

Bridging the gap between atomistic and mesoscopic models of nucleation

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Acknowledgements

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Gareth Tribello (Queen's U Belfast)
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PLUMED



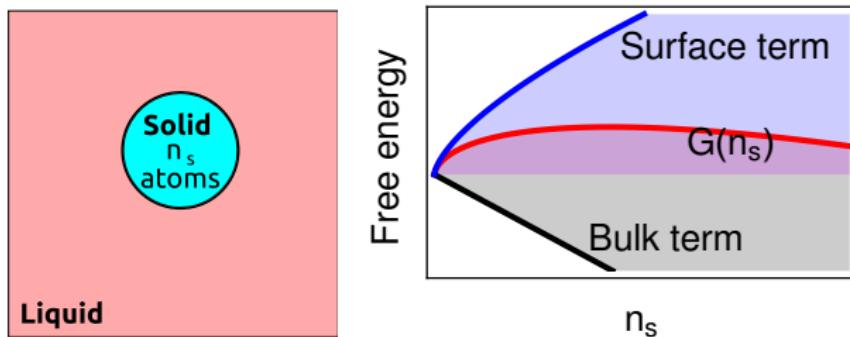
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A thermodynamic model of homogeneous nucleation

Nucleation: the Mesoscopic Picture

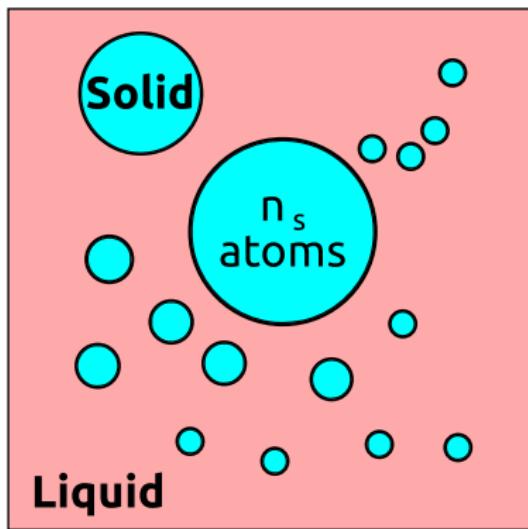
- Contiguous chunks of a stable phase nucleate within a metastable (undercooled, supersaturated, . . .) bulk phase
- Classical nucleation theory is the prototype of a mesoscopic model for the free energy of a nucleus



$$G(n_s) = \mu_{sl} n_s + \gamma \Omega n_s^{2/3}$$

A Tale of Many Nuclei

- The model (formally) predicts the energetics of few-atoms nuclei
- The picture is one in which the metastable phase contains many (p_n) sub-critical nuclei of size n , that form and dissolve dynamically

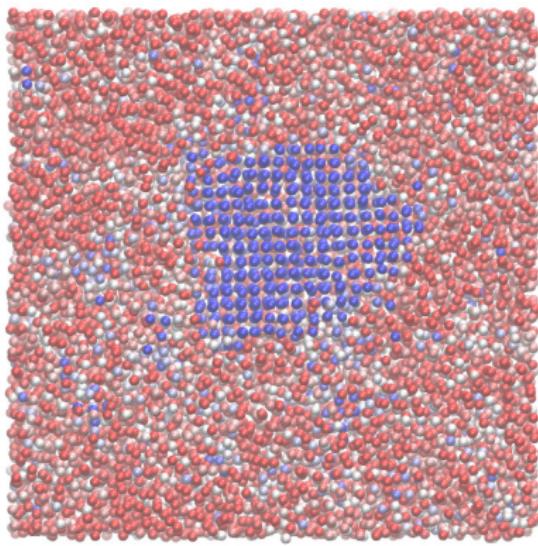
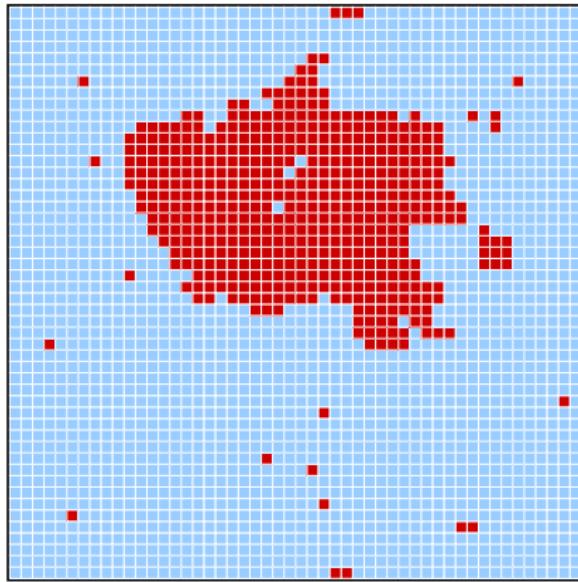


$$P(n, p_n) = \lambda(n)^{p_n} e^{-\lambda(n)} / p_n!, \quad \lambda(n) = N_s e^{-\beta G(n)}$$

Maibaum, PRL 2008

Studying Phase Transitions at the Atomic Scale

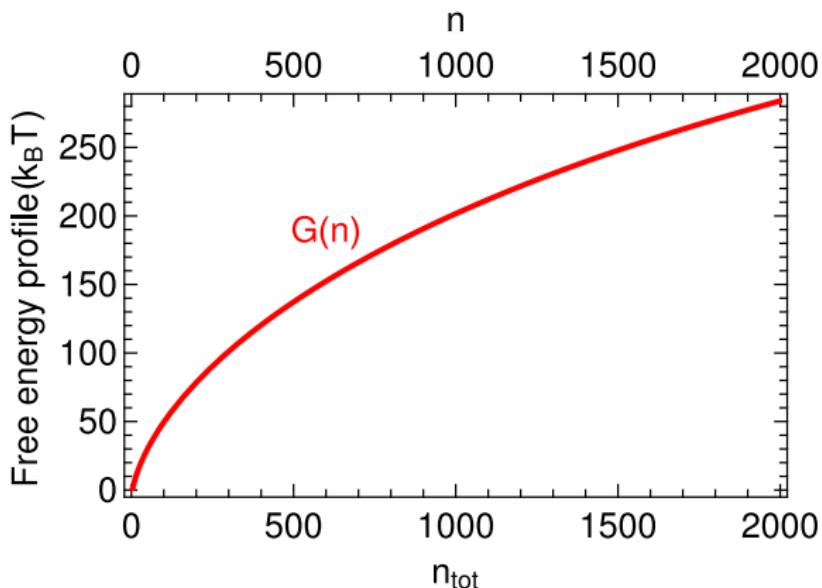
- Difficulties in translating this picture to the atomic scale
- Nuclei of few atoms are not well-defined phases
- Even the stable phase may be inhomogeneous
- Minimize ad-hockery in applying mesoscale models of nucleation to an atomistic simulation: choice of order parameter, clustering, . . .



