CompPhys 18, Leipzig, Nov. 29-30, 2018

Entropy Reduction & Entropy Driven Folding for Confined Polymers

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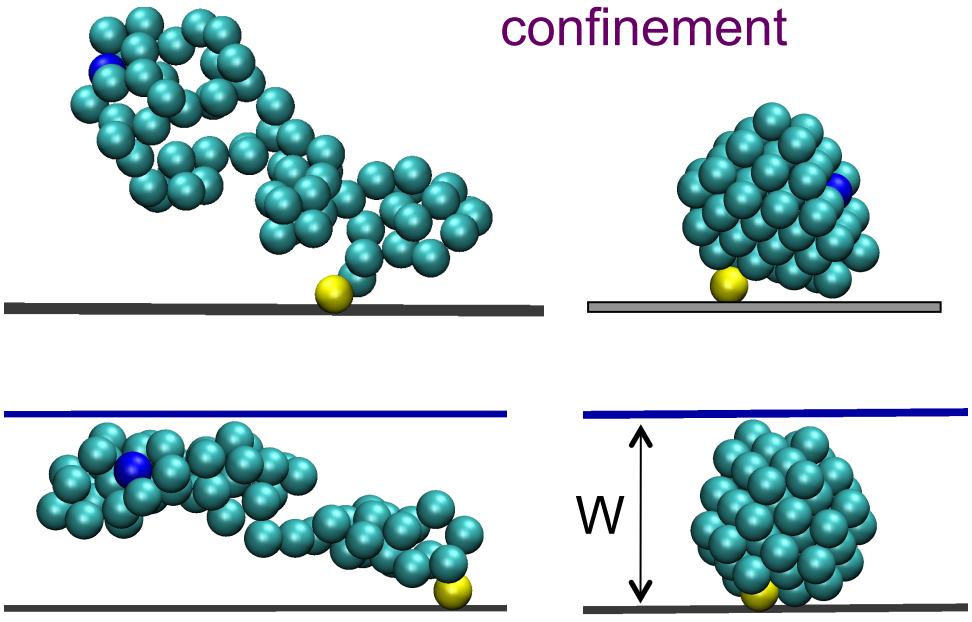
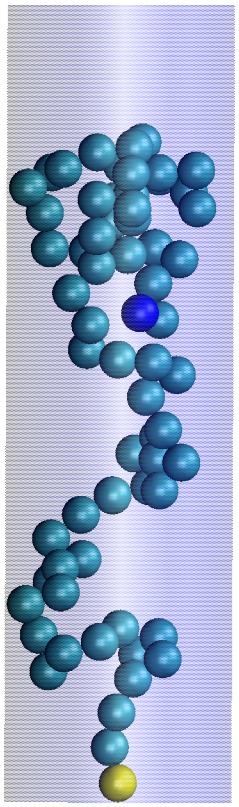
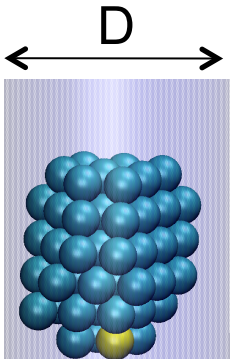
geometric (hard wall) confinement

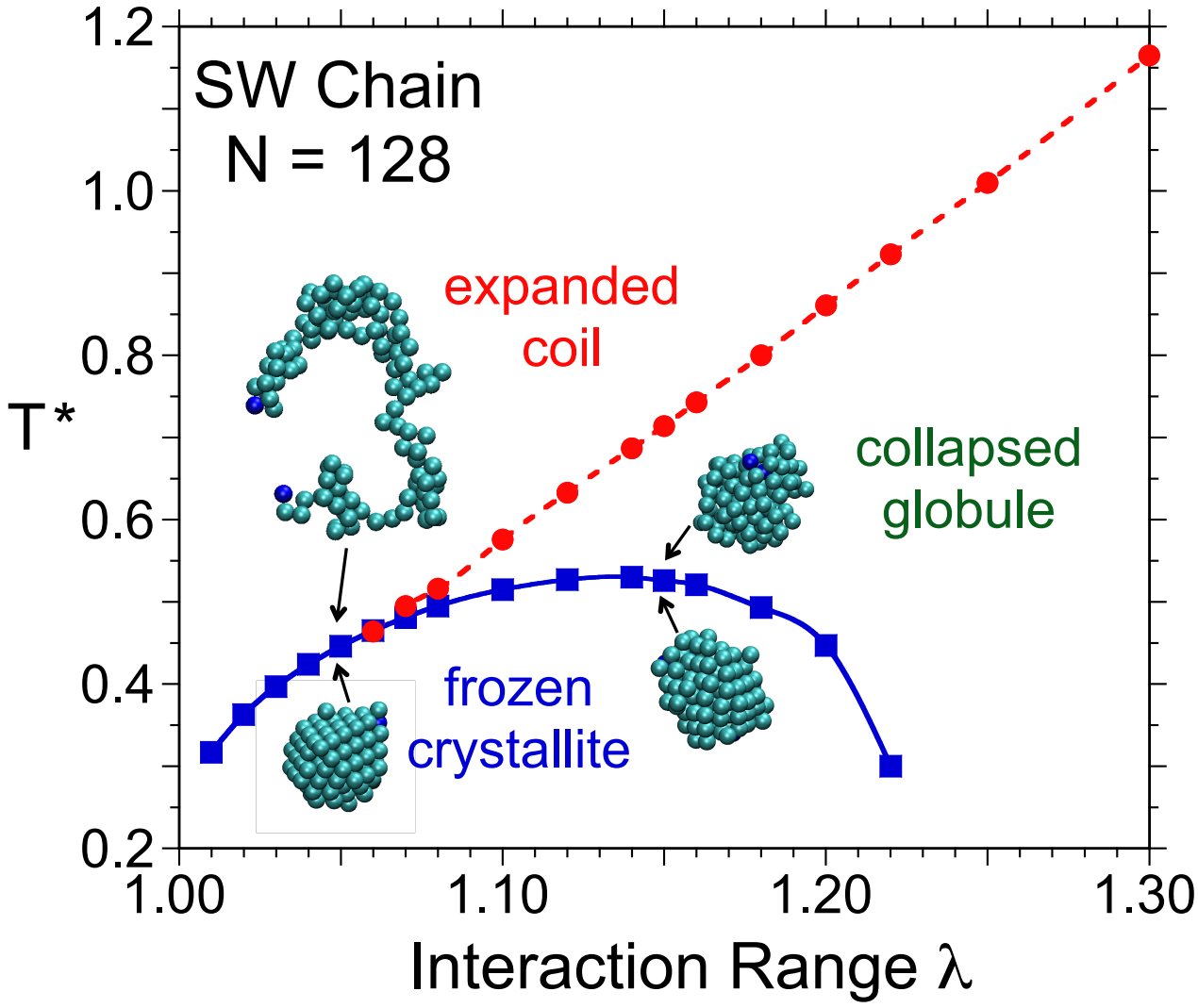




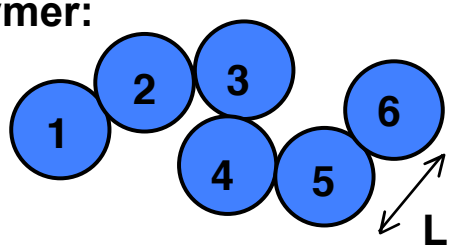
$S = k_B \ln \Omega$



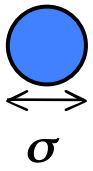
Phase Diagram for a Square-Well-Sphere Polymer



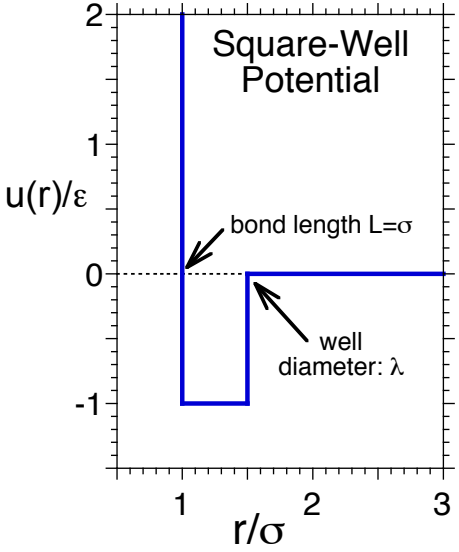
Polymer:



built from simple monomers:

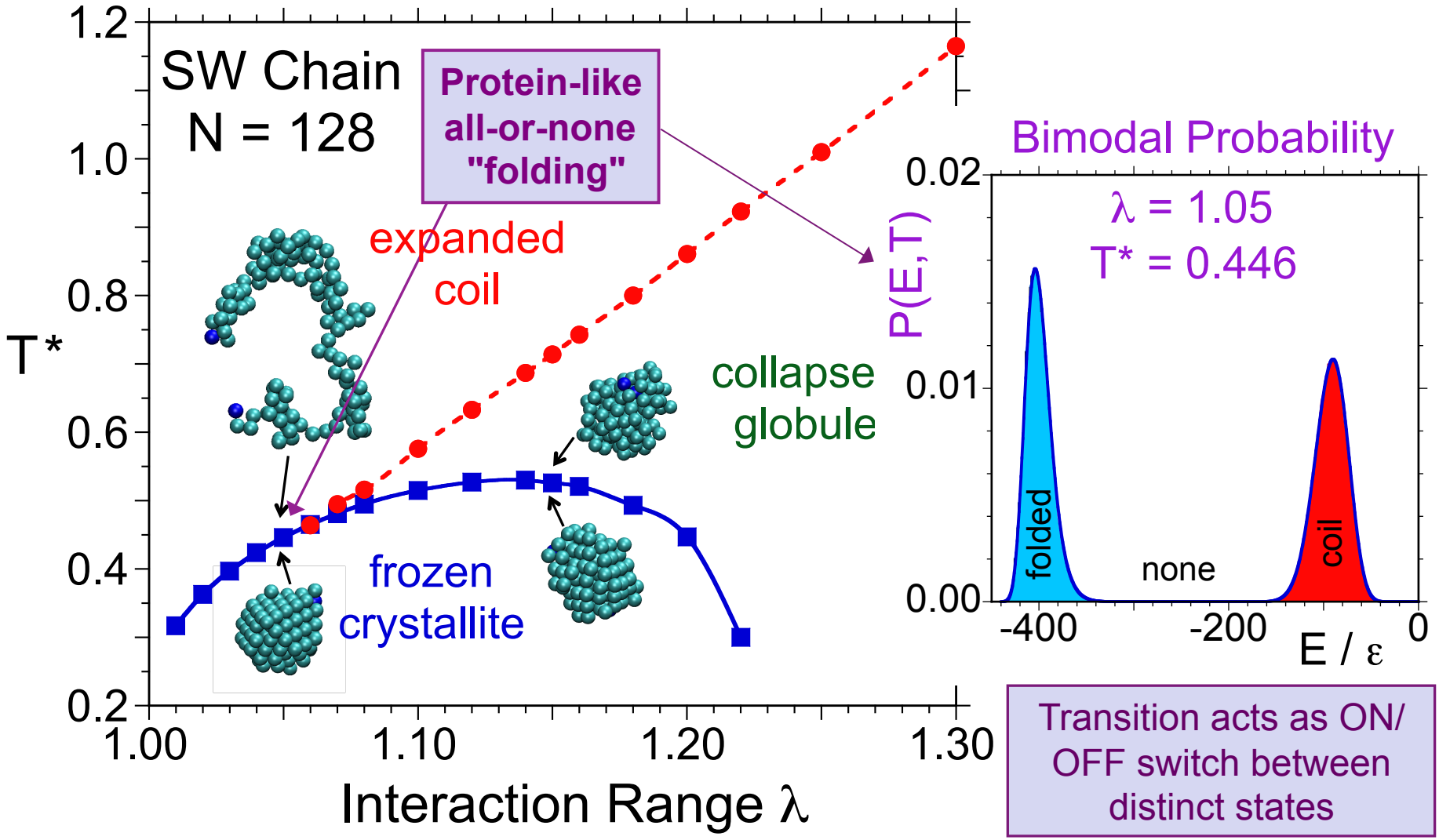


monomer-monomer interaction



Taylor, Paul, & Binder, J. Chem. Phys. **131**, 114907 (2009);
J. Chem. Phys. **145**, 174903 (2016).

