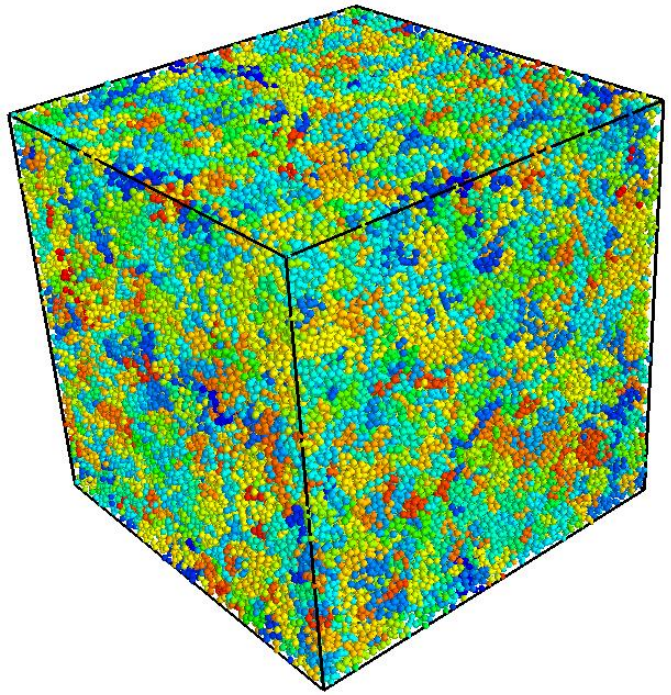
GPU-accelerated Wang-Landau Simulation of Polymer Crystallization

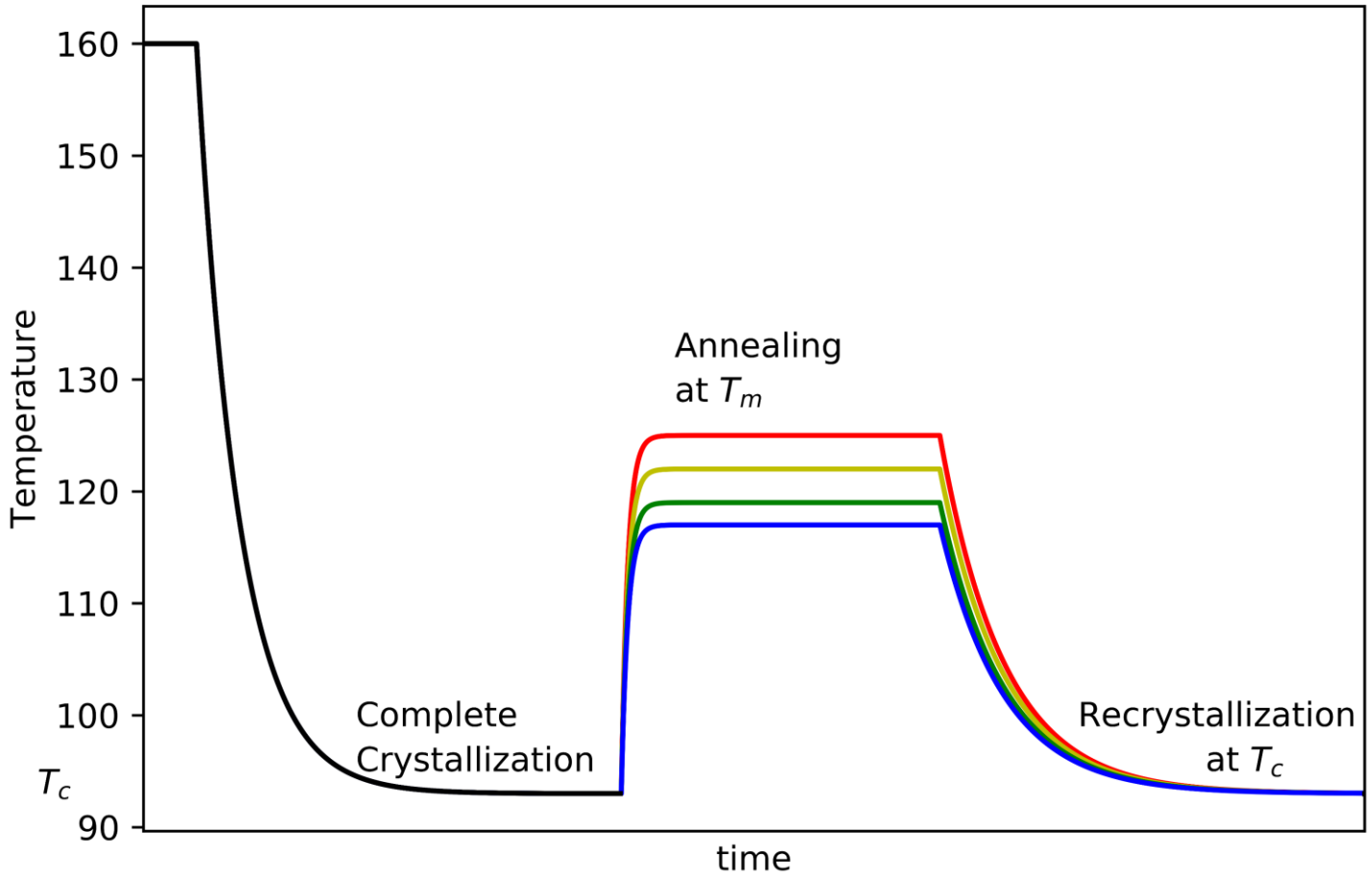
Pierre Kawak, Andrew S. Gibson, Logan S. Brown,
Beverly Delgado, Dakota S. Banks, Douglas R. Tree



19th March 2021

APS March Meeting

Melt memory is indicative of unusual crystallization behavior



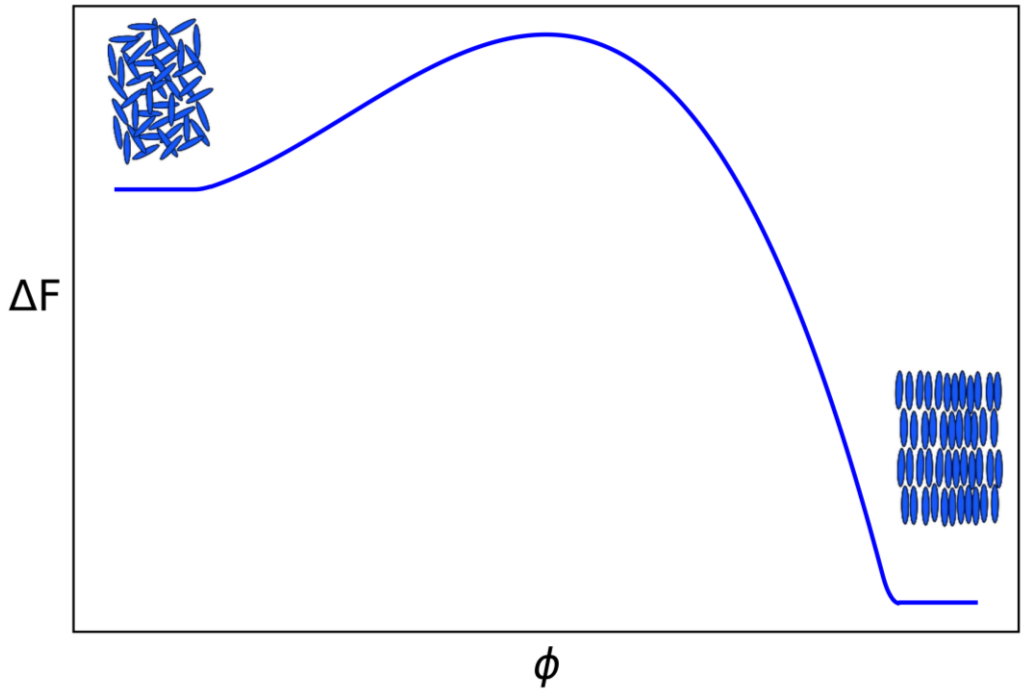
Other Observations:

- Initial larger scale ordering in SAXS/WAXS measurements
- Deviant Crystallization and Recrystallization line
- Intermediate Phase Observations
- No Copolymer Effect on Crystallization

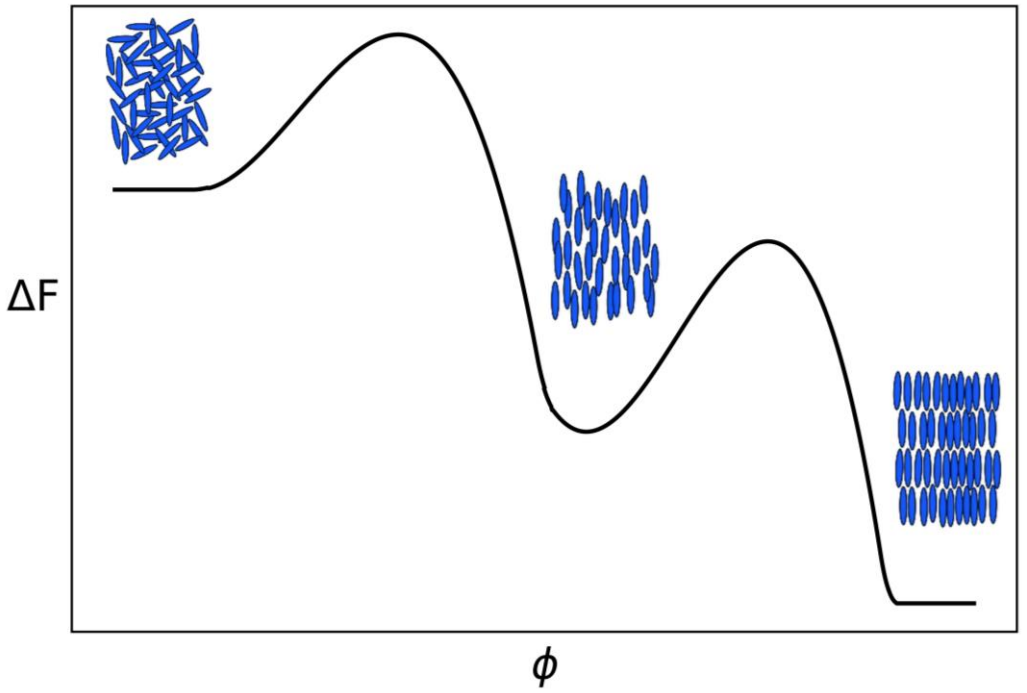
Häfele et al. Eur Phys J E (2005)

Are the previous observations caused by slow kinetics or thermodynamics in the nucleation process?

Scenario 1



Scenario 2



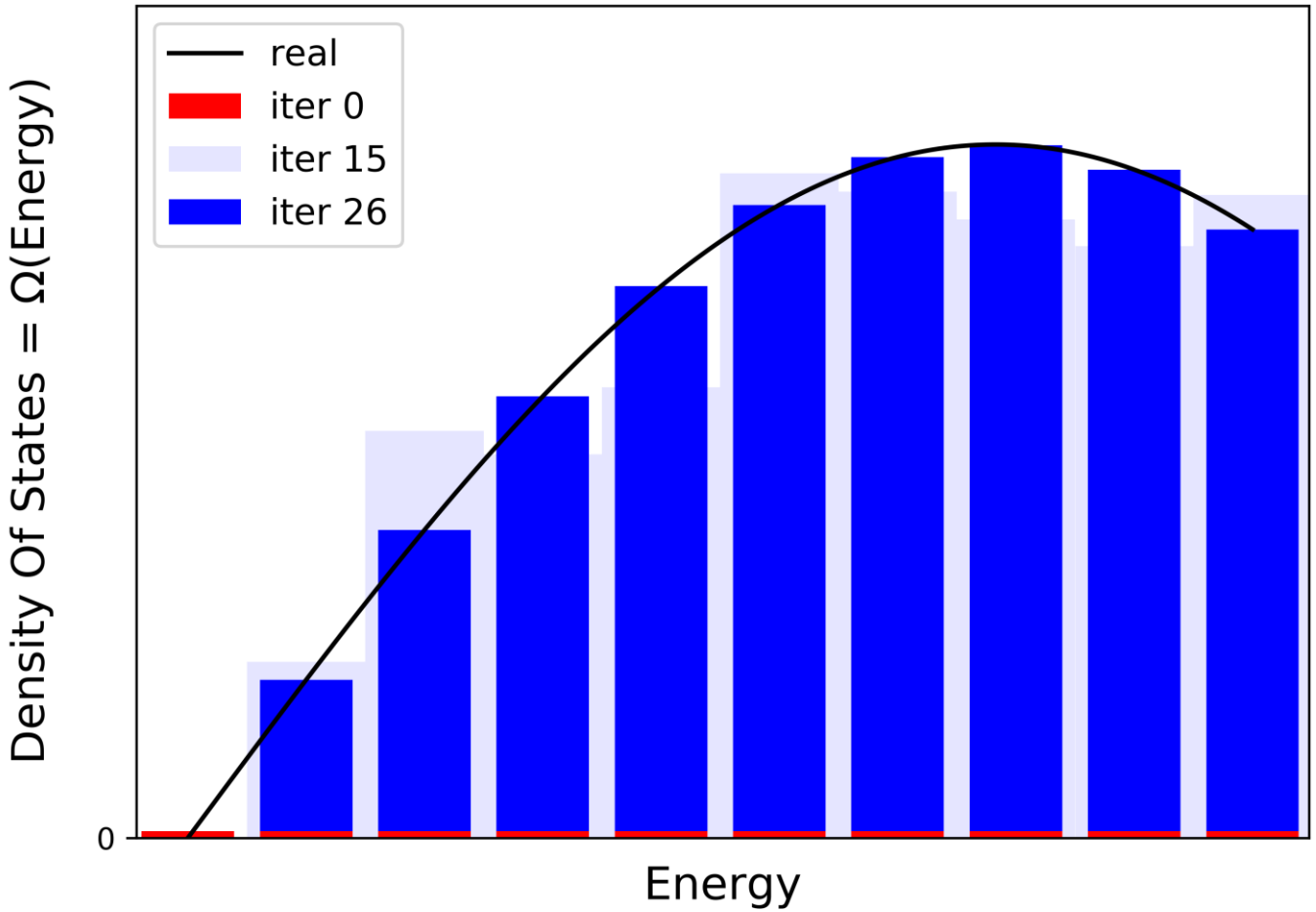
Other scenarios?

