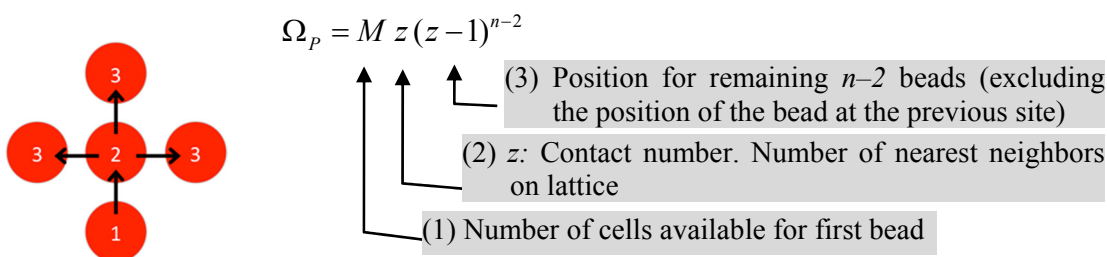# Macromolecules

## 8. Lattice Models for Polymers[1]

Polymer lattice models refer to models that represent chain configurations through the placement of a chain of connected beads onto a lattice. These models are particularly useful for describing the configurational entropy of a polymer and excluded volume effects. However, one can also explicitly enumerate how energetic interactions between beads influences the probability of observing a particular configuration. At a higher level, models can be used to describe protein folding and DNA hybridization.
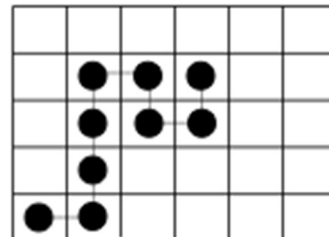
### Entropy of Single Polymer Chain

Calculate the number of ways of placing a single homopolymer chain with $n$ beads on lattice. Place beads by describing the number of ways of adding a bead to the end of a growing chain:

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

(3) Position for remaining $n$–2 beads (excluding the position of the bead at the previous site)

(2) $z$: Contact number. Number of nearest neighbors on lattice

(1) Number of cells available for first bead

A random walk would correspond to the case where we allow the chain to walk back on itself. Then the expression is $\Omega_P = M \, z^{n-1}$

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

$$\text{For } n \to \infty \quad M \gg N \quad \Omega_p \approx M(z-1)^{n-1}$$
$$S_p = k_B \ln \Omega_p$$
$$= k_B \left( (n-1)\ln(z-1) + \ln M \right)$$

This expression assumes a dilute polymer solution, in which we neglect excluded volume, except for the preceding segment in the continuous chain.

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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.

## Self-Avoiding Walks[2]

To account for excluded volumes, one can enumerate polymer configurations in which no two beads occupy the same site. Such configurations are called self-avoiding walks (SAWs). Theoretically it is predicted that the number of configurations for a random walk on a cubic lattice should scale with the number of beads as $\Omega_p(n) \propto z^n n^{\gamma-1}$, where $\gamma$ is a constant which is equal to 1 for a random walk. By explicitly evaluating self-avoiding walks (SAWs) on a cubic lattice it can be shown that

$$\Omega_p(n) = 0.2\alpha^n n^{\gamma-1}$$

where $\alpha = 4.68$ and $\gamma = 1.16$, and the chain entropy is

$$S_p(n) = k_B \left[ n \ln \alpha + (\gamma - 1)\ln n - 1.6 \right].$$

Comparing this expression with our first result $\Omega_P = M\, z\,(z-1)^{n-2}$ we note that in the limit of a random walk on a cubic lattice, $\alpha = z = 6$, when we exclude only the back step for placing the next bead atop the preceeding one $\alpha = (z-1) = 5$, and the numerically determined value is $\alpha = 4.68$.