Phase Diagram for a Square-Well-Sphere Polymer



Transition acts as ON/ OFF switch between distinct states

Taylor, Paul, & Binder, J. Chem. Phys. **131**, 114907 (2009);
J. Chem. Phys. **145**, 174903 (2016).

Density of States and Wang-Landau Sampling I

SW Chain Model has a discrete energy spectrum: $\mathbf{E_n = n\varepsilon}$

Density of States:

$g(E_n)$ = volume of configurational phase space for energy state E_n

Thermodynamics:

microcanonical entropy:

$S(E) = k_B \ln g(E)$

canonical partition function:

$Z(T) = \sum g(E) \exp(-E/k_B T)$

See also:

Yan & de Pablo, PRL **90**, 035701 (2003)

Schneider, Mueller, Janke, Comp. Phys. Comm. **216**, 1 (2017)

Wang-Landau algorithm* ... an iterative simulation method to compute $\mathbf{g(E_n)}$:

Starting w/ $\mathbf{g(E_n)=1}$, $\mathbf{H(E_n)=0\ \forall\ n}$, $\mathbf{f_0 = e}$

Generate sequence of chain conformations using acceptance criteria:

$$P_{acc}(a \to b) = \min\left(1, \frac{g(E_a)}{g(E_b)}\right)$$

iterate m levels

we use m=30

Update DOS: $\mathbf{g(E_n) \to f_m\, g(E_n)}$

Update visitation histogram: $\mathbf{H(E_n) \to H(E_n)+1}$

When histogram ~flat ...

reduce modification factor: $\mathbf{f_{m+1} = (f_m)^{1/2}}$

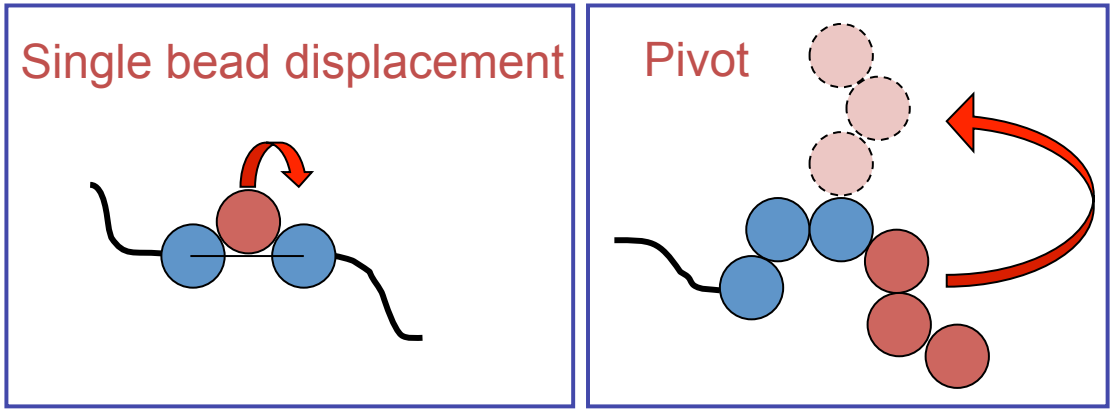
reset histogram to zero: $\mathbf{H(E_n) = 0\ \forall\ n}$

***Wang & Landau, PRL 86, 2050 (2001); PRE 64, 056101 (2001).**

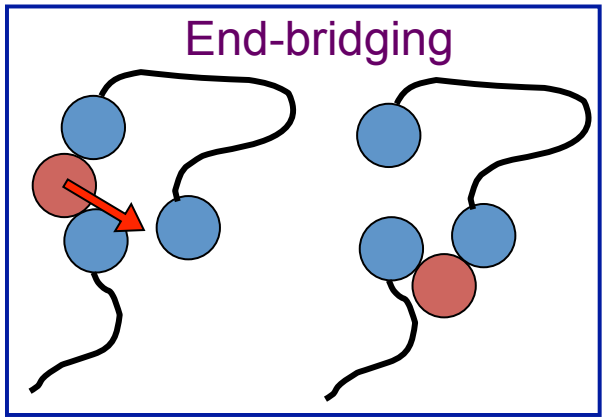
Wang-Landau Sampling II – MC Move Set

Success of the WL methods depends on underlying MC move set

These moves sample most of configuration space:

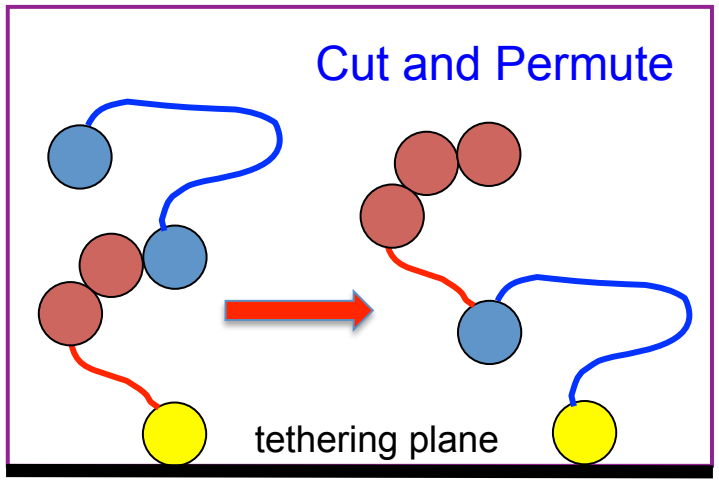


To achieve highly compact conformations:



Escobedo & de Pablo, JCP **102**, 2636 (1995)

For good sampling near the tethering point:

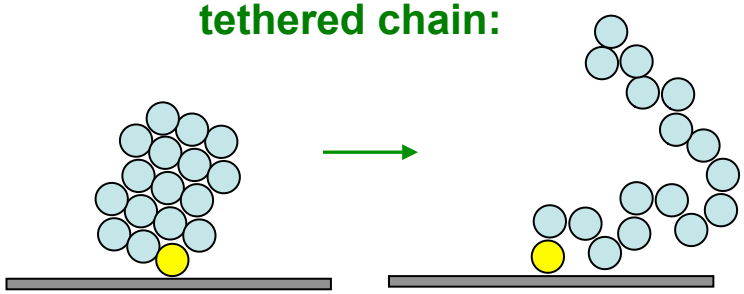


This move swaps upper/lower segments while preserving chain end-to-end vector.

Causo, J. Stat. Phys. **108**, 247 (2002)

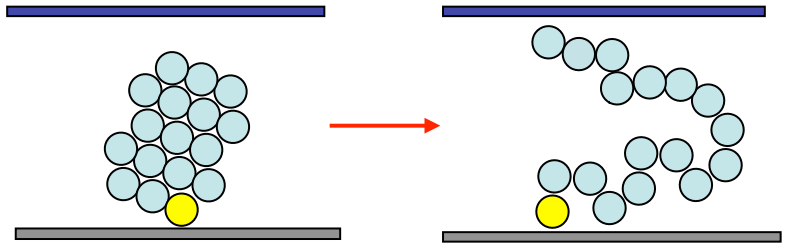
Confined Chain: What do we expect?

unfolding of a tethered chain:

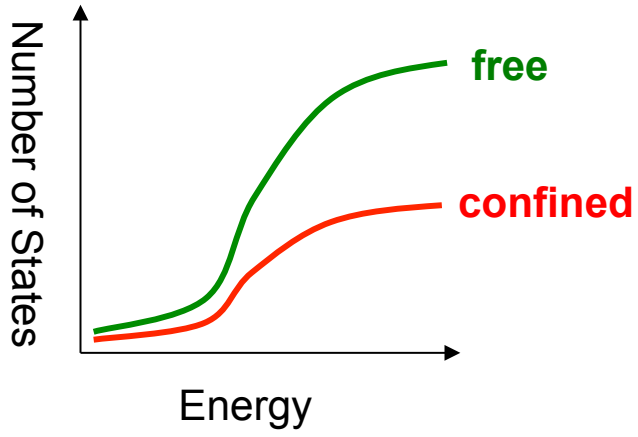


"few" states many states

unfolding of a confined chain:



"few" states many states ... BUT, **MANY** now excluded



entropy reduction: $\ln(g_{confined} / g_{free})$

Fewer states to "unfold into" shifts equilibrium towards folded state:

Entropic Stabilization of Folded State

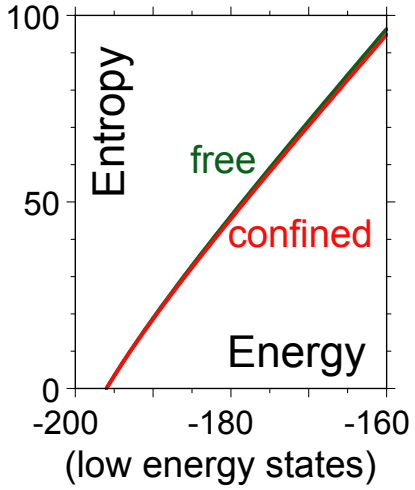
Minton, Biophys. J. **78**, 101 (2000)

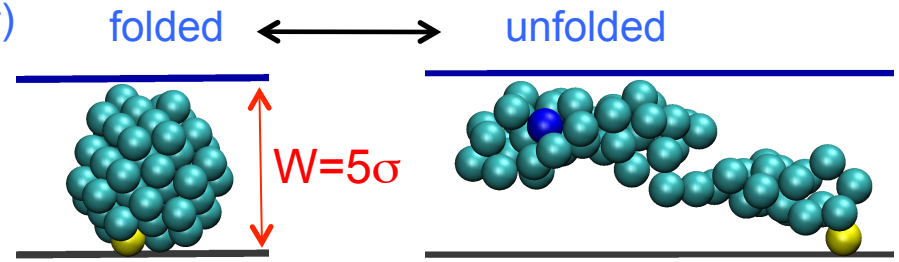
Zhou and Dill, Biochem. **40**, 11289 (2001)

Confinement effects for Square-Well Chain

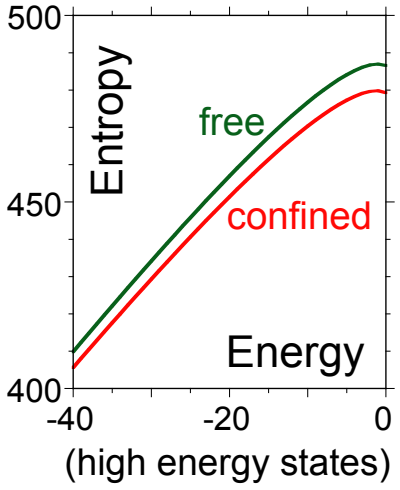
Unfolding of a tethered chain (N=64) in a slit:

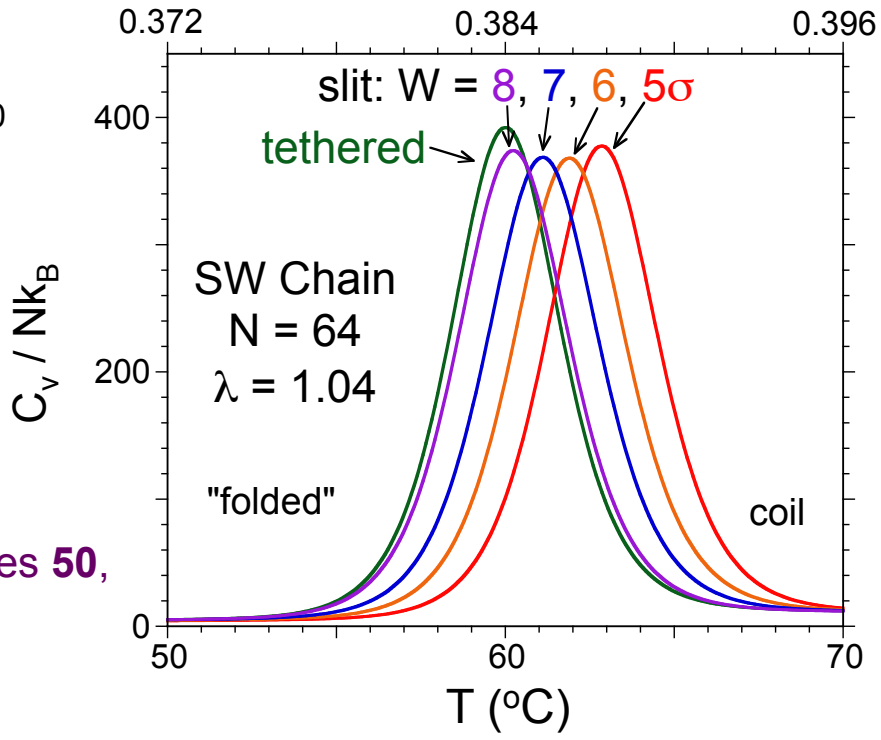
Upper wall does not affect **folded** ensemble (W≥5σ)





Entropy reduction for **unfolded** ensemble

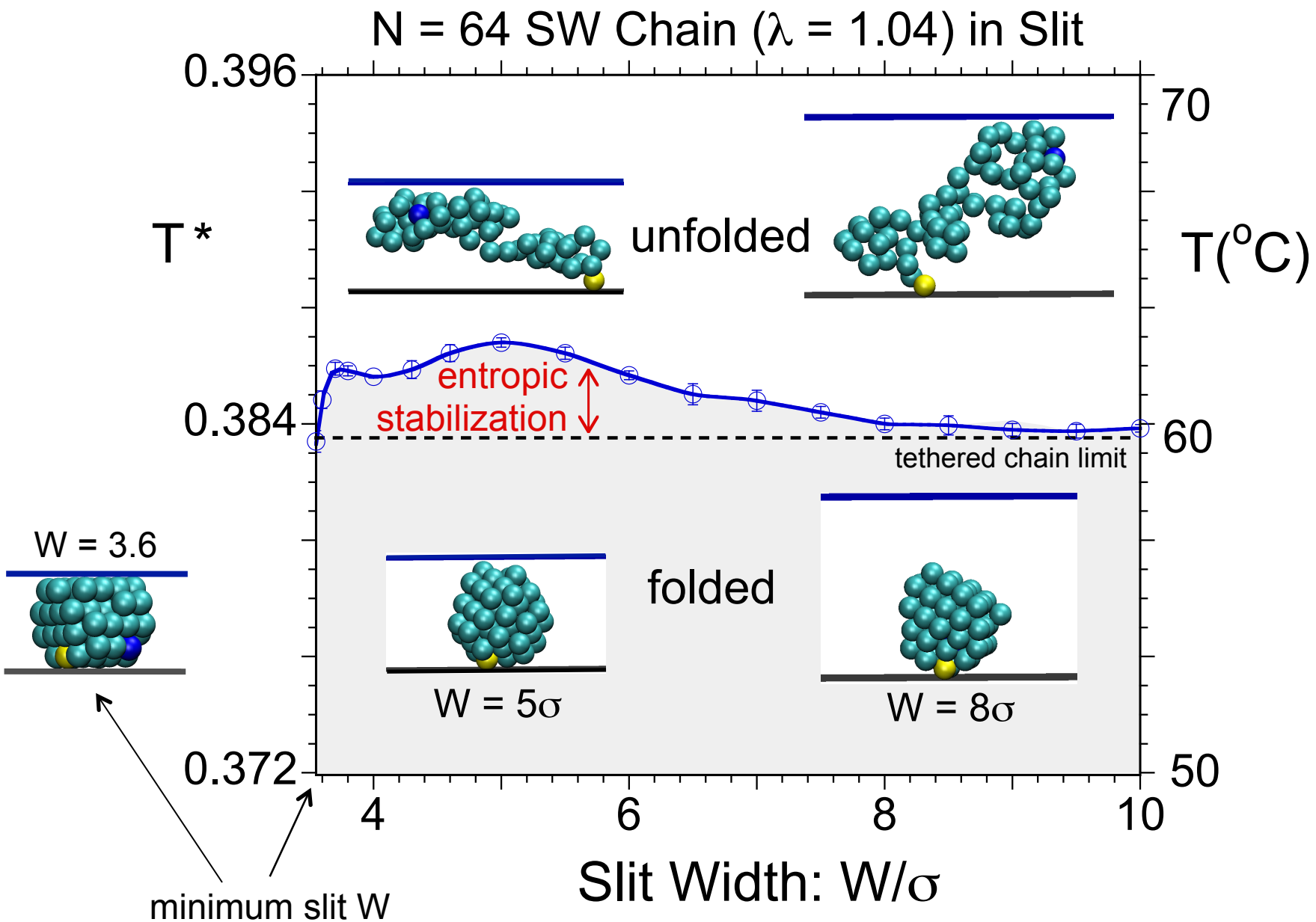




transition shifted to higher T ...

expected result for **entropic stabilization**

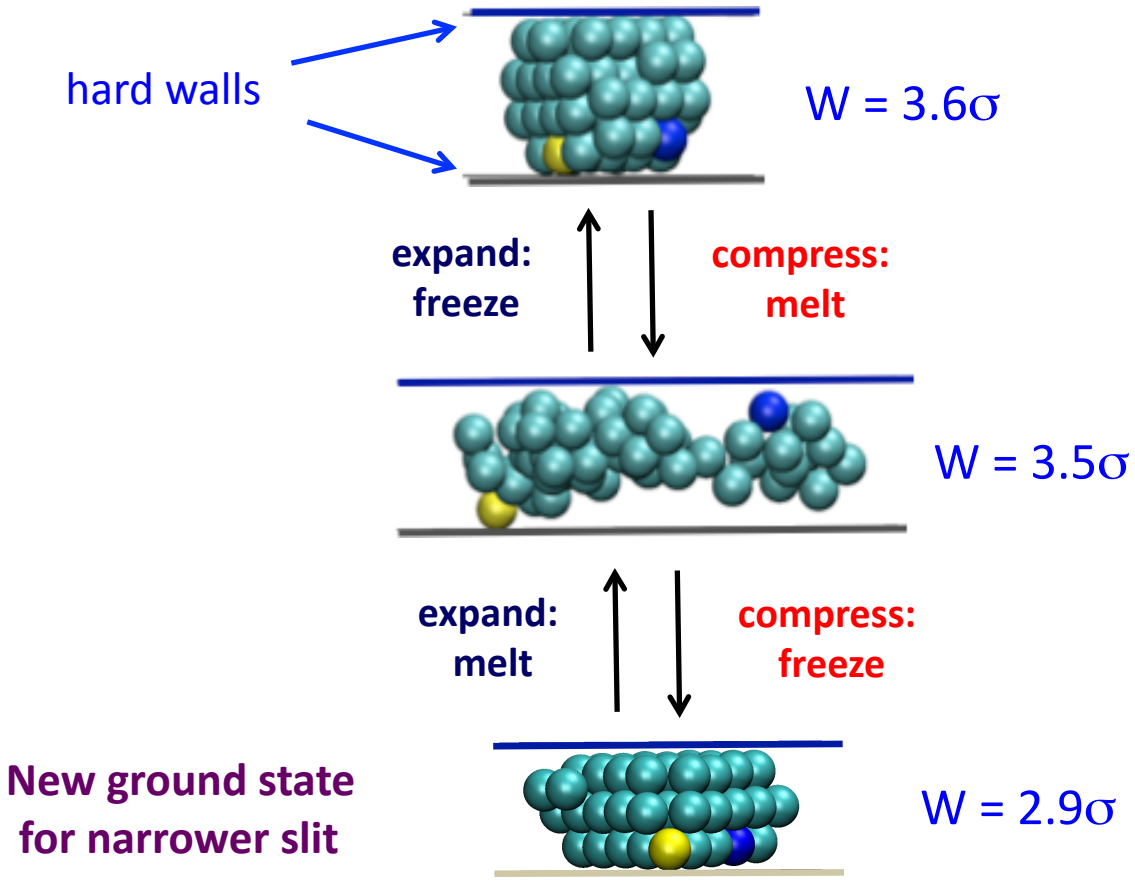
Taylor, Macromolecules **50**, 6967 (2017)

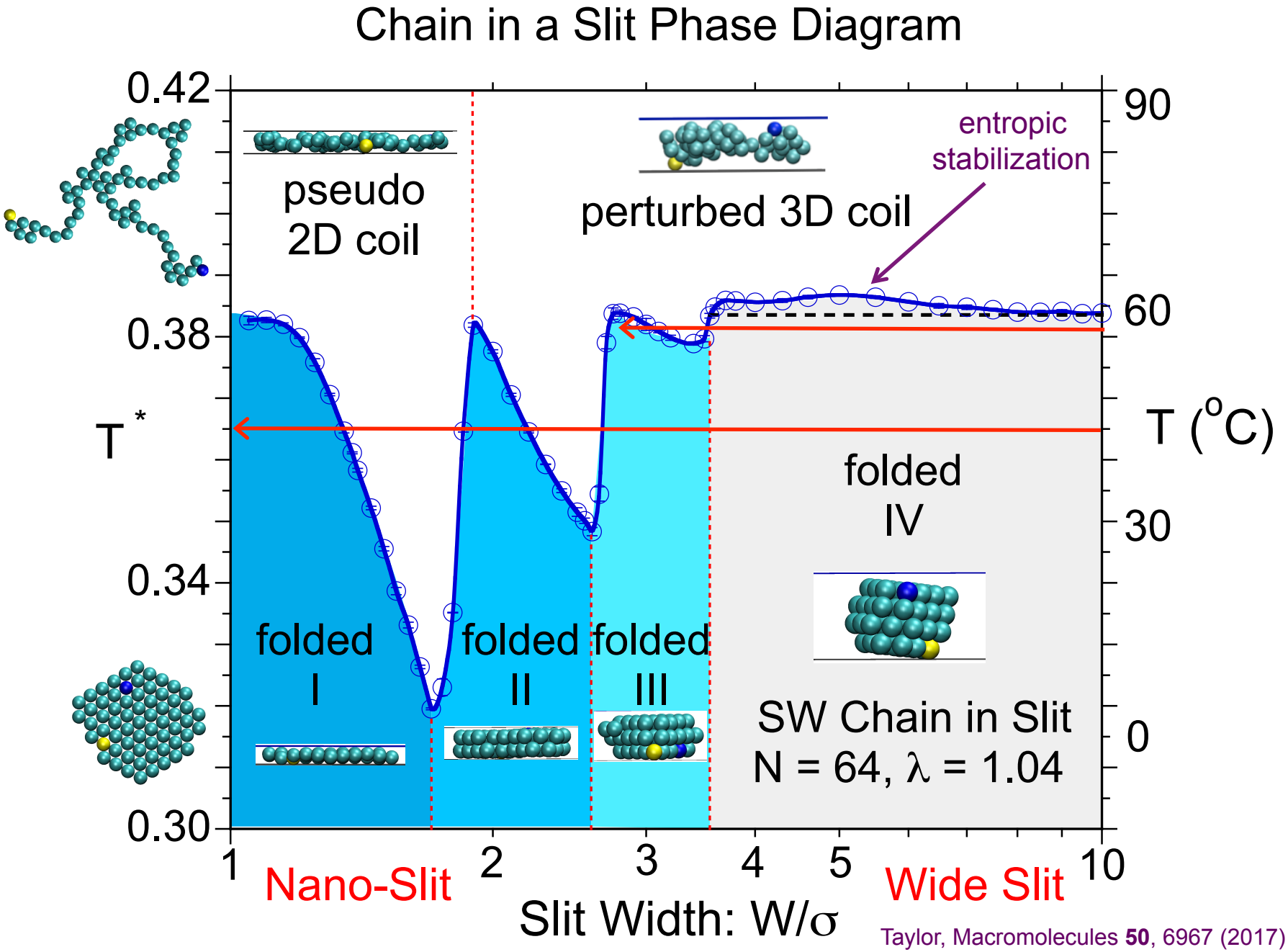


Taylor, Macromolecules **50**, 6967 (2017)

