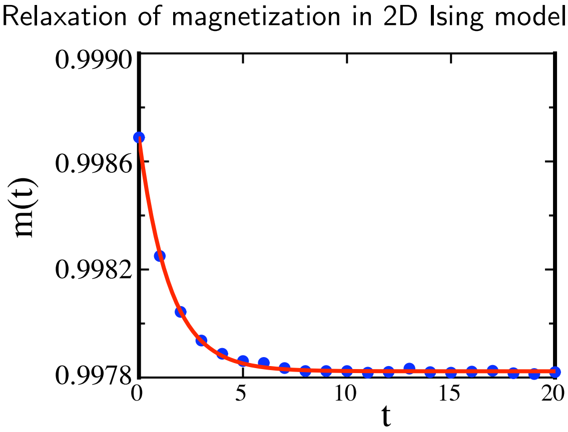
  Assume that $\lambda\Delta t \ll 1$ and let $n = t/\Delta t$. Hence

$$P(t)\Delta t = (1-\lambda\Delta t)^{t/\Delta t}\lambda\Delta t \to e^{-\lambda t}\lambda\Delta t.$$

$$\boxed{P(t) \propto e^{-\lambda t}}$$

  $P(t)\Delta t$ is the probability that the system nucleates between t and $t+\Delta t$ after the change of field.
- $P(t)$ is an *exponentially decreasing* function of time.

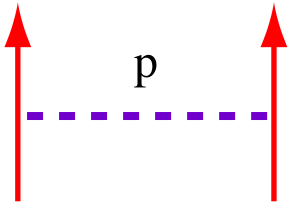
Approach to equilibrium of global quantities



- The magnetization relaxes exponentially.
- According to $m(t)$ and other global quantities, the system has reached metastable equilibrium after $\approx 5\,\mathrm{mcs}$.

Clusters in the Ising model

- Need to determine nucleation time.
- Define clusters by a rigorous mapping between the Ising/Potts models and site-bond percolation (Coniglio and Klein, 1980).

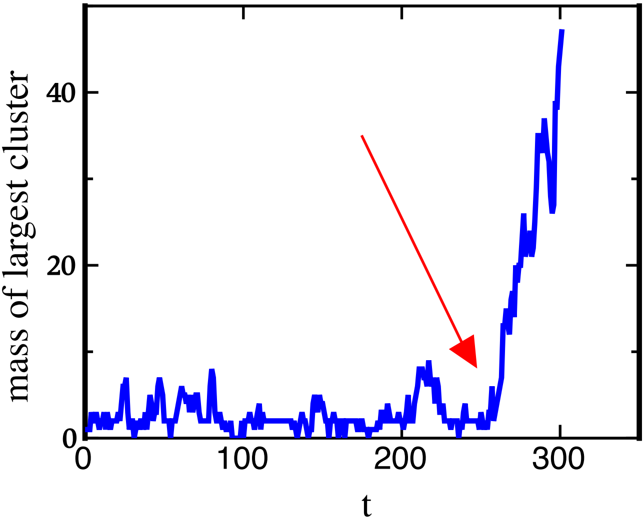


- Two parallel spins within the interaction range are connected by a bond with probability

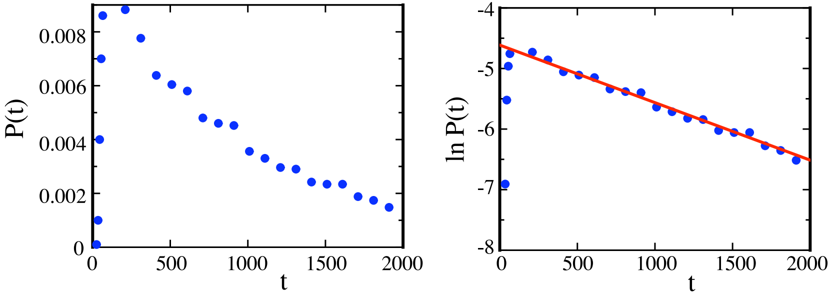
$$p = 1 - e^{-2\beta J}.$$

- Any two spins that are connected via bonds are in the same cluster.
- Clusters are statistical objects. Average over bond realizations to find the distribution of clusters.