2.  C. Vanderzande, *Lattice Models of Polymers* (Cambridge University Press, Cambridge, UK, 1998).

## Conformational Changes with Temperature

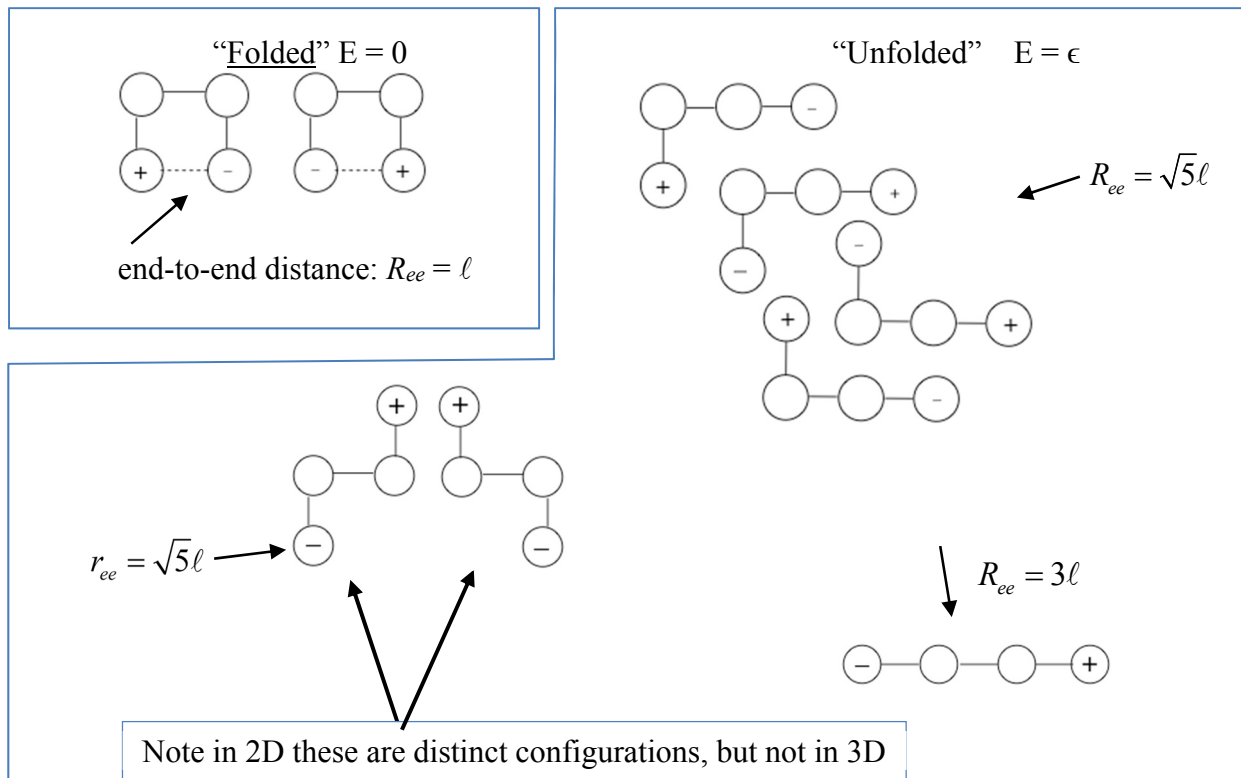4 bead polymer on a two-dimensional lattice



Neighboring non-bonded beads have favorable contact energy $-\epsilon$
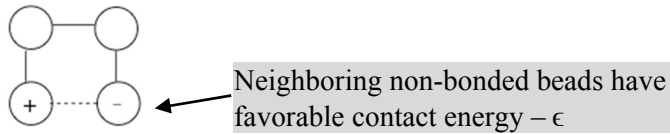
Place polymer on lattice $\quad z = 4 \qquad n = 4$

in 2D (with distinguishable end beads):

$$\Omega_p = 36M$$
$$\Omega_{conf} = 9 \quad \longleftarrow \text{Distinguishable beads}$$
$$\Omega_{conf} = 6 \quad \longleftarrow \text{Indistinguishable beads}$$

"Folded" E = 0



end-to-end distance: $R_{ee} = \ell$

"Unfolded"  E = $\epsilon$



$R_{ee} = \sqrt{5}\ell$

$r_{ee} = \sqrt{5}\ell$



$R_{ee} = 3\ell$

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

## Configurational Partition Function

Number of thermally accessible microstates.

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

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

$$\underbrace{\phantom{\sum}}_{microstates} \qquad \underbrace{\phantom{\sum}}_{energy\,levels}$$

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

## Probability of Being "Folded"

Fraction of molecules in the folded state.