Mission: Characterize transitions using free energy methods in simulation

Monte Carlo methods can build a free energy profile!

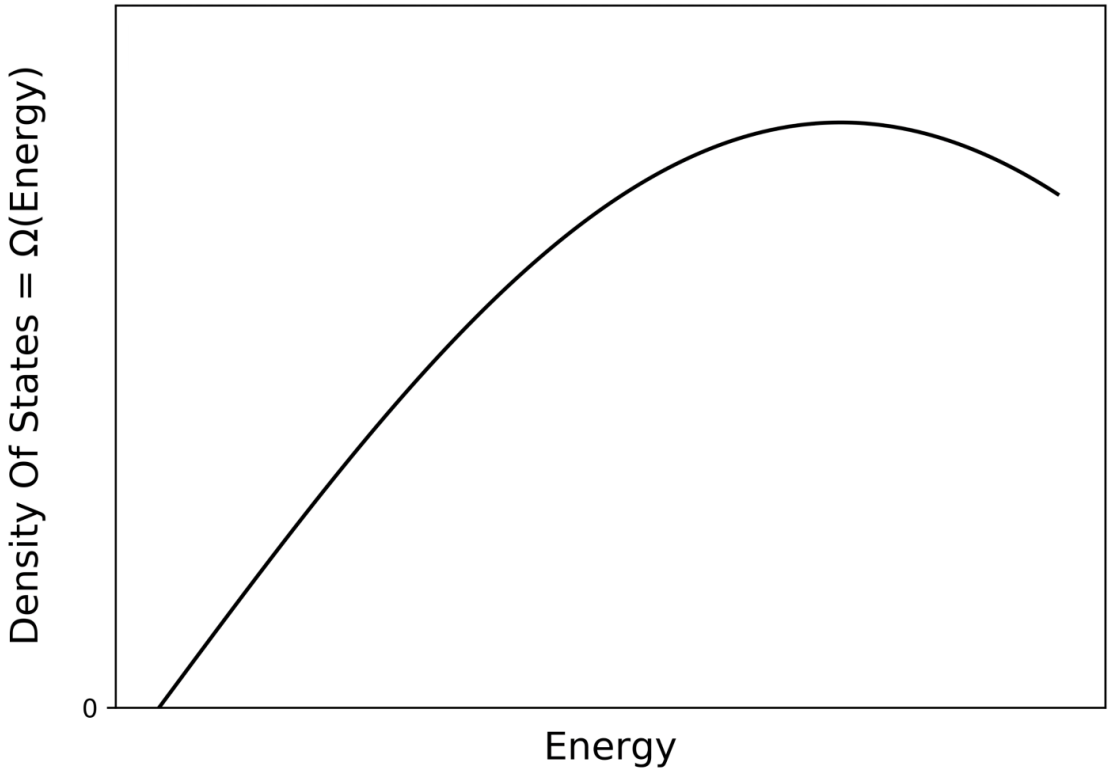
Wang Landau Monte Carlo (WLMC)

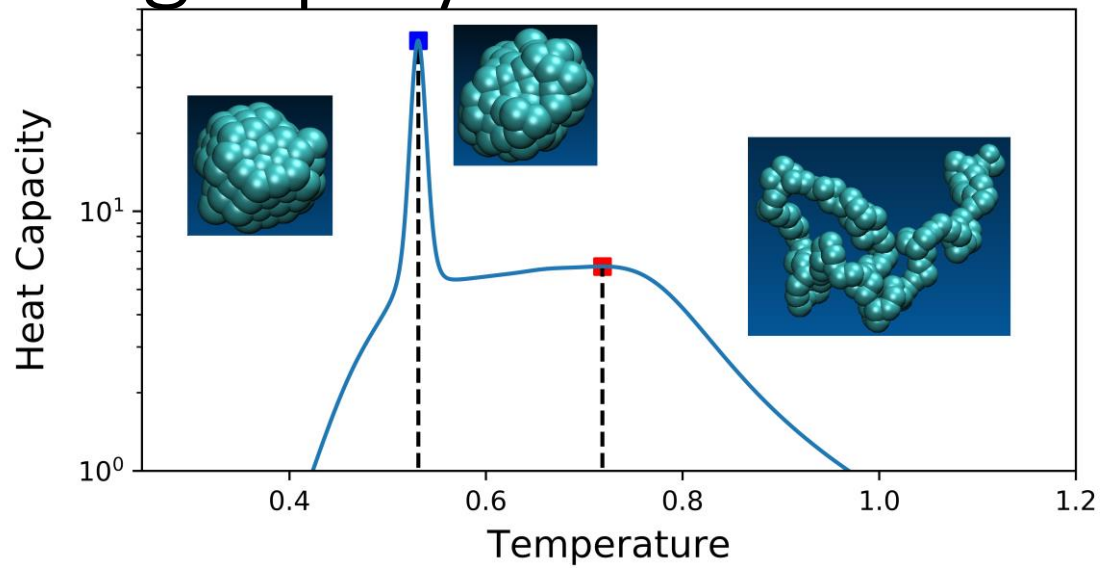
- **Bond-breaking moves**
- **No dynamic considerations**
- **Faster and simpler**
- **Can be massively parallel**
- **Direct access to free energy**

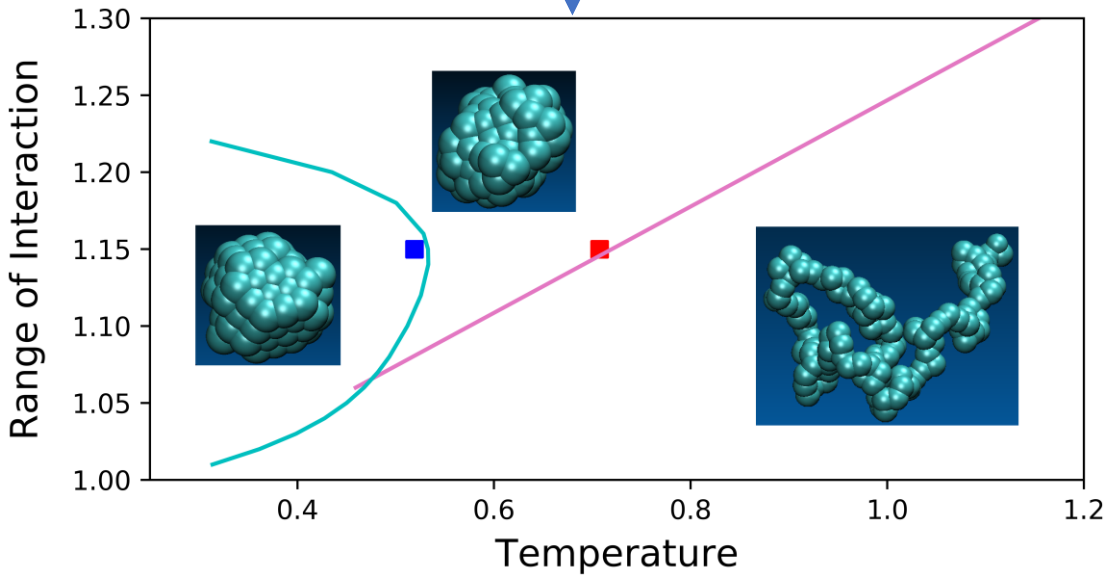


F vs T, Cp vs T, etc.

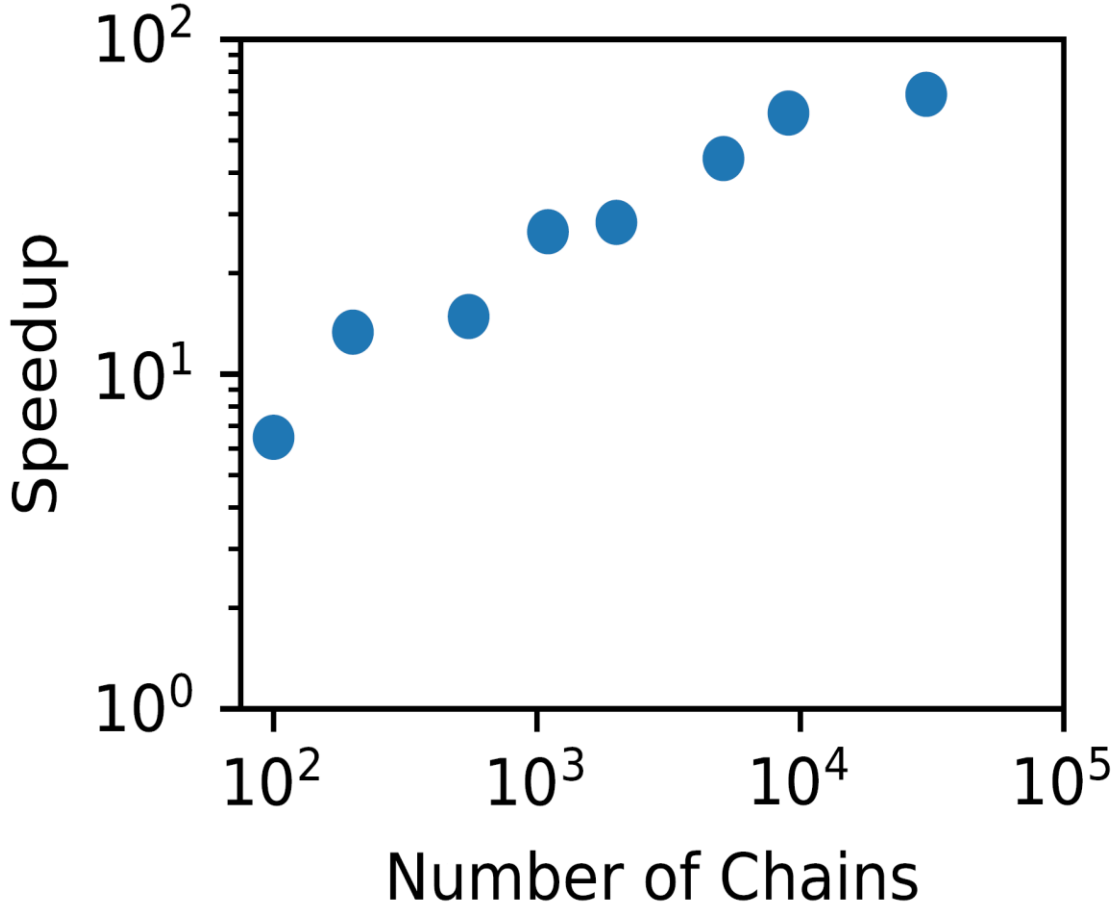
A Wang Landau generated Density of States can characterize crystallization for a single polymer chain