Confinement can drive conformational transitions

Polymer in a slit:
Isothermal melting/freezing (T* = 0.383)

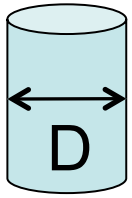


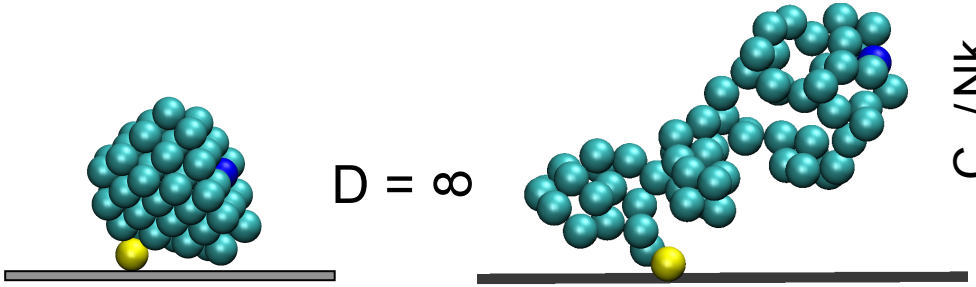


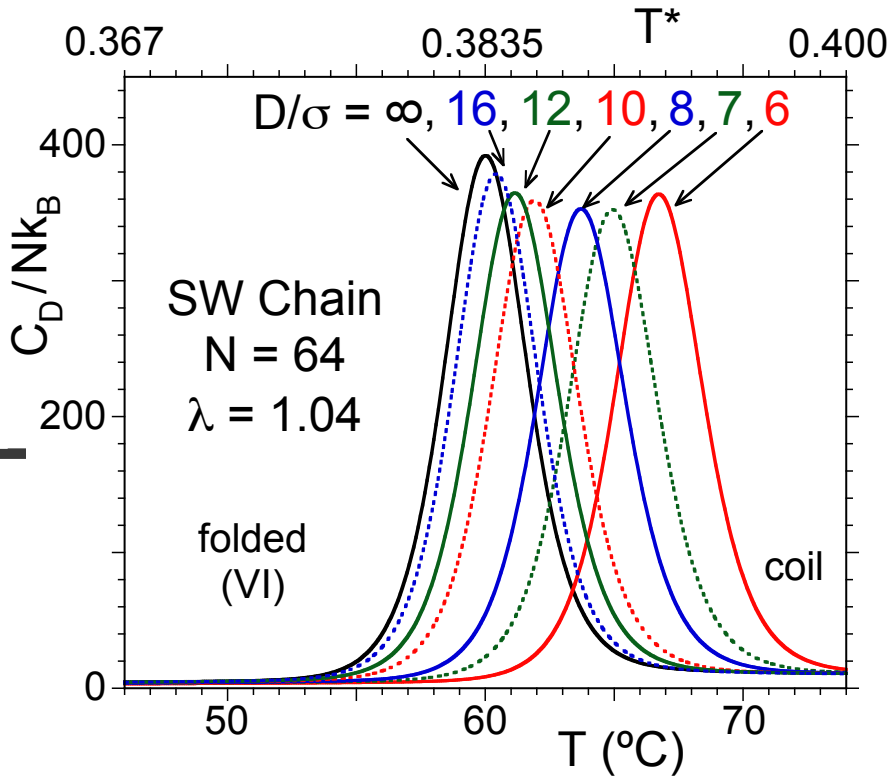
Taylor, Macromolecules **50**, 6967 (2017)