Nucleation time



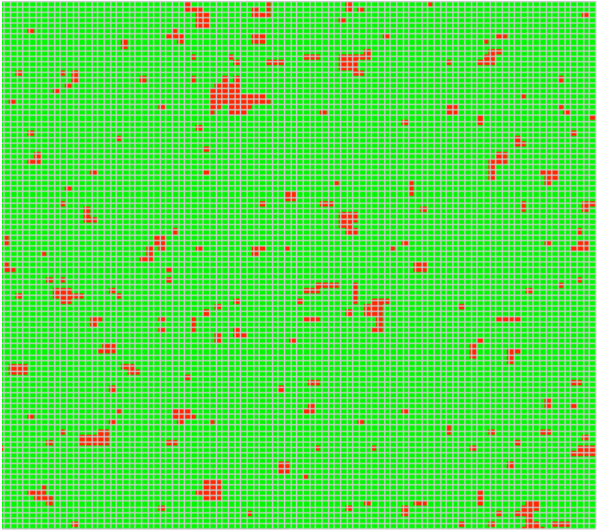
Distribution of nucleation times



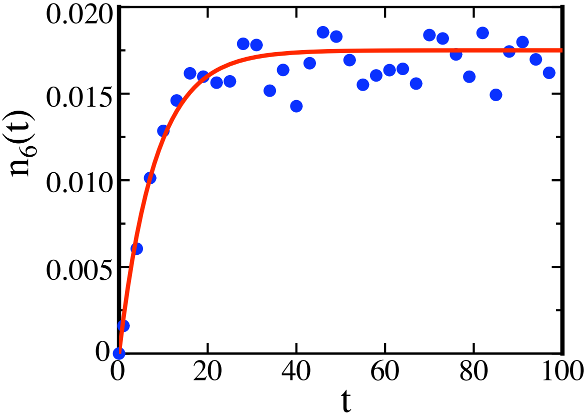
- The nucleation rate becomes a constant only after $t \gtrsim 60\,\mathrm{mcs}$.
- Using global quantities as indicators for metastable equilibrium is not appropriate in general.

Distribution of clusters

Count the number of clusters of size n_1, n_2, ..., and determine their time dependence.



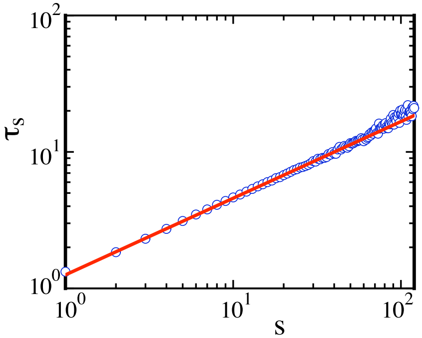
Number of clusters



$$n_s(t) \approx n_{s,\infty}[1 - e^{-t/\tau_s}] \tau_s \approx 8\,\mathrm{mcs}.$$

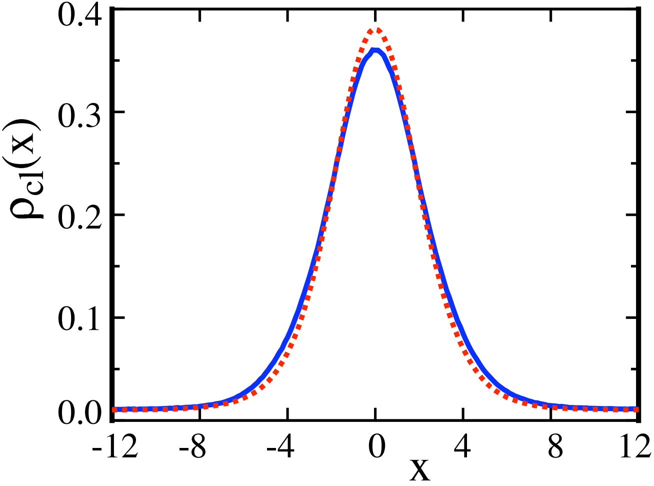
τ_s is time for the number of clusters with s spins to reach its time independent value.