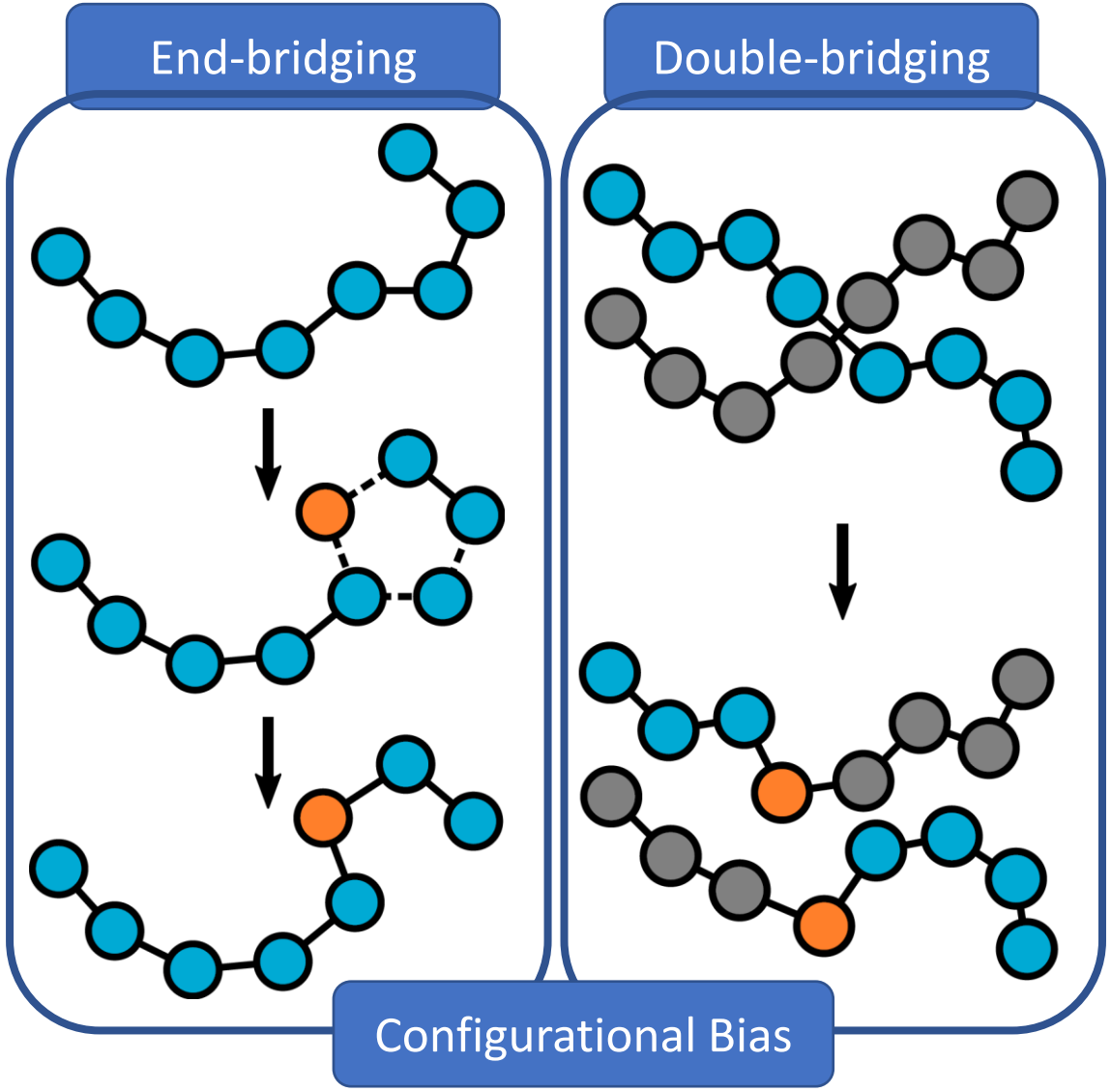




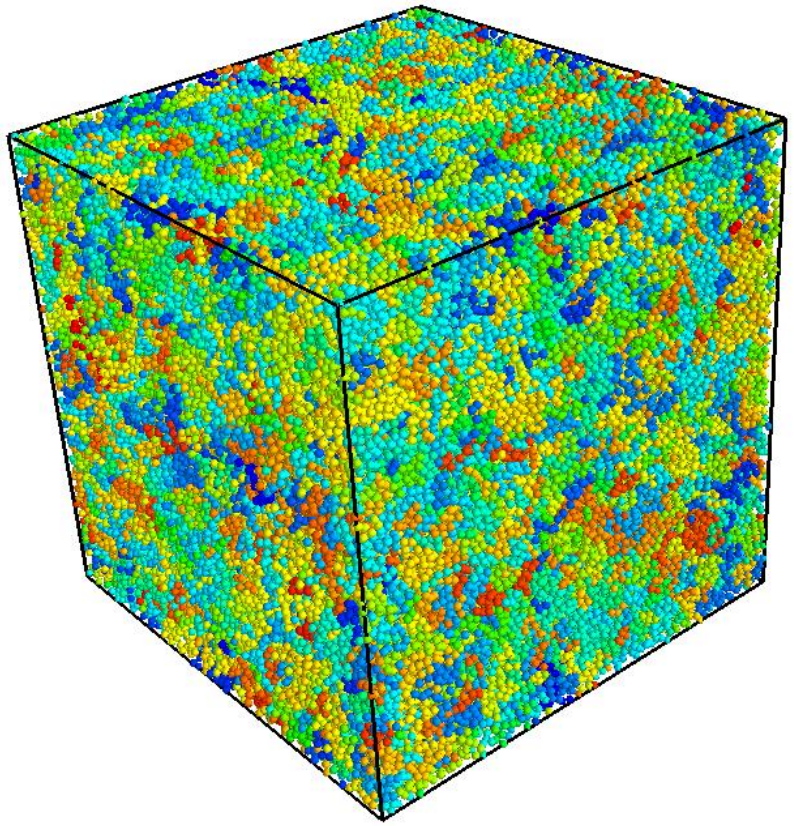
For a melt, we needed to have a faster, more efficient simulation to overcome slow equilibration



Anderson et al. J. Comp. Phys. (2013)

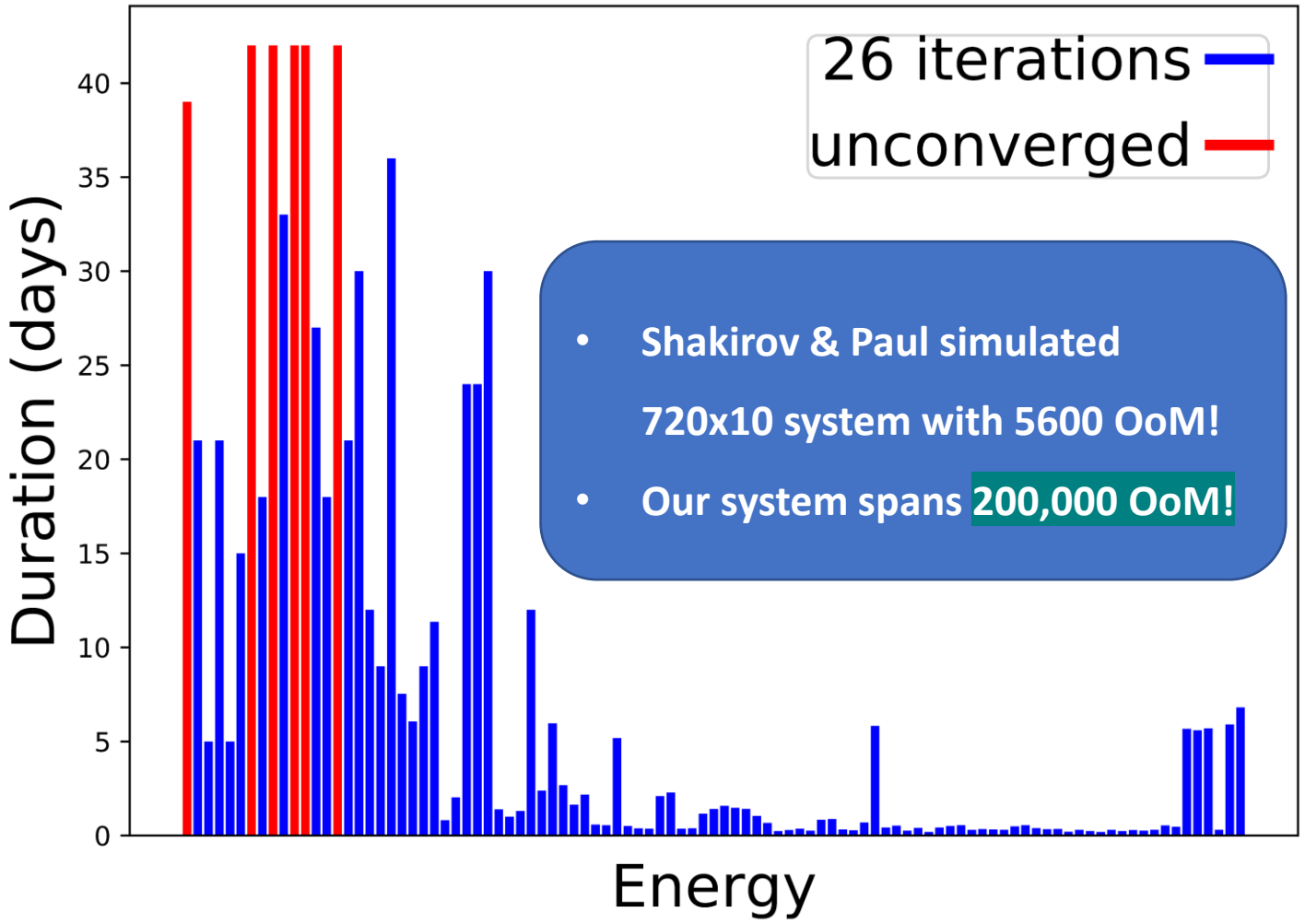


Although slow equilibration was overcome, the system spanned too many OoM to be solved in reasonable time



2000 Chain

100 Bead Melt



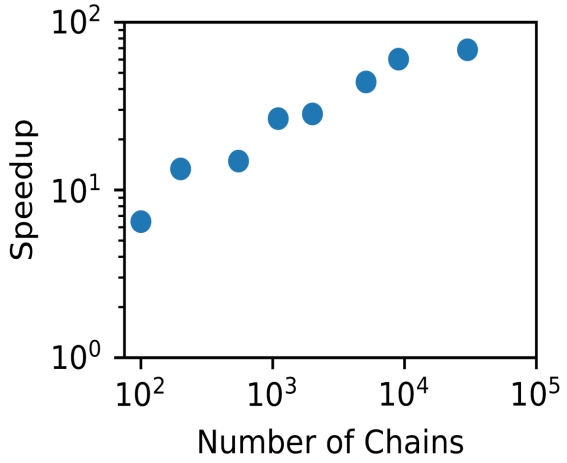
Conclusion and Future Work

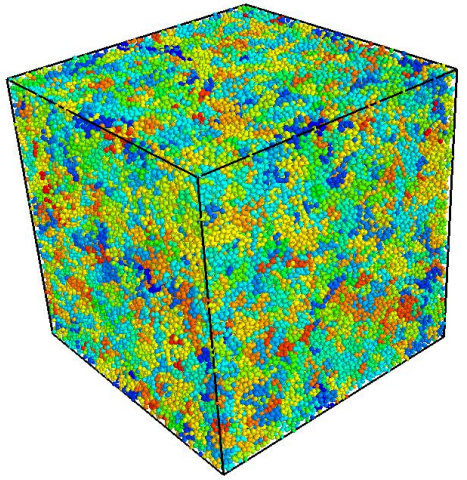
Current Work

- **Built GPU-accelerated WLMC**
- Domain decomposition
- Advanced polymer moveset

Lessons learnt

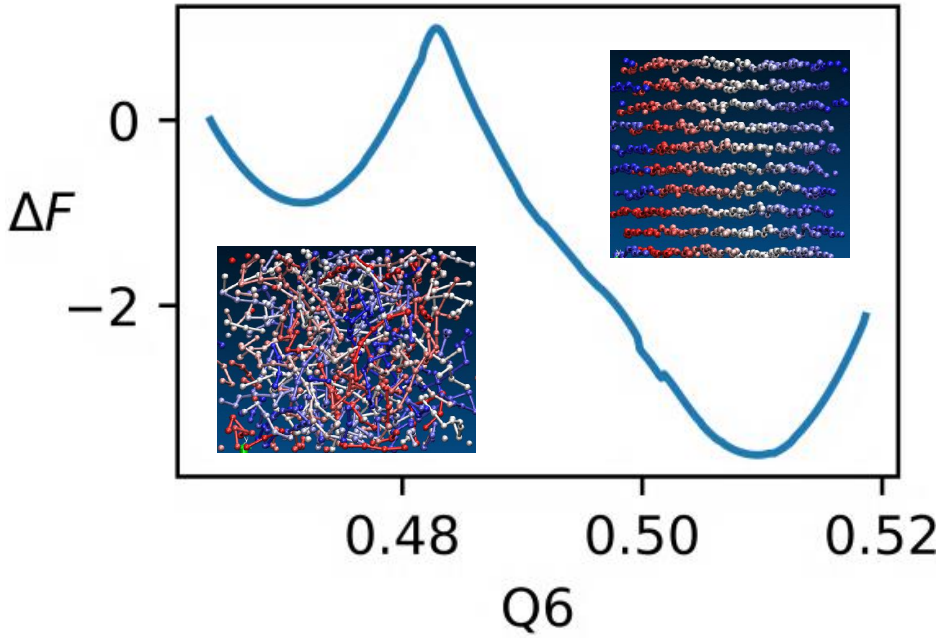
- **Problem**: Too many OoM
- Specific process versus entire DOS





Future Work

- Obtain free energy directly using **Order Parameter Wang Landau**
- Investigate Q6 and P2
- Investigate small nuclei



