Dynamics versus thermodynamics in two-step nucleation

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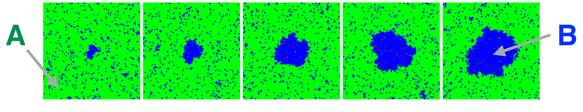
abstract

Nucleation is the process by which a bulk metastable phase undergoes a phase transition to a stable phase via the formation of a local fluctuation (the critical nucleus) of sufficient size to be able to grow spontaneously to macroscopic scale. In the case of `two-step nucleation" (TSN), the first step in the phase transformation process consists of the appearance in the bulk metastable phase of a local fluctuation that resembles an intermediate phase distinct from the stable phase. In the second step of TSN, this intermediate fluctuation undergoes a transition in which the stable phase emerges from within the intermediate phase. Evidence for TSN has been observed experimentally in a wide range of molecular and colloidal systems, including important cases relevant to understanding protein crystallization and biomineralization. In a recent work, the free energy surface (FES) describing TSN as it occurs in a simple 2D model of a metamagnet was evaluated [1]. This FES shows that at a well-defined size for the growing nucleus, the stable phase becomes more stable than the intermediate phase, providing a thermodynamic prediction for the nucleus size at which the second step of TSN begins. Here we identify conditions at which the spontaneous transition within the nucleus occurs at much larger size than predicted by thermodynamics, demonstrating that the system dynamics can have a dramatic impact on how TSN is observed in practice.

[1] D. James, S. Beairsto, C. Hartt, O. Zavalov, I. Saika-Voivod, R.K. Bowles and P.H. Poole, J. Chem. Phys. 150, 074501 (2019).

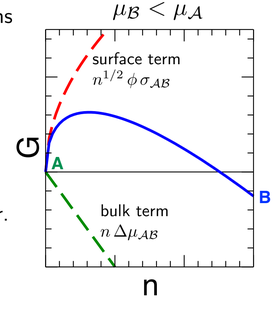
Free energy of a fluctuation in classical nucleation theory



- Consider a bulk phase $\mathcal{A}$ in which fluctuations correspond to another bulk phase $\mathcal{B}$.
- CNT expressions $(d = 2)$ for free energy to form a $\mathcal{B}$ fluctuation of size n:

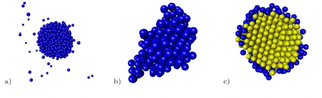
$$G_{\mathcal{AB}} = n^{1/2}\,\phi\,\sigma_{\mathcal{AB}} + n\,\Delta\mu_{\mathcal{AB}}$$

- $\sigma_{\mathcal{AB}}$ is $\mathcal{AB}$ surface tension, ϕ is shape factor.
- $\Delta\mu_{\mathcal{AB}} = \mu_{\mathcal{B}} - \mu_{\mathcal{A}}$ is chemical potential difference between bulk $\mathcal{B}$ and $\mathcal{A}$ phases.

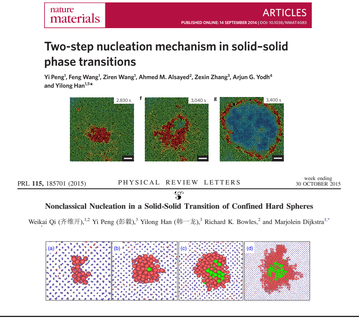


Two-step nucleation

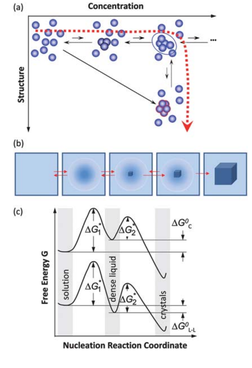
Vapour-crystal nucleation via liquid intermediate



A. van Meel, A. J. Page, R. P. Sear, and D. Frenkel, J. Chem. Phys. **129**, 204505 (2008).



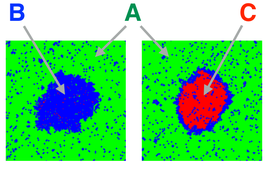
Protein nucleation via dense intermediate



