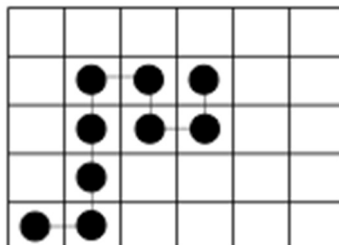


## 6. Lattice Models for Polymers

### Flory–Huggins Model of Polymer Solutions<sup>1</sup>

Chain of connected beads on a lattice. Useful for describing configurational entropy of polymer and excluded volume.



$M$ : total number of lattice cells

$N_p$ : number of polymer molecules

$n$ : number of beads per polymer

$N_s$ : number of solvent cells

$nN_p$  = total number of polymer beads.

$$M = nN_p + N_s$$

Volume fractions of solvent and polymer:  $\phi_s = \frac{N_s}{M}$      $\phi_p = \frac{nN_p}{M}$      $\phi_s + \phi_p = 1$

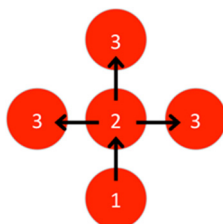
The mole fraction of polymer

$$x_p = \frac{N_p}{N_s + N_p}$$

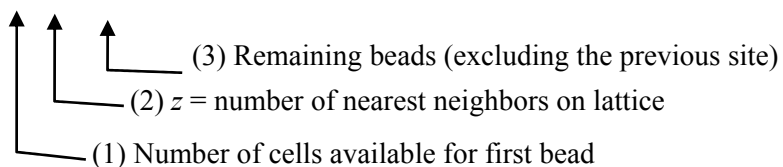
is greatly reduced even if the volume fraction is high.

### Entropy of Mixing

1) Number of ways of placing a single polymer chain on lattice:



$$\Omega_p = M z (z - 1)^{n-2}$$



Note mapping of terms in  $\Omega_p = M z (z - 1)^{n-2}$  onto  $\Omega_p = \Omega_{\text{trans}} \Omega_{\text{rot}} \Omega_{\text{conf}}$ .

$$\text{For } n \rightarrow \infty \ M \gg N \quad \Omega_p \approx M(z-1)^{n-1}$$

1. K. Dill and S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*. (Taylor & Francis Group, New York, 2010); S. F. Sun, *Physical Chemistry of Macromolecules: Basic Principles and Issues*, Array ed. (J. Wiley, Hoboken, N.J., 2004), Ch. 4.

$$S_{\text{mix}} = k \ln \Omega_p$$

This assumes that a dilute polymer solution, in which we neglect excluded volume, except for the direction of the preceding segment.

This does not properly treat excluded volume and it becomes difficult to account for. If you do not watch configurations explicitly (self-avoiding walks or SAWs), you can account for loss of cells in general. Better estimate for chain configurations that partially accounts for excluded volume:

$$\Omega_p = M \left[ z \left( \frac{M-1}{M} \right) \right] \left[ (z-1) \left( \frac{M-2}{M} \right) \right] \dots \left[ (z-1) \frac{(M-n+1)}{M} \right]$$

1<sup>st</sup> bead
3<sup>rd</sup> bead
n<sup>th</sup> bead

Second bead on reduced lattice space counting only fraction of empty cells

$$\Omega_p \approx \frac{(z-1)^{n-1}}{M} \frac{M!}{(M-n)!}$$

## 2) Multiple Chains

$$\Delta S_{\text{mix}} = -Mk \left( \phi_S \ln \phi_S + \frac{\phi_P}{n} \ln \phi_P \right)$$

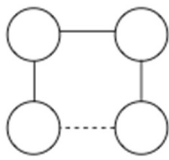
$$\phi_P = nN_P / M$$

$$\phi_S = N_S / M$$

Again,  $\Delta S_{\text{mix}}$  is always positive since  $\phi_i < 1$ . Still does not account for explicit clashes  $\rightarrow$  “self-avoiding chain”.

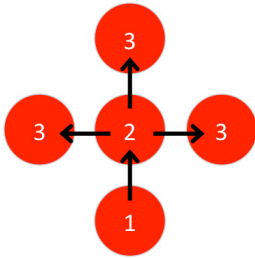
## Example: Conformational Transitions with Temperature

4 bead polymer ( $n = 4$ ) on a two-dimensional lattice ( $z = 4$ )



