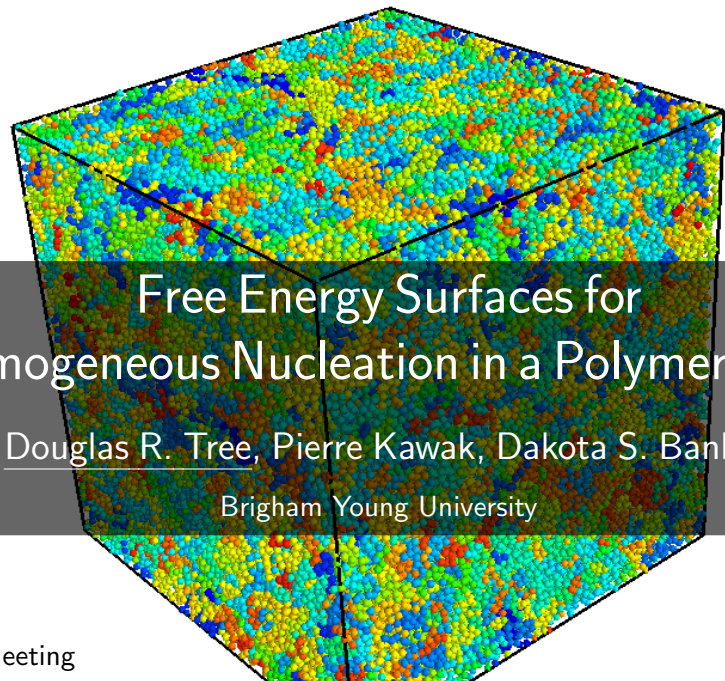


Free Energy Surfaces for Homogeneous Nucleation in a Polymer Melt

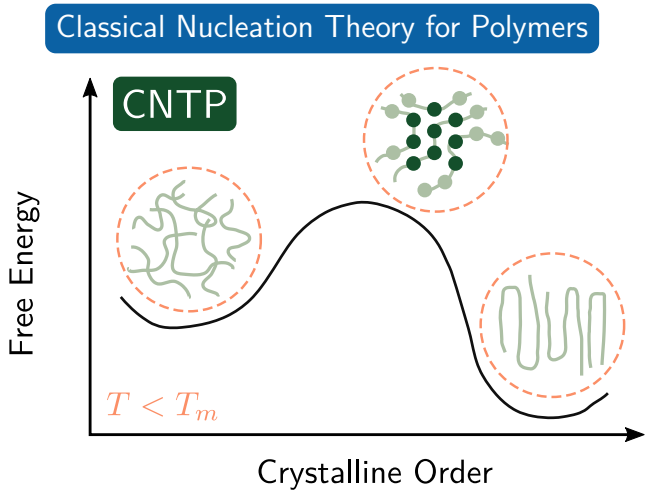
Douglas R. Tree, Pierre Kawak, Dakota S. Banks

Brigham Young University

AIChE Annual Meeting

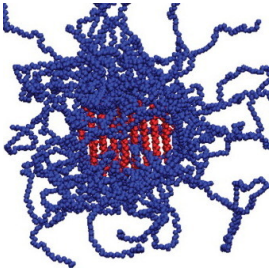
November 7, 2021

How does a polymer crystal nucleate from a melt?



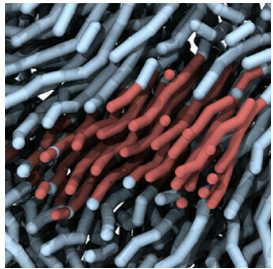
Schultz. Polymer Crystallization. (2001)
Yi. J. Chem. Phys. (2009)

Controversy in non-equilibrium MD simulations of polyethylene



- Cylindrical crystal nucleus
- Crystal size is a good order parameter
- No intermediate phases/states
- General agreement with classical models

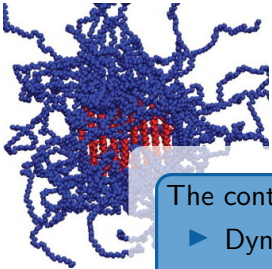
Yi et al. Macromolecules (2013)

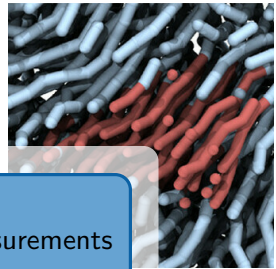


- Anisotropic crystal nucleus
- Crystal size is not only order parameter
- Crystal nucleates inside nematic droplet
- Disagrees with classical models