Multiple-cluster Model \Rightarrow Macroscopic Variables

- Easy to see how a multiple-cluster model would look like in terms of the *total* fraction of solid atoms

$$n_{\text{tot}} = \sum_{n=1}^{\infty} np_n, \quad e^{-\beta \tilde{G}(n_{\text{tot}})} = \sum_{p_1, p_2, \dots, p_{n^*}} \delta \left(n_{\text{tot}} - \sum_{n=1}^{\infty} np_n \right) \prod_{n=1}^{n^*} P(n, p_n)$$

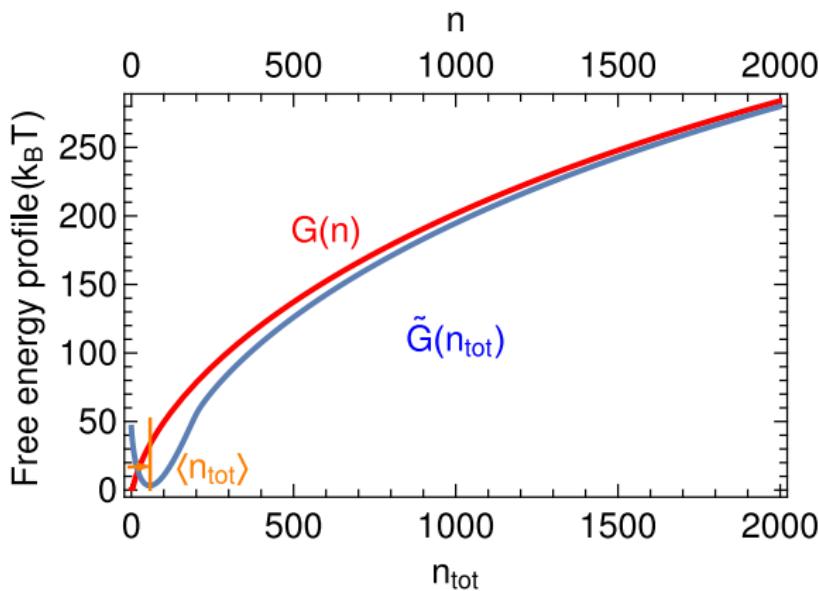


B. Cheng & MC, JCP (2017) DOI:10.1063/1.4973883

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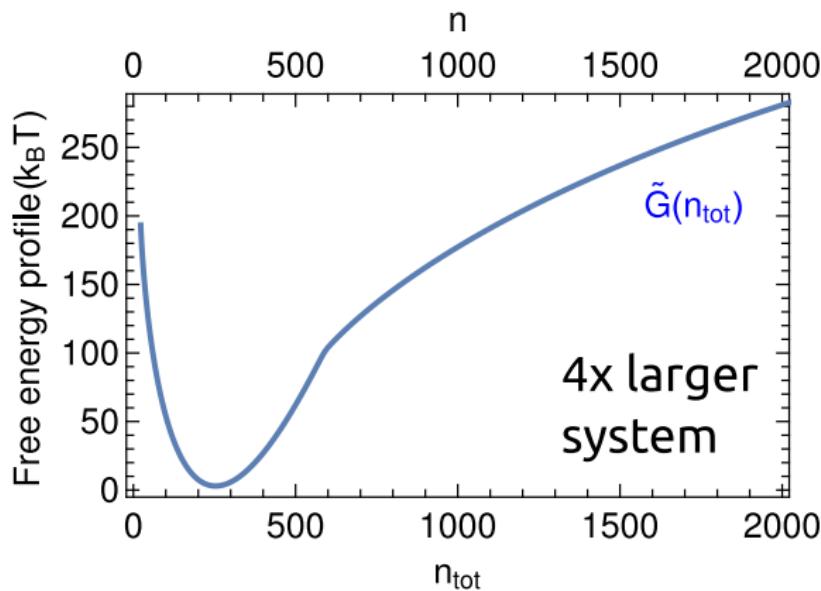


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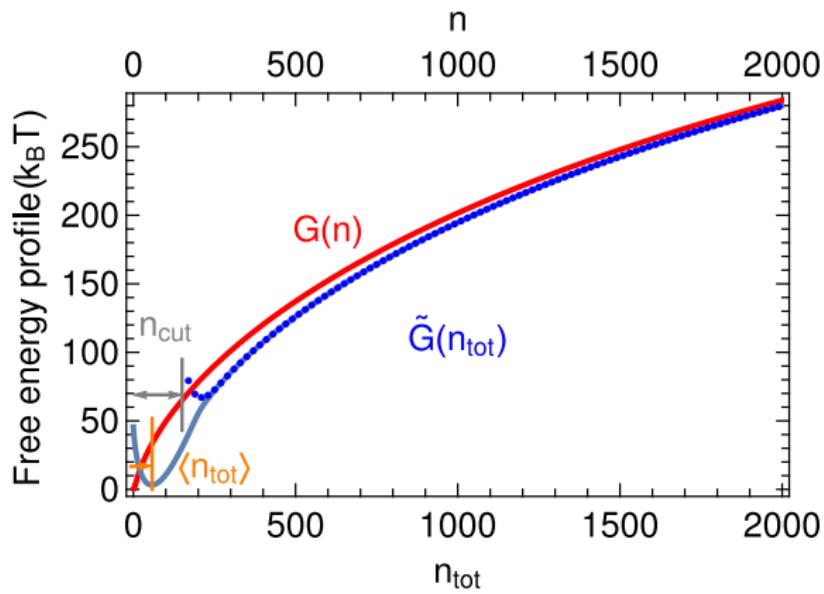
Bhimalapuram et al., PRL 98, 206104 (2007); B. Cheng & MC, JCP (2017) DOI:10.1063/1.4973883

Multiple-cluster Model \Leftarrow Macroscopic Variables

- In a **finite-size** simulation, there are two different regimes: for $n_{\text{tot}} > n_{\text{cut}} \gg \langle n_{\text{tot}} \rangle$, it is overwhelmingly more likely to have one “large” cluster on a background of small clusters. The expression then simplifies

$$e^{-\beta \tilde{G}(n_{\text{tot}})} = N_s \sum_{n=n_{\text{cut}}}^{n_{\text{tot}}} e^{-\beta G(n)} e^{-\beta \tilde{G}(n_{\text{tot}}-n)}$$

... meaning one can extract $G(n)$ from knowledge of $\tilde{G}(n_{\text{tot}})$!

