Wang-Landau Simulation of the Free Energy Surface of Crystallization in a Polymer Melt

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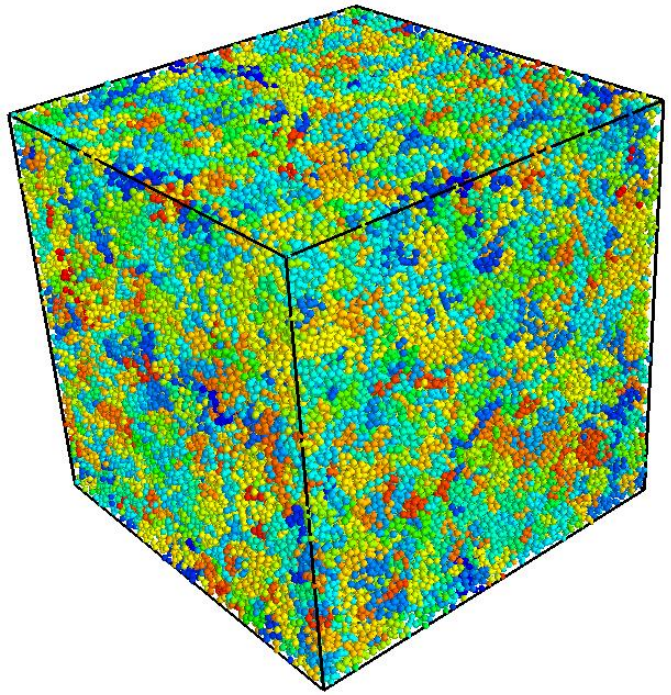


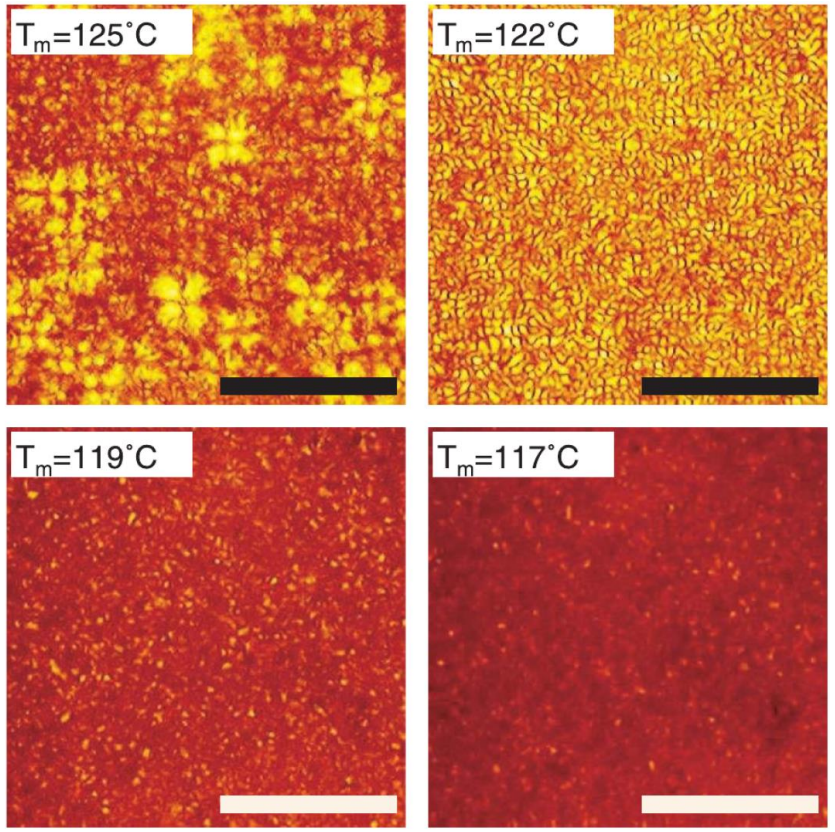
6th March 2020

APS March Meeting 2020

There is a controversy in the polymer crystallization literature

Melt Memory Effect & Primary Nucleation

- *Häfele et al. Eur Phys J E (2005)*
- Final crystalline state depends on T_m
- Influenced by slow dynamics or thermodynamic phenomena?