Hall et al. J. Phys. Chem. B. (2020)

Controversy in non-equilibrium MD simulations of polyethylene





The controversy extends to:

- Dynamic SAXS/WAXS measurements
- Recrystallization and melt memory experiments

- Cylindrical crystal
- Crystal size is a good order parameter
- No intermediate phases/states
- General agreement with classical models

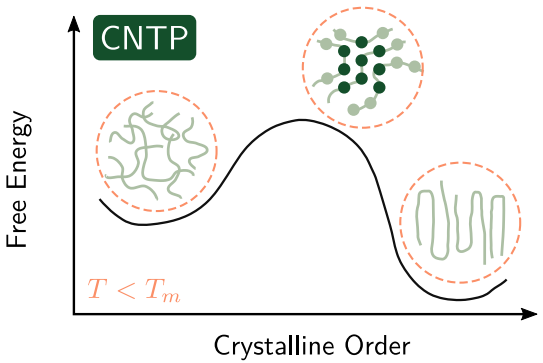
Yi et al. Macromolecules (2013)

- nucleus
- Crystal size is not only order parameter
- Crystal nucleates inside nematic droplet
- Disagrees with classical models

Hall et al. J. Phys. Chem. B. (2020)

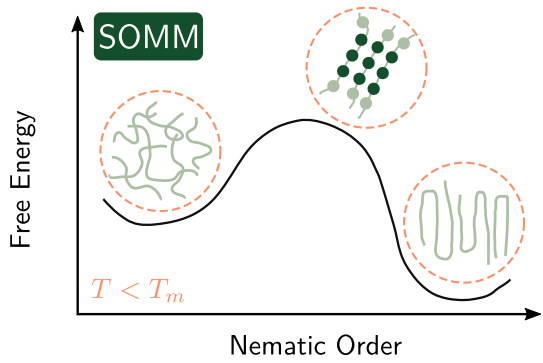
Contradictions in simulations and experiments have led to new theories

Classical Nucleation Theory for Polymers



Schultz. Polymer Crystallization. (2001)
Yi et al. J. Chem. Phys. (2009)

"SOMM" Hypothesis

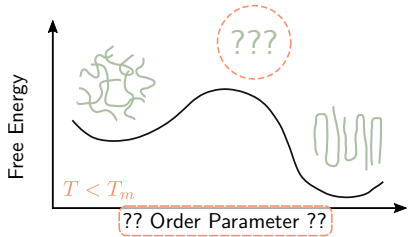


Strobl. The Physics of Polymers. (2007)
Olmsted. Phys. Rev. Lett. (1998)
Milner. Soft Matter. (2011)
Welch and Muthukumar. Phys. Rev. Lett. (2001)

A way forward? Calculate the free energy landscape (FEL)

Key idea

- All theories are based on a free energy landscape
- An FEL is a near-equilibrium concept



Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

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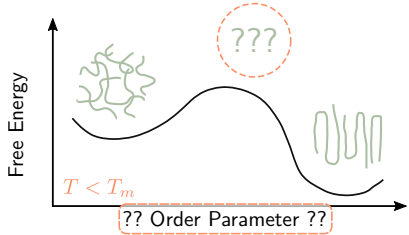
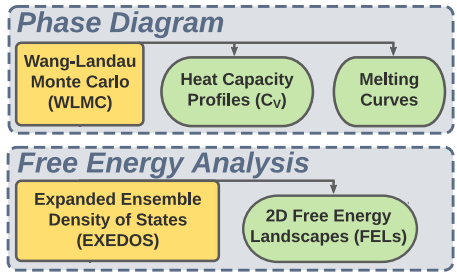


Our Approach

Use equilibrium Monte Carlo methods

- Construct a phase diagram (WLMC)
- Calculate FELs (EXEDOS)
- Study crystalline (Q_6) and nematic (P_2) order parameters



Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

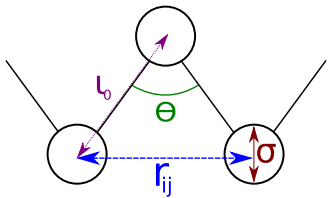
We have started with a simple model of semiflexible oligomers

$$U_{tot} = U_{hs}(r_{ij}) + U_{bond}(l) + U_{bend}(\theta)$$

$$U_{hs} = \begin{cases} \infty & r_{\mathrm{ij}} < \sigma \\ 0 & r_{\mathrm{ij}} \geq \sigma \end{cases}$$

$$U_{bond} = \begin{cases} 0 & l = l_0 \\ \infty & l \neq l_0 \end{cases}$$

$$U_{bend} = \begin{cases} -\epsilon & \theta \leq \theta_{\mathrm{s}} \\ 0 & \theta > \theta_{\mathrm{s}} \end{cases}$$