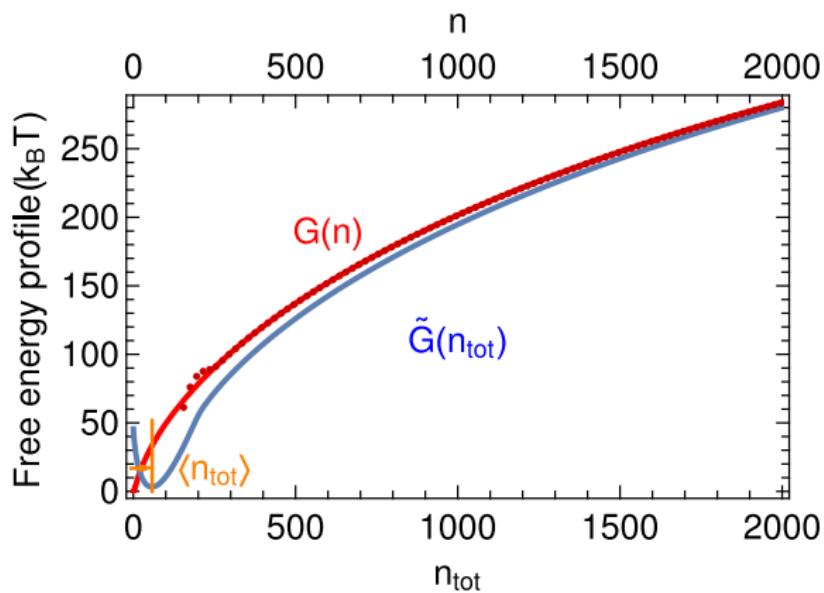


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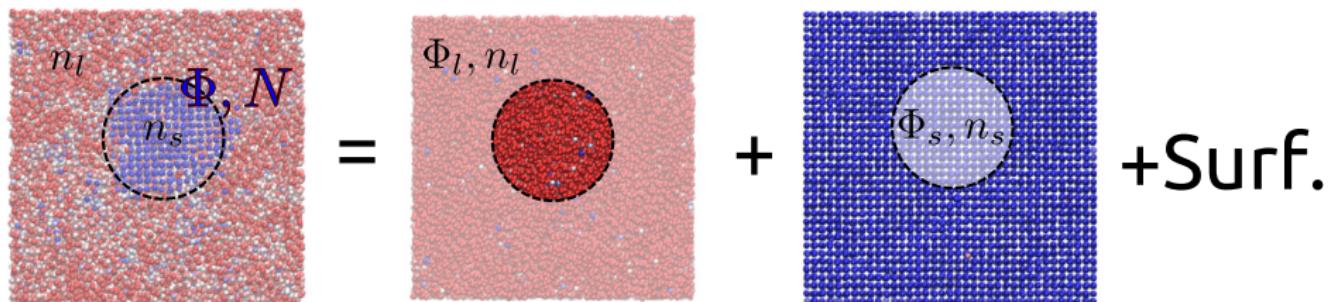
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A Generalized Gibbs Dividing Surface

- How to determine n_{tot} in an atomistic simulation? We can rely on any extensive order parameter Φ that distinguishes solid and liquid and require zero surface excess
- Assuming bulk phases can be represented by the average value of the order parameter, we can obtain n_s as a linear rescaling of Φ



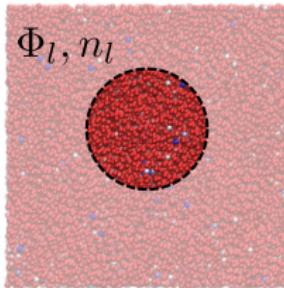
$$N = n_s + n_l + 0$$

$$\Phi = \Phi_s + \Phi_l + 0 = n_s \bar{\phi}_s + n_l \bar{\phi}_l$$

$$n_s = \frac{\Phi - N \bar{\phi}_l}{\bar{\phi}_s - \bar{\phi}_l}$$

Accounting for the Fluctuations

- For any realistic system the order parameters will exhibit fluctuations. We can build these in the framework with a probabilistic version of the Gibbs dividing surface construction
- The bulk phases can be characterized from unbiased simulations
- In a 2-phase system, zero-surface excess can be expressed in terms of the distribution of ϕ

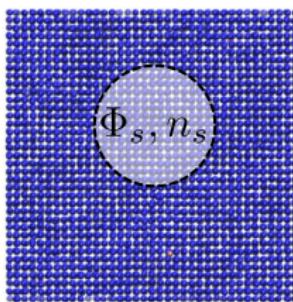


The liquid is characterized by a distribution of values of ϕ , for each size n

$$\rho_l(\phi|n) = \int d\Omega_n^{(l)} \delta(\phi(\Omega_n^{(l)}) - \phi)$$

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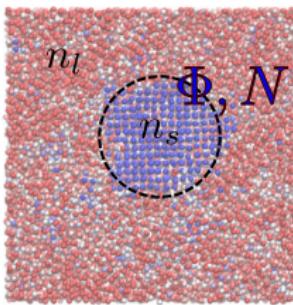


The solid is characterized by another distribution

$$\rho_s(\phi|n) = \int d\Omega_n^{(s)} \delta(\phi(\Omega_n^{(s)}) - \phi)$$

Accounting for the Fluctuations

- For any realistic system the order parameters will exhibit fluctuations. We can build these in the framework with a probabilistic version of the Gibbs dividing surface construction
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Assuming no “probabilistic surface excess”,

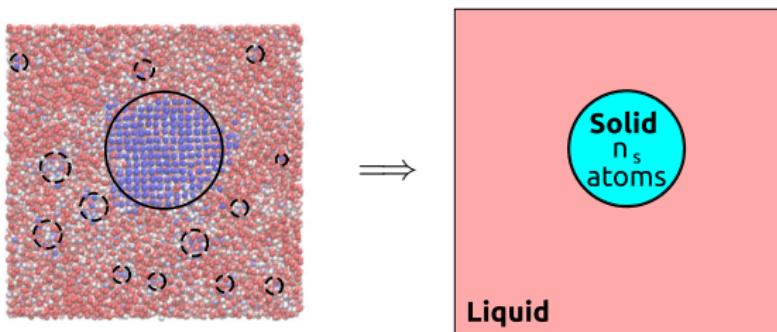
$$\rho(\Phi|n_s, n_l) = \int d\varphi \rho_s(\varphi|n_s) \rho_l(\Phi - \varphi|n_l)$$

A Link Between Atomistic and Mesoscale Models

- Much like for the multiple-cluster model, we can make a link between $G(n_s)$ and a "thermodynamic" $\tilde{G}(\Phi)$

$$e^{-\beta \tilde{G}(\Phi)} = \int_{n_{cut}}^{n^*} dn_s \rho(\Phi | n_s, n_l = N - n_s) N_s e^{-\beta G(n_s)}$$

- The expression can be inverted with a fixed-point iteration - so $G(n_s)$ can be obtained from $\tilde{G}(\Phi)$