Equilibration time



- Time τ_s for mean number of clusters of size s to become time independent increases linearly with s.
- The magnitude of the time τ_s for clusters whose size is the order of the nucleating droplet is the same order of magnitude as time for the nucleation rate to become time independent.
- Non-equilibrium distribution of nucleation times is due to the longer time required for the mean number of larger clusters to become time independent.

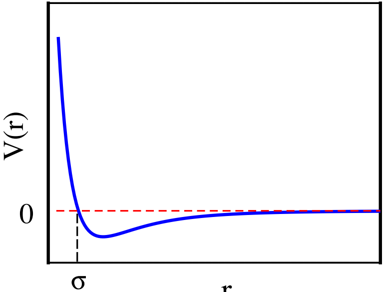
Structure of nucleating droplets: Does equilibrium make a difference?



The transient droplets occur in a slightly lower background magnetization and compensate by being denser and more compact.

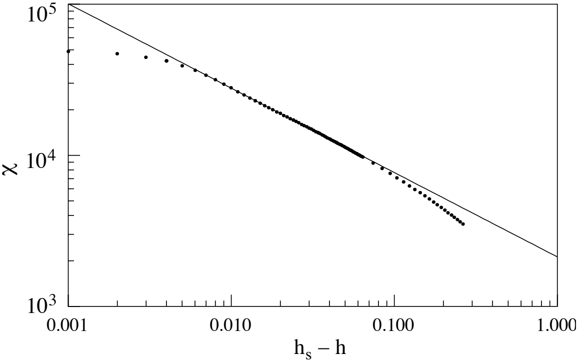
Supercooled Lennard-Jones liquid

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$



- Classical nucleation theory: Droplets are compact, isotropic and have a well-defined surface. Expect classical theory to hold near coexistence.
- What happens for deeper quenches?
  For short-range interactions the lifetime of the metastable state becomes shorter and eventually $\Delta F \sim kT$ and the system reaches the Becker-Doring limit.

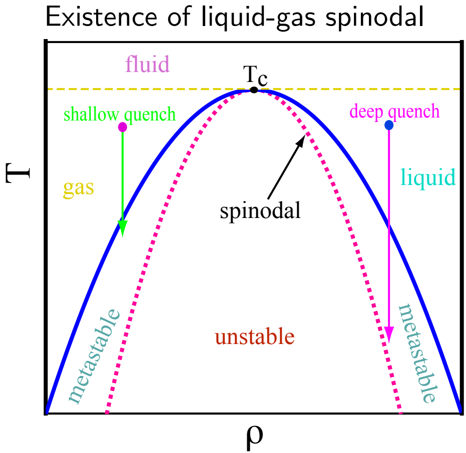
What happens for long-range interactions?



Ising model with long-range interaction.

- Spinodal separates metastable and stable regions.
- Spinodal well defined only in the mean-field limit.
- Shallow quench: classical nucleation.
- Deep quench: spinodal nucleation.

van der Waals phase diagram



- Spinodal nucleation: liquid → solid
  - Surface tension of droplet vanishes.
  - Nucleating droplets are diffuse and ramified.
  - Nucleating droplets are bcc or stacked hexagonal planes.
  - Radius of gyration of the nucleating droplets diverges in 3D.

Difficulties

- No theoretical definition of (solid-like) clusters in continuum systems unlike for Ising models.
- Nucleation events are rare near coexistence. Molecular dynamics and conventional sampling techniques are impractical. Typical nucleation barrier ΔF ranges from $0 \rightarrow 60\, kT$. The probability of nucleation $\propto e^{-\beta \Delta F}$.