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

## Mean End-to-End Distance

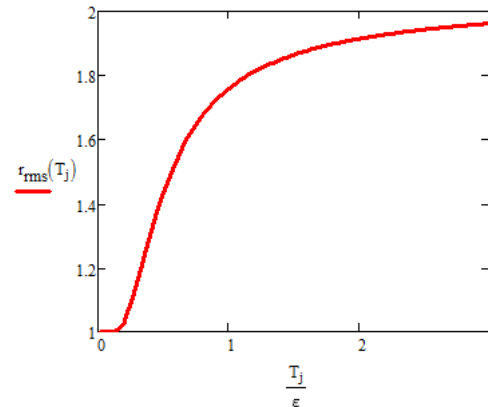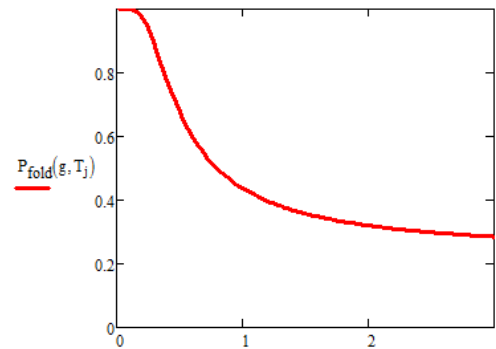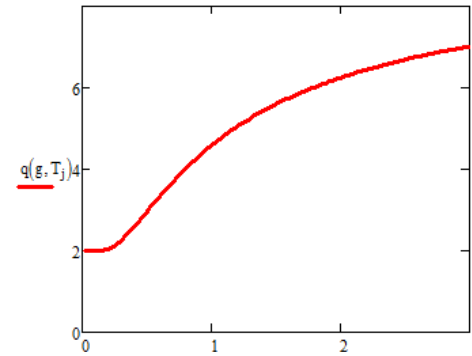$$\langle r_{ee} \rangle = \sum_{i=1}^{9} \frac{r_i\, e^{-E_i/kT}}{q_{conf}}$$

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

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

Also, we can access other thermodynamic quantities:

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

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



$q(g, T_j)$



$P_{fold}(g, T_j)$



$r_{rms}(T_j)$

$\dfrac{T_j}{\varepsilon}$

## Flory–Huggins Model of Polymer Solutions
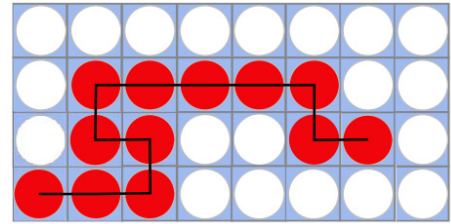
Let's being by defining the variables for the lattice:

$M$ : 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

The total number of lattice sites is then composed of the fraction of sites occupied by polymer beads and the remaining sites, which we consider occupied by solvent:

$$M = nN_P + N_S$$

Volume fractions of solvent and polymer:

$$\phi_S = \frac{N_S}{M} \qquad \phi_P = \frac{nN_P}{M} \qquad \phi_S + \phi_P = 1$$

The mole fraction of polymer:

$$x_P = \frac{N_P}{N_S + N_P}$$

$x_P$ is small even if the volume fraction is high.

### *Excluded Volume for Single Polymer Chain*

Generally, excluded volume is difficult to account for if you don't want to elaborate configurations explicitly, as in self-avoiding walks. However, there is a mean field approach we can use to account for excluded volume.

A better estimate for chain configurations that partially accounts for excluded volume:

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

1st bead

3rd bead

$n^{\text{th}}$ bead

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

Large $n$:  $\Omega_P \approx \frac{(z-1)^{n-1}}{M}\frac{M!}{(M-n)!}$

### *Entropy of Multiple Polymer Chains*

For $N_P$ chains, we count growth of chains by adding beads one at a time to all growing chains simultaneously.

1) First bead. The number of ways for placing the 1$^{st}$ bead for all chains:

$$v^{(1)} = M(M-1)(M-2)\rightarrow(M-(N_P-1)) = \frac{M!}{(M-N_P)!}$$

1$^{st}$ bead 1$^{st}$ chain    1$^{st}$ bead 2$^{nd}$ chain    1$^{st}$ bead on $N_P{}^{th}$ chain

2) Place the second bead on all chains. We assume the solution is dilute and neglect collisions between chains.

$$v^{(2)} = \left[z\left(\frac{M-N_P}{M}\right)\right]\left[z\left(\frac{M-N_P-1}{M}\right)\right]\ldots\left[z\left(\frac{M-2N_P+1}{M}\right)\right]$$

Ways of placing 2$^{nd}$ bead on 1$^{st}$ chain with a volume reduced by the number of beads present from the 1$^{st}$ beads. Volume fraction excluded: $(M-N_P)/M$

$$= \frac{(z)^{N_P}}{M}\left(\frac{(M-N_P)!}{(M-2N_P)!}\right)$$

3) For placing the $n^{th}$ bead on $N_P$ growing chains. Here we neglect collisions between site $i$ and sites $>(i+4)$, which is the smallest separation that one can clash on a cubic lattice.