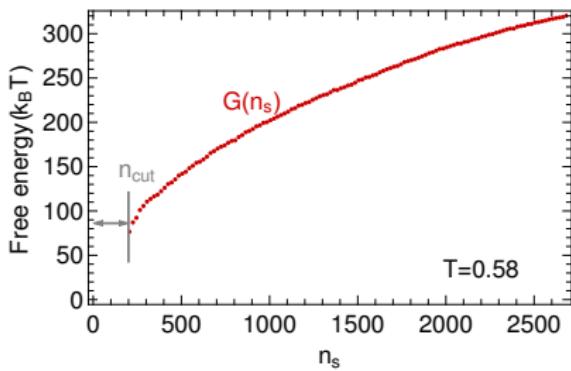
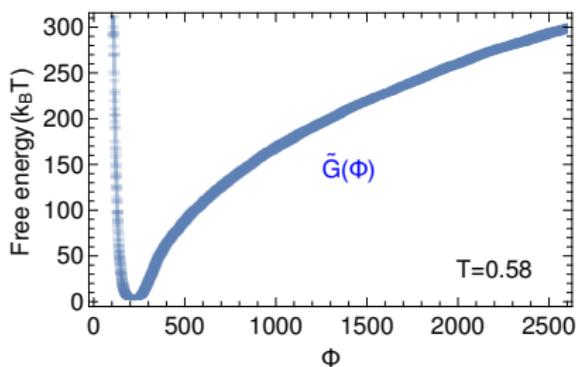


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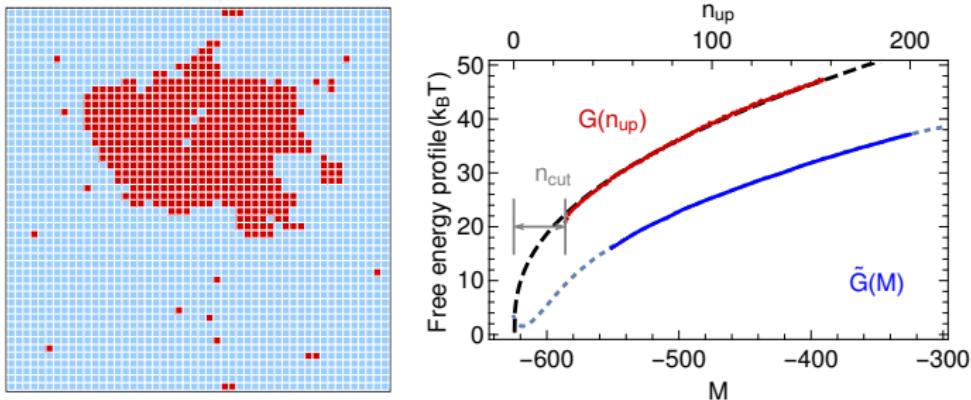
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Simulations for a Lennard-Jones potential at $T = 0.58$ ($T_m = 0.6185$)

A General & Predictive Framework

- This approach is generally applicable to different phase transitions.
An example with the 2D Ising model ($L = 25$, $T = 1.5$, $H = 0$)



Comparison with analytical results for $G(n)$

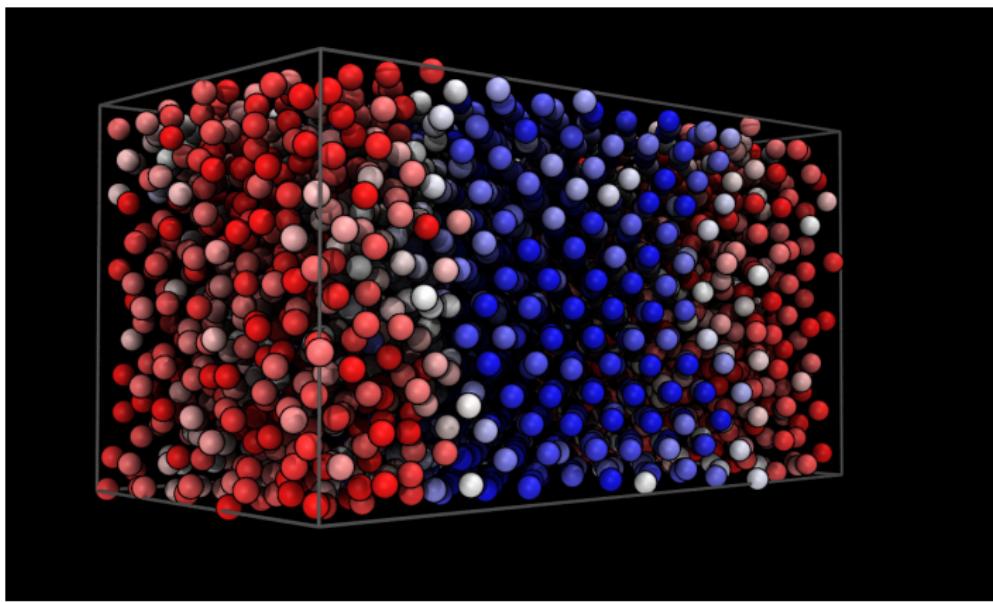
$$G(n) = 2\sigma\sqrt{n\pi} + \tau k_B T \ln n + d$$

[S. Ryu and W. Cai, Phys. Rev. E 81, 030601 (2010)]

Solid-liquid interface free energies, out of equilibrium

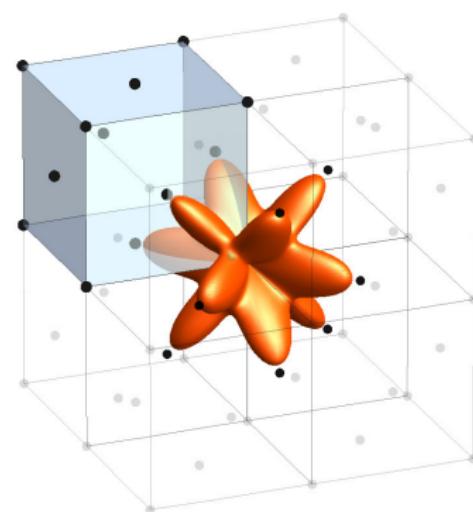
Using metadynamics to compute γ_{SL}

- Can we use bias to remove the energy barrier to the formation of a solid-liquid interface in a periodic simulation box?
- Must simulate with fluctuating z dimension to accommodate change in volume upon freezing



The basic ingredients

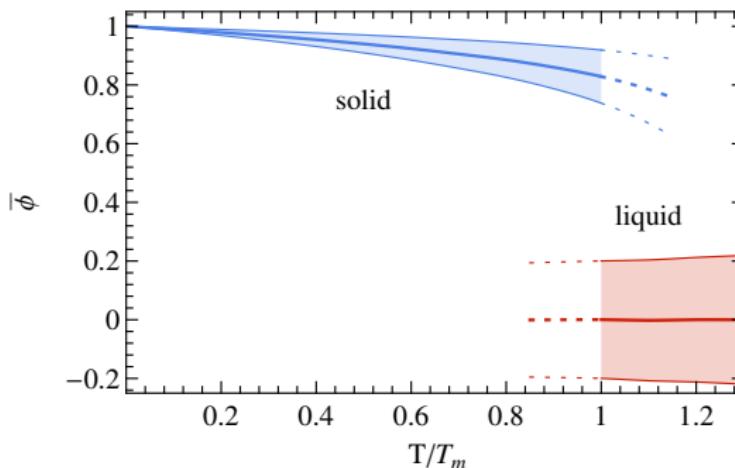
- Must be able to tell the solid and the liquid apart
 - Use an order parameter ϕ that forces nucleation in an orientation consistent with the cell periodicity
 - Verify that the typical values for solid and liquid do not overlap
- Distinguish LL, SS and LS configurations by averaging ϕ over two halves of the box