What to do?

- Introduce umbrella sampling.
- Define solid-like particles and clusters (ad hoc).

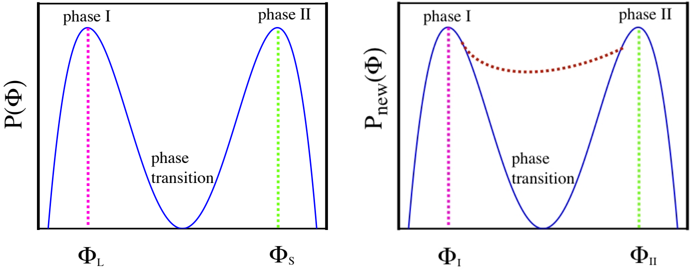
Umbrella sampling: Increase the probability of rare events

- Introduce order parameter Φ.
- Introduce bias potential $V_b(\Phi)$. Total potential energy becomes $\tilde{V} = V + V_b$.
- Sample states according to Boltzmann probability $\tilde{P}$

$$\tilde{P} = e^{-\tilde{V}/kT} = P\, e^{-V_b/kT}.$$

- From the relation $P = e^{-\beta F}$, find

$$F = -kT \ln \tilde{P} + \beta^{-1} V_b.$$



Define solid-like particles

- For each particle i, compute the complex vector

$$\tilde{q}_{\ell=6m}(i) = \frac{1}{n_i} \sum_{j=1}^{n_i} Y_{6m}(\hat{r}_{ij}).$$

  Y_{6m} is spherical harmonic; n_i is # of neighbors of particle i.

- Define $q_{lm}(i)$ as

$$q_{lm}(i) = \frac{\tilde{q}_{lm}(i)}{[\sum_{m=-l}^{l} |\tilde{q}_{lm}(i)|^2]^{1/2}}.$$

- Form the dot product

$$c_{ij} = \sum_{m=-6}^{6} q_{6m}(i) q_{6m}(j)^*.$$

  Two particles i and j are *coherent* if $c_{ij} \geq 0.5$.

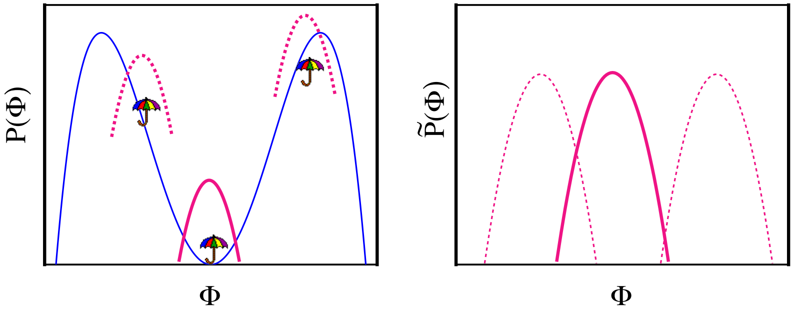
- A particle with more than 11 coherent bonds is *solid-like*.

Order parameter

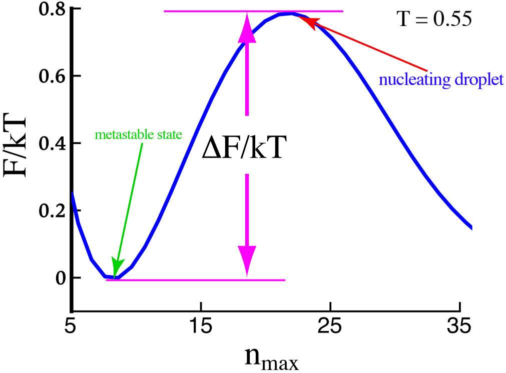
- Choose the order parameter Φ to be $n_{\max}$, size of largest cluster.

$$V_b = \frac{1}{2}\kappa(\Phi - \Phi_0)^2$$

- Φ_0 specifies the position of the bias and κ controls its strength.
- Determine $\tilde{P}$ in each window and then match the values of $\tilde{P}$ in each window.