P. Vekilov, Nanoscale 2, 2346 (2010).

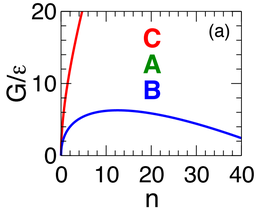
phase transition in a fluctuation

Free energy of a fluctuation in a three-phase system



$$\sigma_{\mathcal{AB}} < \sigma_{\mathcal{AC}}$$

$$\mu_{\mathcal{B}} < \mu_{\mathcal{A}} < \mu_{\mathcal{C}}$$



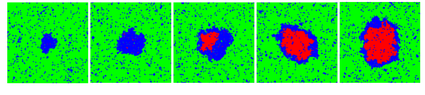
- Consider a bulk phase $\mathcal{A}$ in which fluctuations correspond to two other bulk phases $\mathcal{B}$ and $\mathcal{C}$.
- CNT expressions ($d = 2$) for free energy to form a $\mathcal{B}$ or $\mathcal{C}$ fluctuation of size n:

$$G_{\mathcal{AB}} = n^{1/2}\,\phi\,\sigma_{\mathcal{AB}} + n\,\Delta\mu_{\mathcal{AB}}$$

$$G_{\mathcal{AC}} = n^{1/2}\,\phi\,\sigma_{\mathcal{AC}} + n\,\Delta\mu_{\mathcal{AC}}$$

- $\sigma_{\mathcal{AC}}$ is $\mathcal{AC}$ surface tension.
- $\Delta\mu_{\mathcal{AC}} = \mu_{\mathcal{C}} - \mu_{\mathcal{A}}$ is chemical potential difference between bulk $\mathcal{C}$ and $\mathcal{A}$ phases.

Phase transition in a fluctuation



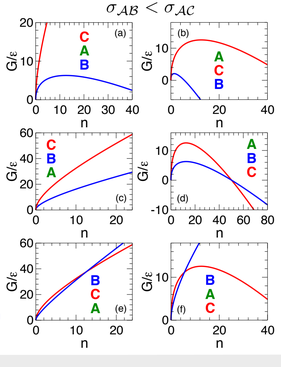
- $G_{\mathcal{AB}}$ and $G_{\mathcal{AC}}$ cross at $n = n_c$

$$n_c^{1/2} = \phi\,\frac{\sigma_{\mathcal{AC}} - \sigma_{\mathcal{AB}}}{\Delta\mu_{\mathcal{AB}} - \Delta\mu_{\mathcal{AC}}}$$

if quotient is positive.

- Assume $\sigma_{\mathcal{AB}} < \sigma_{\mathcal{AC}}$:
- Then n_c exists when $\Delta\mu_{\mathcal{AB}} > \Delta\mu_{\mathcal{AC}}$,
- and $\mathcal{B}$ fluctuations always dominate at small n.
- The most probable small fluctuation corresponds to the phase with the lowest surface tension. Russo, Romano, Tanaka, PRX (2018).
- If the phase with the lowest σ is not the phase with the lowest μ, then the fluctuation exhibits a phase transition at $n = n_c$.

$\sigma_{\mathcal{AB}} < \sigma_{\mathcal{AC}}$



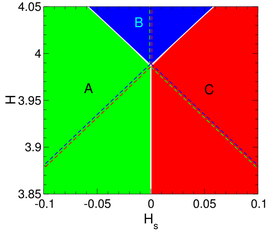
simulation of fluctuations in a 2D lattice model

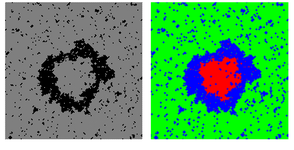
2D lattice model - the metamagnet

- Metamagnet Hamiltonian on a 2D square lattice with nn and nnn interactions:

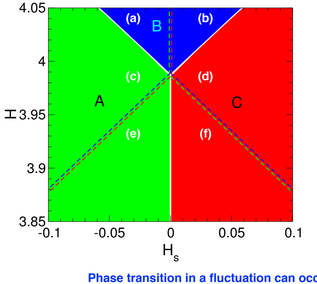
$$\frac{E}{J} = \sum_{\langle \mathrm{nn}\rangle} s_i s_j - \frac{1}{2}\sum_{\langle \mathrm{nnn}\rangle} s_i s_j - H\sum_{i=1}^{N} s_i - H_s \sum_{i=1}^{N} \lambda_i s_i$$