$$v^{(n)} = \left(\frac{z-1}{M}\right)^{N_P(n-1)}\frac{(M-N_P)!}{(M-n\cdot N_P)!}$$

4) Total number of configurations of $N_P$ chains with $n$ beads:

$$\Omega_P = \frac{v^{(1)}v^{(n)}}{N_P!} \longleftarrow \text{indistinguishablity of polymer chains}$$

$$\Omega_P = \left(\frac{z-1}{M}\right)^{N_P(n-1)}\frac{M!}{(M-nN_P)!N_P!}$$

$N_S!$

6

### *Entropy of Polymer Solution*

Entropy of polymer/solvent mixture:

$$S_{\text{mix}} = k_B \ln \Omega_P$$

Calculate entropy of mixing:

$$\Delta S_{\text{mix}} = S_{\text{mix}} - S^0_{\text{solvent}} - S^0_{\text{polymer}}$$

pure solvent      pure polymer

$$S^0_{\text{solvent}} = 0 \text{ since } \Omega_{\text{solvent}} = 1$$

The pure polymer has many possible entangled configurations $\Omega^0_P$, and therefore a lot of configurational entropy: $S^0_{\text{polymer}}$. But we can calculate $\Omega^0_P$ just by using the formula for $\Omega_P$ with the number of cells set to the number of polymer beads $M = nN_P$.

$$\Omega^0_P = \left( \frac{z-1}{N_P \cdot n} \right)^{N_P(n-1)} \frac{(N_P \cdot n)!}{N_P!}$$

$$\frac{\Omega_P}{\Omega^0_P} = \left( \frac{N_P \cdot n}{M} \right)^{N_P(n-1)} \frac{M!}{N_S!(N_P \cdot n)!}$$

Since $\Delta S_{\text{mix}} = k_B \ln \dfrac{\Omega_P}{\Omega^0_P}$

$$\Delta S_{\text{mix}} = -k_B N_S \ln \left( \frac{N_S}{M} \right) - k_B N_P \ln \left( \frac{N_P \cdot n}{M} \right)$$

$$= -M k_B \left( \phi_S \ln \phi_S + \frac{\phi_P}{n} \ln \phi_P \right)$$
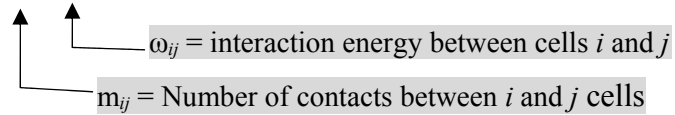
where the volume fractions are:

$$\phi_S = \frac{N_S}{M} \qquad\qquad \phi_P = \frac{nN_P}{M} = 1 - \phi_S$$

Note for $n = 1$, we have original lattice model of fluid.

## Polymer–Solvent Interactions

- Use same strategy as lattice model of a fluid.
- Considering polymer ($P$) and solvent ($S$) cells:

$$U = m_{SS}\omega_{SS} + m_{PP}\omega_{PP} + m_{SP}\omega_{SP}$$

$\omega_{ij}$ = interaction energy between cells $i$ and $j$

$m_{ij}$ = Number of contacts between $i$ and $j$ cells

- Number of solvent cell contacts:

$$zN_S = 2m_{SS} + m_{SP}$$

- Number of polymer cell contacts:

$$\approx (z-2)\cdot N_P \cdot n \approx z\cdot N_P n = 2m_{PP} + m_{SP}$$

each bead connects to 2 other beads

- Mean field approximation: Substitute the average number of solvent/polymer contacts.

$$m_{SP} \approx \frac{zN_S N_P \cdot n}{M} = \langle m_{SP} \rangle$$

$$U_{mix} = k_B T\left\{ \frac{z\omega_{SS}}{2k_B T}N_S + \frac{z\omega_{PP}}{2k_B T}N_P n + \chi_{SP}\frac{N_S N_P}{M}n \right\}$$

$$\chi_{SP} = \frac{z}{k_B T}\left( \omega_{SP} - \frac{\omega_{SS} + \omega_{PP}}{2} \right) \quad \text{solvent-polymer bead exchange parameter}$$

$$\vdots$$

$$F_{mix} = N_S k_B T \ln \phi_S + N_P k_B T \ln \phi_P + \frac{z}{2}\left( \omega_{SS}N_S + \omega_{PP}N_P \right) + \chi_{SP}\frac{N_S N_P n}{M}$$

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

| 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 | $\chi = 0.5$ | $\sqrt{\langle r^2 \rangle} \sim \dfrac{2N\ell^2}{3} = R_0$ |