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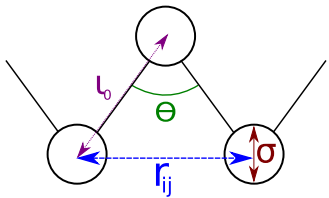
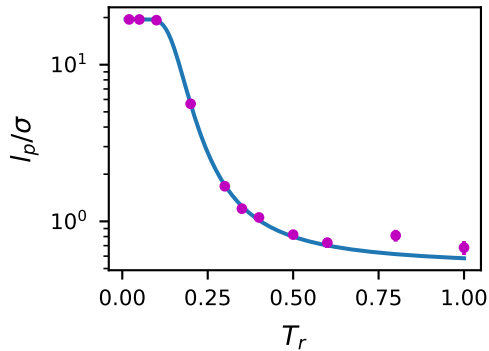
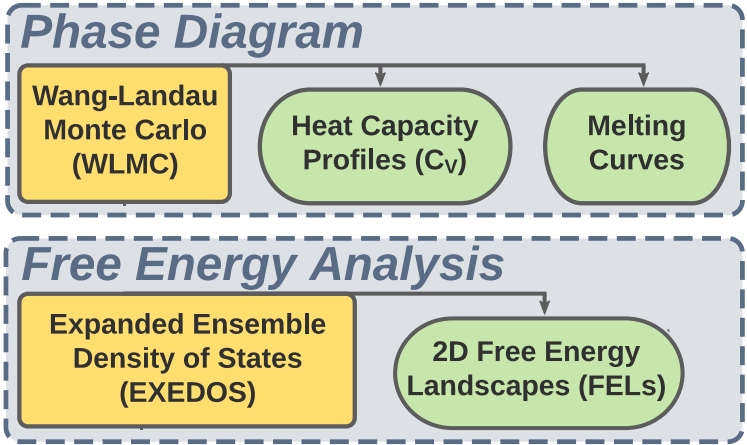


2 Degrees of Freedom

- Volume Fraction ϕ
- Reduced Temperature $T_r = kT/\epsilon$ (equivalent to persistence length l_p)



Overview



WLMC: Wang. Phys. Rev. Lett. (2001)
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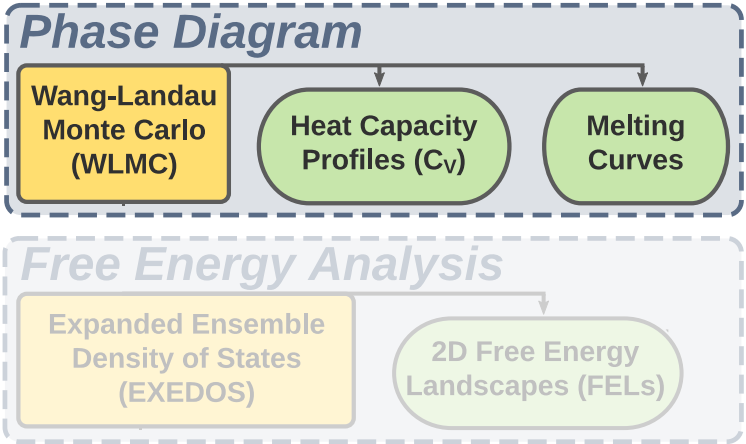