- Ising spins $s_i = \pm 1$
- Lattice variable $\lambda_i = (-1)^{x_i + y_i}$ defines a reference checkerboard.
- Direct field H and staggered field H_s
- $\mathcal{A}$ is an antiferromagnetic phase with $s_i \simeq -\lambda_i$.
- $\mathcal{B}$ is a ferromagnetic phase with $s_i \simeq 1$.
- $\mathcal{C}$ is an antiferromagnetic phase with $s_i \simeq \lambda_i$.
- Fixed $kT/J = 1$.
- All phase transitions are first order.
- Lattice sizes up to $L = 200$.

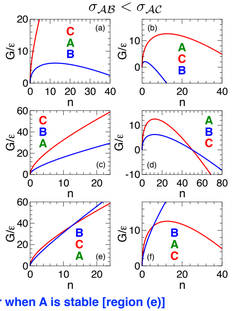




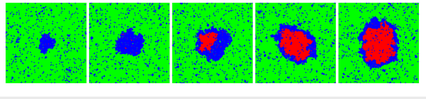
Thermodynamic regions



$\sigma_{\mathcal{AB}} < \sigma_{\mathcal{AC}}$



Phase transition in a fluctuation can occur when A is stable [region (e)] or metastable [regions (d) and (f)]:

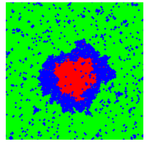


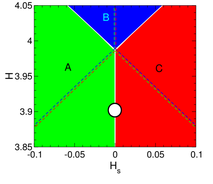
Free energy surface for fluctuations

- $n_{\max}$ = size of largest non-$\mathcal{A}$ cluster in the bulk $\mathcal{A}$ phase
- f = fraction of largest cluster occupied by $\mathcal{C}$ sites
- Free energy surface

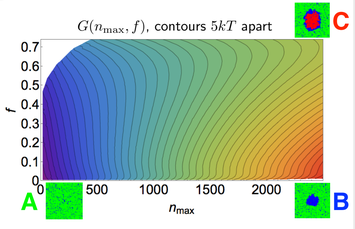
$$G(n_{\max}, f) = -kT\log[P(n_{\max}, f)] + \text{const}$$

evaluated using 2D umbrella sampling with respect to $n_{\max}$ and f.