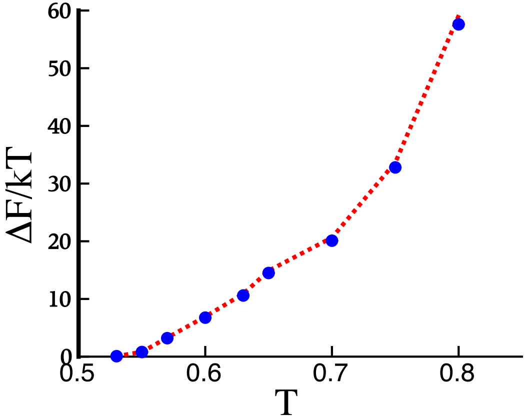


Free energy



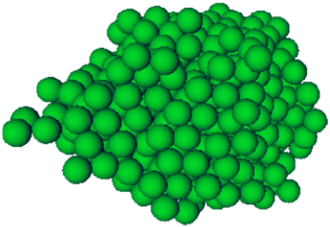
- 3D simulation of 4000 Lennard-Jones particles at density $\rho = 0.95$; $T_{\mathrm{melt}} \approx 1.18$; ≈ 5 hours per window, and 10–20 windows for each temperature.

Temperature dependence of the free energy barrier

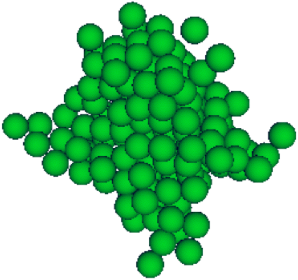


- Free energy barrier vanishes at $T \approx 0.53$.

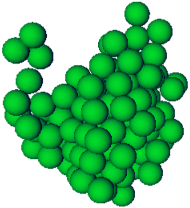
Snapshots of nucleating droplets



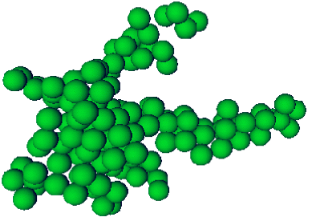
$T = 0.75.$



$T = 0.65.$



$T = 0.60.$

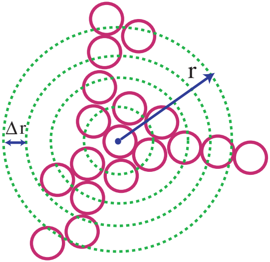


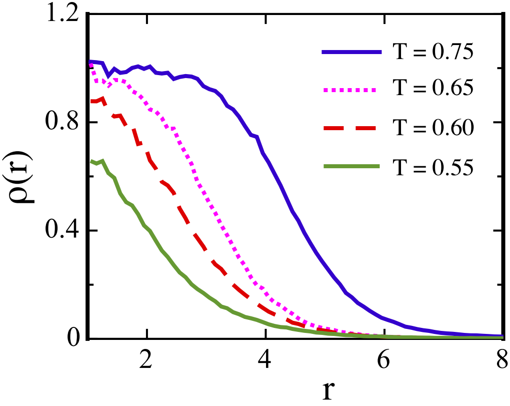
$T = 0.55.$

Evidence for spinodal effects

- Density profile of nucleating droplets

$$\rho(r)4\pi r^2 dr = N(r).$$





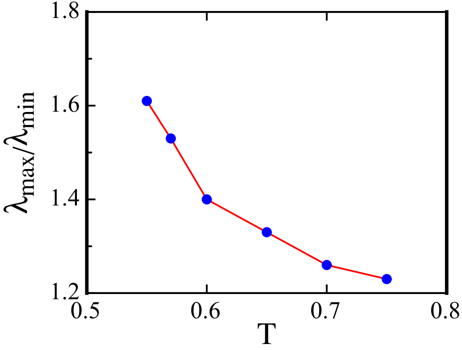
- Nucleating droplets become more diffuse for deeper quenches.