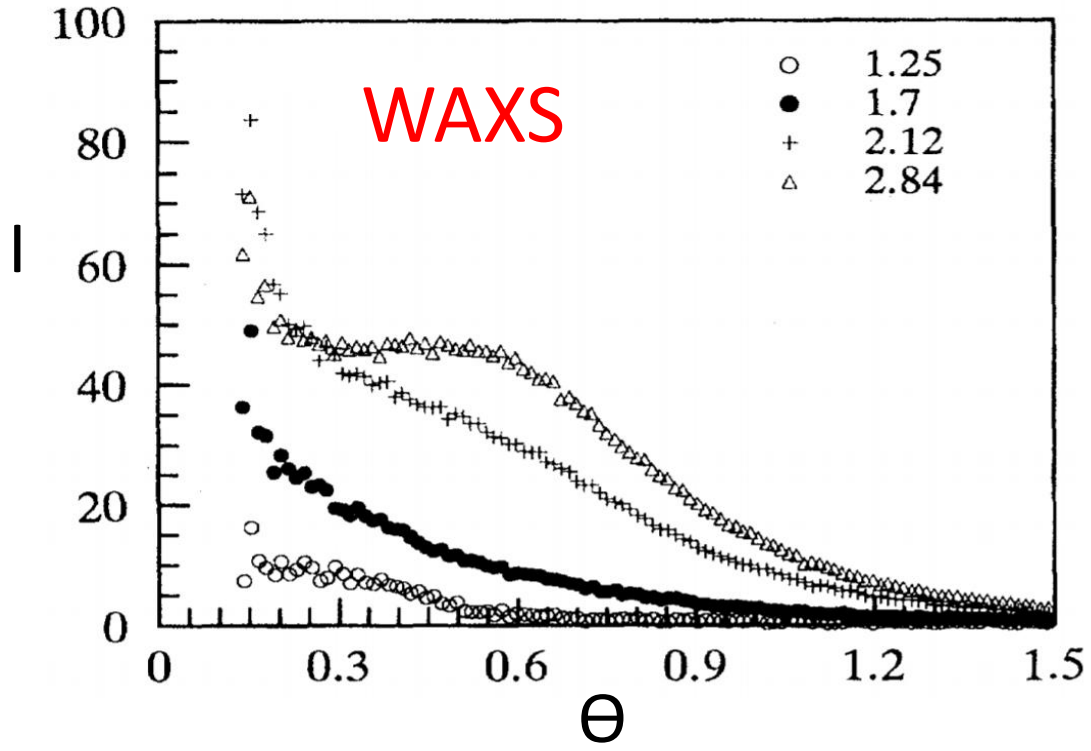


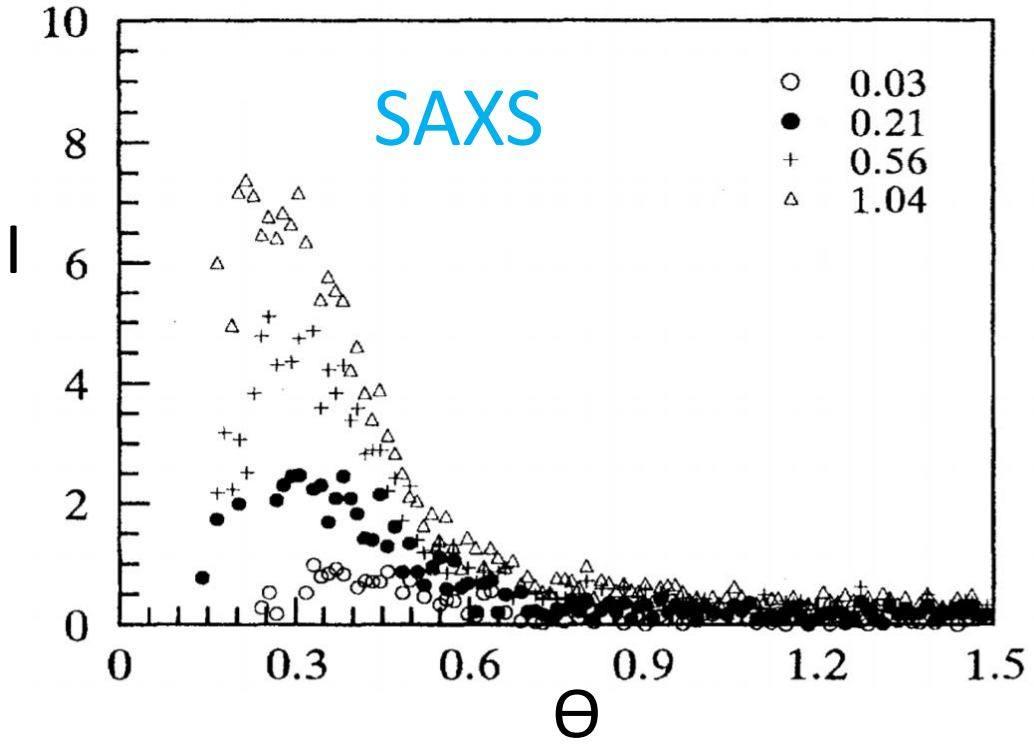
Other Observations:

Initial larger scale ordering in SAXS and WAXS	*Imai et al. Physica B Condens (1995)*
Deviant Crystallization and Recrystallization	*Strobl Rev Mod Physics (2009)*
Intermediate Phase Observations	*Kanig Colloid Polym Sci (1991), Rastogi et al. Macromol (1991)*
No Copolymer Effect on Crystallization	*Hauser et al. Macromol (1998)*

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

Imai et. al, 1995, Phys. Rev. B, 52





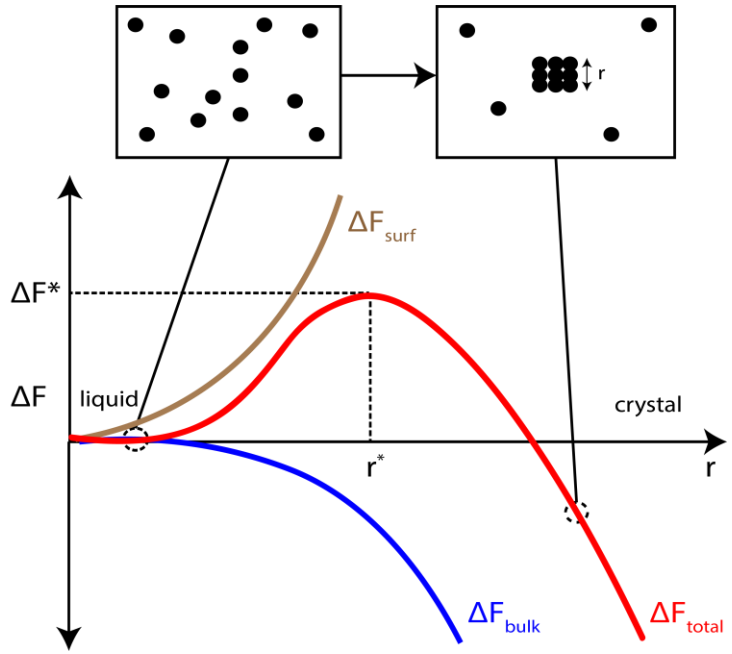
- Probes Å-scale behavior
- Order at t = 2.84

- Probes nm-scale behavior
- Order at t = 1.04

Can the previous observations be explained by CNT?

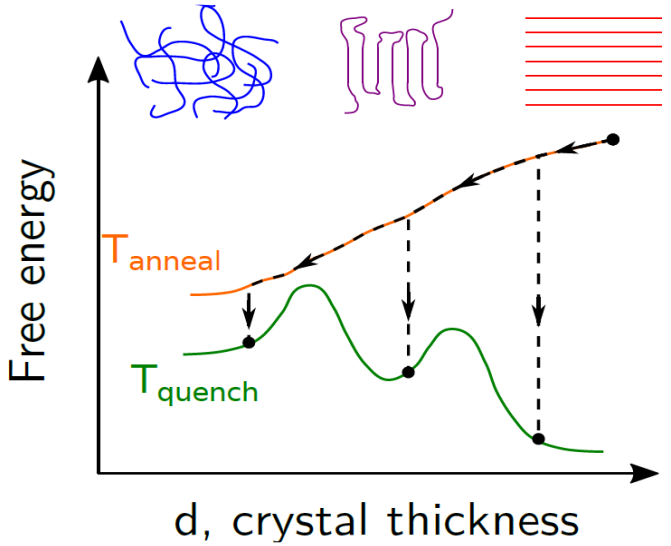
Classical Nucleation Theory (CNT)

- Single energy barrier predicted
- No intermediate mesophases
- Could more than one barrier explain prior observations?



Current Hypothesis

- Strobl, Olmsted, Milner and Muthukumar (SOMM) propose intermediate nematic phase
- SOMM is controversial; some authors believe slow entanglement dynamics cause these observations