Simulations powered by PLUMED2 <http://plumed.org>

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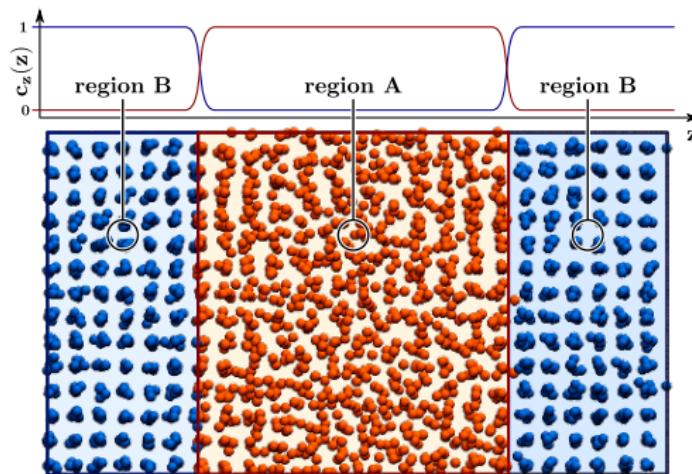
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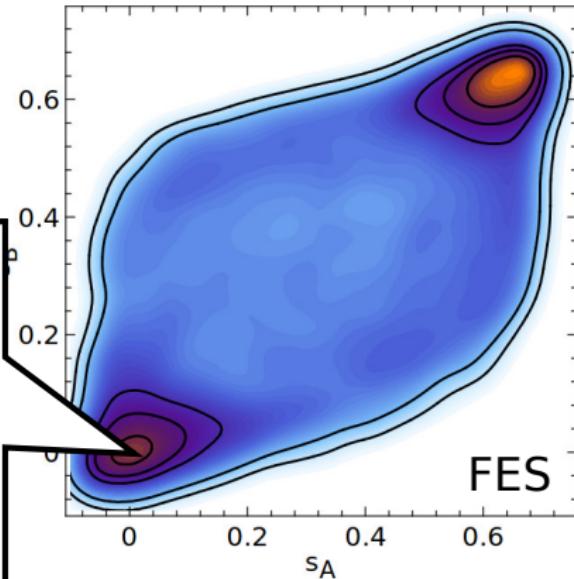
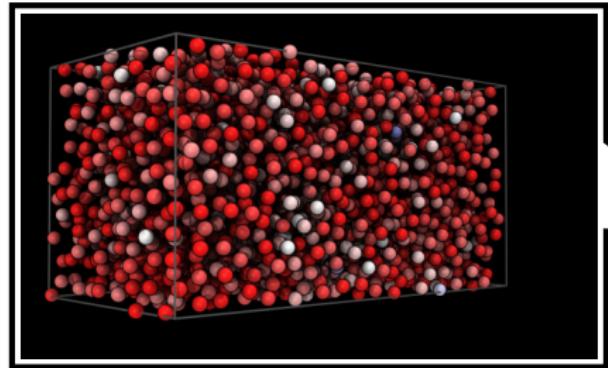
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An example simulation

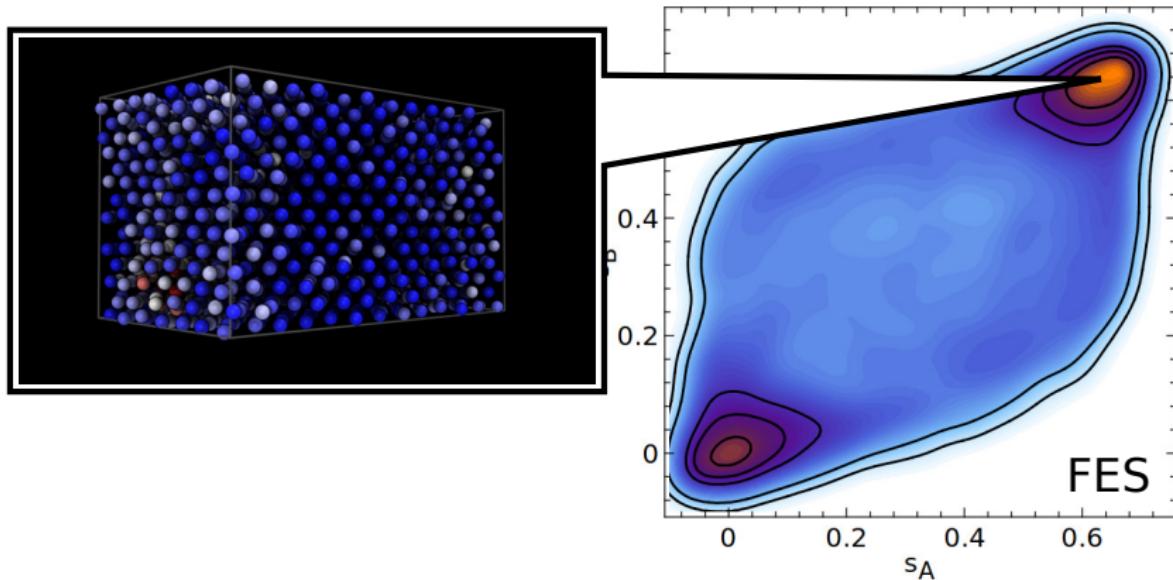
- Minima in the FES (computed by metadynamics) correspond to LL and SS configurations
- There is a large free energy barrier, that can be removed by biasing the simulation in a controlled way



Angioletti-Uberti, Ceriotti, Lee, Finnis, PRB (2010)