Cylindrical Confinement & Entropic Stabilization

N = 64 SW Chain
(λ = 1.04) in a Cylinder

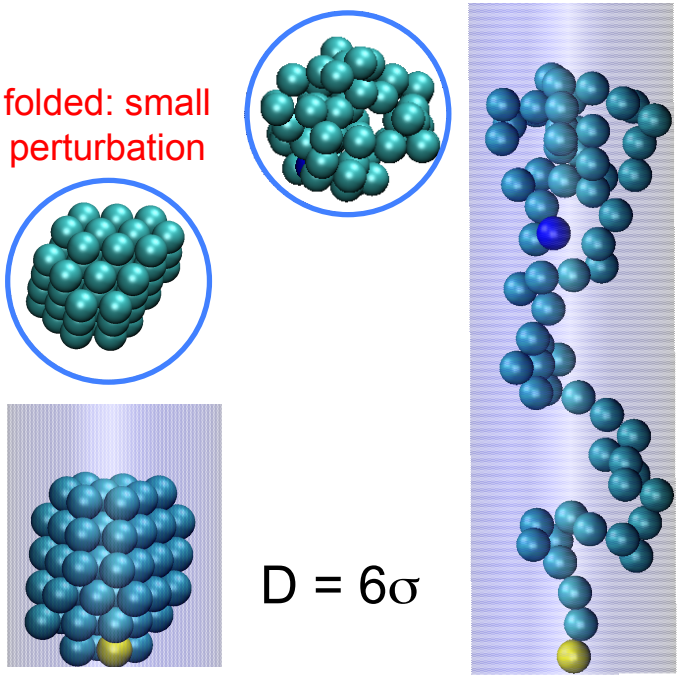






unfolded: large perturbation

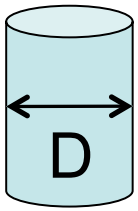
folded: small perturbation

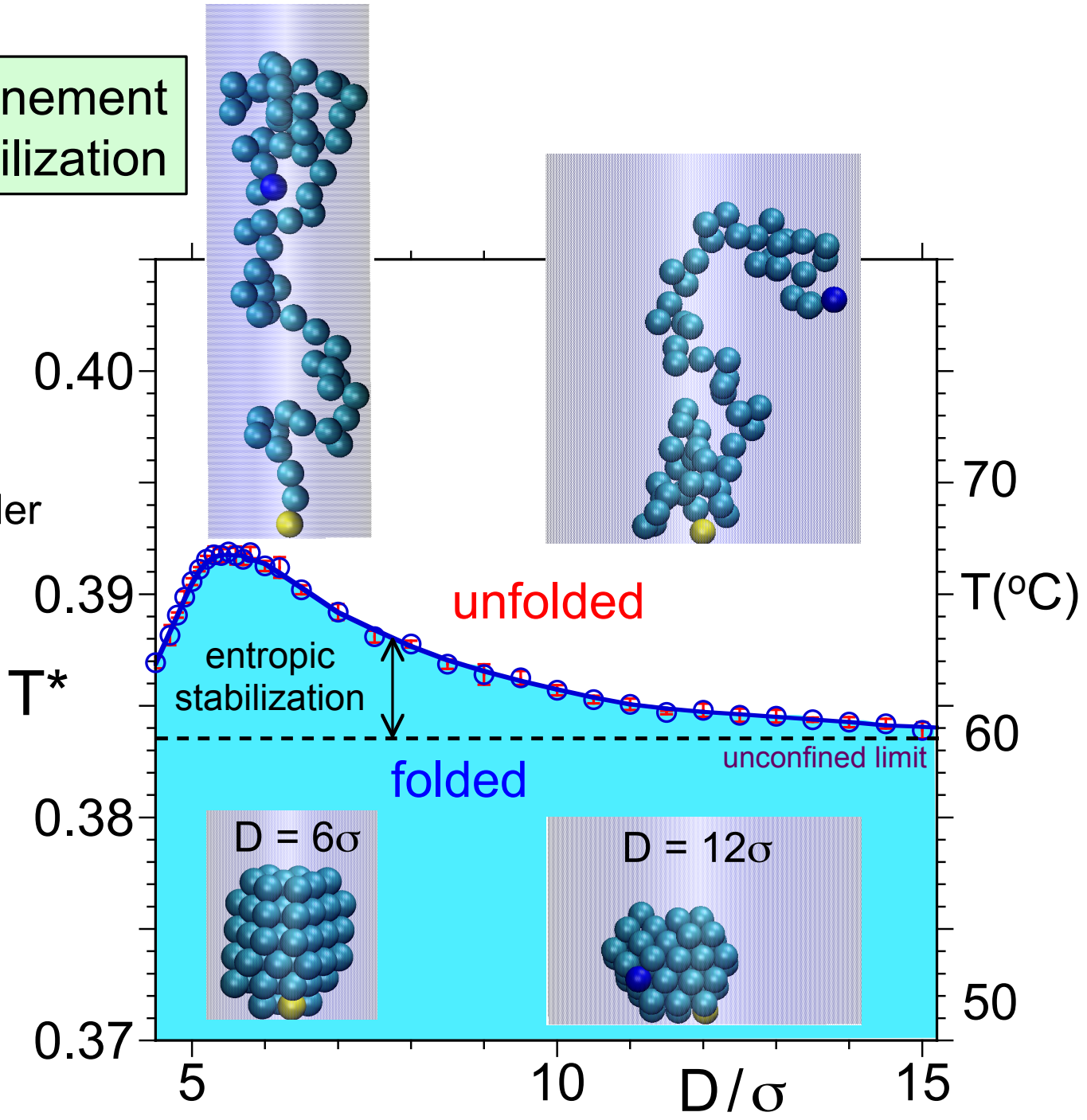


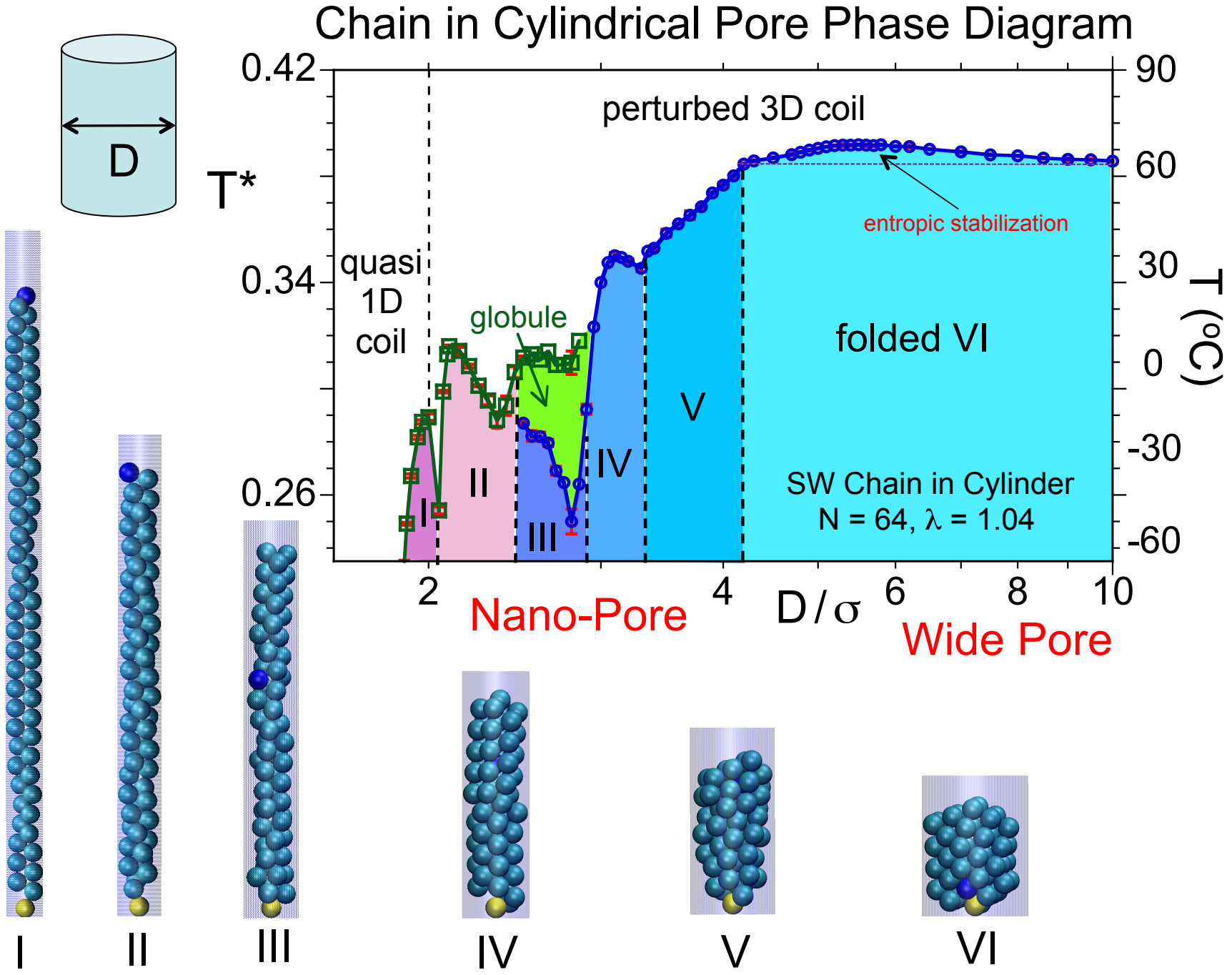
Christian O'Neil Troy Prunty

Cylindrical Confinement & Entropic Stabilization

N = 64 SW Chain
(λ = 1.04) in Cylinder

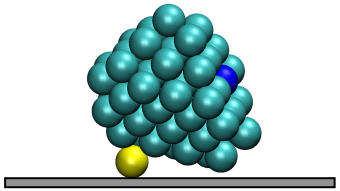




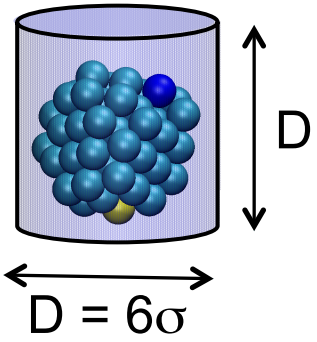

Chain in Cylindrical Pore Phase Diagram
D
T*
0.42
0.34
0.26
90
60
30
0
-30
-60
T (°C)
perturbed 3D coil
quasi
1D
coil
globule
folded VI
entropic stabilization
SW Chain in Cylinder
N = 64, λ = 1.04
I
II
III
IV
V
2
4
6
8
10
D / σ
Nano-Pore
Wide Pore
I
II
III
IV
V
VI

Chain in a Cylindrical Box (3D confinement)

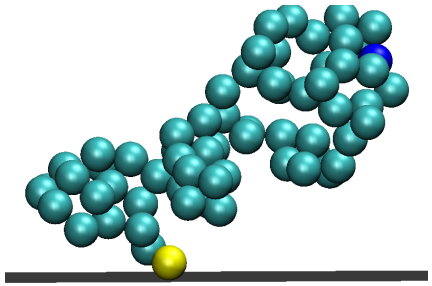
folded: small perturbation

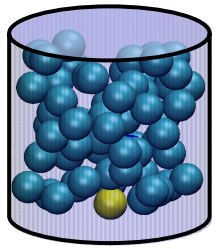


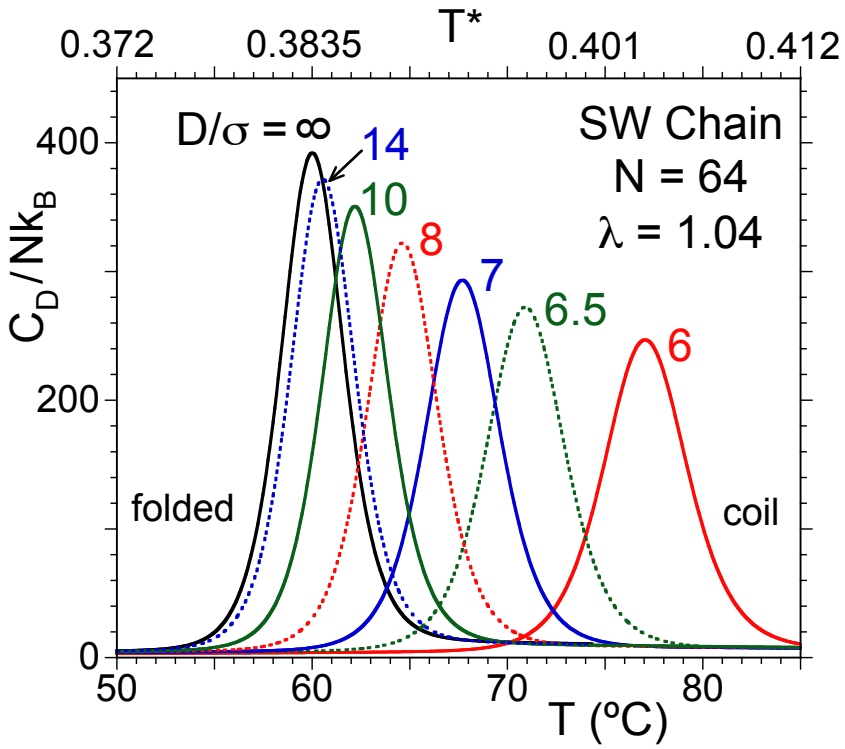
D = ∞



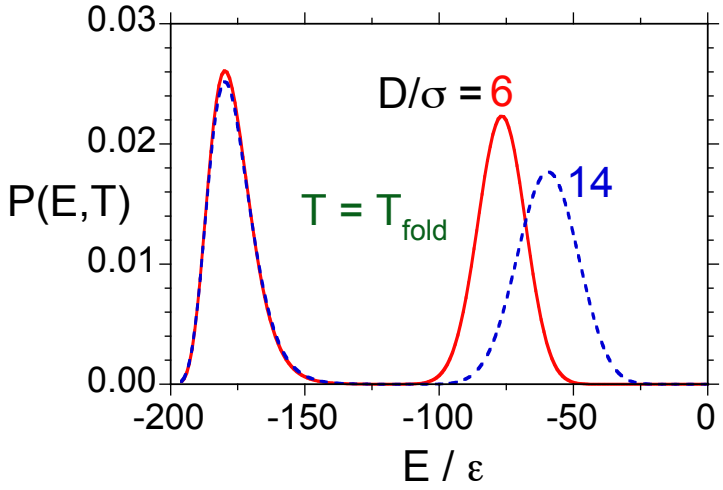
unfolded: large perturbation







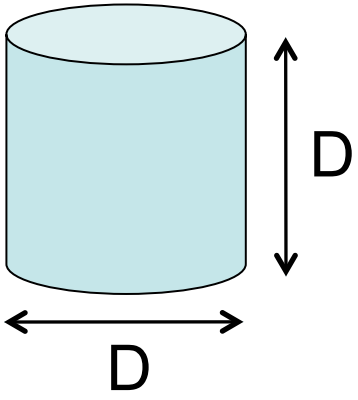
Probability distribution at transition:
Bimodal, even in strong confinement
... 1st order like transition

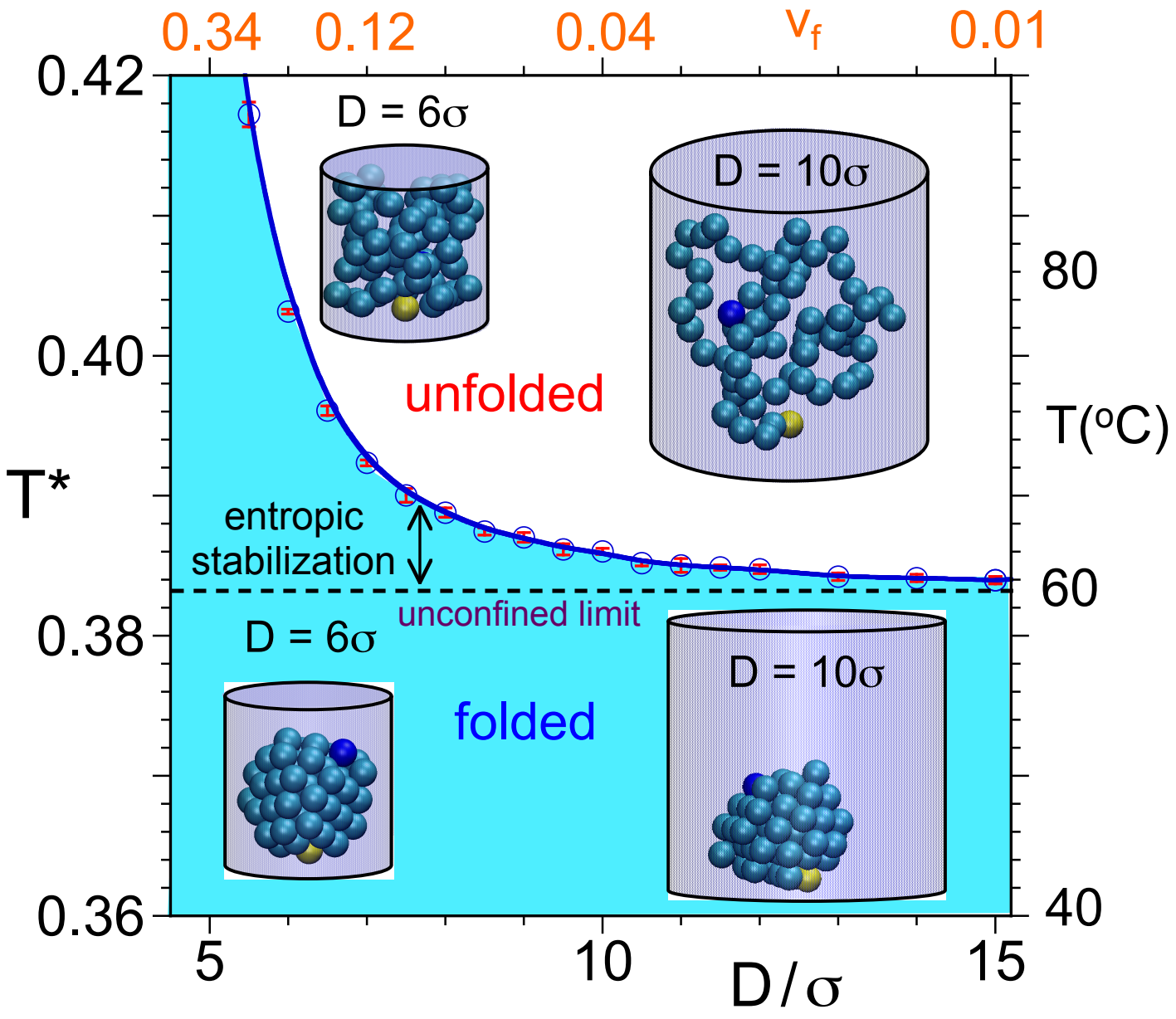


For chain collapse in Spherical Confinement see:
Marnez et al., Conds. Matt. Phys. (2012)
Marnez & Janke, Physics Procedia (2014)