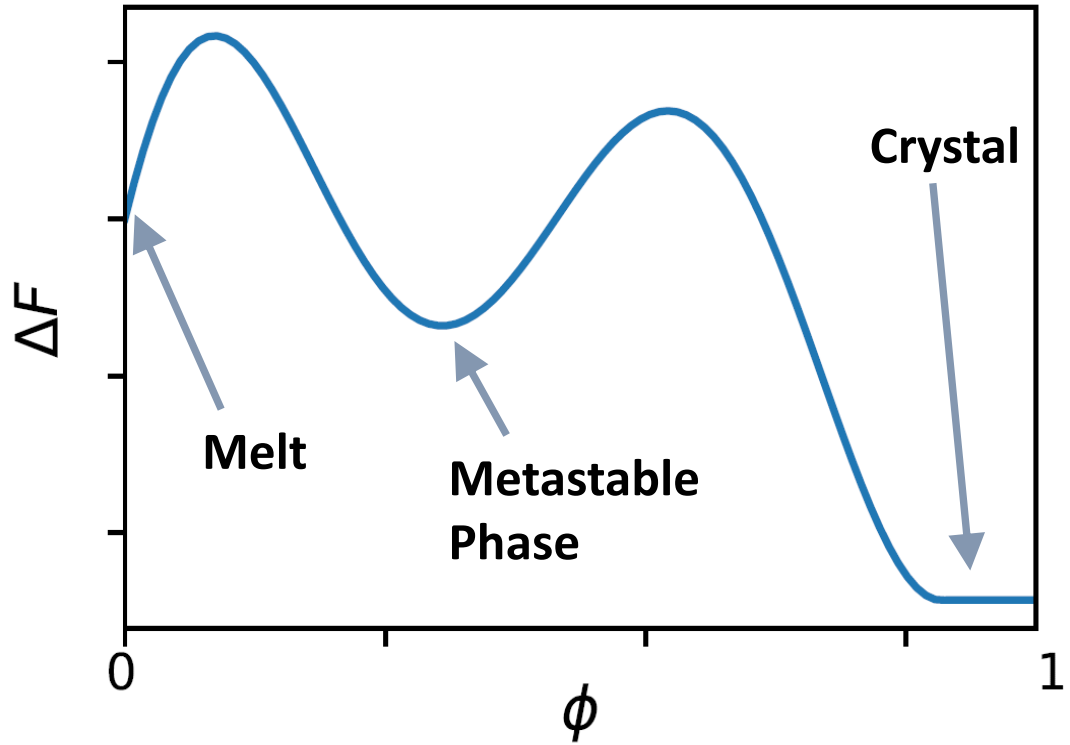
The literature and our approach

Current State of the Literature

- Very smart people are trying: Sommer, Rutledge, Milner, Hoy, Yamamoto, Sirota, Zhang, Paul, etc.
- We have an interesting approach; build a Free Energy Surface (FES) for:
  - Appropriate system sizes
  - Homogeneous nucleation from amorphous melt

Advantages of FES

- Direct test of CNT/SOMM
- Equilibrium calculation
- No dynamic considerations
- $F(\phi_1, \phi_2, \phi_3, \dots, \phi_n)$



What simulation techniques can build an FES?

Molecular Dynamics (MD)

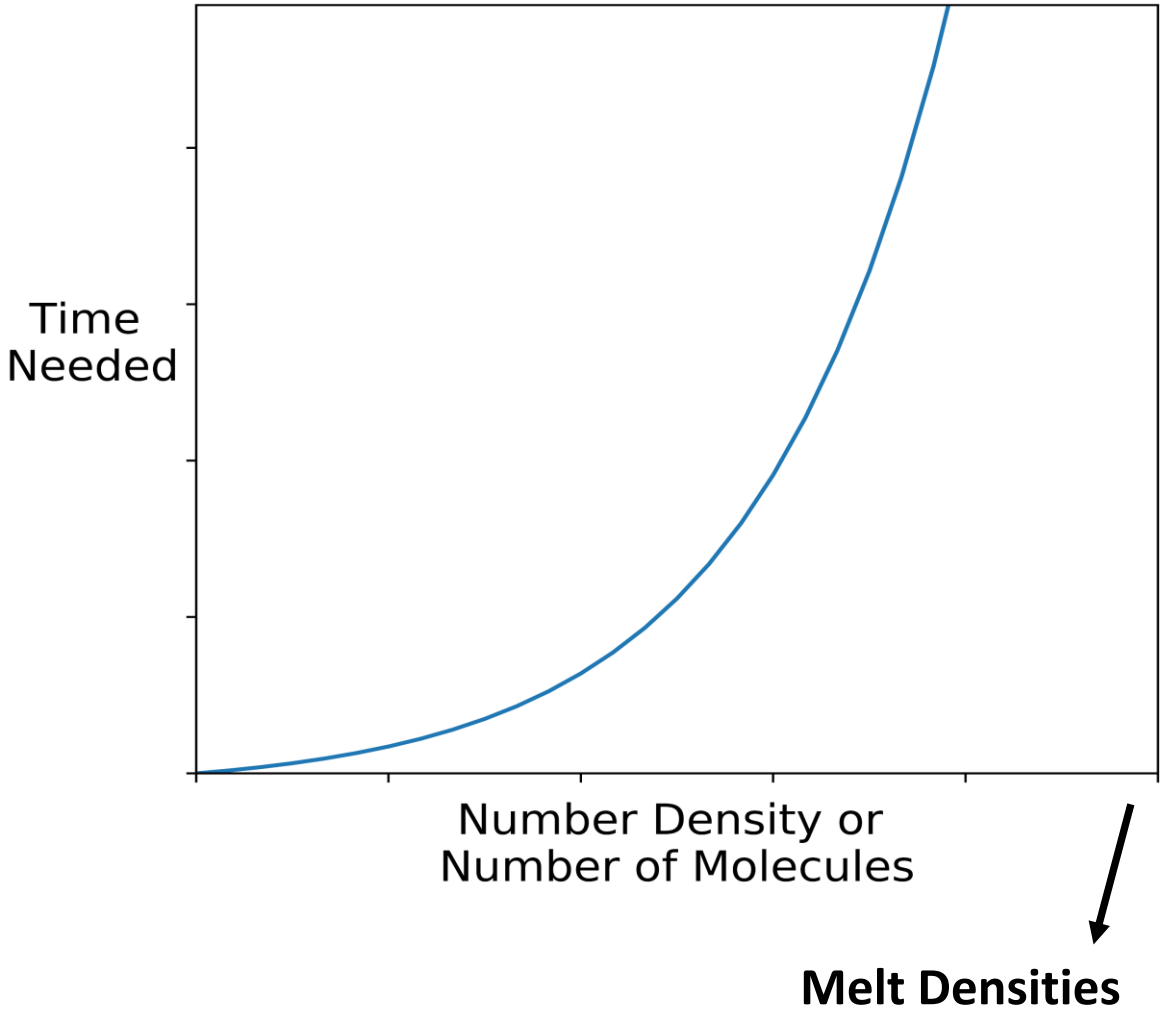
- **Access to dynamic properties**
- **Readily available (e.g. LAMMPS)**
- **Limited by entanglement dynamics**
- **Very slow equilibration**

Wang-Landau Monte Carlo (WLMC)