Acknowledgements

- ACS **Petroleum Research Fund**

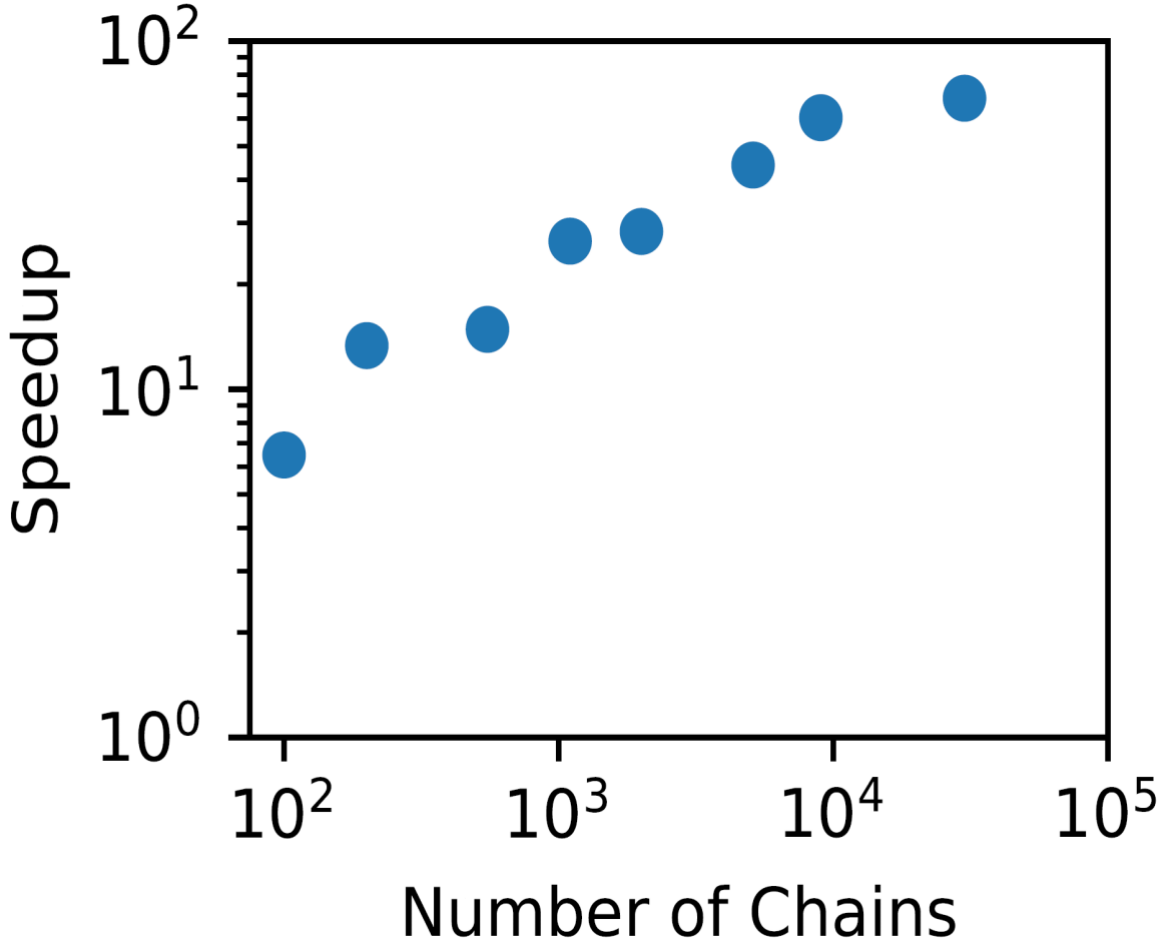
  (PRF# 59244-DN16**)**

- BYU **Board of Trustees**

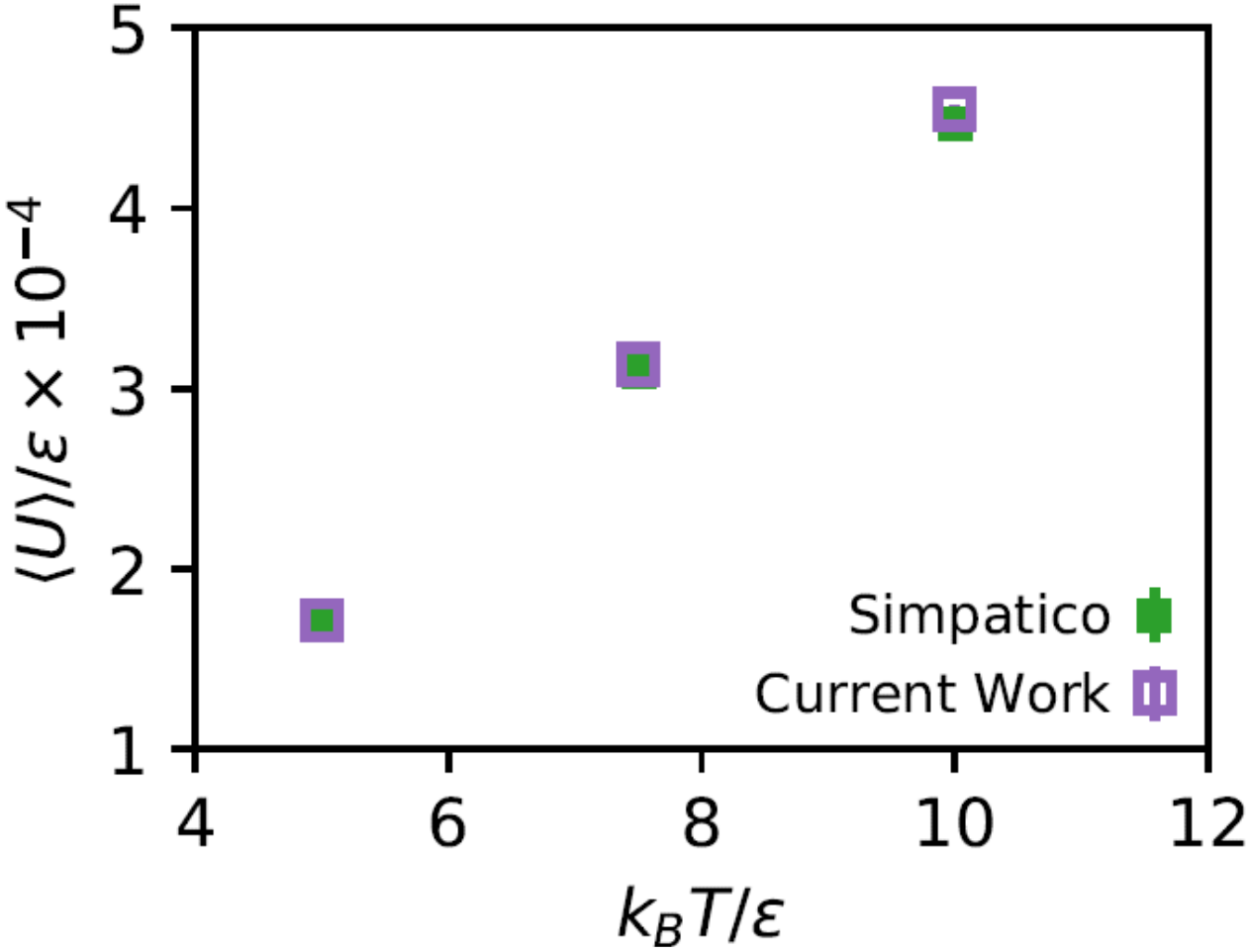
- BYU **Office of Research Computing**

BYU ORC

Parallel simulations are 2 orders of magnitude faster



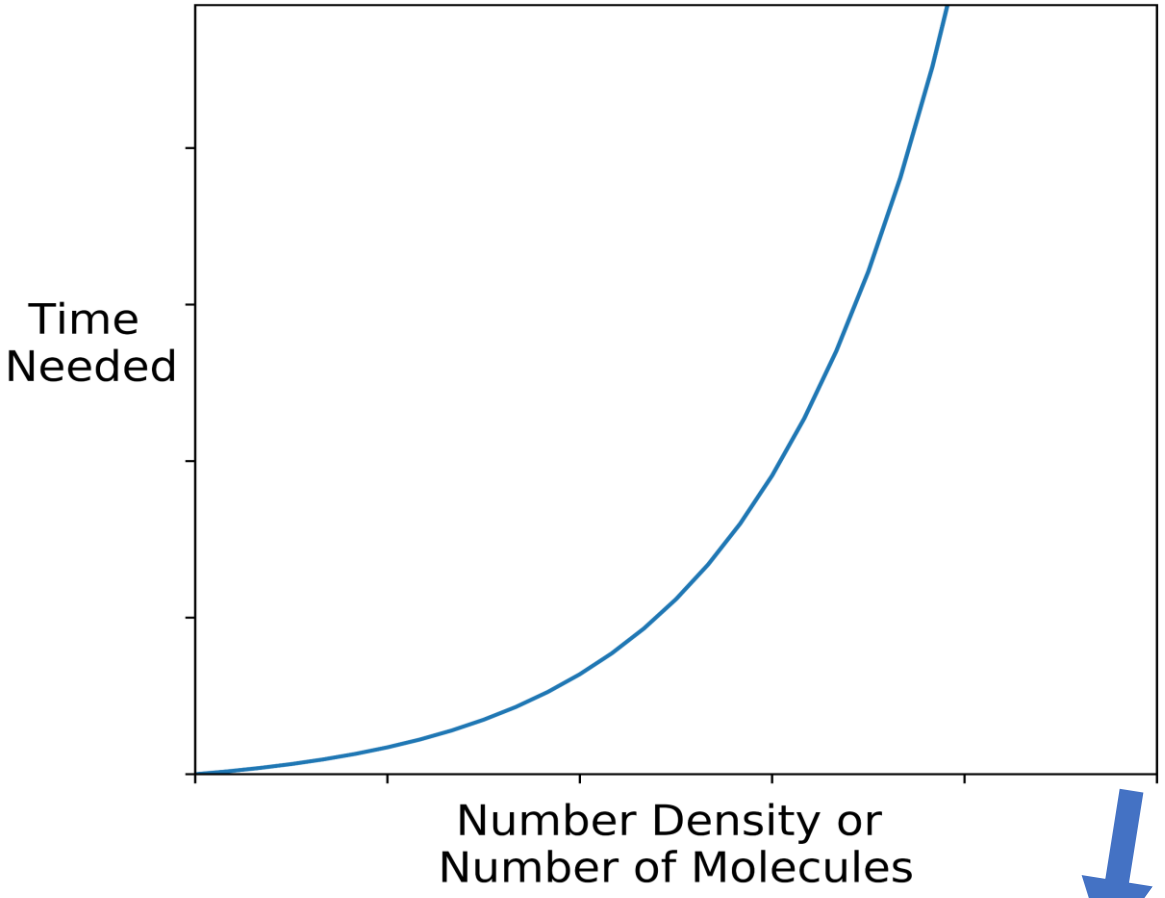
Simpatico [Computer software]. (2010).



$$Speedup = \frac{time\ per\ move_{serial}}{time\ per\ move_{parallel}}$$

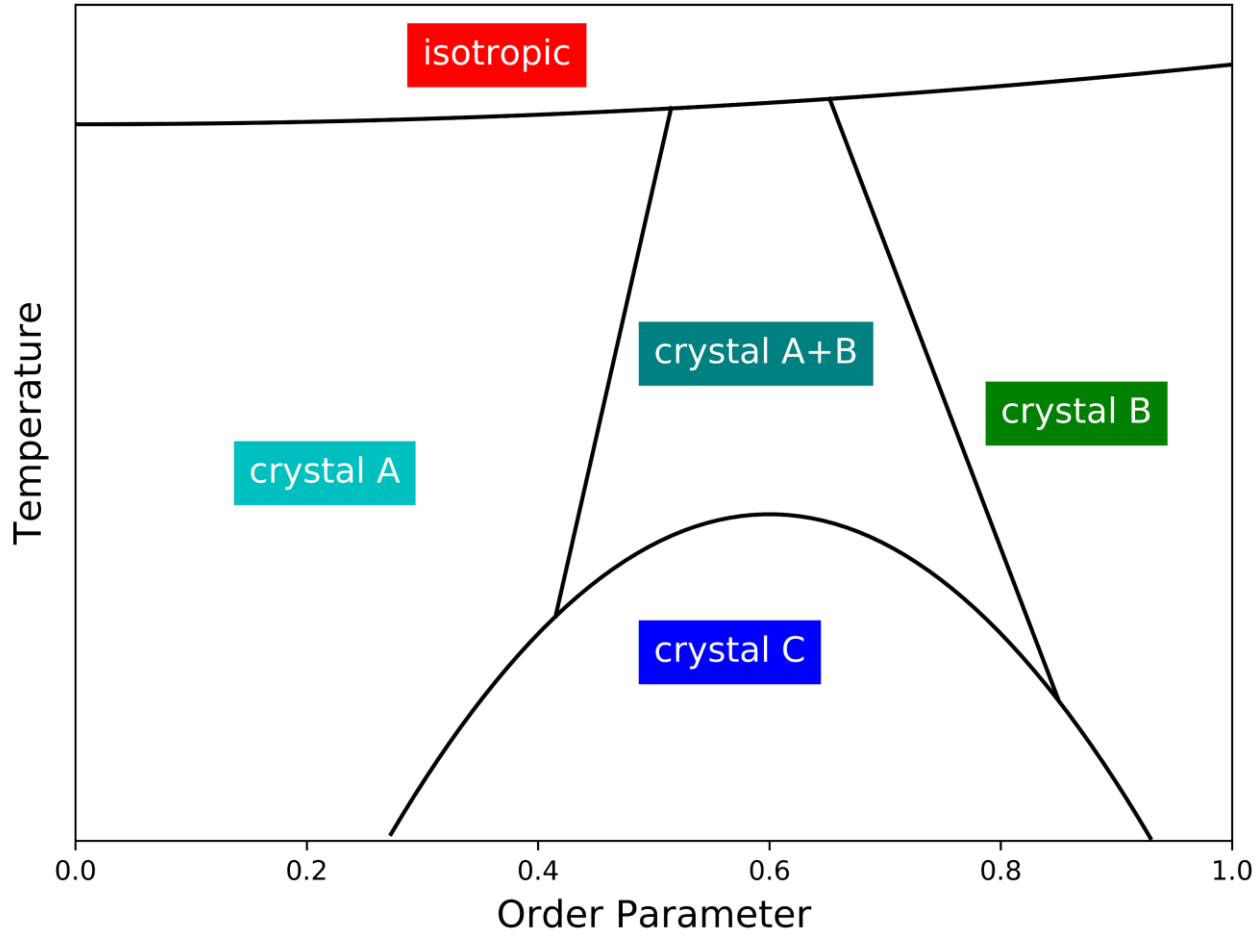
There are 2 major obstacles to overcome to better understand crystallization