3D Confinement: Folding in a Cylindrical Box (D=H)

N = 64
SW Chain
(λ = 1.04)





Entropy reduction for a confined hard-sphere chain

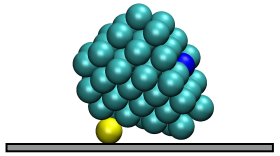
HS-chain free energy (entropy) is given by the SW-Chain density of states:

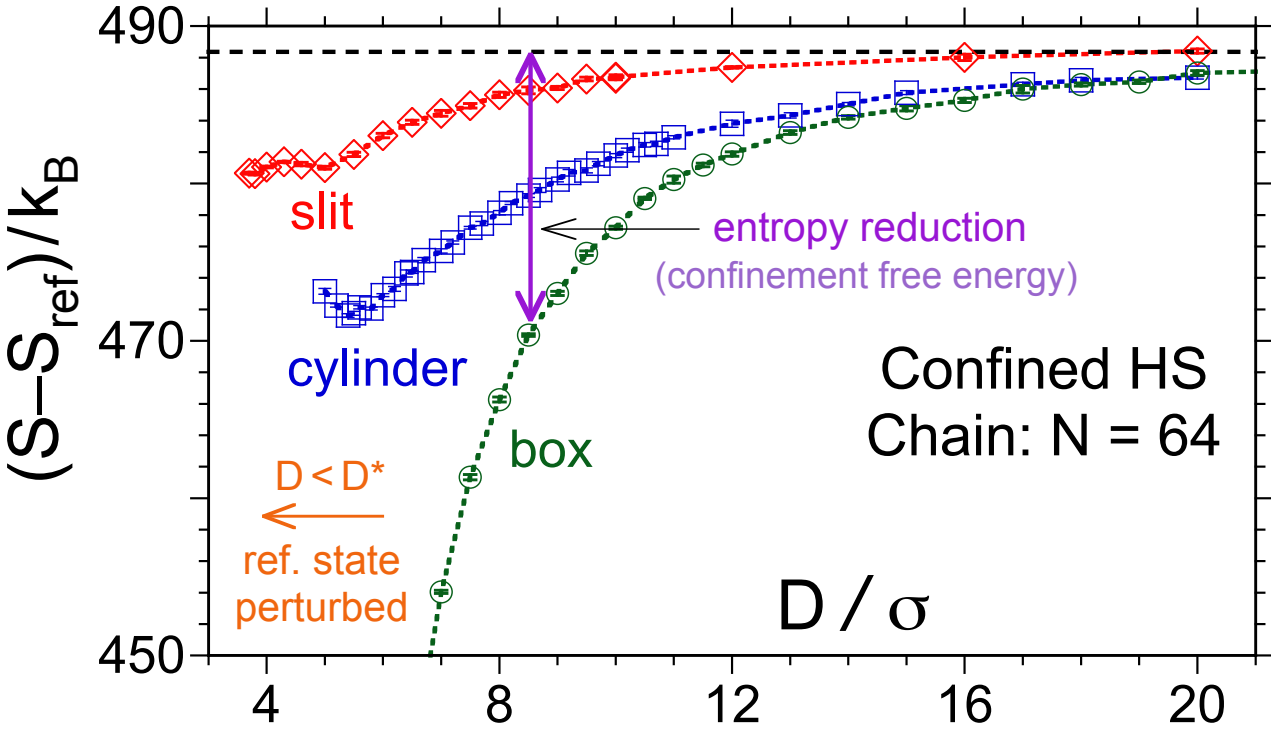
$$Z_{SW}(T) = \Sigma\, g(E)\, e^{-E/kT}$$

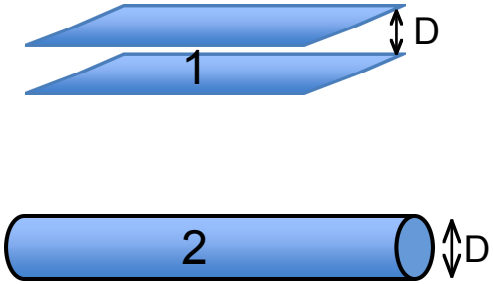
$$T \to \infty \quad \ldots \quad Z_{HS} = \Sigma\, g(E)$$

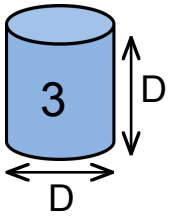
$$\ln Z_{HS} = -\beta F_{HS} = S_{HS}/k_B$$

In WL we compute $g(E)/g(E_{ref})$ ... reference state used here:

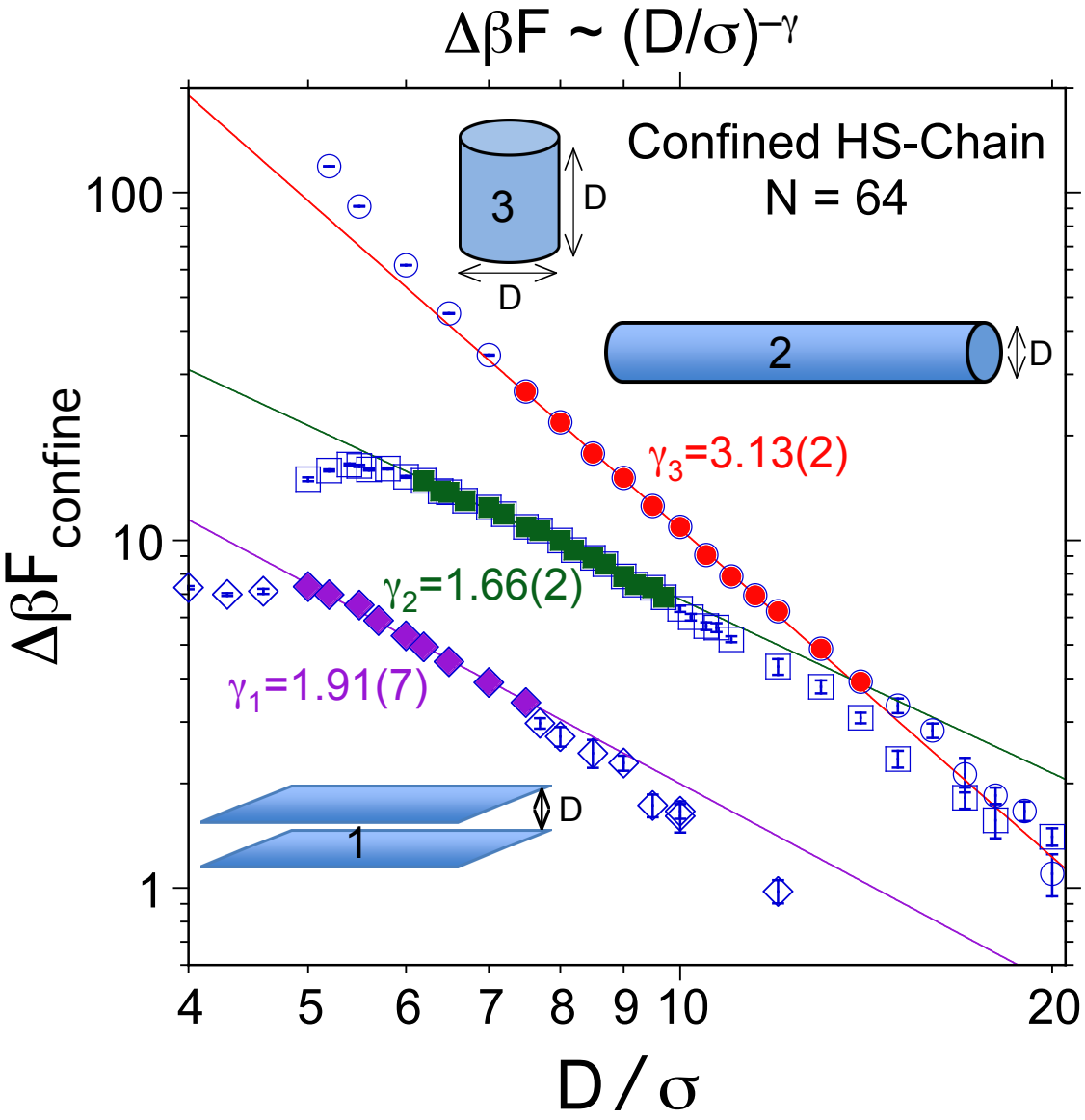








Confinement Free Energy: Scaling Properties*



Scaling regime: $D^* < D < 2R_g$

For 3D confinement $\rho \sim N/D^3$
Density expansion gives:

$$\Delta\beta F \sim N\rho\sigma^3 \sim N^2 (D/\sigma)^{-\gamma}$$

$$\gamma \approx 3$$

Cylinder / Slit set blob size ≈ D
Scaling analysis gives:

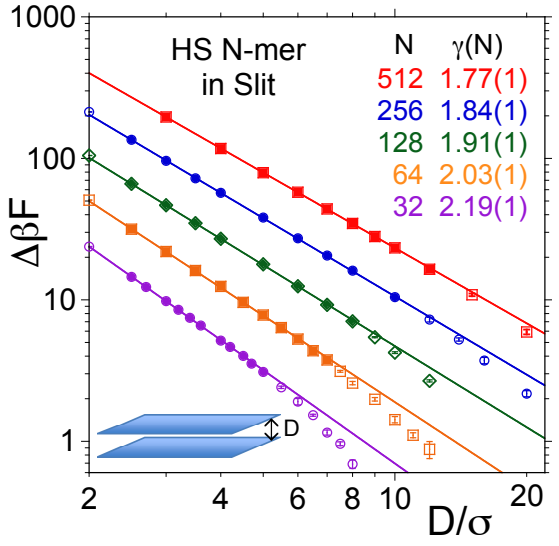
$$\Delta\beta F \sim N (D/\sigma)^{-\gamma}$$