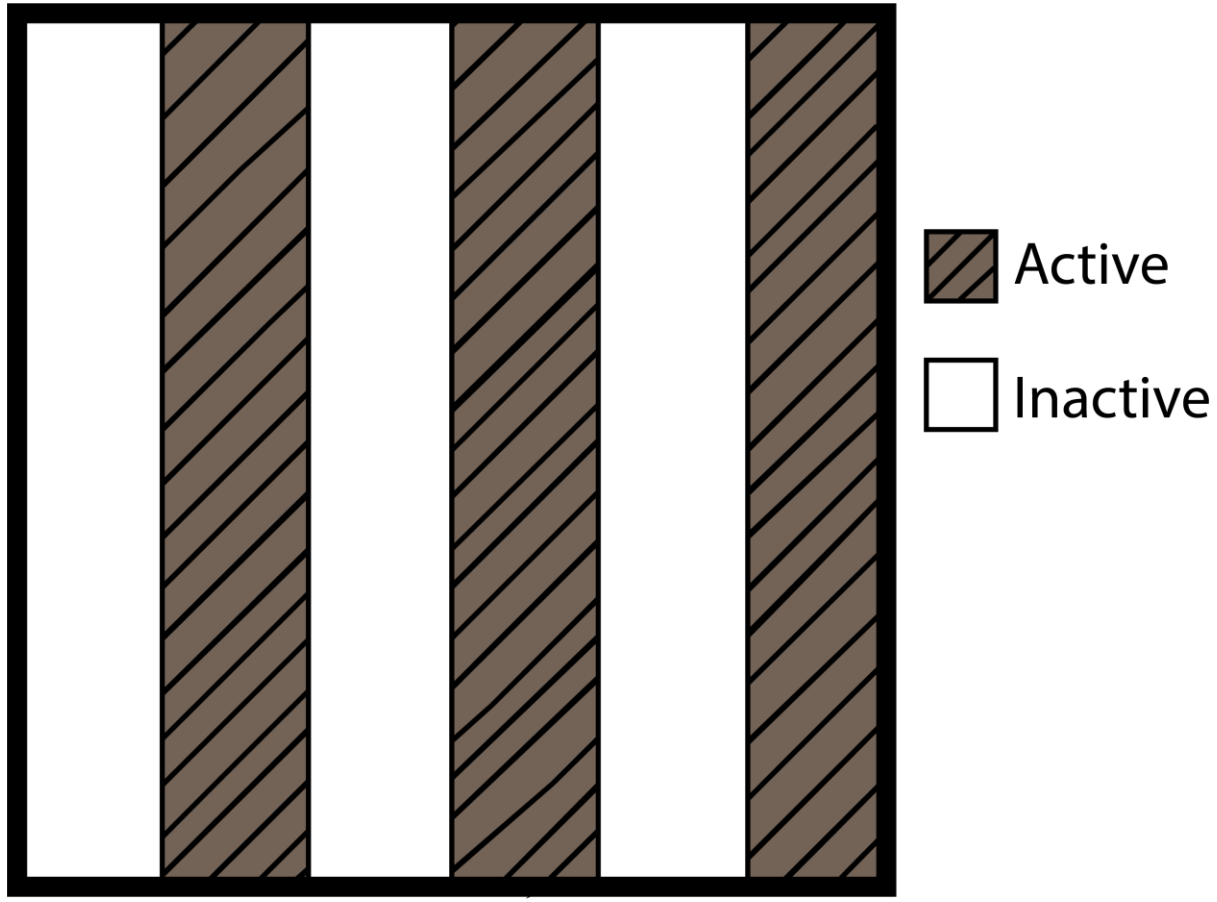
- **Bond-breaking moves**
- **Overcomes energy barriers**
- **Direct density of states (Ω) computation**
- **That is, direct FES computation**