Polymer simulations are expensive



Melt Densities

Relative stability of different phases

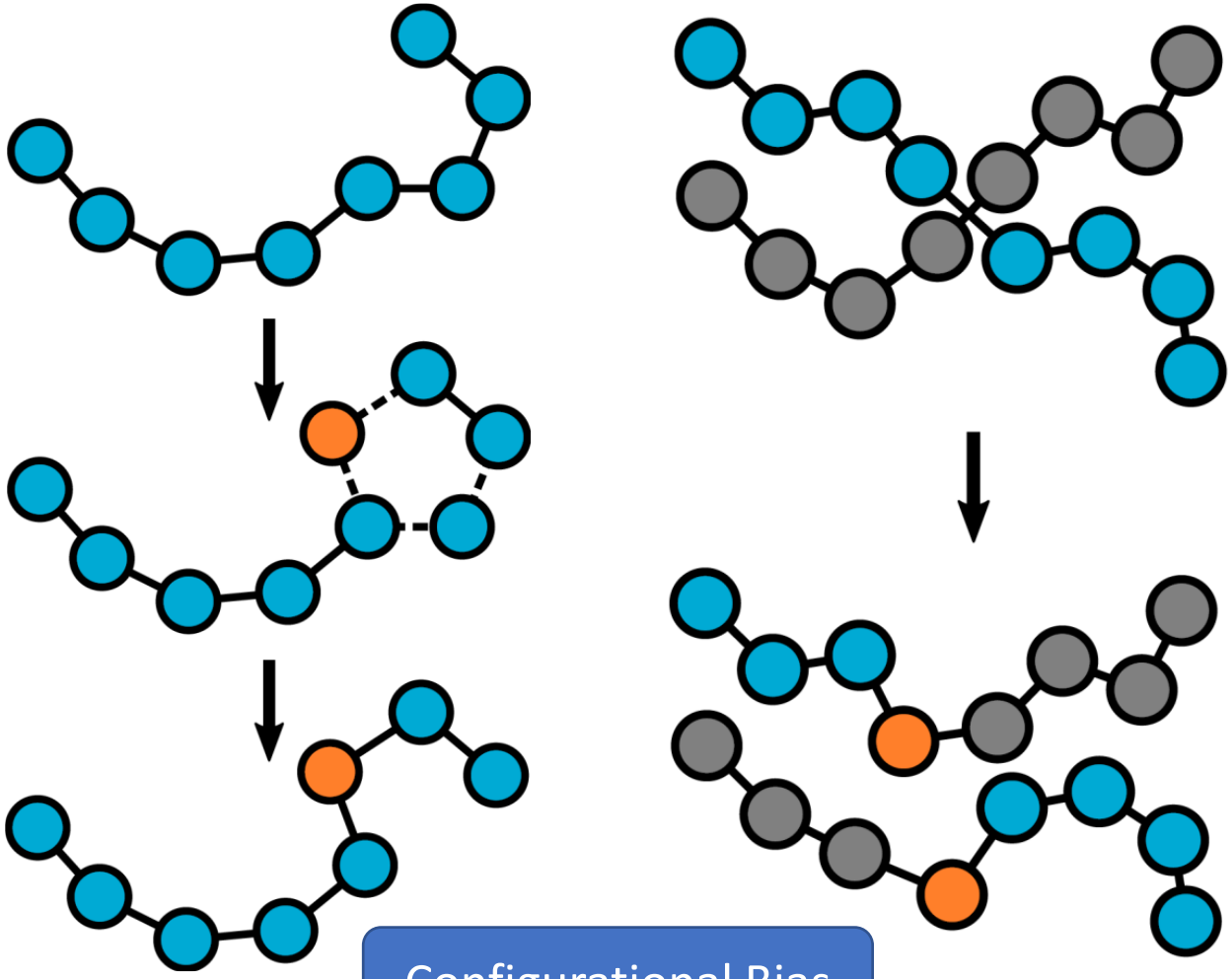


We can use advanced move set and domain decomposition to speed equilibration

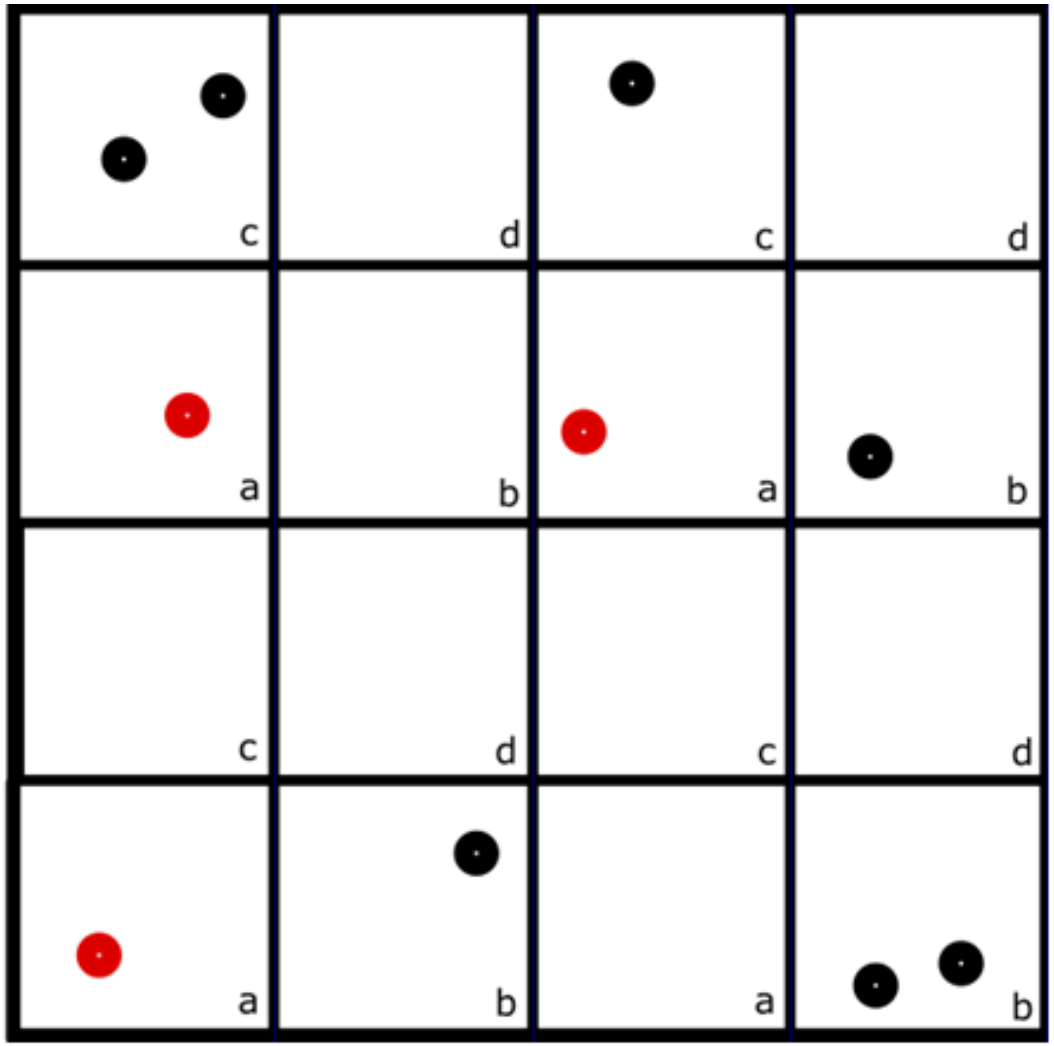
Anderson et al. J. Comp. Phys. (2013)

End-bridging

Double-bridging



Configurational Bias

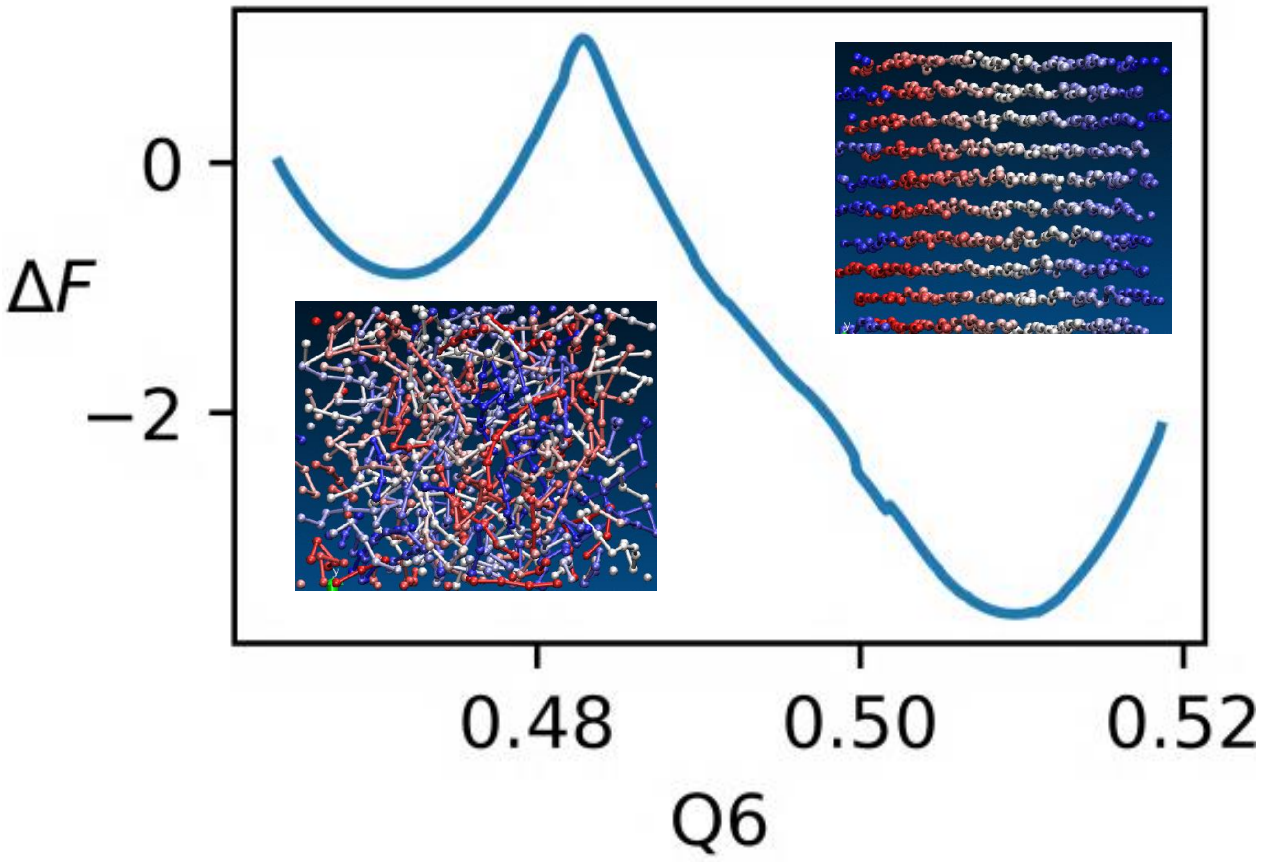


Checkerboard MC

Future work will involve Order Parameter Wang Landau

Future Work

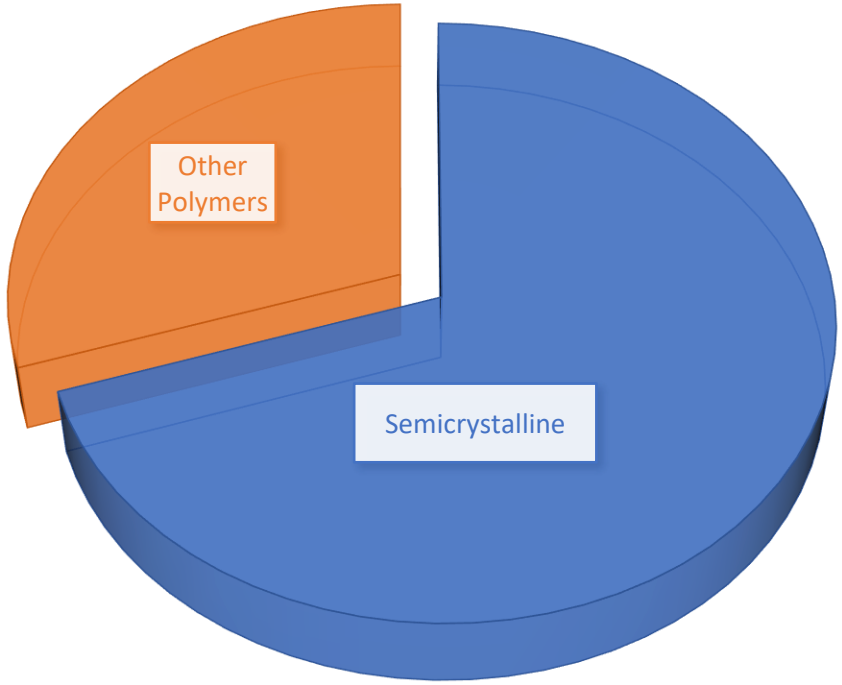
- Build FES directly using Order Parameter Wang Landau
- Specific molecular order parameters such as Q6 and P2
- Study relevant emergent small nuclei