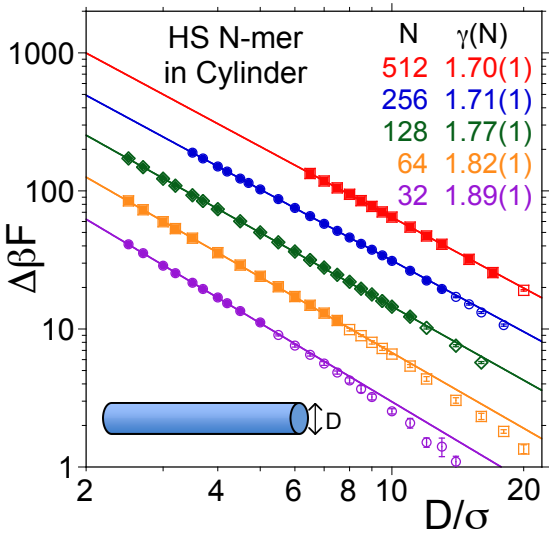
$$\gamma = 1/\nu \approx 1.7$$

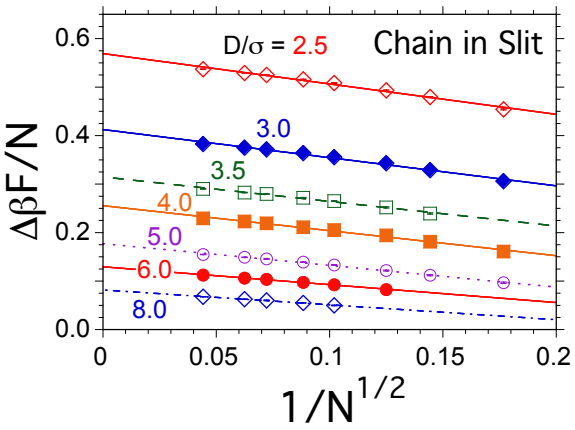
*See, for example:
de Gennes, Scaling Concepts in Polymer Physics
Grosberg & Khokhlov, Stat. Phys. of Macromolecules

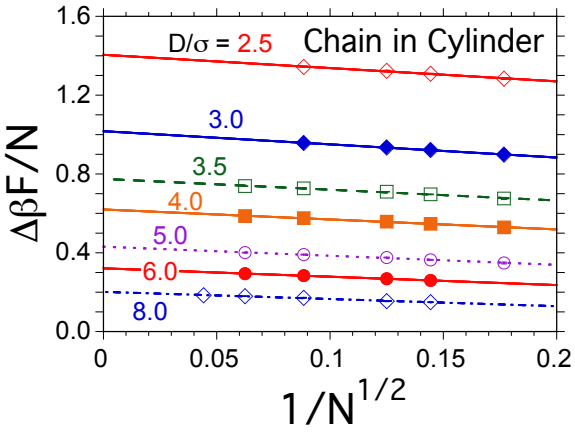
Scaling Properties & Finite Size Effects

Corrections to scaling: $\Delta\beta F/N = A\,(D/\sigma)^{-\gamma}\,(1-b/N^{1/2})$





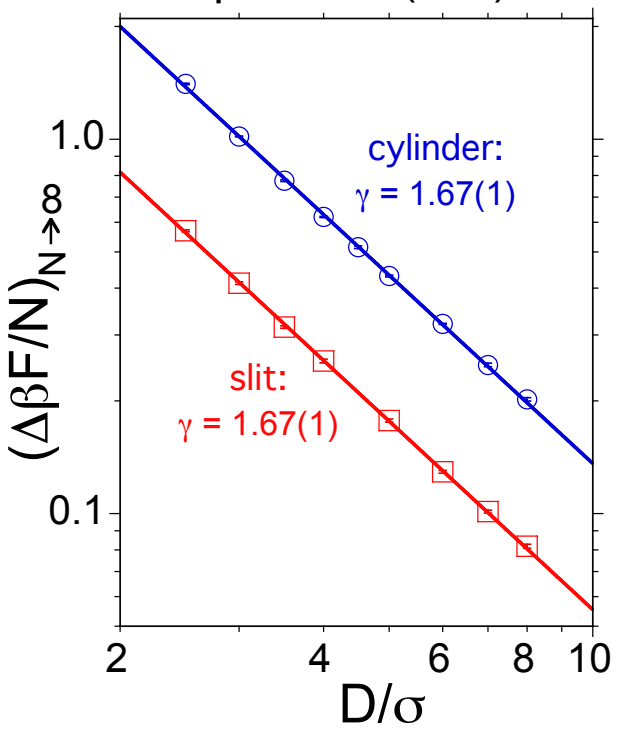




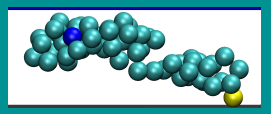
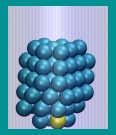
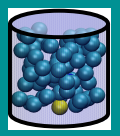
Slit Ref. state:
Adsorbing Wall

Cylinder Ref. state:
Adsorbing Axial Line

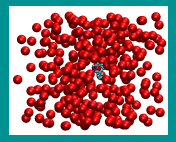
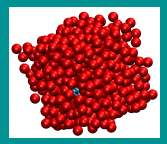
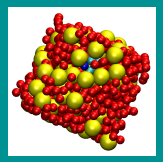
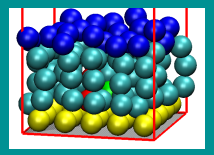
Confined Hard-Sphere Chain
Asymptotic (N→∞) scaling
$\Delta\beta F/N = A(D/\sigma)^{-\gamma}$



See also: Cacciuto & Luijten,
Nano Letters **6**, 901 (2006)

Summary

Confinement Effects on Polymer Folding/Unfolding

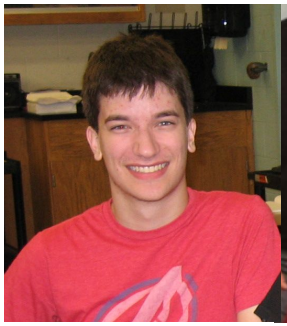
-Hard wall confinement provides entropic stabilization of folded state

-Folding transitions maintain "all-or-none" character in confinement

-Increasing confinement can lead to isothermal freezing/melting

-Finite size effects important for confinement free energy of HS-chains

Christian O'Neil



Troy Prunty

Beth Breen

Christopher Vinci

Norah Ali

Jaden Slovensky

Funding: NSF (DMR-1607143)

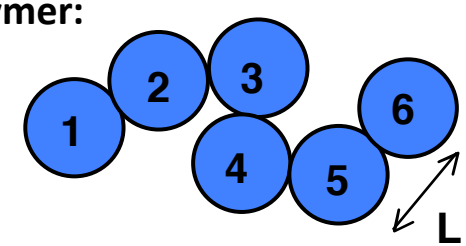
NSF

HIRAM COLLEGE

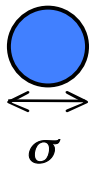
Extra Slides

Square-Well Chain Model

Polymer:



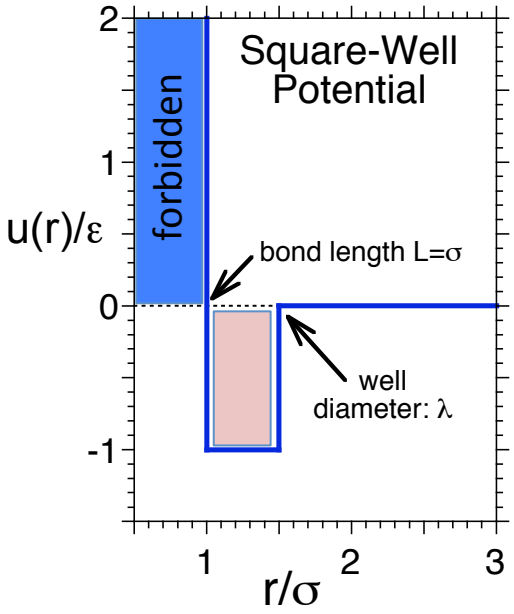
built from simple monomers:



Model Parameters:

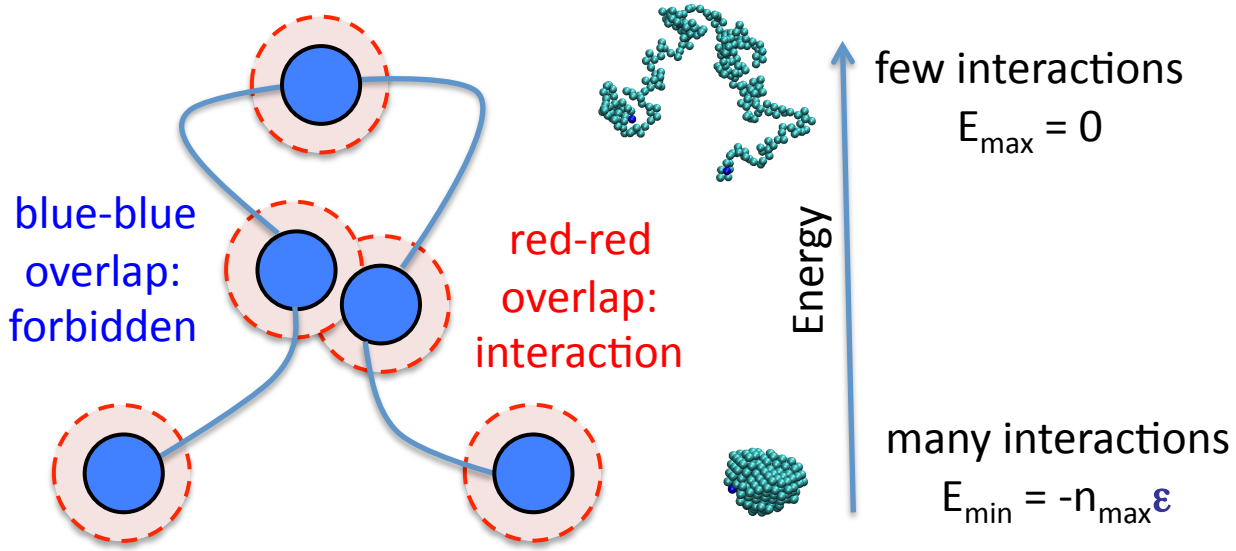
- ε = well depth (sets energy scale)
- σ = hard-sphere diameter
- L = bond length (L = σ)
- **λ = interaction range/σ**
- $T^* = k_B T/\varepsilon$ = reduced temperature

monomer-monomer interaction



Model has a discrete energy spectrum: $\mathbf{E_n = -n\varepsilon}$

(**n** = number of monomer-monomer interactions)



The entropy of the model is given by

S = k ln [g(E)] where g(E) is :

$$g(E) = \frac{\varepsilon}{V} \int \cdots \int \prod_{k=1}^{N-1} \frac{\delta(r_{k,k-1} - L)}{4\pi L^2} \; \delta\left(E - \sum_{i<\, j+1}^{N} u(r_{ij}) \right) d\vec{r}_1 \ldots d\vec{r}_N$$

This 3N-dimensional integral (3N=192 for N=64) presents a daunting numerical challenge!