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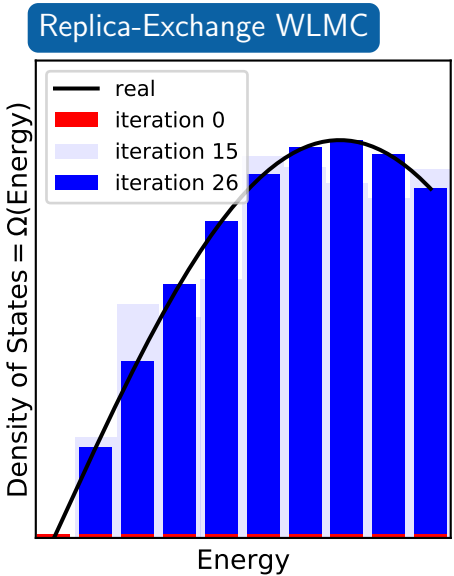
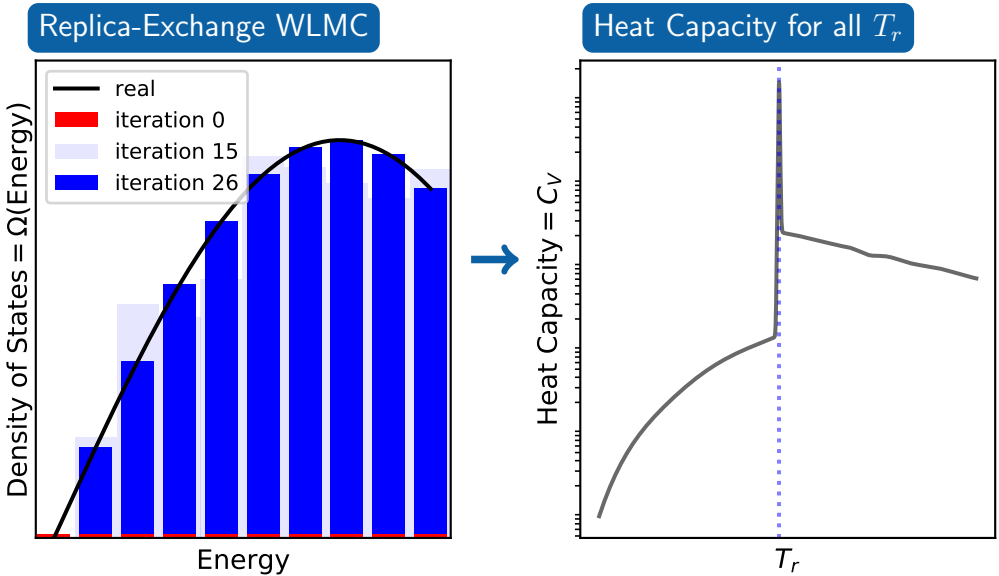
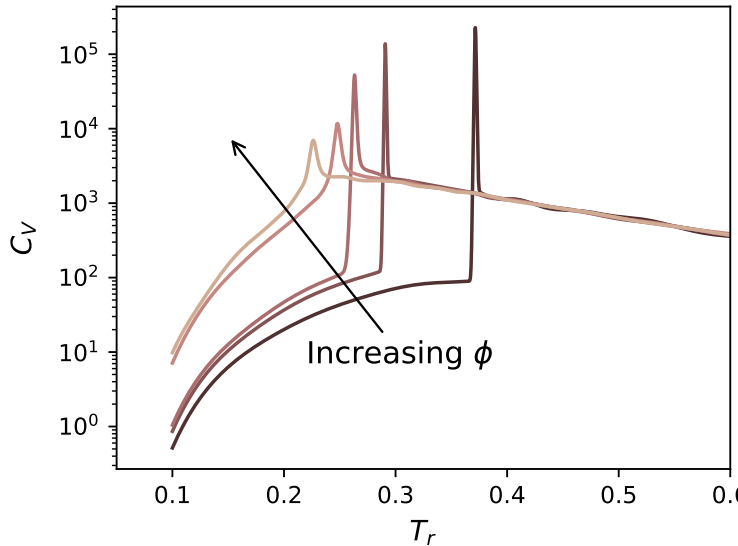
Wang–Landau captures the T-dependent thermodynamics at fixed ϕ



Wang–Landau captures the T-dependent thermodynamics at fixed ϕ

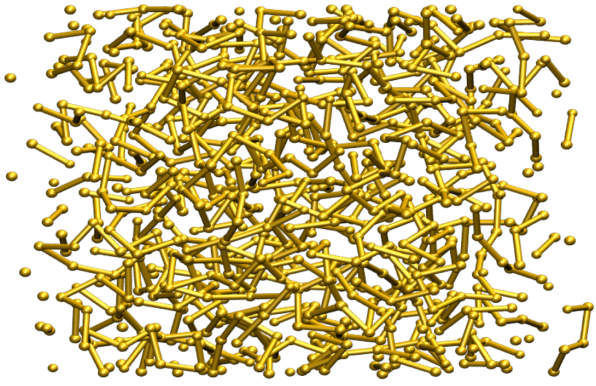


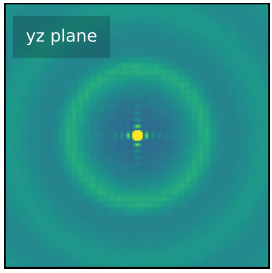
Sweeping volume fraction (ϕ) shows a single first-order phase transition