Parallel simulations reduce required simulation times

Polymer simulations are expensive

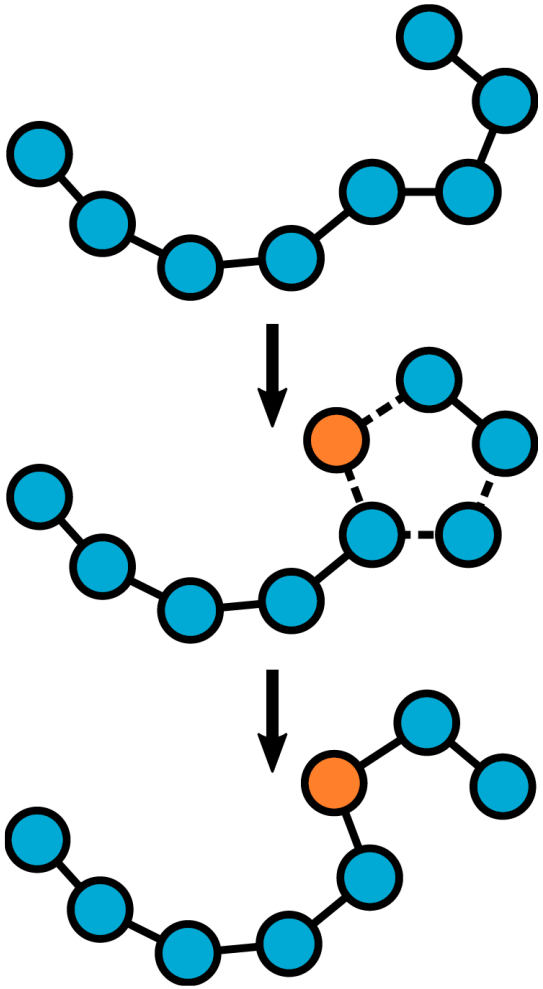


Domain decomposition parallel construct

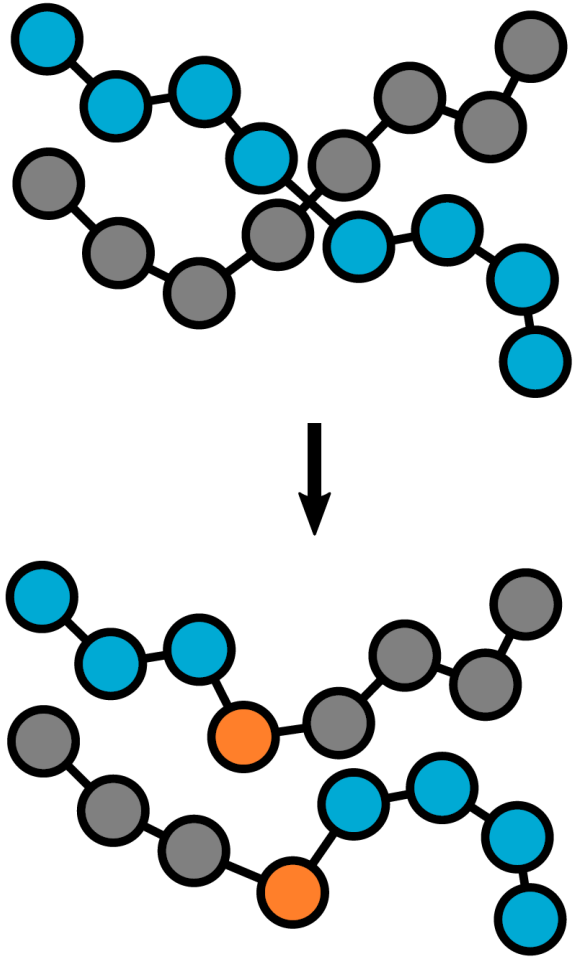


Advanced moves help break entanglement dynamics