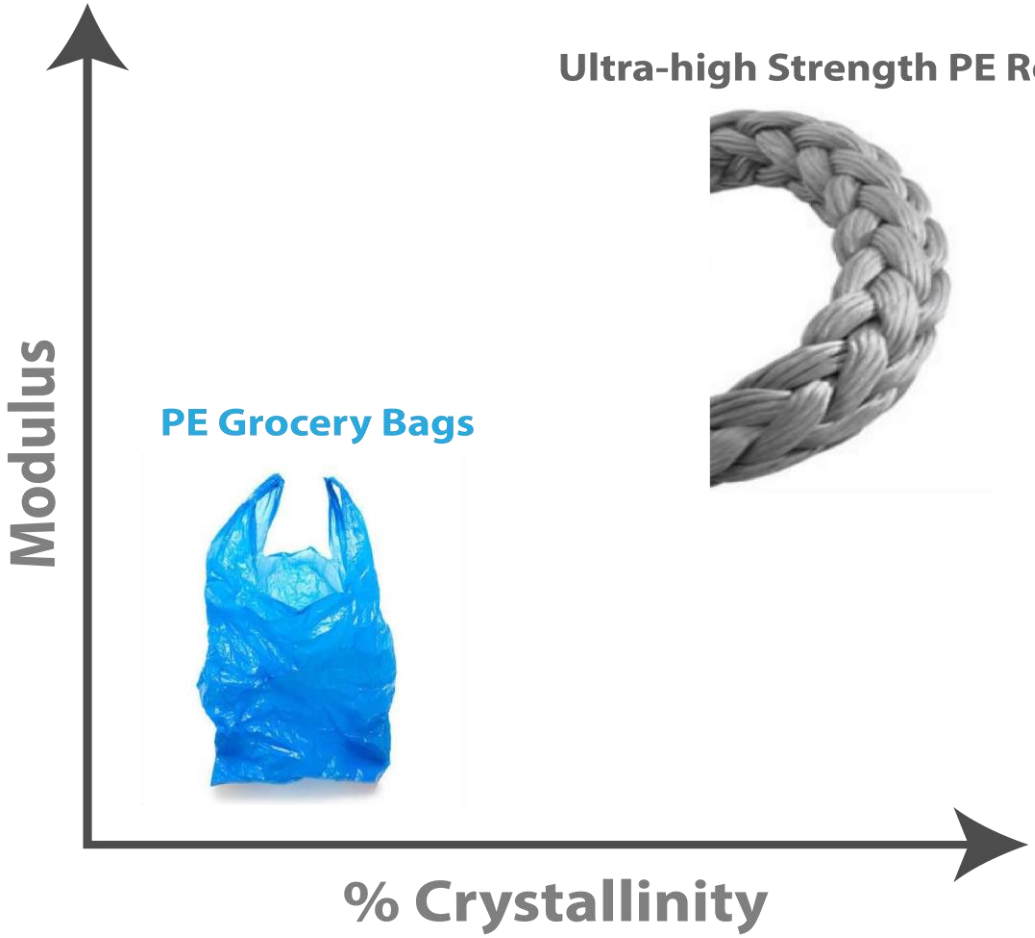
Kawak et al. Unpublished

Crystallinity is an important polymer property

% Industrial Production



Variation in Strength of PE Products



https://www.indiamart.com/proddetail/plastic-grocery-bag-13175987991.html
https://www.dsm.com/products/dyneema/en_GB/industries/maritime/whitepaper-safety-factors-innovation-in-ropes-and-cables.html

Crystallization is a multi-step process

Primary Nucleation

Secondary Nucleation

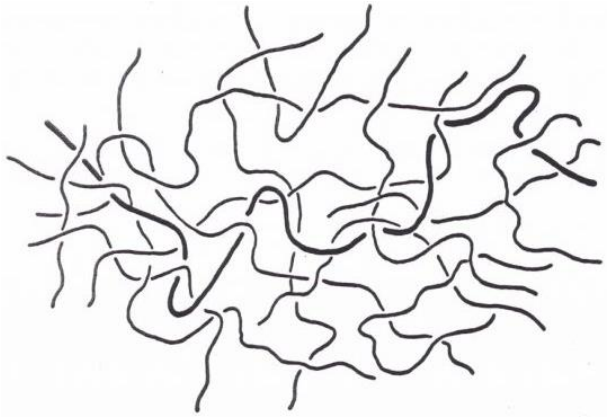
Coalsening

Amorphous Melt

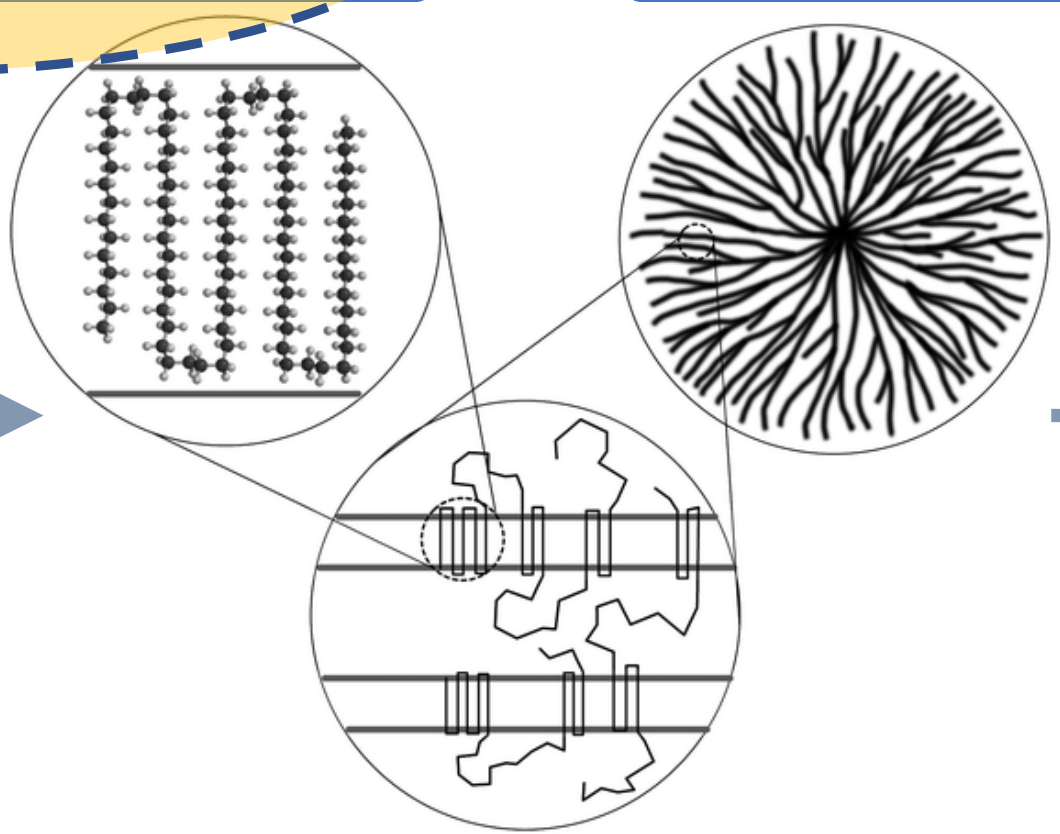
Lamellar Crystal

Spherulite

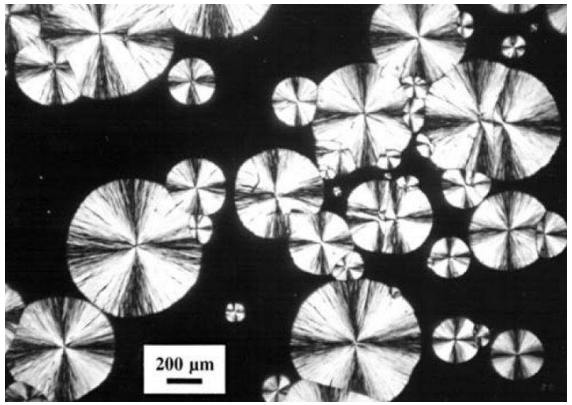
Semicrystalline Materials



https://polymerinnovationblog.com/polymers-electronic-packaging-types-polymers-used/

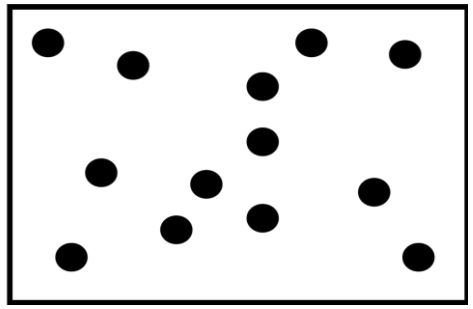


S. T. Milner, “Polymer crystal-melt interfaces and nucleation in polyethylene,” Soft Matter, vol. 7, no. 6, pp. 2909–2917, 2011.

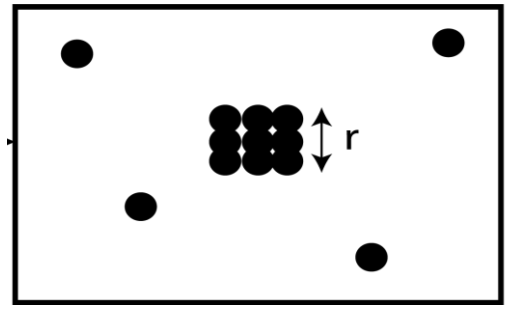


Winkler, Anders & Kloosterman, Gertjan. (2015). A critical review of fracture mechanics as a tool for multiaxial fatigue life prediction of plastics. Frattura ed Integrita Strutturale. 9.

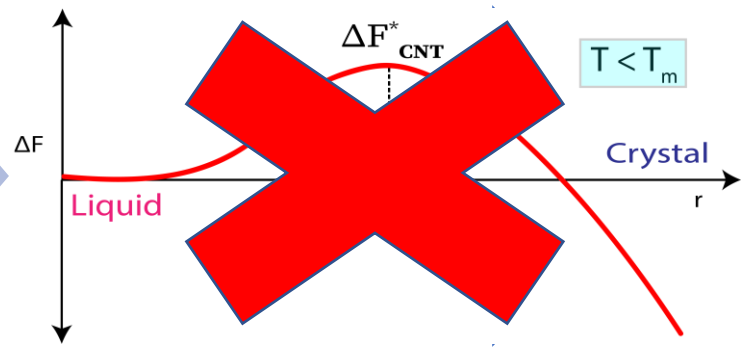
Conventional models poorly describe primary nucleation