Anisotropy of nucleating droplets

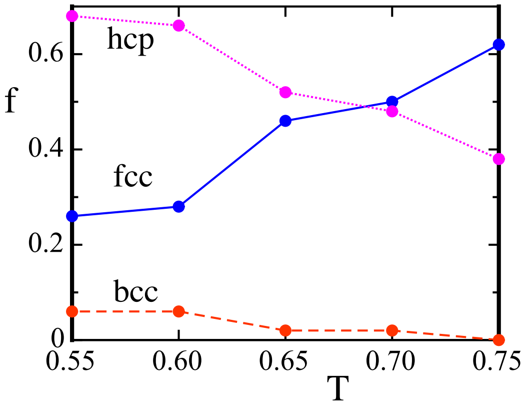
- Moment of inertia tensor:

$$I_{\alpha\beta} = \sum_k (r_k^2 \delta_{\alpha\beta} - r_{k,\alpha} r_{k,\beta}).$$

- Eigenvalues of $I_{\alpha\beta}$ correspond to principal radii of ellipsoid.
- Ratio of the maxima and minima eigenvalues ($\lambda_{\mathrm{max}}/\lambda_{\mathrm{min}}$): measure of anisotropy.

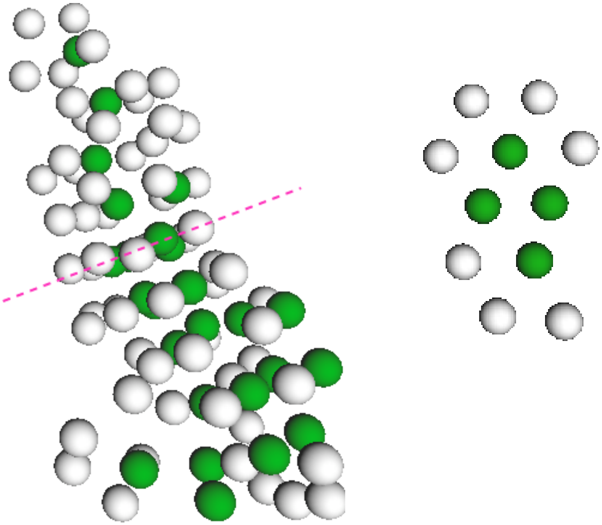


Symmetries of particles in the nucleating droplet



- Near coexistence nucleating droplets are compact and core has fcc symmetry, consistent with classical nucleation.
- For deep quenches, core becomes smaller and droplets have a larger bcc and hcp component.

The nucleating droplet and its immediate neighborhood form stacked hexagonal planes

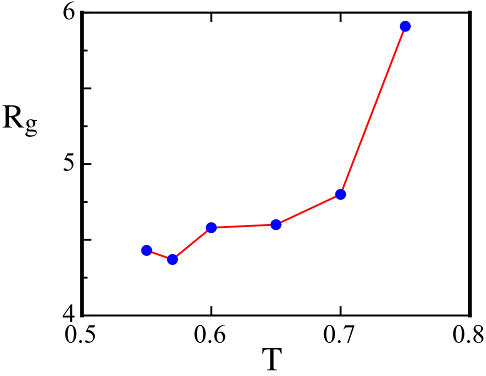


(a) A nucleating droplet (green) and the surrounding liquid (gray).

(b) An intersection.

The jury is still out: Radius of gyration

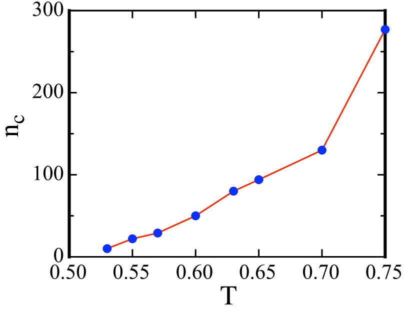
- Theory: $R_g \sim \epsilon^{-1/2}$; R_g should decrease for quenches away from coexistence and then begin to increase for deep quenches near the spinodal.
- Simulation: Radius of gyration R_g decreases as T is decreased. How deep is deep?