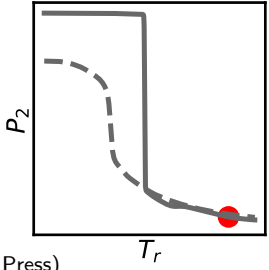


Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

At high T and all ϕ the system is an isotropic melt

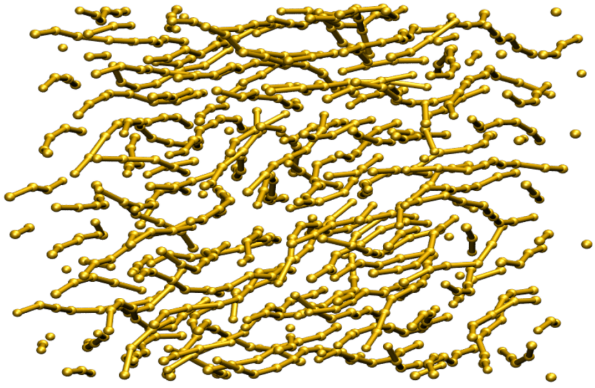


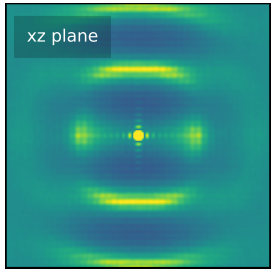


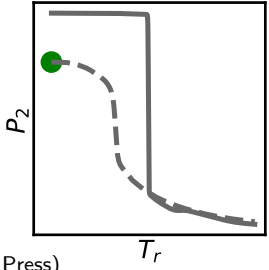


Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

At low T and low ϕ the system is nematic

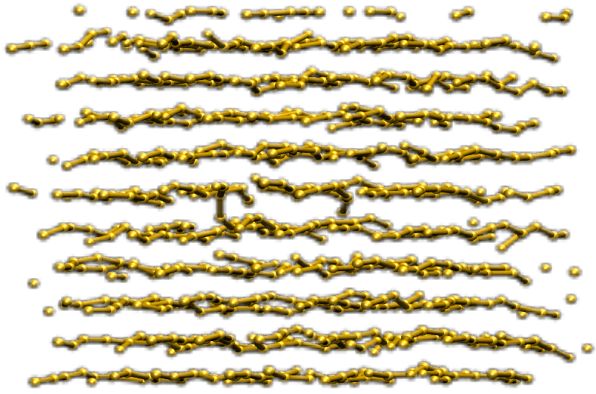


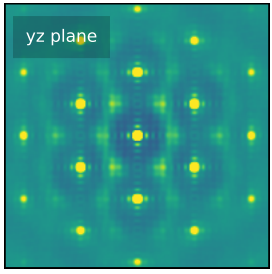


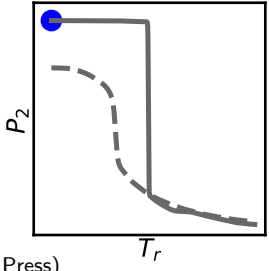


Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

At low T and high ϕ the system is crystalline

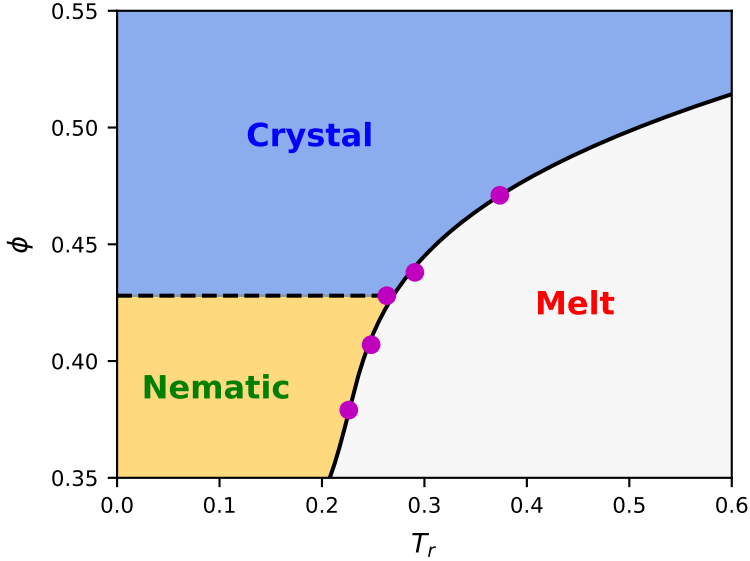






Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

Melt–nematic–crystal phase diagram



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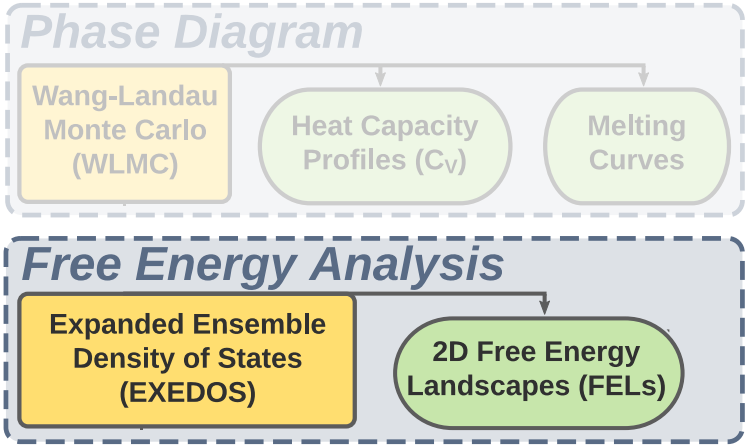

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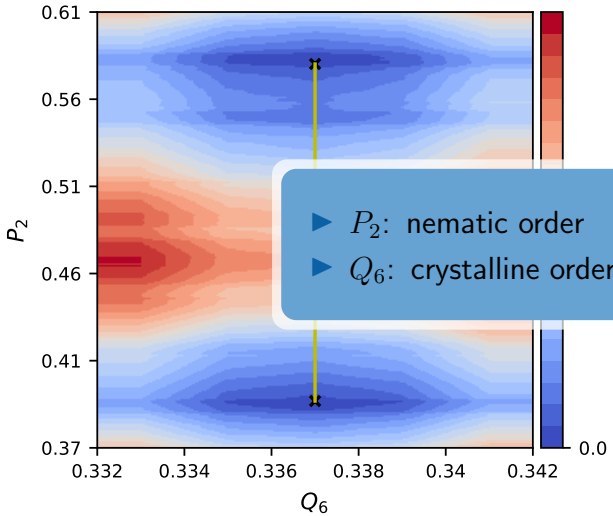
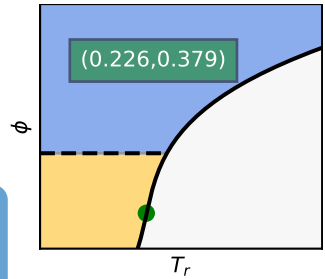
The FEL of the melt–nematic transition is along P_2



- P_2: nematic order
- Q_6: crystalline order



- Minimum Free Energy Path (MFEP)
- Melt at low P_2
- Nematic at high P_2

Fu et al. J. Chem. Inf. Model. (2020)

Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

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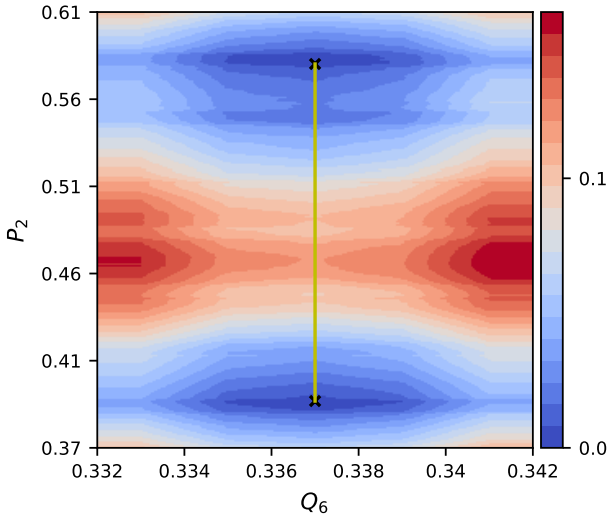