Neighboring non-bonded beads have favorable contact energy  $\epsilon$

Place polymer on lattice



$$\Omega_p = M z (z-1)^{n-2}$$

$$= \Omega_{\text{trans}} \Omega_{\text{rot}} \Omega_{\text{conf}}$$

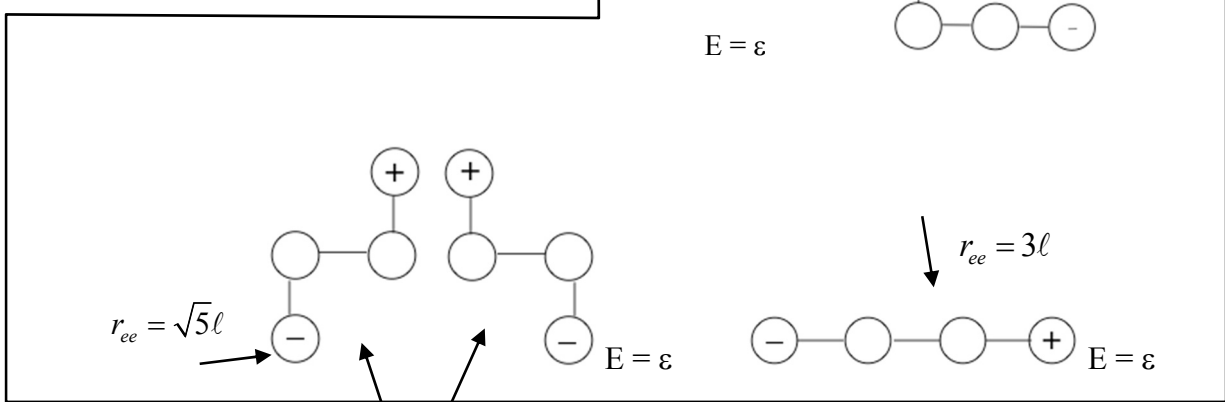
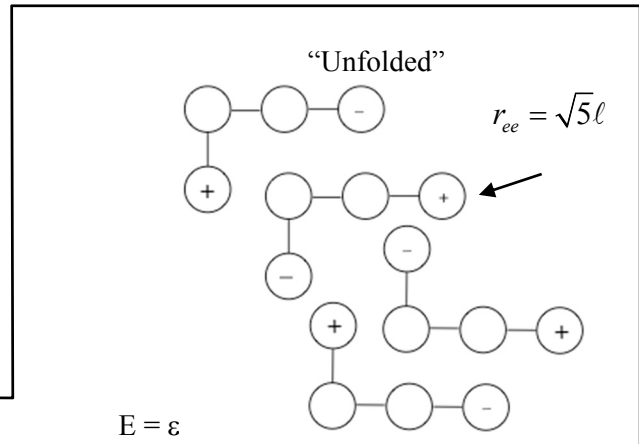
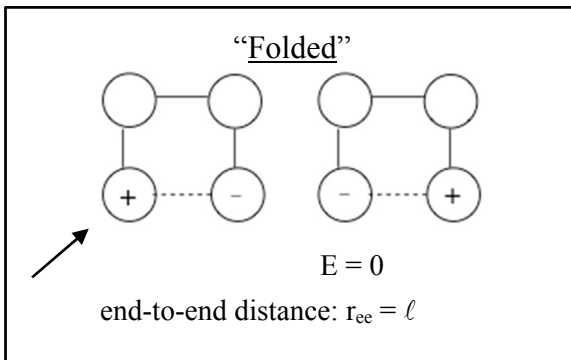
in 2D (with distinguishable beads)

$$z = 4 \quad n = 4$$

$$\Omega_p = 36M$$

$$\Omega_{\text{conf}} = 9 \quad \leftarrow \text{Distinguishable beads}$$

$$\Omega_{\text{conf}} = 6 \quad \leftarrow \text{Indistinguishable beads}$$



Note in 2D these are distinct configurations, but not in 3D

### Configurational Partition Function

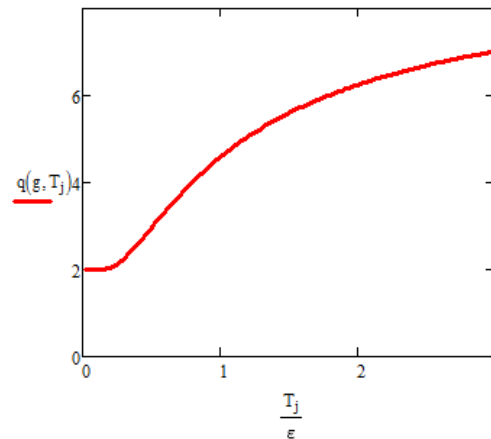
Number of thermally accessible microstates.

$$Q = (q_{\text{conf}})^N$$

$$q_{\text{conf}} = \sum_{i \text{ states}=1}^9 e^{-E_i/kT} = \sum_{j \text{ levels}=1}^2 g_j e^{-E_j/kT}$$

microstates      energy levels

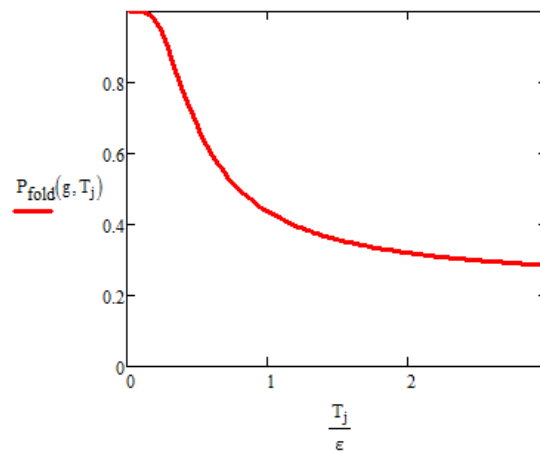
$$= 2 + 7e^{-\varepsilon/kT}$$



### Probability of Being "Folded"

Fraction of molecules in the folded state.

