Cannot cover everything today!

2

Ideal Chain – Basics

- Monomers separated by *enough* bonds do not interact

- Random walk where bonds are *steps*

$$\mathbf{R}_{\text{e2e}} = \mathbf{r}_N - \mathbf{r}_0 = \sum_{i=1}^{N} \mathbf{b}_i$$

$\langle \mathbf{R}_{\text{e2e}} \rangle = \mathbf{0}$ *Bonds have no preferred direction!*

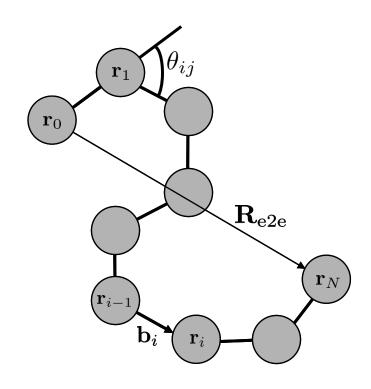$\langle \cdots \rangle$ *Indicates ensemble average (over many chains or over many conformations)*

3

Ideal Chain – Characteristic Size

Mean-Square End-to-End Distance

$$\langle R_{\text{e2e}}^2 \rangle \equiv \langle \mathbf{R}_{\text{e2e}} \cdot \mathbf{R}_{\text{e2e}} \rangle = \left\langle \left(\sum_{i=1}^{N} \mathbf{b}_i \right) \cdot \left(\sum_{j=1}^{N} \mathbf{b}_j \right) \right\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle$$
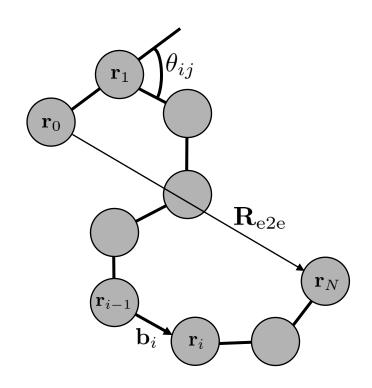
If all bonds have the same length, l

$$\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = l^2 \langle \cos \theta_{ij} \rangle$$

1. If bonds i and j are *correlated* : $\quad \langle \cos \theta_{ij} \rangle \neq 0$

2. If bonds i and j are *uncorrelated* : $\quad \langle \cos \theta_{ij} \rangle = 0$

3. If $i = j$: $\quad \langle \cos \theta_{ij} \rangle = 1$

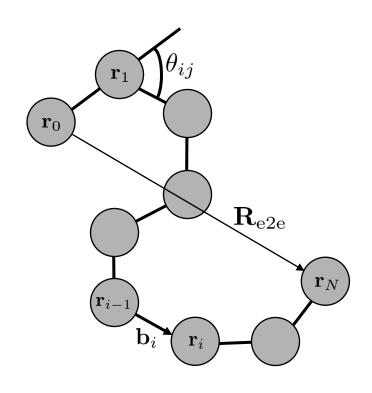# Ideal Chain – No Correlations

Mean-Square End-to-End Distance

$$\langle R_{\text{e2e}}^2 \rangle \equiv \langle \mathbf{R}_{\text{e2e}} \cdot \mathbf{R}_{\text{e2e}} \rangle = \left\langle \left(\sum_{i=1}^{N} \mathbf{b}_i \right) \cdot \left(\sum_{j=1}^{N} \mathbf{b}_j \right) \right\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle$$

$$\langle R_{\text{e2e}}^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \cos \theta_{ij} \rangle = N l^2 + l^2 \sum_{i=1}^{N} \sum_{j \neq i} \langle \cos \theta_{ij} \rangle$$