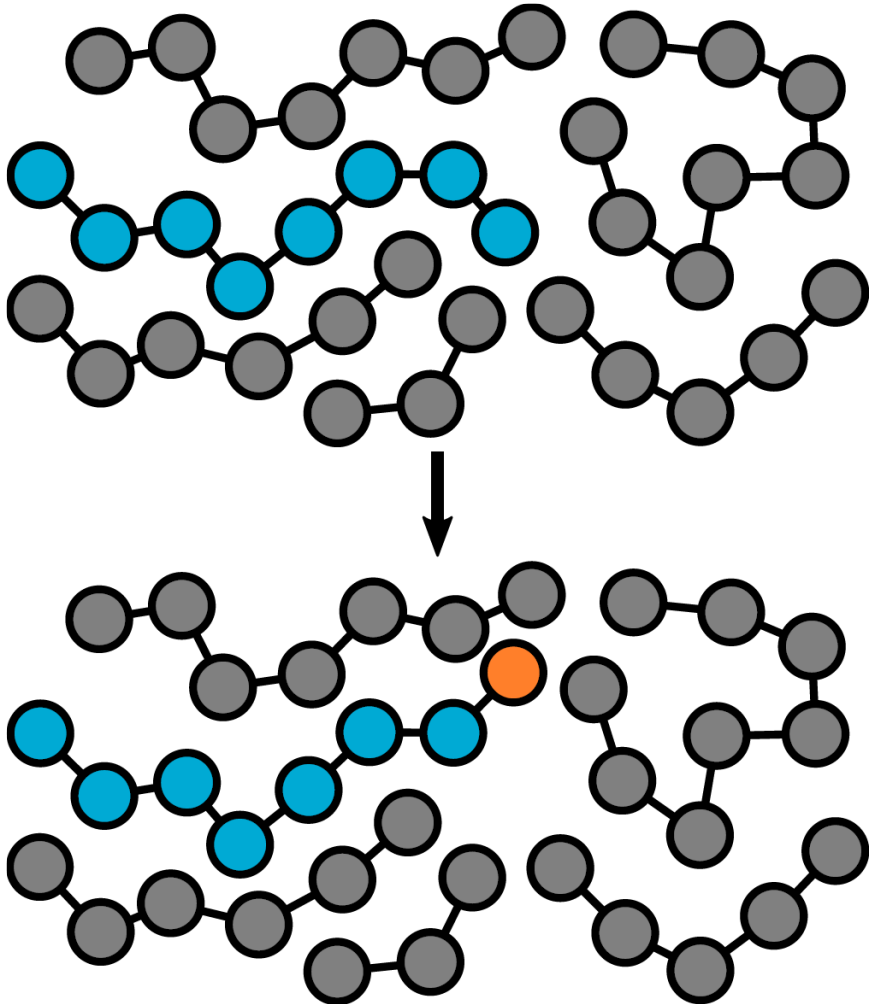
End-bridging



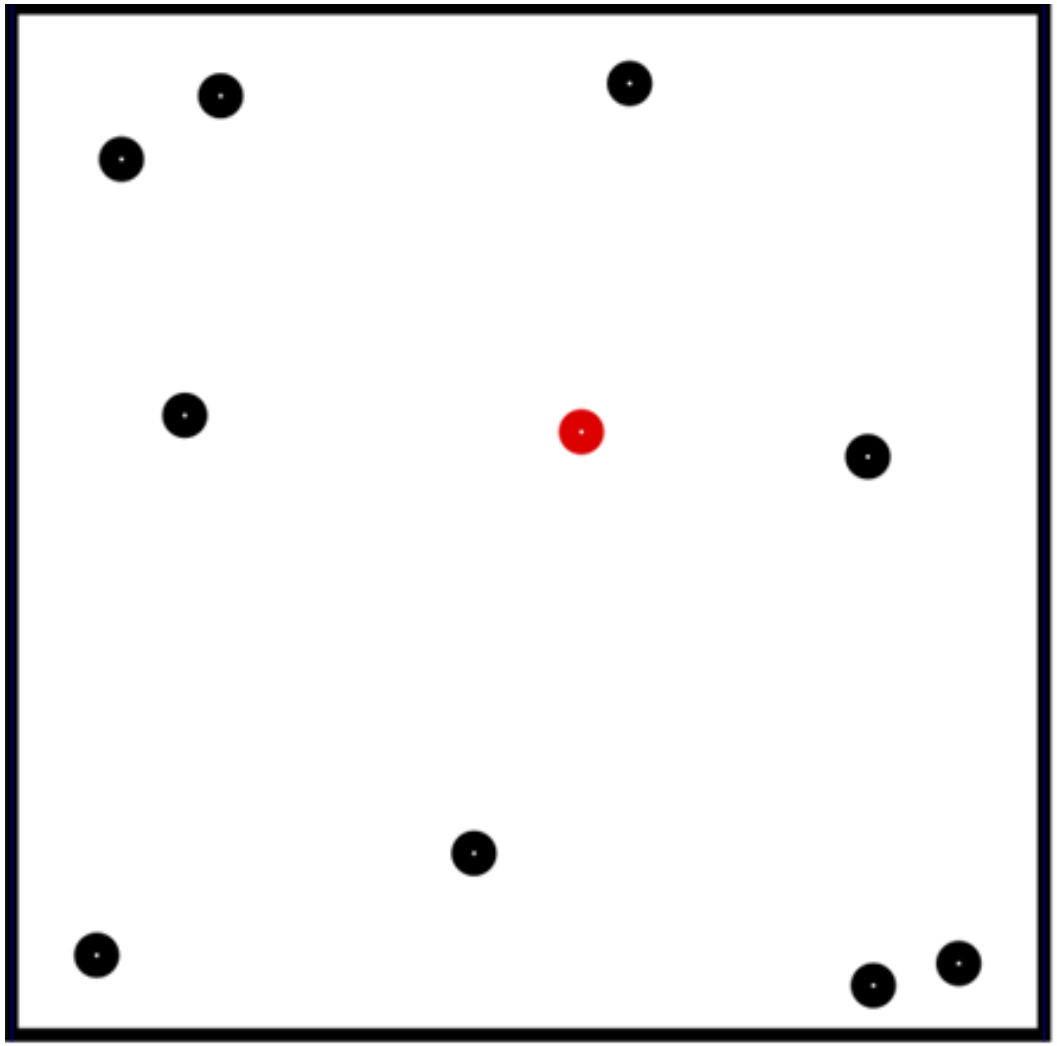
Double-bridging



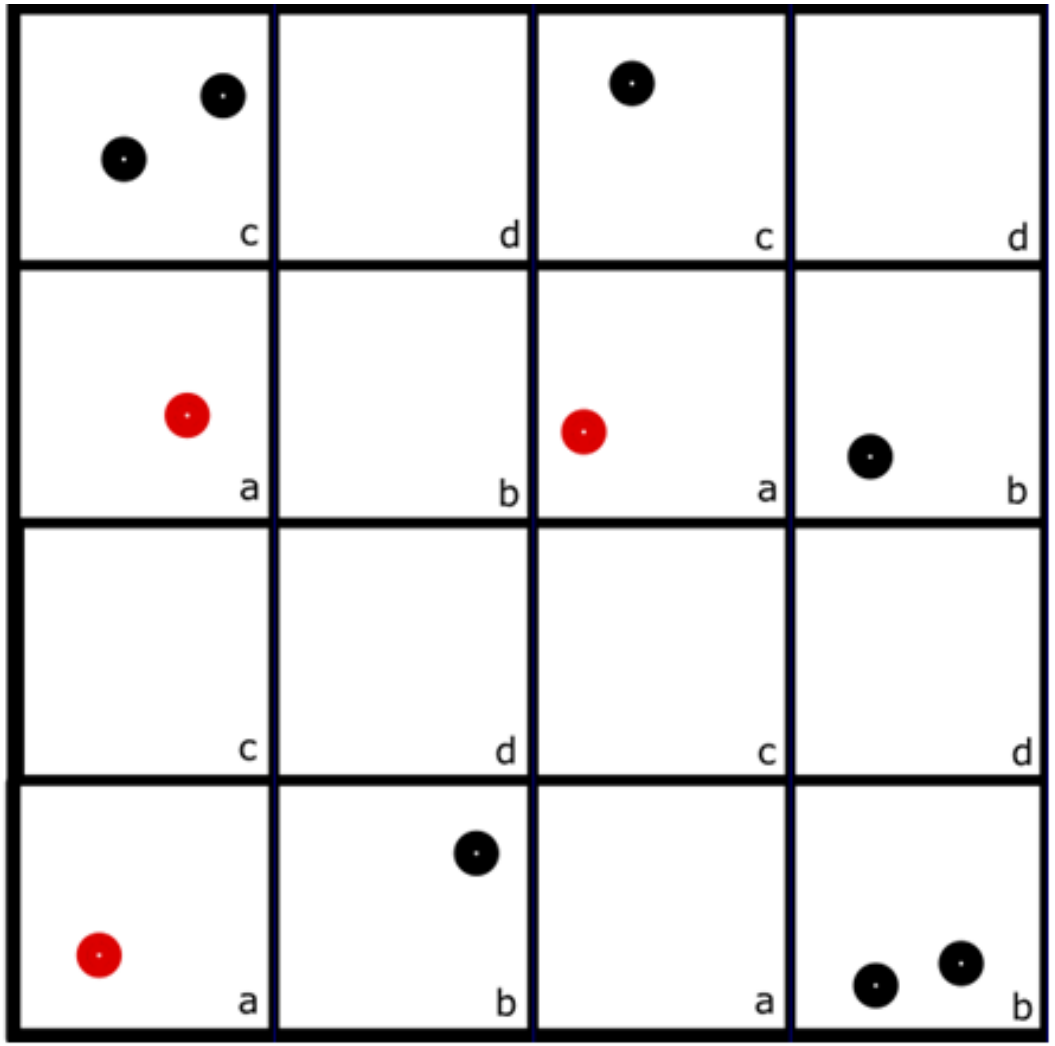
Configurational Bias



Domain decomposition breaks up the simulation volume



Conventional MC



Checkerboard MC

Anderson et al. J. Comp. Phys. (2013)