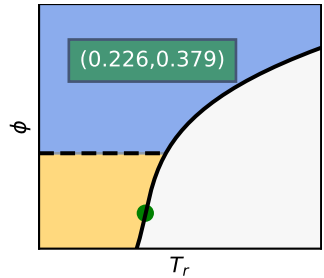

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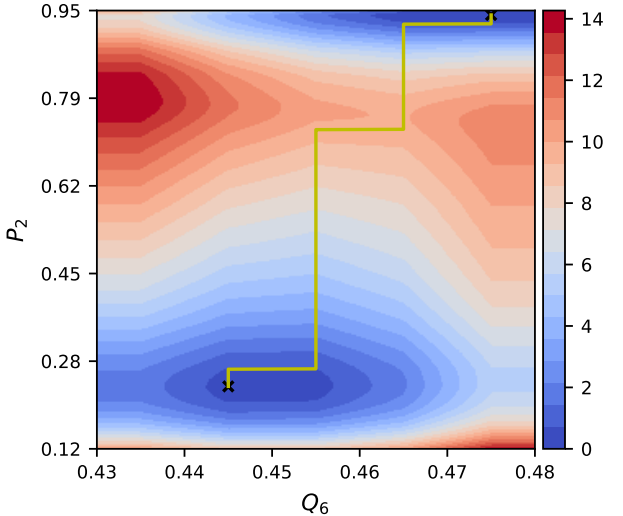
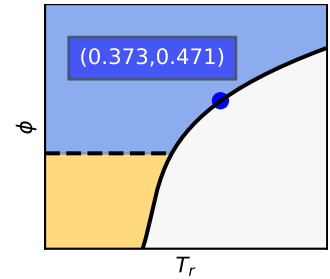
Fu et al. J. Chem. Inf. Model. (2020)

Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

The FEL of the melt–crystal transition is cooperative between P_2 and Q_6





- MFEP
- Melt at low P_2, Q_6
- Crystal at high P_2, Q_6

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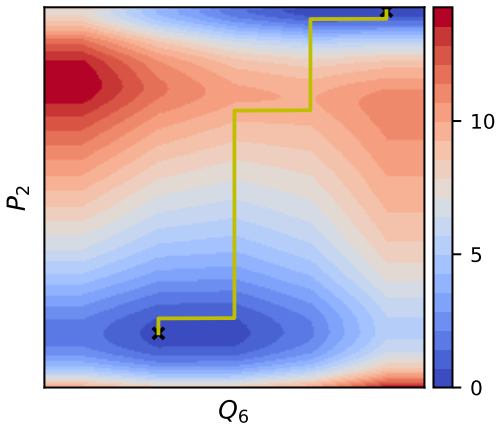
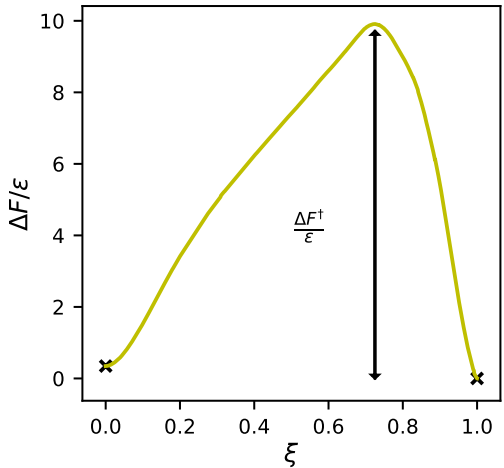
Extracting the barrier height $\Delta F^\dagger$ from the MFEP





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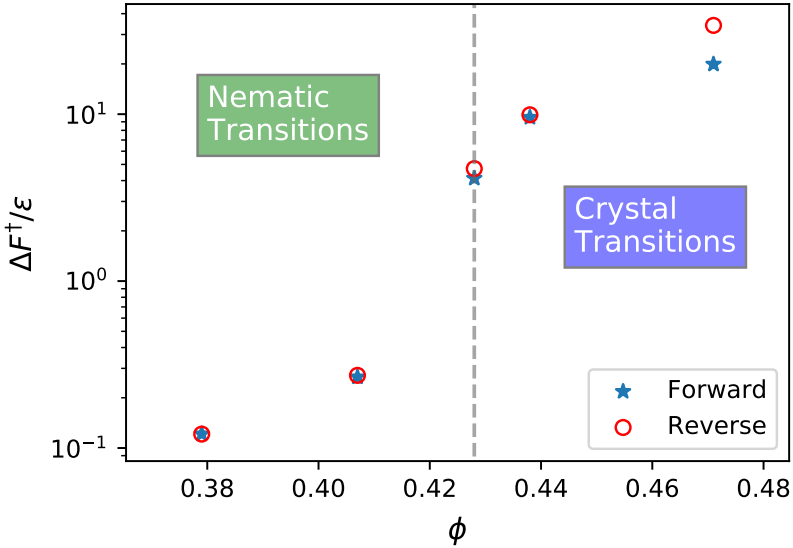
The barrier height $\Delta F^{\dagger}$ is strong function of ϕ



Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

Conclusion: "This work opens more questions than it answers"

Conclusions

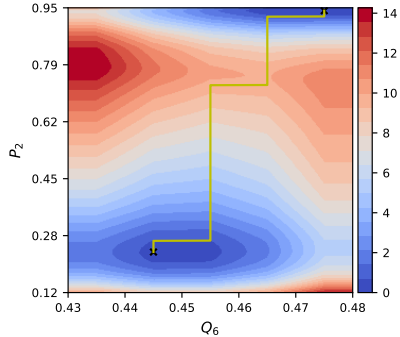
For a system of simple semiflexible oligomers:

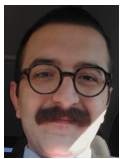
- Equilibrium FELs are valuable
- No intermediate between melt and crystal
- Nematic and positional ordering cooperate in crystallization mechanism

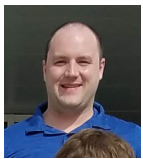
Kawak, Banks, & Tree. J. Chem. Phys. (In Press)

How general are our conclusions?

- Molecular weight?
- More complex intermolecular potentials?







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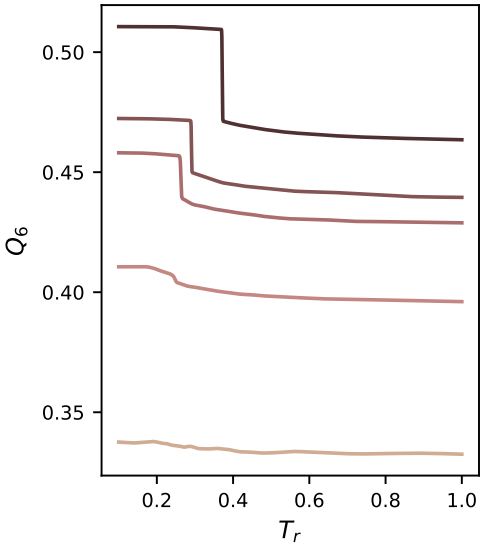
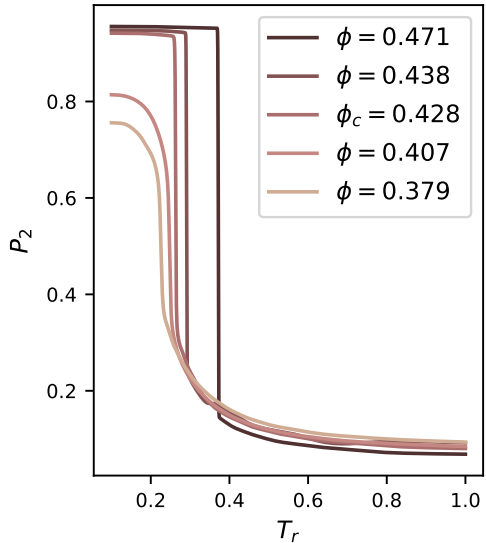
Order parameters reveal two types of transitions





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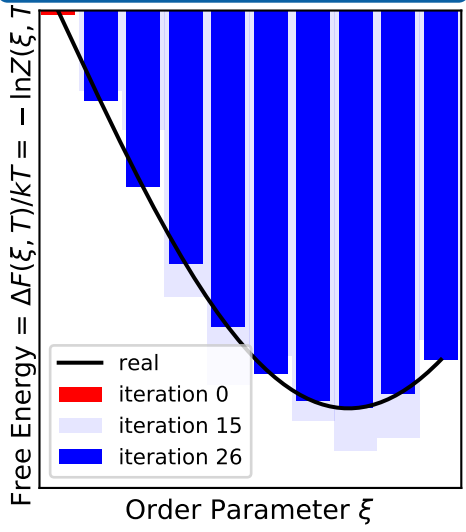
To understand interplay of Q_6 and P_2, we need 2D FELs

EXEDOS algorithm builds 1D FEL



Our algorithm incorporates 2 OPs