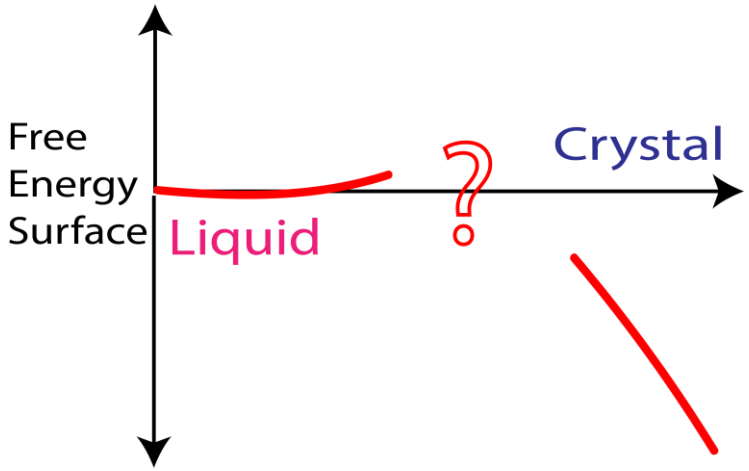
Classical Nucleation Theory



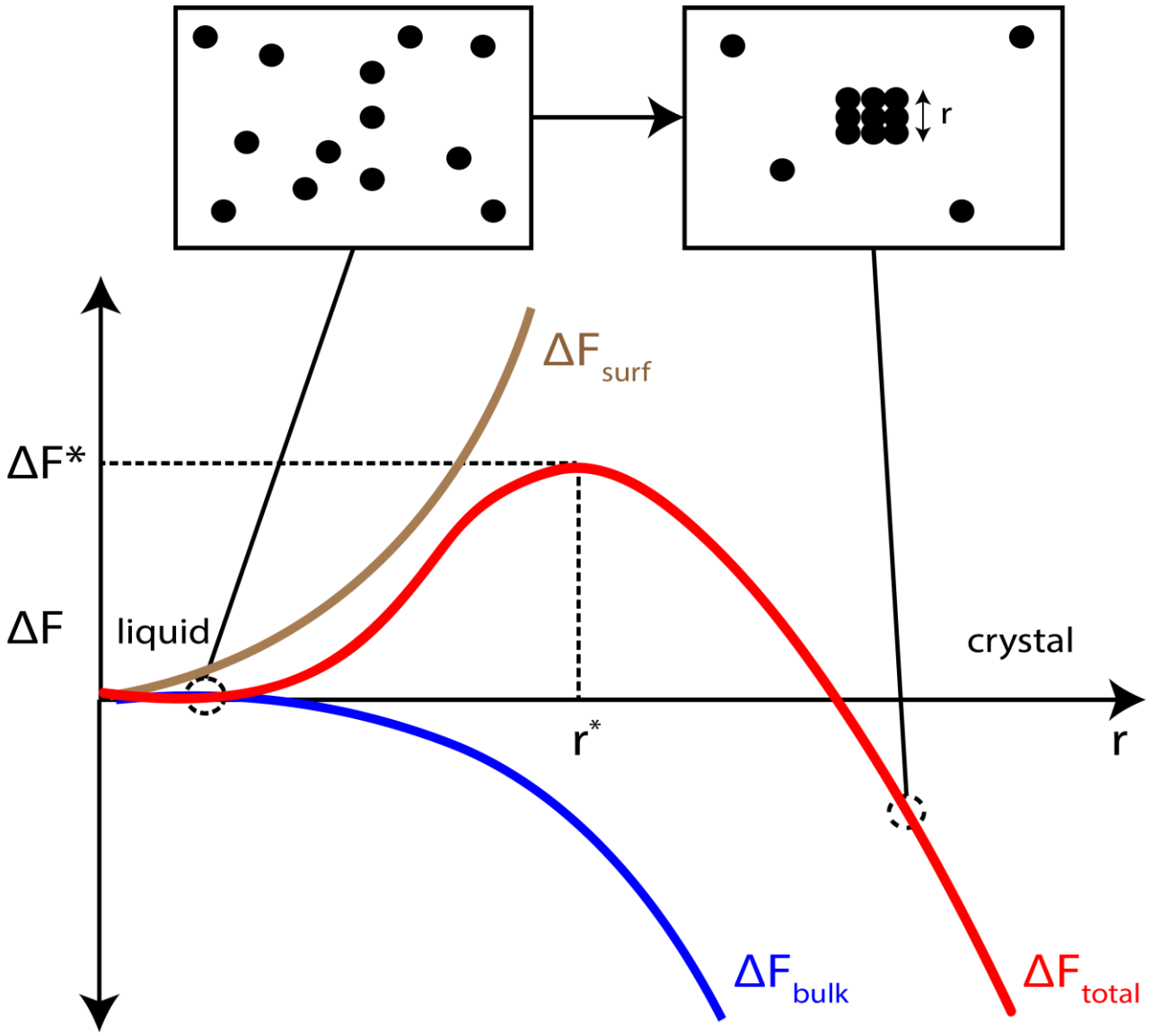
Amorphous Melt

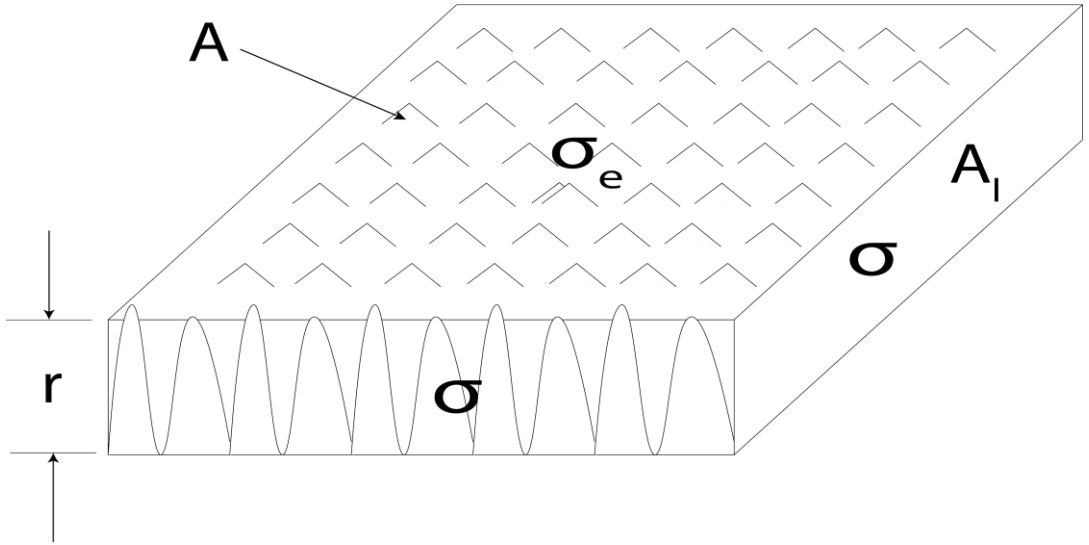


Lamellar Crystal



CNT explains some features of primary nucleation



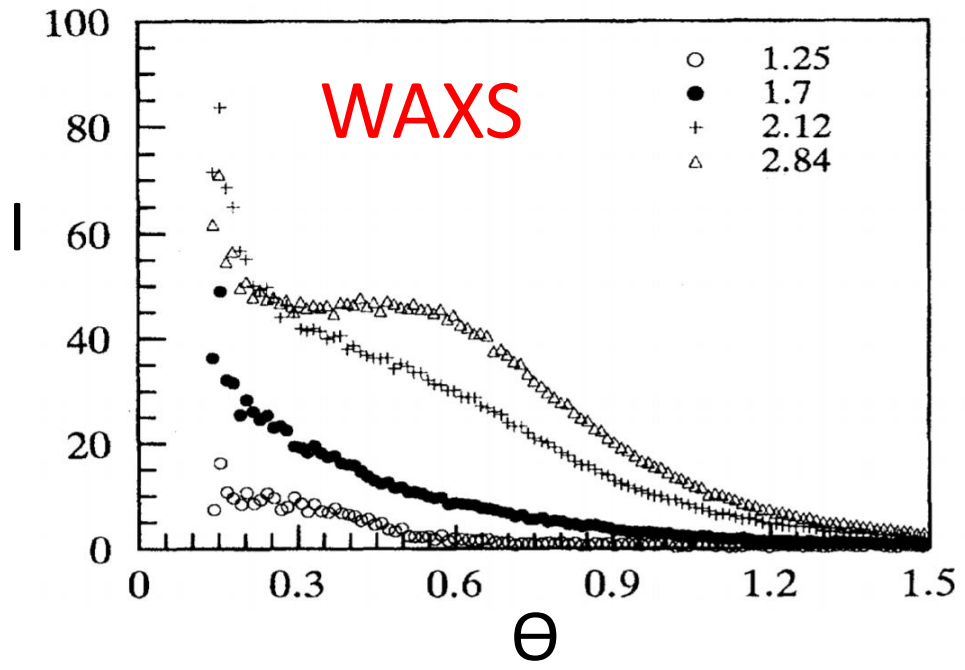


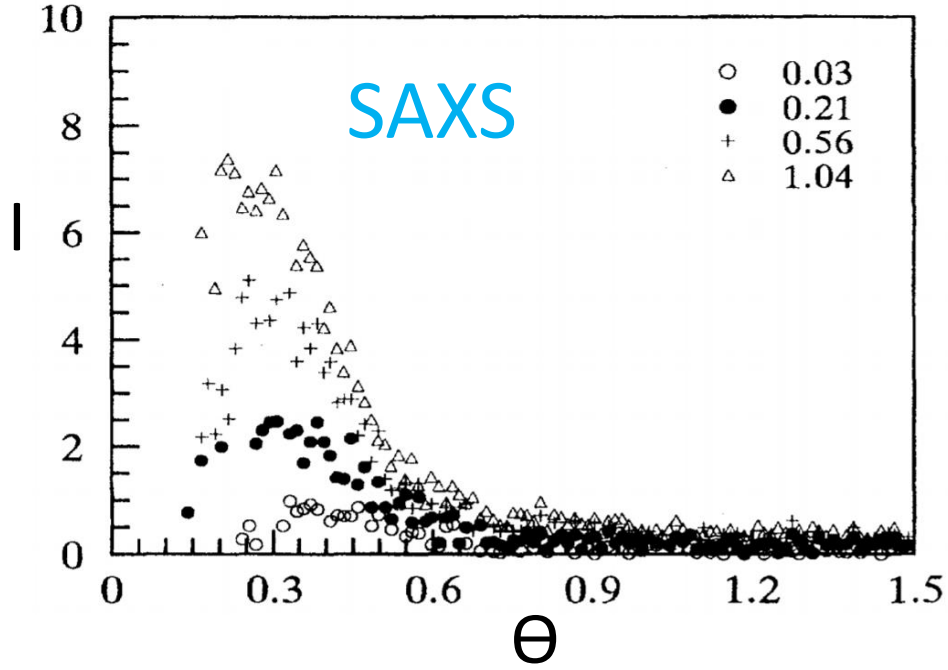
Gibbs-Thompson Equation

$$F = F_{SURFACE} + F_{BULK}$$

$$r^* = \frac{2\sigma_e {T_m}^{\infty}}{\Delta {H_m}^{\infty} \Delta T_m}$$

Small- and Wide- Angle X-ray Scattering reveals initial ordering prior to crystallization

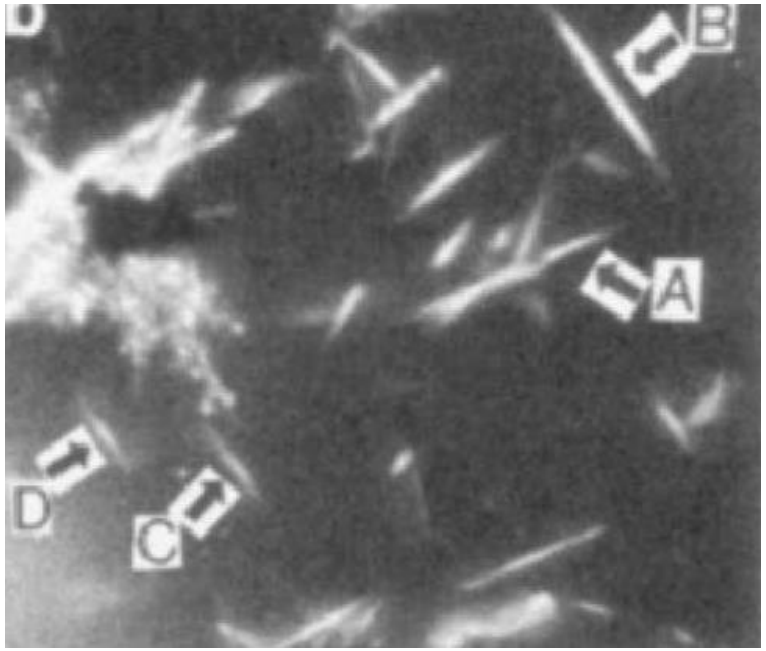


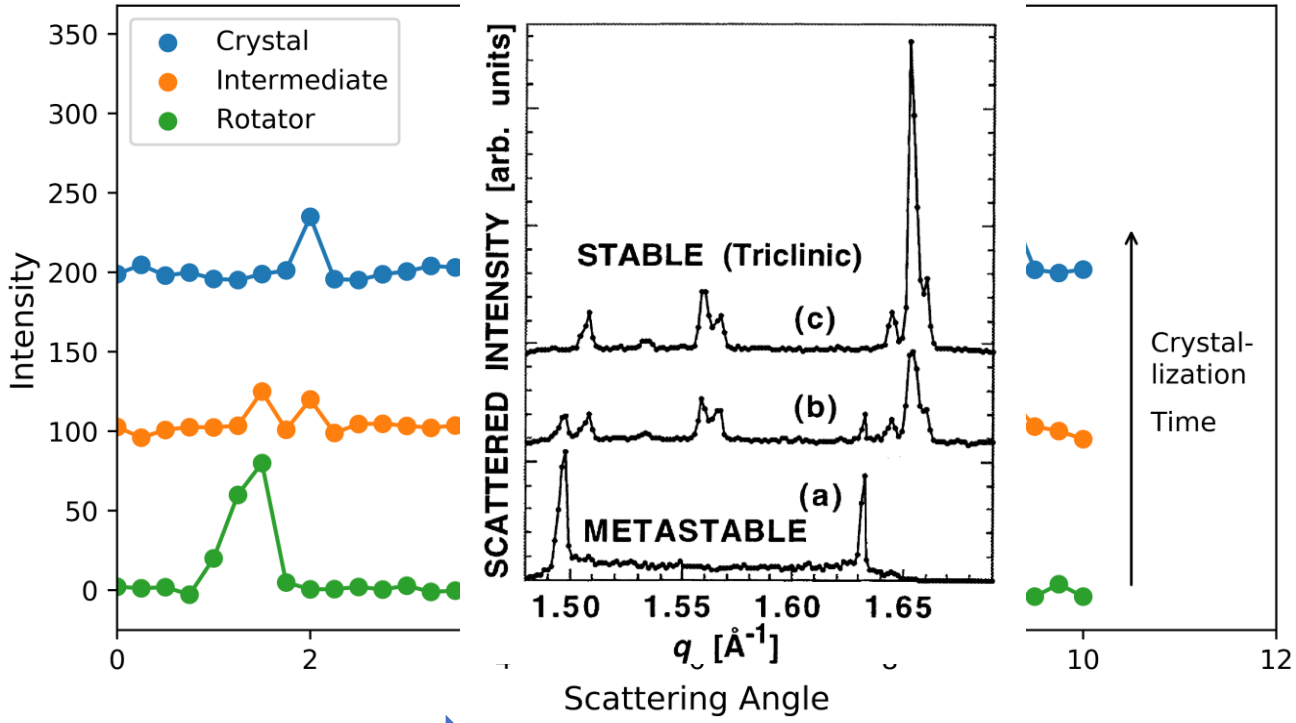


Amorphous Melt → Nematic Crystal → Lamellar Crystal

M. Imai, K. Kaji, T. Kanaya, and Y. Sakai, Physical Review B, vol. 52, no. 17, pp. 12 696–12 704, 11 1995

Intermediate phase observations before crystal transition





Amorphous Melt

Hexagonal Crystal (High P)