Radius of gyration.

Mass of nucleating droplet

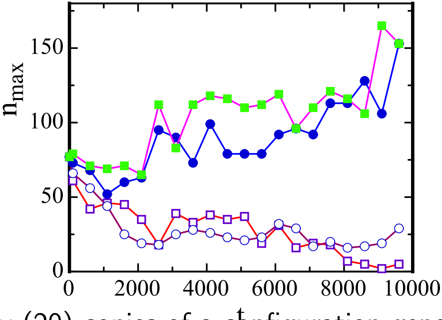
- Theory: $n_c \sim \epsilon^{1-d/2}$; n_c should decrease for quenches away from coexistence and increase for deep quenches near the spinodal in 3D and be constant in 2D.
- Simulation: Number of particles in nucleating droplet decreases as T is decreased.
- Is the nucleating droplet essentially 2D?



Number of particles in nucleating droplet.

Consistency check: Is the nucleating droplet a saddle point object?

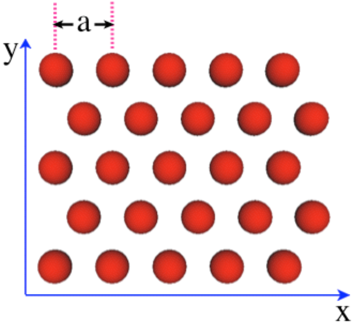
The nucleating droplet is a saddle point object. Intervention should give a 50% probability of growing or shrinking.



- Make many (20) copies of a configuration generated at Φ corresponding to free energy maximum..
- Introduce randomness, e.g., change random number seed.
- Turn off the bias and determine if the droplet grows with $\approx 50\%$ probability at about the same time and place.
- Meaning of $\Delta F \approx 0$ at $T = 0.53$?

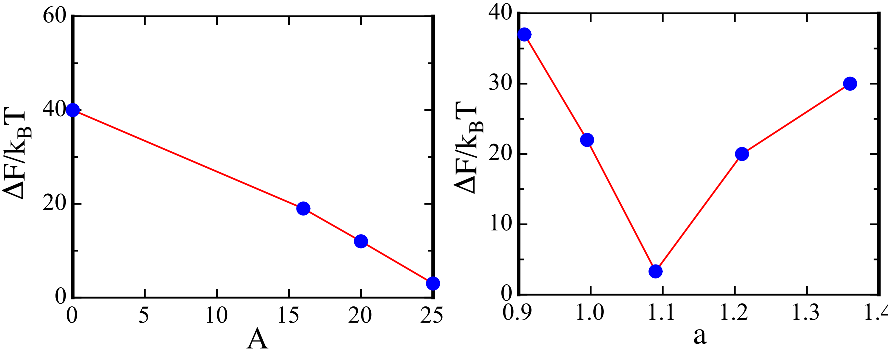
Heterogeneous nucleation

- Types of Impurities:
  - Foreign particles, (pre-critical) nucleus.
  - Rough surface (e.g., container wall), interface between phases.
- Presence of impurity can greatly lower the nucleation barrier.