$$P_{\text{fold}} = \frac{g_{\text{fold}} e^{-E_{\text{fold}}/kT}}{q_{\text{conf}}} = \frac{2}{2 + 7e^{-\varepsilon/kT}}$$

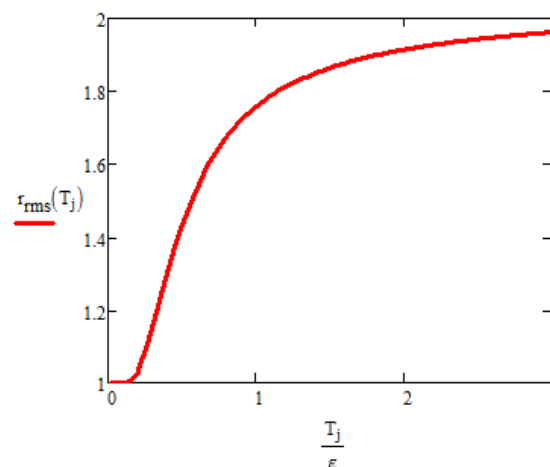


### Mean End-to-end Distance

$$\langle r_{ee} \rangle = \frac{\sum_{i=1}^9 r_i e^{-E_i/kT}}{q_{\text{conf}}}$$

$$= \frac{(1)(2) + (\sqrt{5})6e^{-\varepsilon/kT} + 3e^{-\varepsilon/kT}}{q_{\text{conf}}}$$

$$= \frac{2 + (6\sqrt{5} + 3)e^{-\varepsilon/kT}}{q_{\text{conf}}}$$



Also, we can access other thermodynamic quantities:

$$A = -kT \ln Q \quad U = \langle E \rangle = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$S = - \left( \frac{\partial A}{\partial T} \right)_{V,N} = k \ln Q + kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

## Extensions for Hydrophobic Collapse and Protein Folding

### HP model<sup>2</sup>

H (hydrophobic) beads

P (polar) beads

Favorable contacts: H next to H, but not P next to H (Energy penalty:  $\epsilon_{HY}$ )

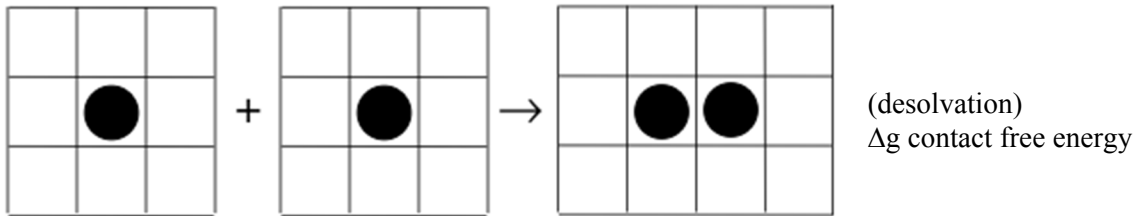
more H  $\rightarrow$  collapse to compact state, but many collapsed structures

more P  $\rightarrow$  well-solvated, does not fold

$\sim 1:1$  H:P optimal.

### Flory–Huggins model for polymer solvation

Polymers expand in good solvents, collapse in bad solvents, retain Gaussian random coil behavior in neutral solvents ( $\theta$  solvents).



$$\Delta g = -\frac{2}{z} \chi kT$$

As before,  $\chi$  is the exchange parameter:  $\chi = \frac{1}{kT} \left( \omega_{AB} - \frac{\omega_{AA} + \omega_{BB}}{2} \right)$

$\chi$ : Balance of monomer–monomer attraction and excluded volume.

Good solvents	$\chi < 0.5$	$\sqrt{\langle r^2 \rangle} \sim N^{3/5} \sim R_0 N^{3/5}$
Bad solvents (collapse)	$\chi > 0.5$	$R \sim R_0 N^{1/3}$
Theta solvents	$\chi = 0.5$	$\sqrt{\langle r^2 \rangle} \sim \frac{2N\ell^2}{3} = R_0$

$$F_{\text{solvation}} = NkT\rho \left( \frac{1}{2} - \chi \right)$$

$\rho = N/M$  density—probability of an adj. segment



2. K. F. Lau and K. A. Dill, A lattice statistical mechanics model of the conformational and sequence spaces of proteins, *Macromolecules* **22**, 3986-3997 (1989).