Rotator Crystal (Oligomers)

Lamellar Crystal

S. Rastogi, M. Hikosaka, H. Kawabata, and A. Keller, Macromolecules vol. 24, no. 24, pp. 6384–6391, 1991.

E. Sirota and A. Herhold, Polymer, vol. 41, no. 25, pp. 8781–8789, 2000.

WL-MC simulation can calculate an FES

Metropolis MC:

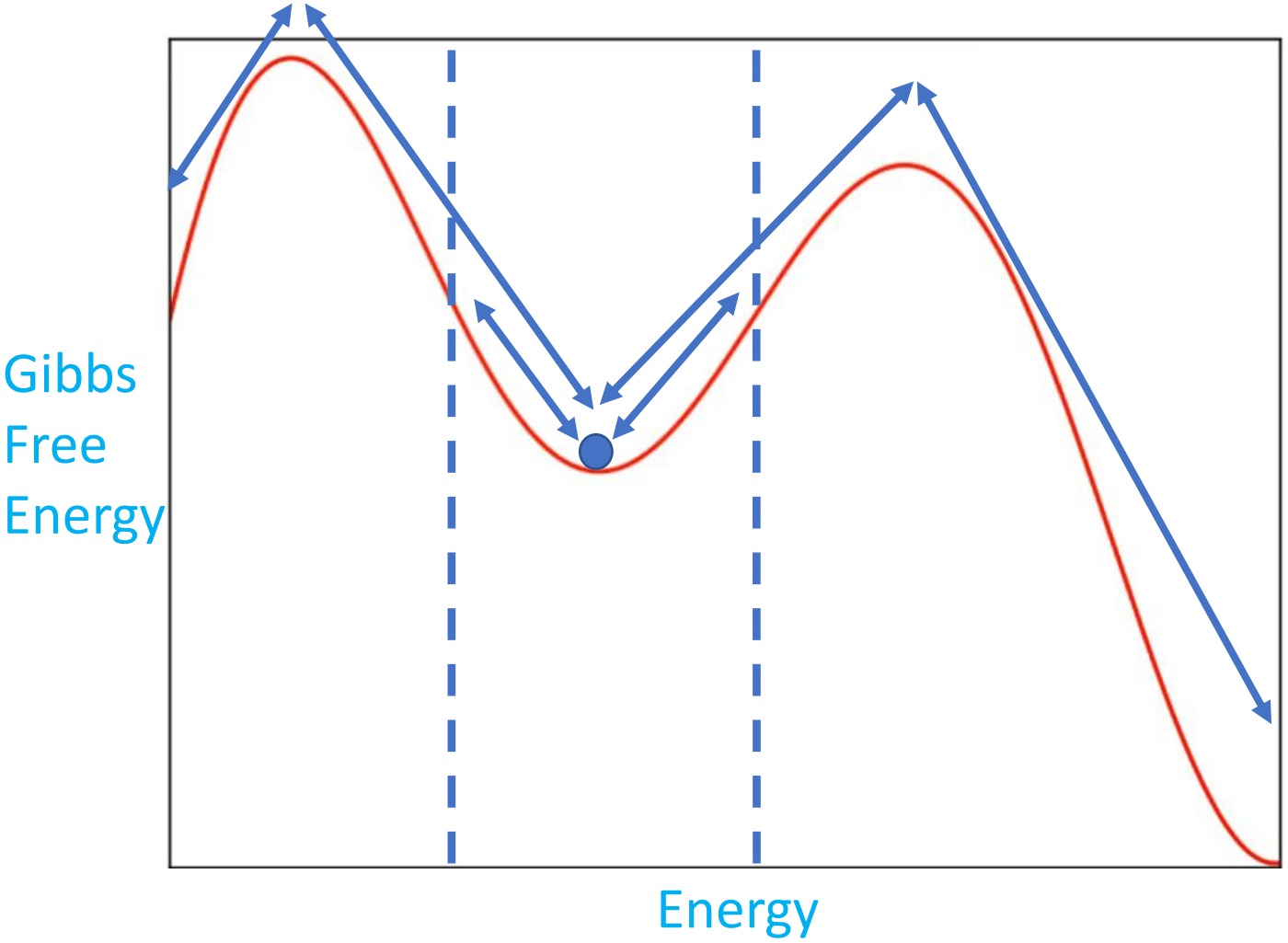
$$P = e^{-\Delta E/T}$$

Wang-Landau MC:

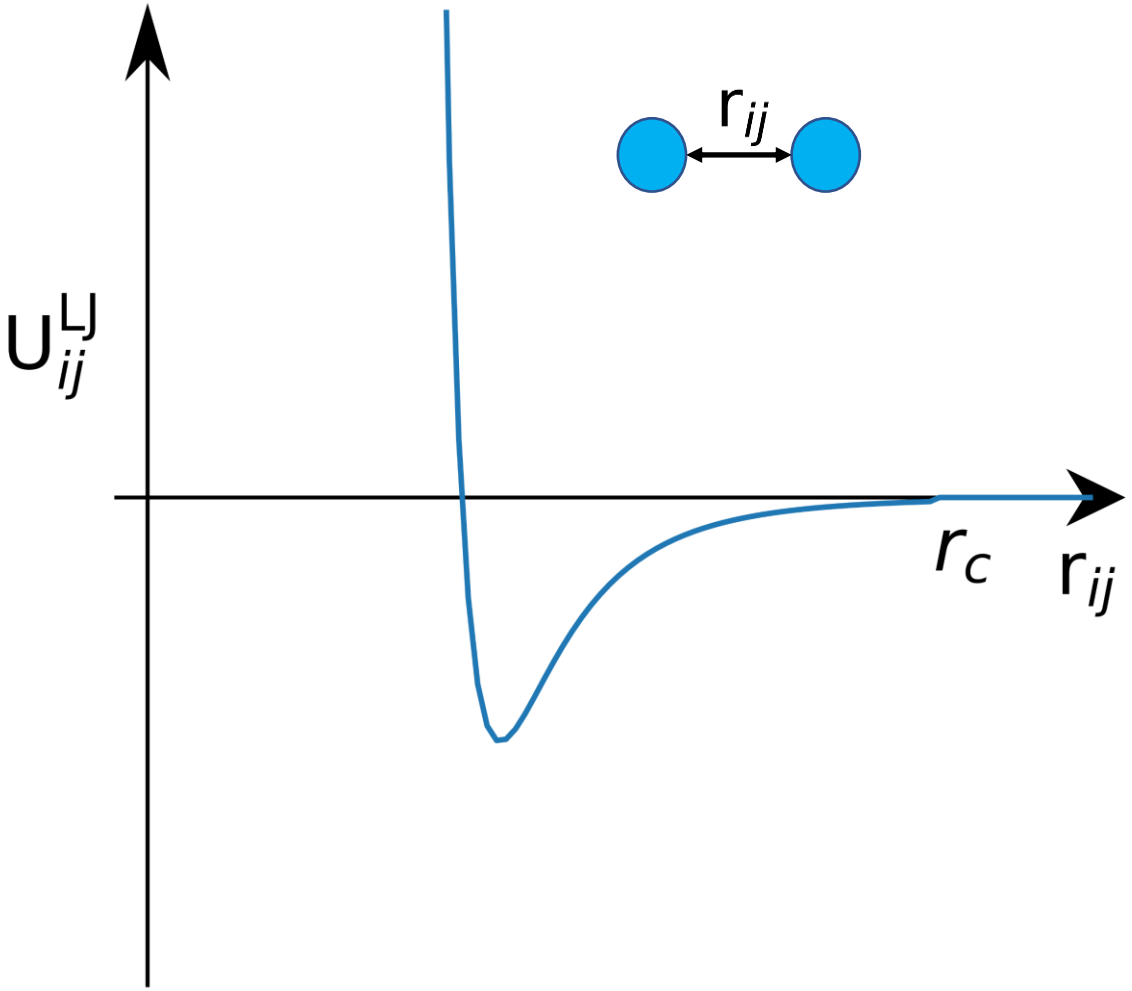
$$P = e^{\Omega(E_{old})-\Omega(E_{new})}$$

$$F(E) = E - kTln\big(\Omega(E)\big)$$

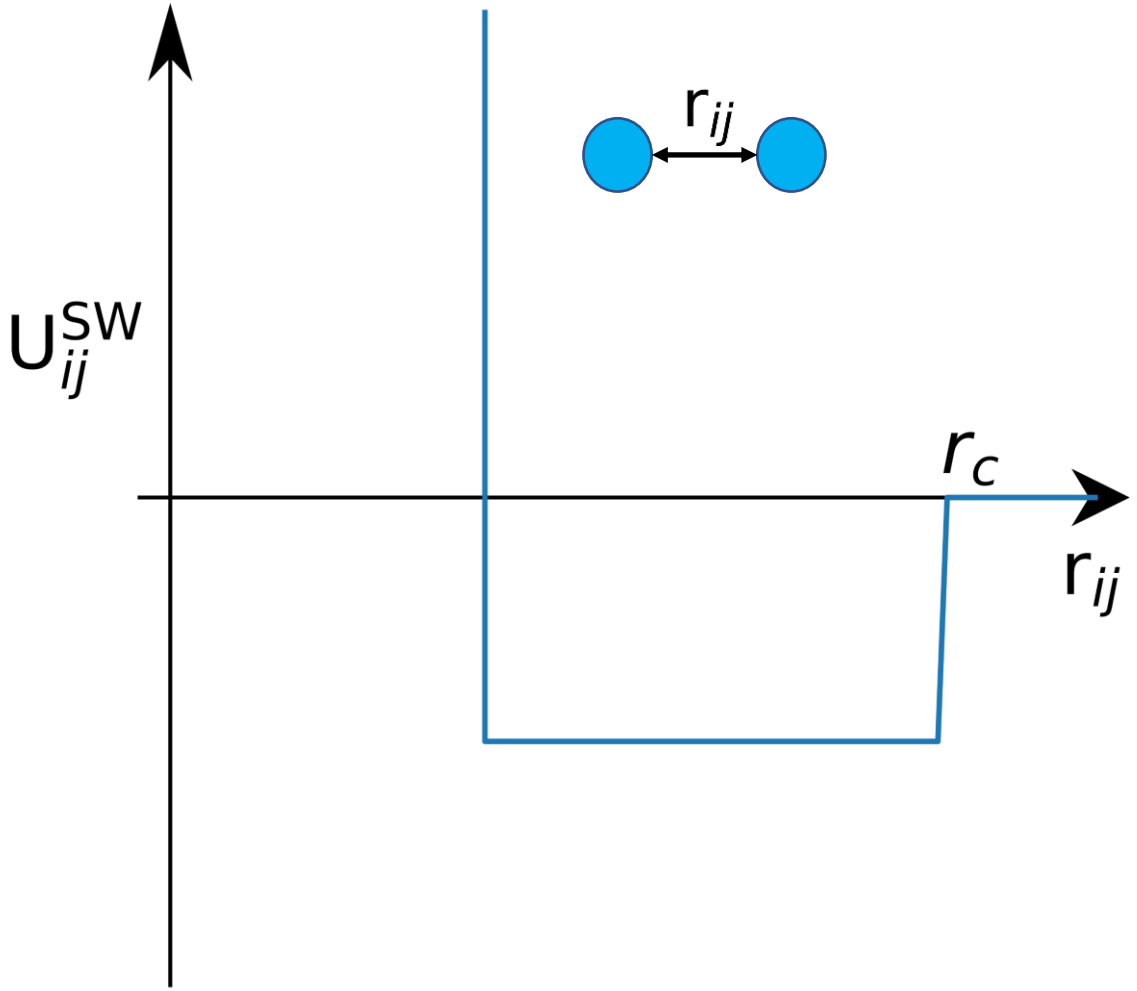
$$F(\phi_1, \phi_2, \phi_3, \ldots, \phi_n)$$



Potential models simulate bead-bead interaction



Lennard-Jones Potential



Square-Well Potential

Deviant crytallization and recrystallization lines

Legend:
- Agreement with convention
- Disagreement with convention

- Melting line = Gibbs-Thomson
- $T_m{}^{\infty}$ = Equilibrium Melting T
- B = Melting at constant thickness
- $T_c{}^{\infty}$ = Another Equilibrium T
- A = No crystals observed
- C = Crystal thickening during melting