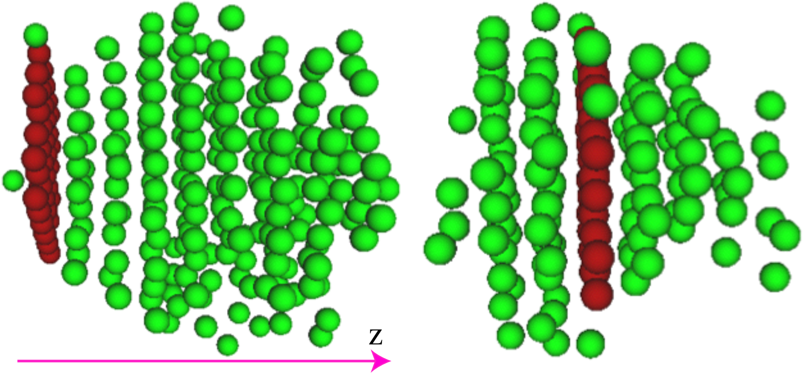
- The positions of the particles in the impurity are fixed and form a $m \times n$ hexagon.
- Vary the size and lattice spacing a.

Dependence of the nucleation barrier on area and lattice spacing of impurity



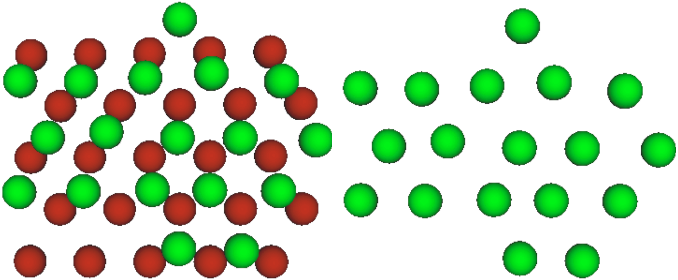
- Nucleation barrier decreases for bigger area (and fixed a).
- For fixed area ΔF is a minimum when $a = 1.09$.
- The optimal spacing $a_c = 1.09$ coincides with the lattice spacing in homogeneous nucleation.
- $\Delta F/kT$ lowered by a factor of 30 compared to homogeneous case at $T = 0.75$. Probability of nucleation enhanced by 10^{13}.

Droplets grow by forming layers



(a) $a = 0.908$.　(b) $a = 1.09$.

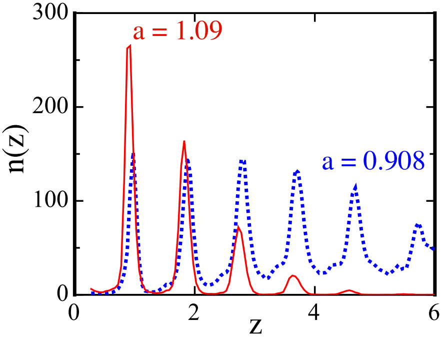
Each layer is hexagonal



(a) Impurity and the first layer (b) First layer

- Lattice spacing in each layer equals a_{c}, even when $a \neq a_{\mathrm{c}}$.

Density profile



- Solid line for $a = a_c$, dashed line for $a = 0.908$.
- Sharp peaks indicate layered structure.
- When $a = a_c$, droplet prefers to grow on the impurity; When $a \neq a_c$, the crystal prefers to grow into the bulk.

Summary of Lennard-Jones results

- An impurity is most efficient when its lattice spacing is equal to that of the crystalline phase.
- Nucleating droplet grows by forming hexagonal layers on impurity.
- When the lattice spacing is not optimal, the droplet grows into the bulk instead of wetting both sides of the impurity.
- Homogeneous nucleation results consistent with the existence of a liquid-solid spinodal:
  - Near coexistence the nucleating droplets are compact, consistent with classical nucleation theory.
  - For deep quenches, the core becomes much smaller, the droplets become more anisotropic, and the droplets have a larger bcc and hcp component.
- Unanswered questions: Why does the radius of gyration and the number of clusters in the nucleating droplet not increase near the spinodal?
- Are there are other signatures of the influence of a liquid-solid spinodal?

Future work

- Study other models where range of interaction can be varied.
- Study transient nucleation in Lennard-Jones and more realistic systems. Is the symmetry of the nucleating droplet affected?
- Develop a "Ginzburg criterion" to determine when mean-field effects should be observable.
- Introduce impurities with different symmetries and study their effect for deeper quenches.
- Do a careful study of umbrella sampling in the Ising model.

Selected References

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