Anderson et al. Comp. Phys. Comm. (2016)

A WLMC-generated FES can characterize crystallization

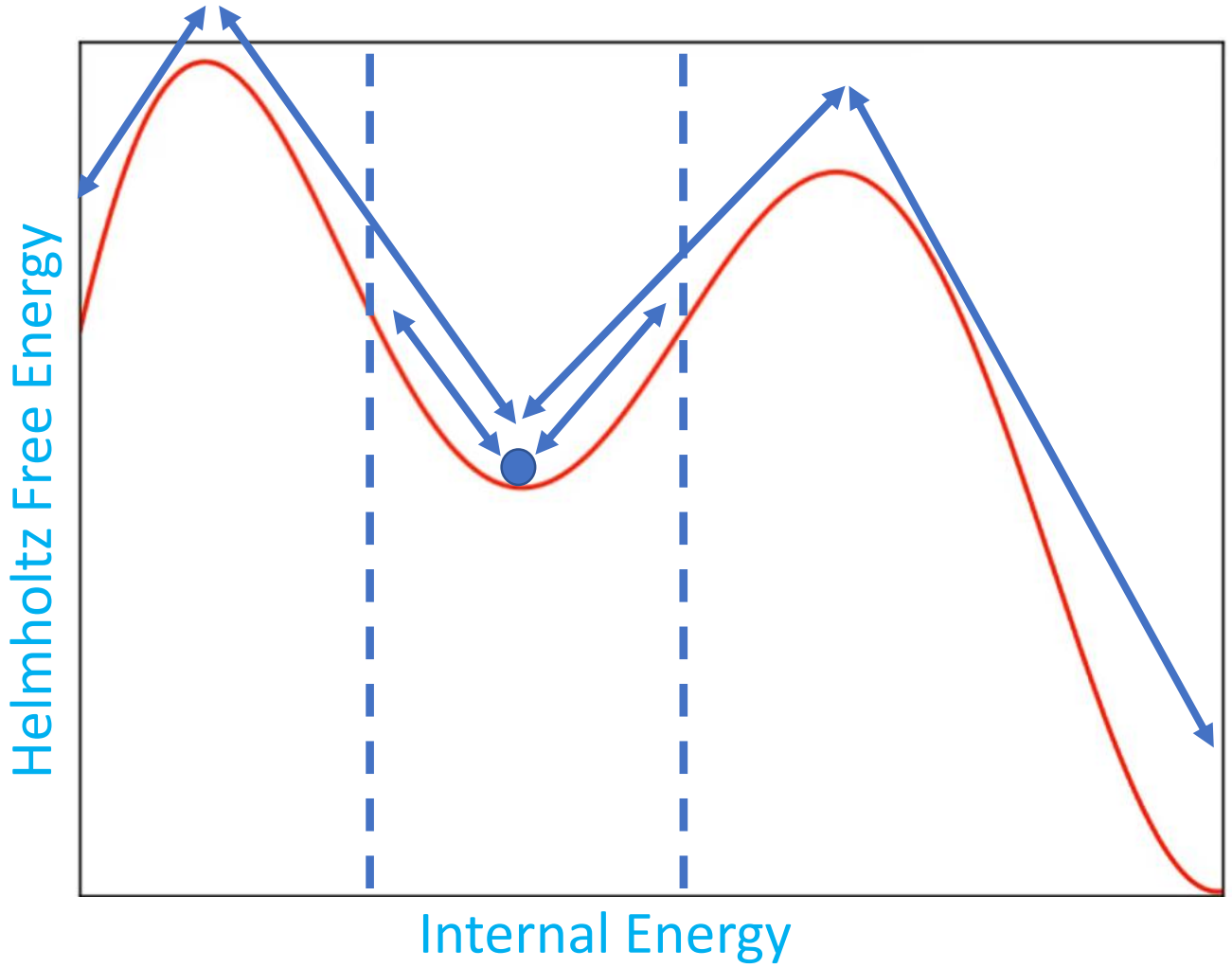
Metropolis MC:

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

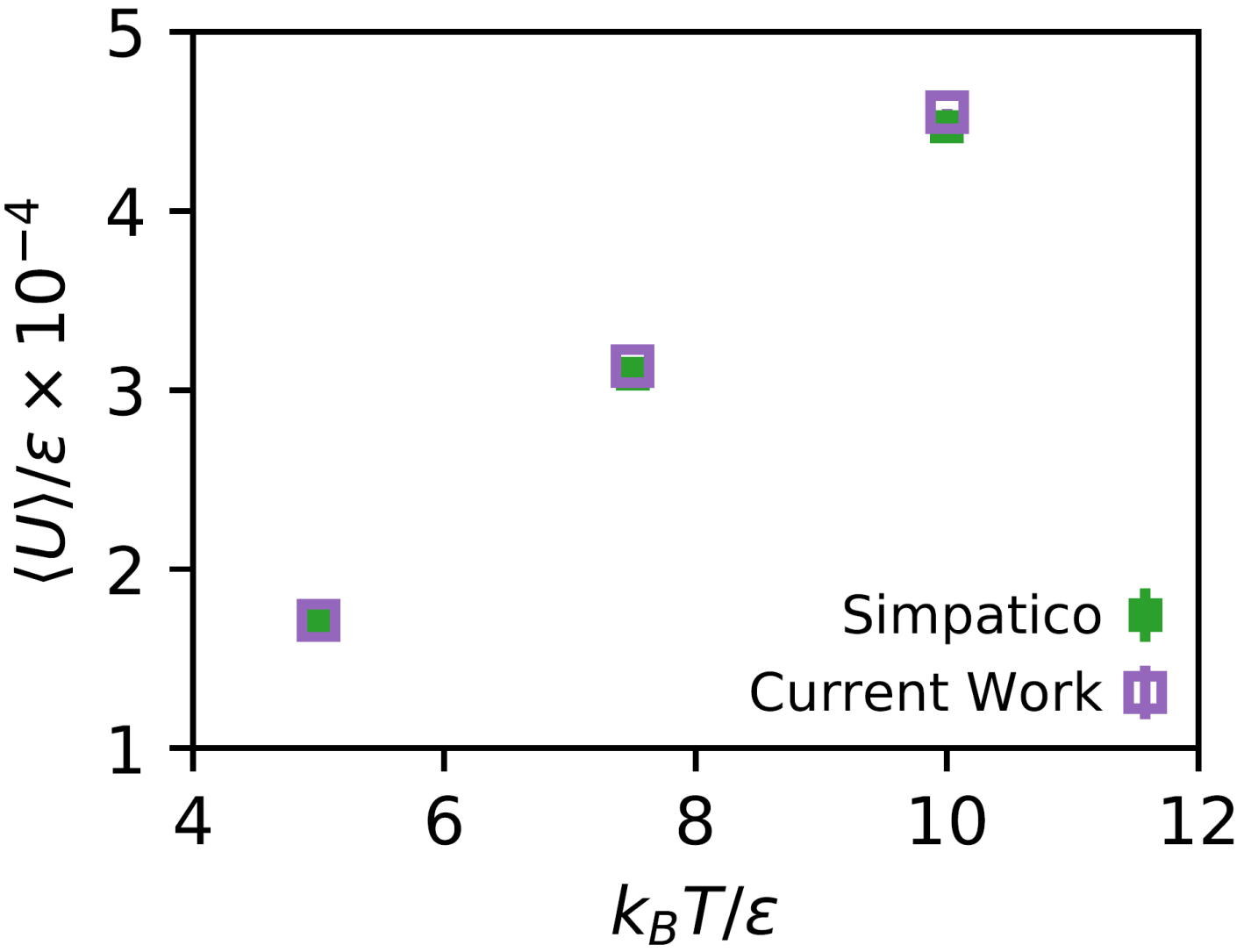
Wang-Landau MC:

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

- Better sampling of phase space
- Overcomes energy barriers
- Direct access to Ω (DOS)



Verification of our results with Simpatico



LJ Bead-Spring System

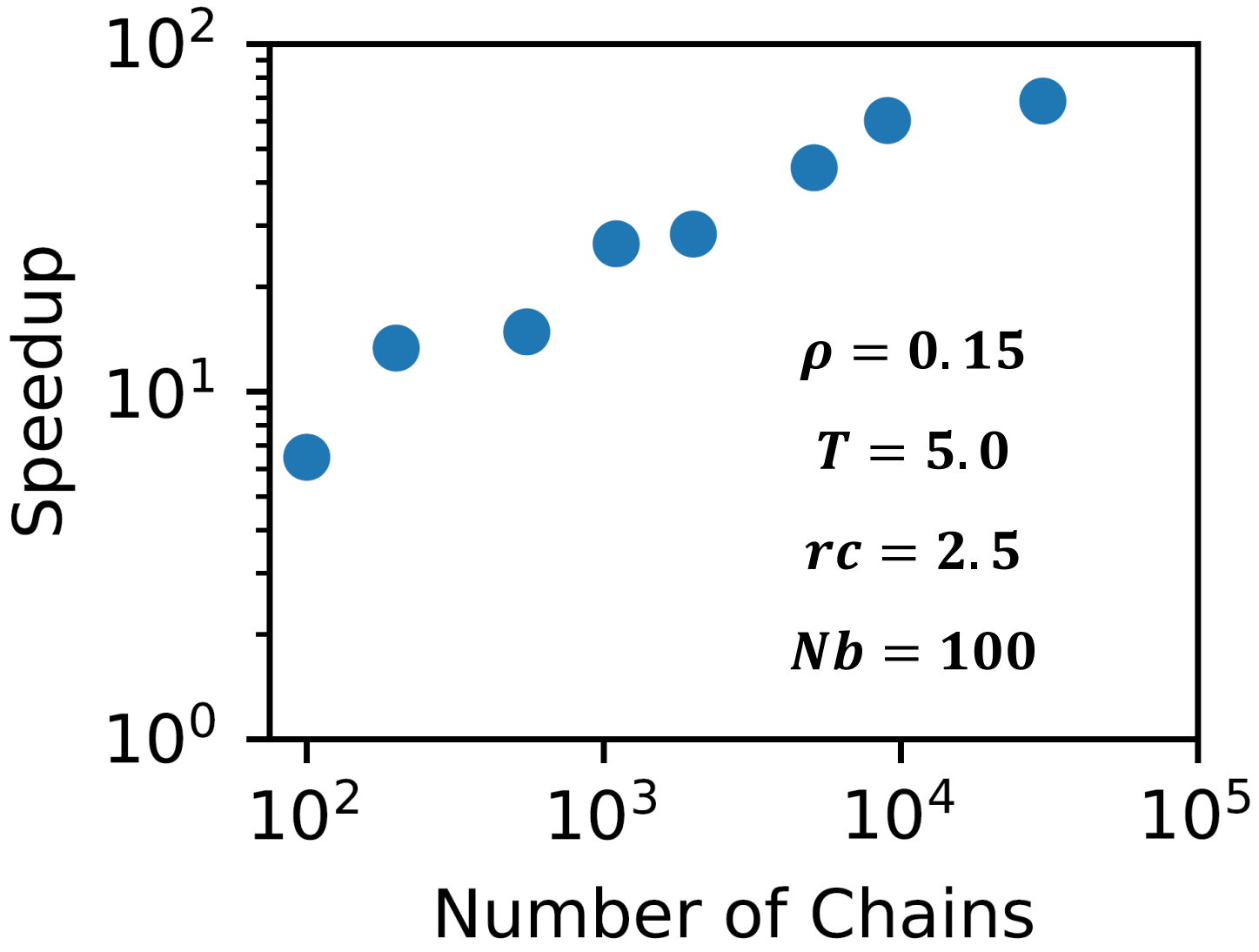
$N_{chains} = 100$

$N_{beads} = 100$

$\rho = 0.15$

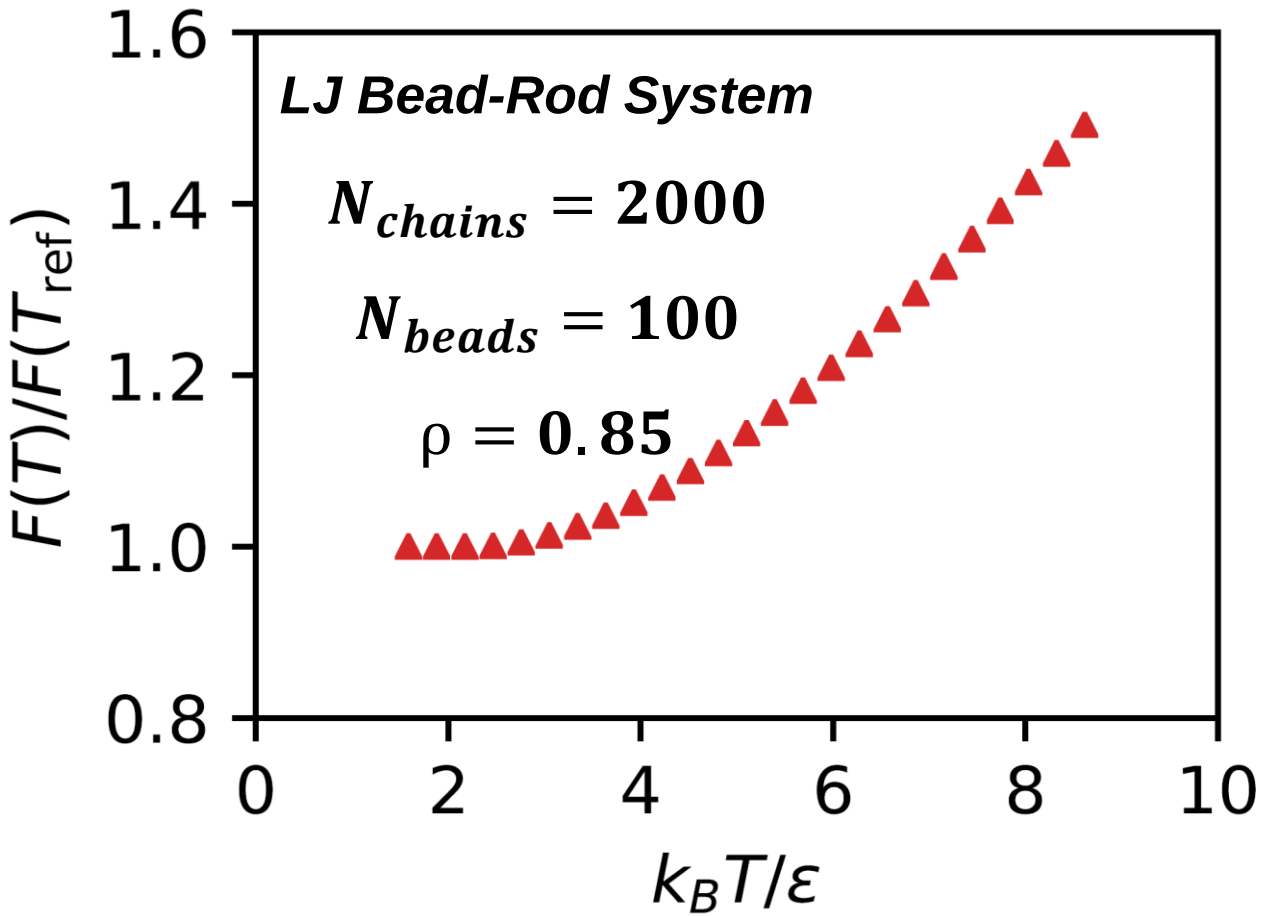
Simpatico [Computer software]. (2010). Retrieved from https://github.com/dmorse/simpatico

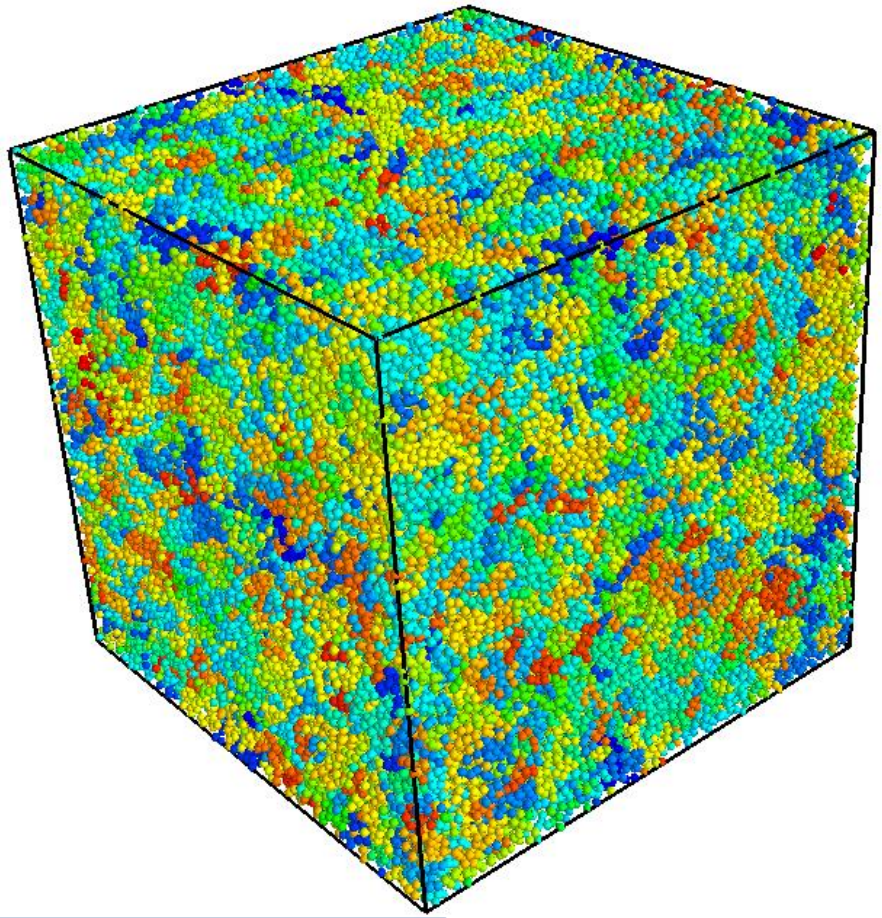
Parallel simulations are 2 orders of magnitude faster



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

WLMC simulation of bead-rods yields single transition FES





Results from bead-rod simulations

- Consistently with Hoy et al.'s work, single transition was observed (RCP)
- CNT is an appropriate description for simple bead-rod systems

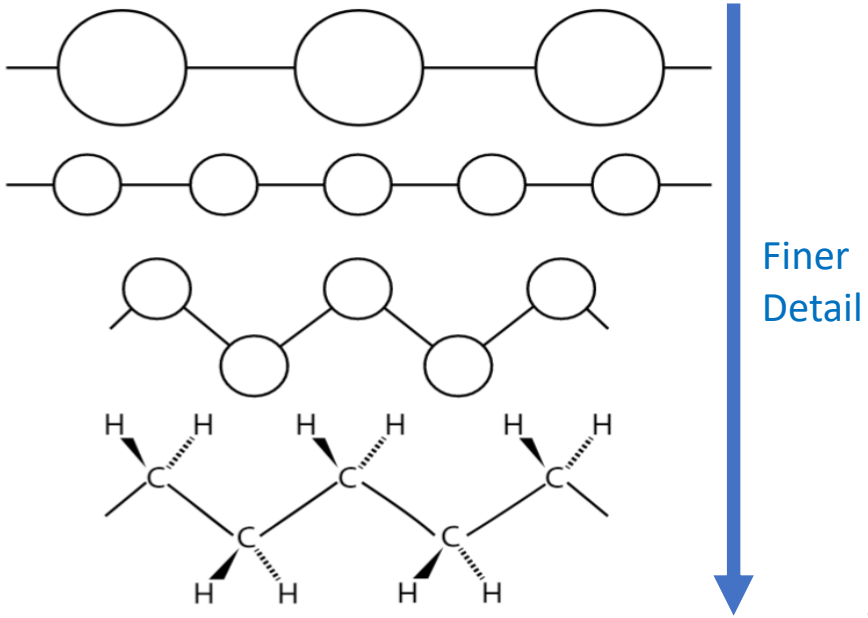
Conclusion and Future Work

Current Work

- We built a **GPU-accelerated WLMC** algorithm from scratch
- CNT is an appropriate description for simple bead-rod systems
- Chain connectivity not enough to capture important polymer phenomena

Future Work

- Explore different **order parameters**
- More realistic detail
  - **Semi-flexible** chains
  - Torsion potentials
- **Long chain** studies capturing entanglement



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