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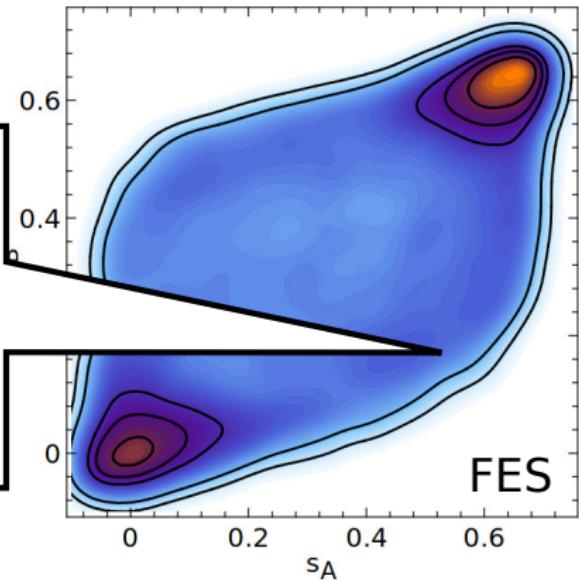
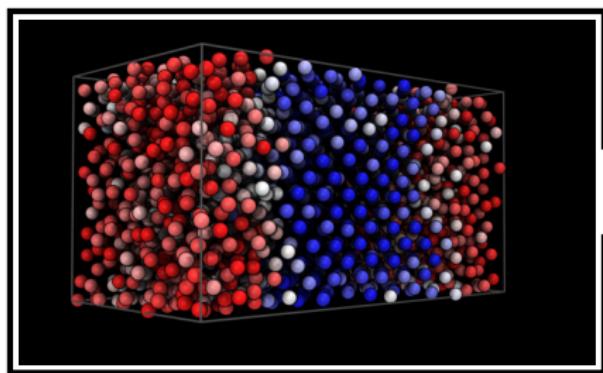
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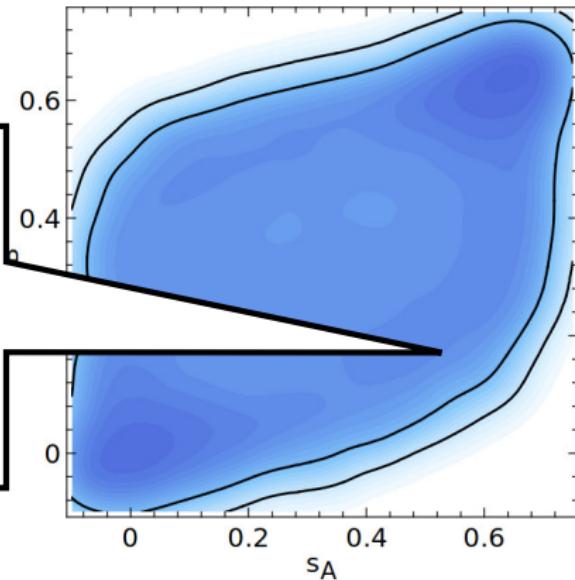
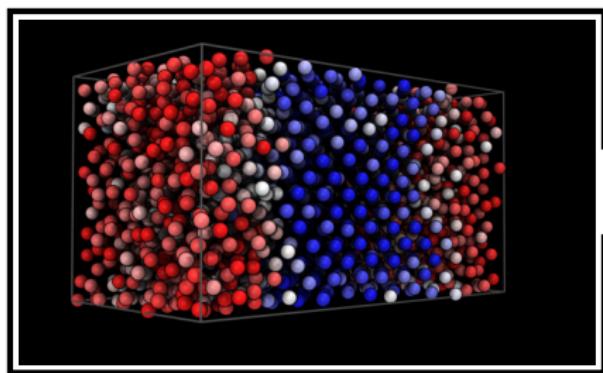
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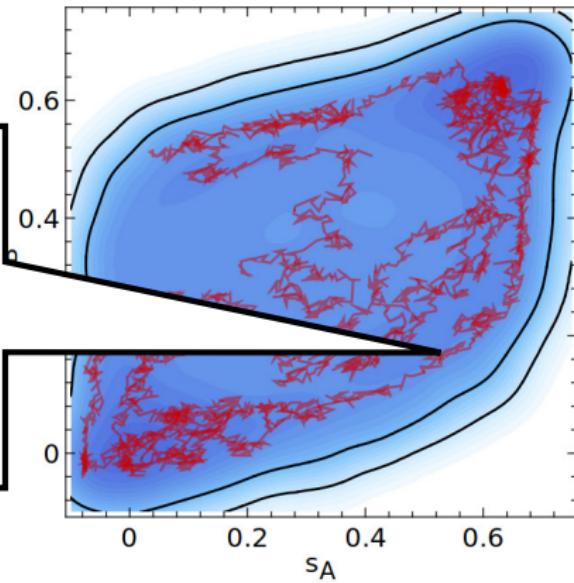
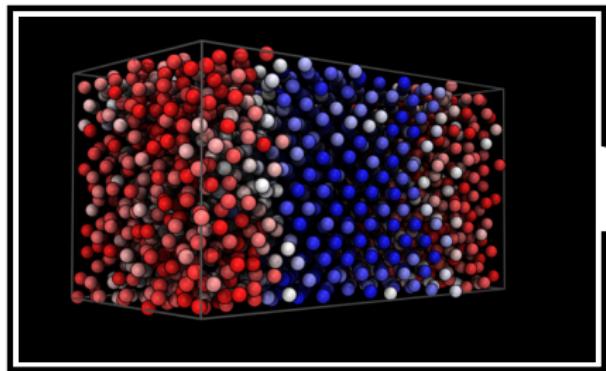
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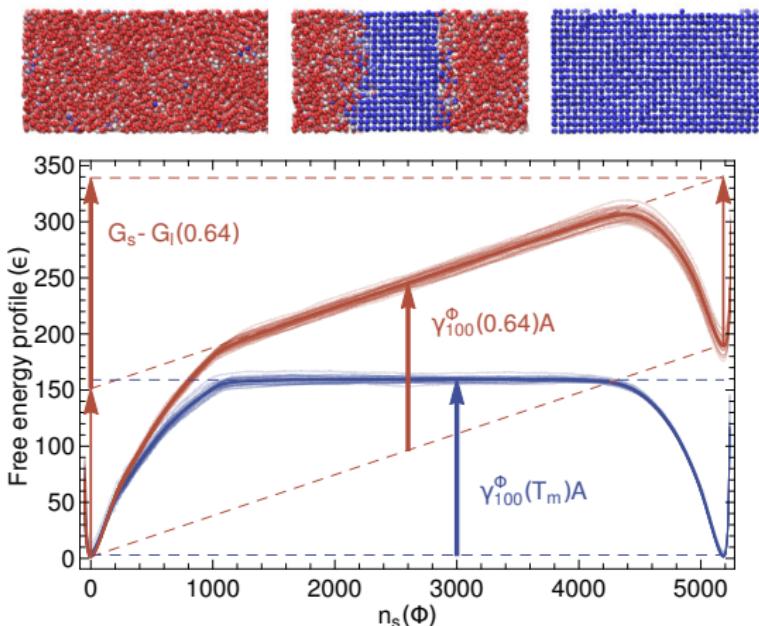
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Evaluating γ_{sl} at $T \neq T_m$