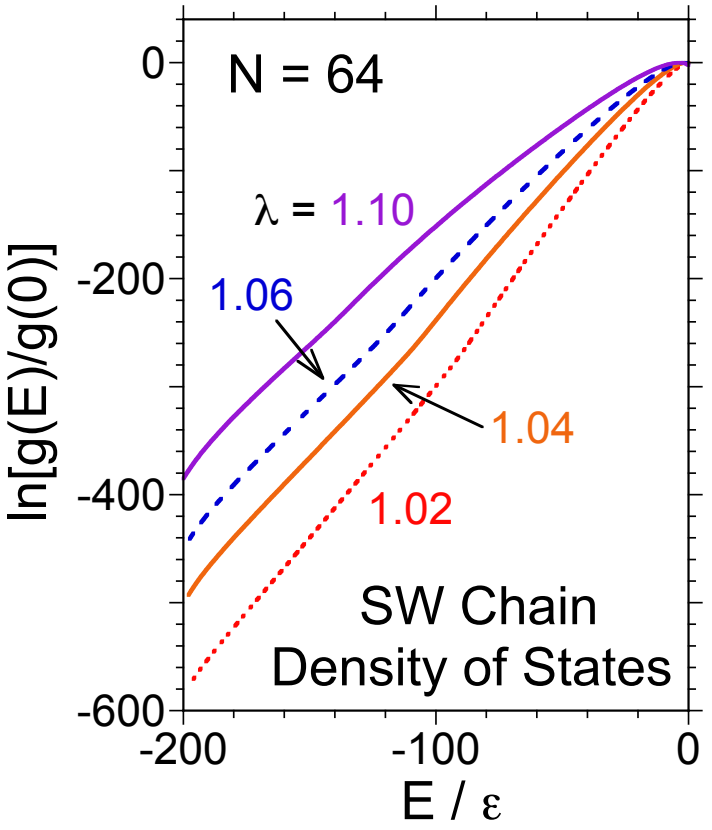
M.P. Taylor, J. Chem. Phys. **118**, 883 (2003)
J. Chem. Phys. **147**, 166101 (2017)

We use **computer simulation methods** (Wang-Landau algorithm) to compute this integral.

F. Wang and D.P. Landau, Phys. Rev. Lett. **86**, 2050 (2001)

Single Chain DOS and Canonical Analysis

Algorithm validated via comparison with exact DOS results for short (n≤6) SW chains.



Taylor, Paul, & Binder,
Polymer Sci., Ser. C **55**, 23 (2013)

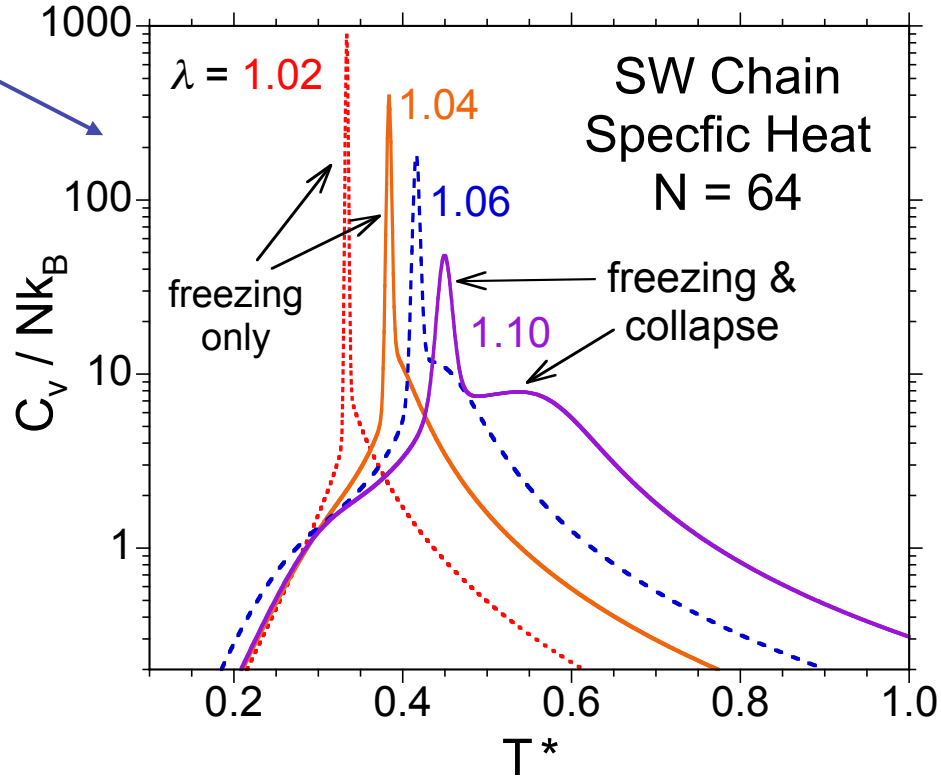
Canonical Analysis

Partition Function: $Z = \sum g(E)\, e^{-E/kT}$

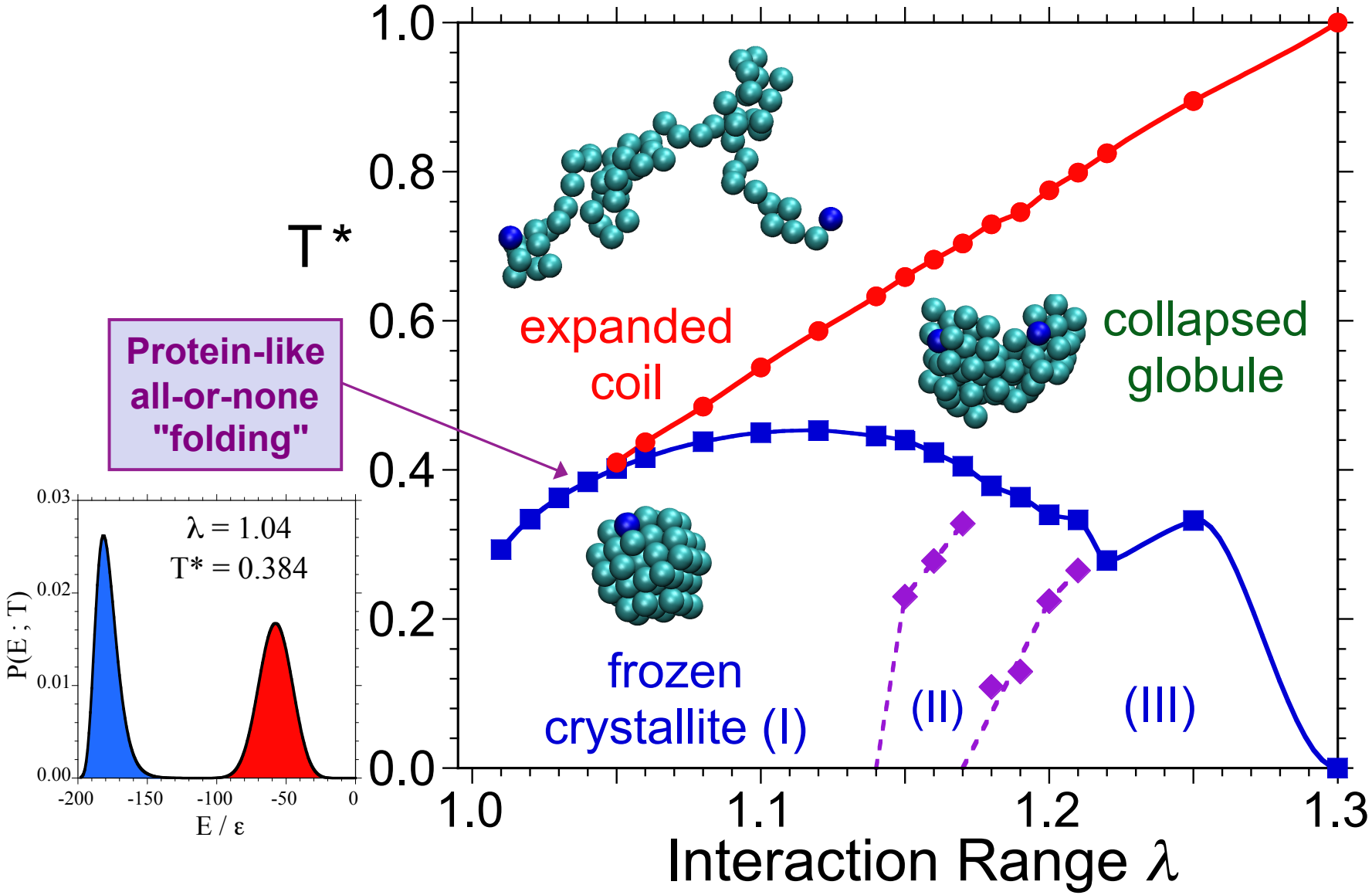
Probability: $P(E,T) = g(E)\, e^{-E/kT} / Z$

Average Energy: $\langle E(T) \rangle = \sum EP(E,T)$

Specific Heat: $C(T) = d\langle E(T) \rangle / dT$



N=64 Square-Well Chain Phase Diagram



Taylor, Paul, & Binder, Polymer Sci., Ser. C **55**, 23 (2013)

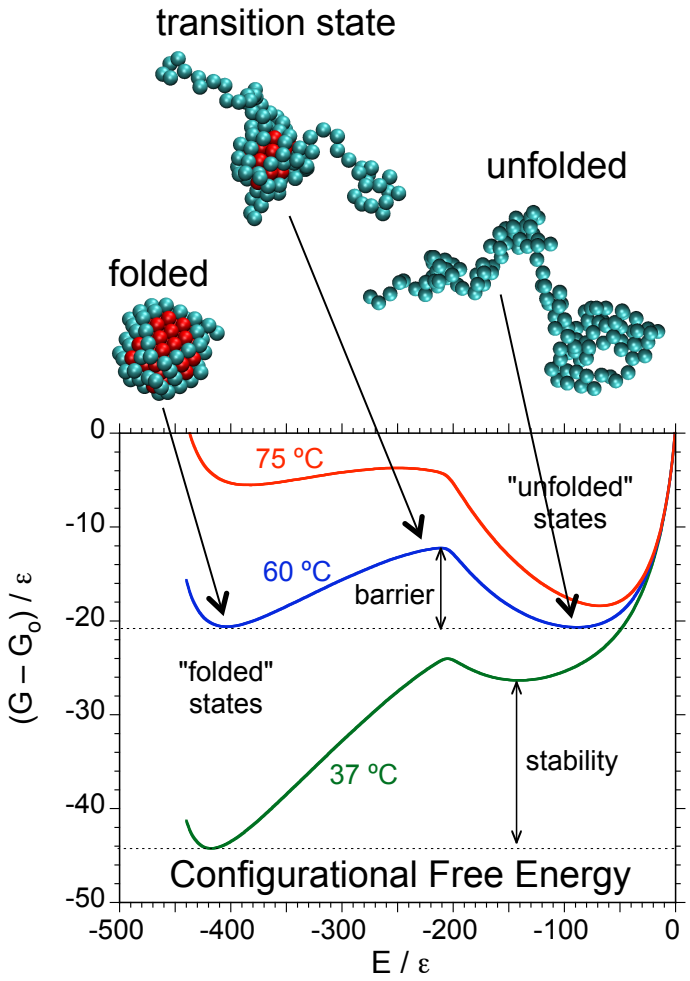
All-or-none polymer "folding" transition

Thermodynamics characteristic of **two-state protein folding** ... simple model for a complex biophysical process.

Taylor, Paul, Binder, JCP **145**, 174903 (2016)

This type of transition useful for **responsive/smart materials** ... provides an "on/off switch" between two distinct states.

Confinement effects are of interest for both of these applications.

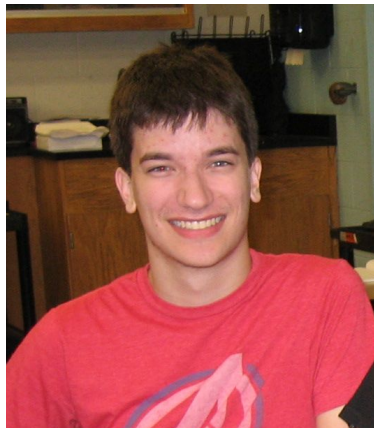


folded/unfolded states separated by a free energy barrier

Jutta Luettmer-Strathmann
Akron

Jaden Slovensky Beth Breen Norah Ali

Wolfgang Paul
Halle



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