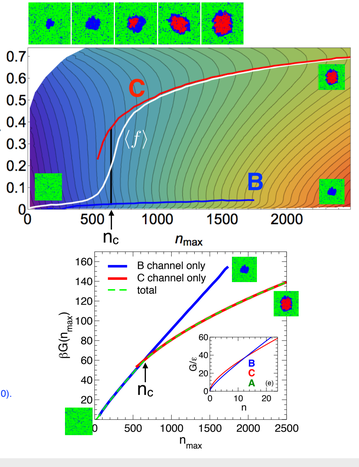


$G(n_{\max}, f)$, contours $5kT$ apart

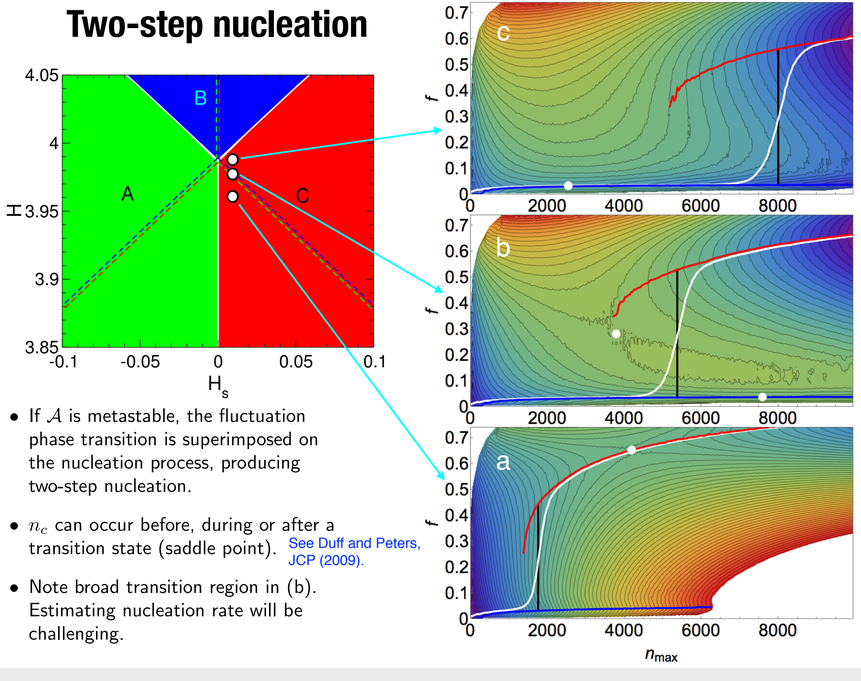


Phase transition in a fluctuation

- Two channels:
  High-f channel for $\mathcal{C}$ fluctuations
  Low-f channel for $\mathcal{B}$ fluctuations
- n_c = coexistence value of $n_{\max}$ for phase transition
- $\langle f\rangle$ = average value of f at fixed $n_{\max}$. Inflection in $\langle f\rangle$ close to n_c.
- 1D free energy $G(n_{\max}) = -kT\log\int_0^1 \exp[-\beta G(n_{\max}, f)]\,df$ has a kink at n_c.
- Each channel has a metastable extension beyond n_c, ending in a spinodal.
- At small n: $\mathcal{C}$ fluctuation is unstable. Only $\mathcal{B}$ is stable. See Harrowell, JPCM (2010).
- At large n: $\mathcal{B}$ fluctuation is unstable. Only $\mathcal{C}$ is stable.



two-step nucleation

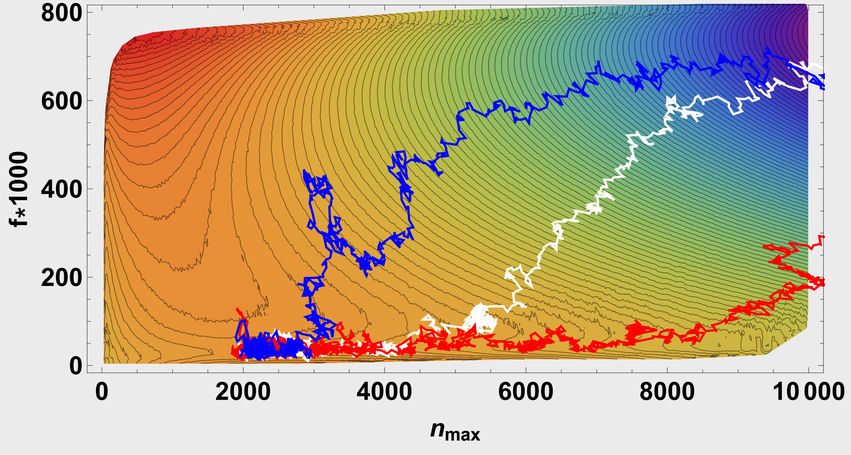


- If $\mathcal{A}$ is metastable, the fluctuation phase transition is superimposed on the nucleation process, producing two-step nucleation.
- n_c can occur before, during or after a transition state (saddle point). See Duff and Peters, JCP (2009).
- Note broad transition region in (b). Estimating nucleation rate will be challenging.

dynamics versus thermodynamics

Unconstrained runs at H=3.975, H_s=0.02:

- Individual runs started at the transition state take widely varying paths to the stable phase.
- This behaviour is consistent with the wide range of pathways observed in many experiments.



Unconstrained run at H=3.983, H_s=0.01:

- Individual run started at the transition state.
- Here the system remains trapped in the lower channel well beyond the cluster size for the transition in the nucleus predicted solely by thermodynamics.
- Demonstrates that dynamics play a key role.
- Consistent with observation of mesoscale pre-nucleation clusters observed in experiments.