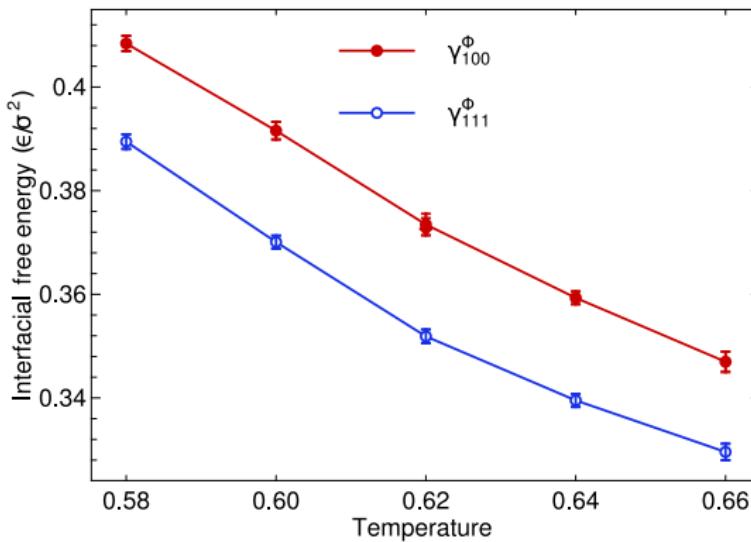
- Planar-interface simulations of freezing can also be performed at $T \neq T_m$
- The slope of the plateau corresponds to μ_{sl} , the vertical shift to γ_{sl}
- We can use planar-interface geometry to compute the temperature dependence of γ_{sl}



B.Cheng, G.A.Tribello, & MC, PRB (2015) DOI: 10.1103/PhysRevB.92.180102

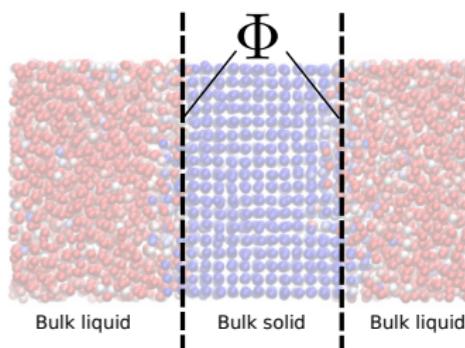
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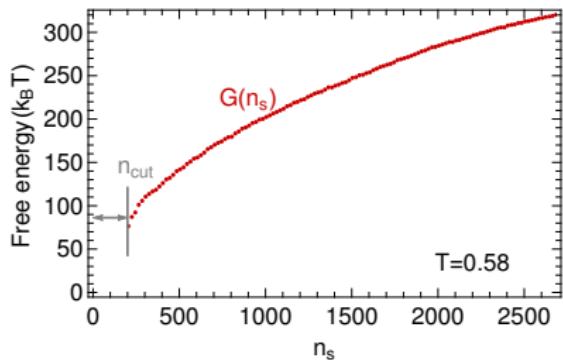
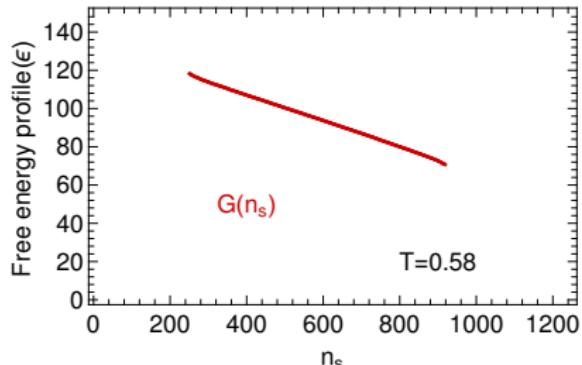
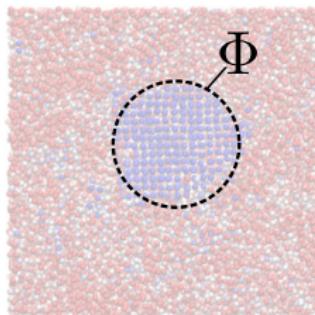


Comparing the Planar Limit and 3D Nuclei

$$G(n_s) = \mu_{sl} n_s + \gamma_\infty^\Phi A$$



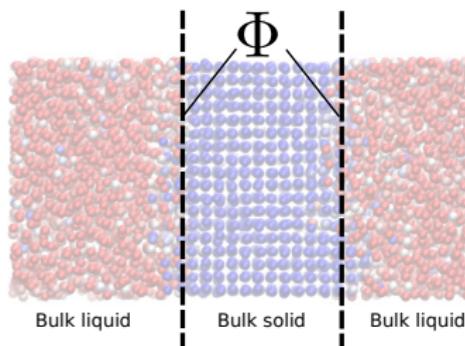
$$G(n_s) = \mu_{sl} n_s + \gamma_\infty^\Phi \Omega n_s^{2/3} \left(1 + \zeta n_s^{-1/3}\right)$$



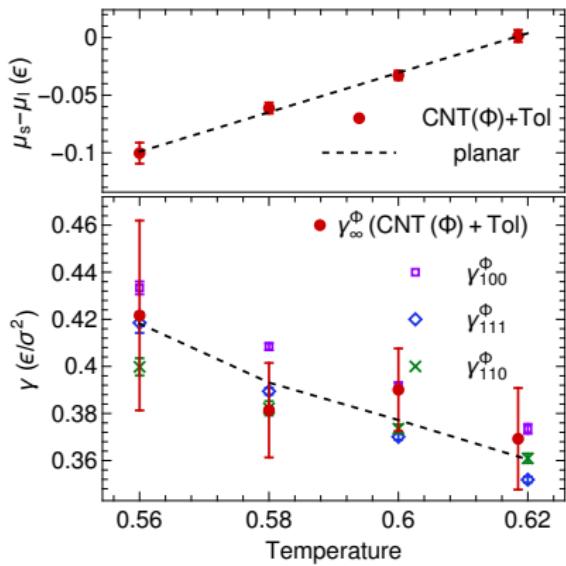
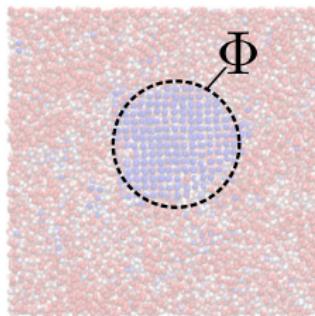
Prestipino et al. PRL (2012) DOI: 10.1103/PhysRevLett.108.225701
Cheng, Tribello, MC, arxiv.org/abs/1703.06062

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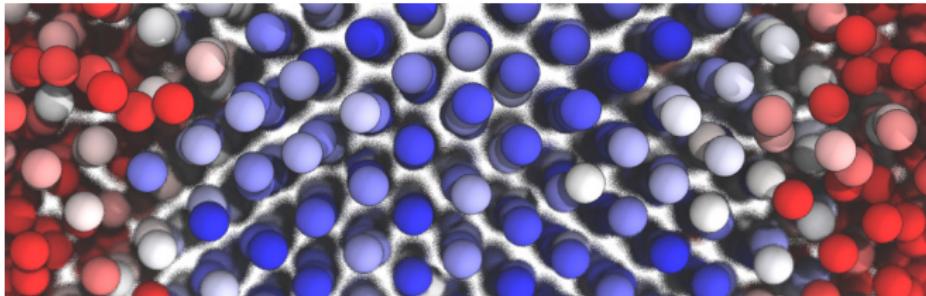


Simulations performed in the planar limit are fully consistent with the 3D nucleation model

Prestipino et al. PRL (2012) DOI: 10.1103/PhysRevLett.108.225701
Cheng, Tribello, MC, arxiv.org/abs/1703.06062

Outlook

- A general framework to map atomic-scale modelling of phase transitions onto a thermodynamic model
- Accelerated sampling makes it possible to study nucleation by molecular dynamics, at realistic levels of undercooling (thanks PLUMED and Multicovar for seamless setup of horribly complex biasing scheme)
- Planar-interface setup reduces the unknowns (and statistical errors) in determining γ_{sl}
- Importance of the choice of dividing surface to link atomistic simulations and classical nucleation theory

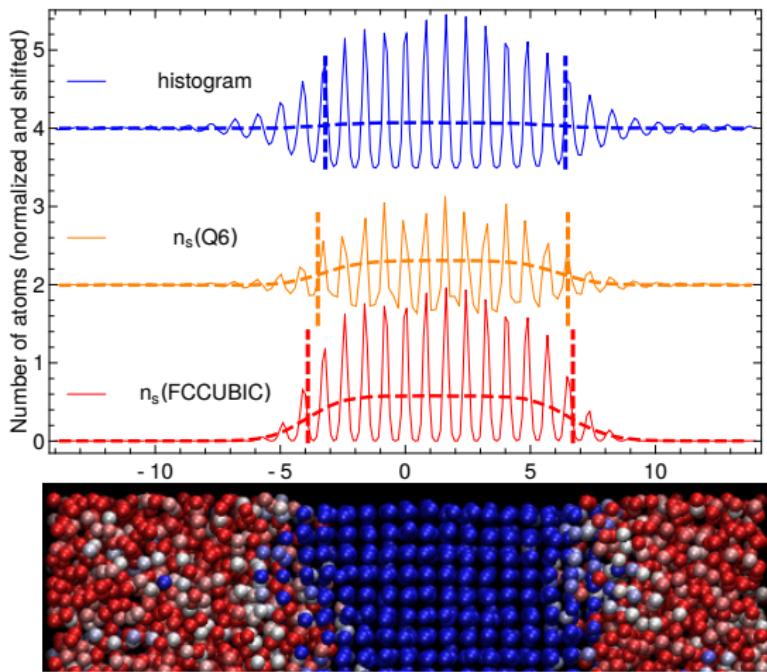


<http://cosmo.epfl.ch/>

A few subtleties...

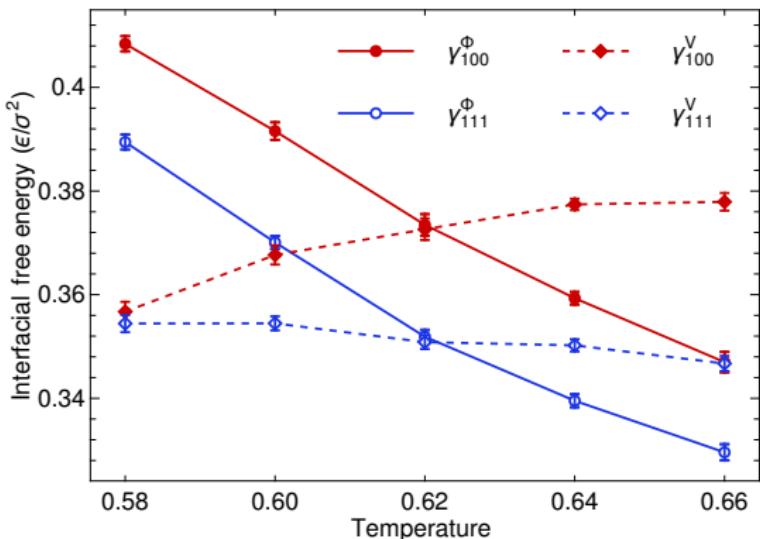
The GDS Depends on the Reference Φ

- Different order parameters may shift the position of the dividing surface
- This is reflected on a dependence of n_s on the choice of Φ



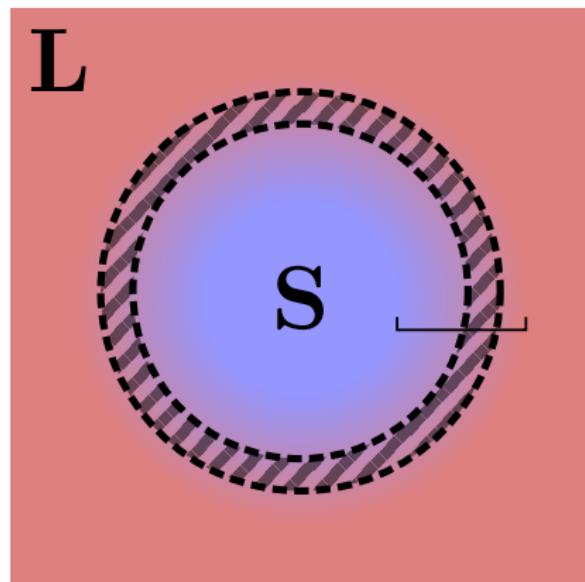
Dependence of γ_{SL} on the GDS

- Shifting the dividing surface change the partitioning of the free energy between chemical potential and surface energy.
- For $T \neq T_m$, the interface energy γ_{SL} depends on the choice of Φ



Dependence of γ_{SL} on the GDS

- This change does not affect the nucleation barrier, if one considers how the shift in dividing surface modifies the density of the solid cluster.
- Using the molar volume to define n_s is the choice that is most consistent with classical nucleation theory
- Other choices result in an additional term in the CNT expression for $G(n_s)$, that has the same form as a Tolman correction



A Fixed-Point Iteration for Deconvoluting $\tilde{G}(\Phi)$

- One can obtain a monotonic relation between the average $\bar{\Phi}$ and n_s

$$\bar{\Phi}(n_s) = \int d\Phi \rho(\Phi | n_s, N - n_s) \Phi$$

- This can be used to cast the relation between $G(n_s)$ and $\tilde{G}(\Phi)$ into a fixed-point iteration

$$G(n_s) = \tilde{G}(\bar{\Phi}(n_s)) + k_B T \ln N_s + k_B T \ln \int_{n_{cut}}^{n^*} dn \rho(\bar{\Phi}(n_s) | n_s, N - n_s) e^{-\beta(G(n) - G(n_s))}$$