In the absence of bond-bond correlations

$$\langle R_{\text{e2e}}^2 \rangle = N l^2$$

Ideal Chain – Correlations
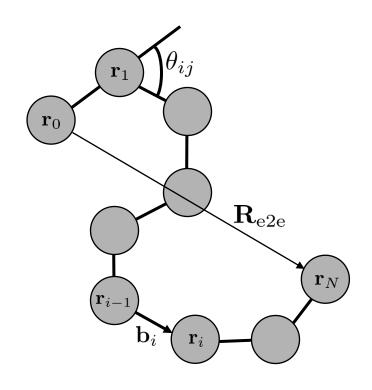
Mean-Square End-to-End Distance

$$\langle R_{\mathrm{e2e}}^2 \rangle = l^2 \sum_{i=1}^{N}\sum_{j=1}^{N}\langle \cos\theta_{ij}\rangle = Nl^2 + l^2 \sum_{i=1}^{N}\sum_{j\neq i}\langle \cos\theta_{ij}\rangle$$

$$= Nl^2\left(1 + \sum_{j\neq i}\langle \cos\theta_{ij}\rangle\right) = C_\infty Nl^2 \geq Nl^2$$

Accounts for correlations due to steric hinderance across chain and augments ideal behavior

Polymer	Structure	C_∞
1,4-Polyisoprene (PI)	–(CH$_2$CH=CHCH(CH$_3$))–	4.6
1,4-Polybutadiene (PB)	–(CH$_2$CH=CHCH$_2$)–	5.3
Polypropylene (PP)	–(CH$_2$CH$_2$(CH$_3$))–	5.9
Poly(ethylene oxide) (PEO)	–(CH$_2$CH$_2$O)–	6.7
Poly(dimethyl siloxane) (PDMS)	–(OSi(CH$_3$)$_2$)–	6.8
Polyethylene (PE)	–(CH$_2$CH$_2$)–	7.4
Poly(methyl methacrylate) (PMMA)	–(CH$_2$C(CH$_3$)(COOCH$_3$))–	9.0
Atactic polystyrene (PS)	–(CH$_2$CHC$_6$H$_5$)–	9.5

Ideal Chain – Correlations Example

(Example) Correlations that decay exponentially

$$\langle \cos \theta_{ij} \rangle = \exp\left(-|i-j|/\xi\right)$$

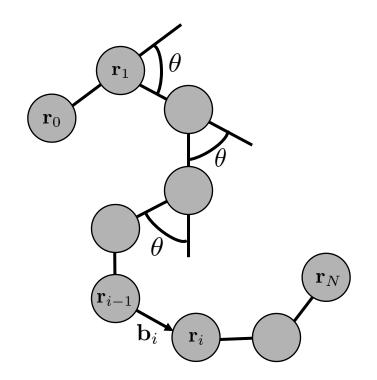Correlation length

$$\langle R_{e2e}^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(-|i-j|/\xi\right) = Nl^2 + l^2 \sum_{i=1}^{N} \left[\sum_{k=1}^{i-1} e^{-k/\xi} + \sum_{k=1}^{N-i} e^{-k/\xi} \right]$$
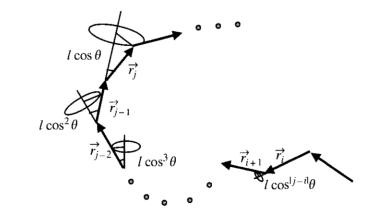
Correlations decay rapidly (small ξ)... extend sums to ∞

$$\langle R_{e2e}^2 \rangle = Nl^2 + 2Nl^2 \sum_{k=1}^{\infty} e^{-k/\xi} = Nl^2 + 2Nl^2 \frac{e^{-1/\xi}}{1 - e^{-1/\xi}}$$

$$\xi = 1 \quad \rightarrow \quad \langle R_{e2e}^2 \rangle \approx 2Nl^2$$

Freely Rotating Chain Model

- Fixed bond length and fixed bond angle

- Torsional angle is random

$$\langle \cos \theta_{ij} \rangle = (\cos \theta)^{|j-i|}$$

$$\langle R_{\text{e2e}}^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} (\cos \theta)^{|j-i|} = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(|j-i| \ln(\cos \theta)\right)$$

Number of bonds in a persistence segment $\quad \xi = -\dfrac{1}{\ln(\cos \theta)}$

Persistence length $\quad l_p = \xi l$

Wormlike Chain

- Very small bond angle

- Double stranded DNA

Taylor expand for small bond angle!

$$l_p = \xi l = -\frac{l}{\ln(\cos\theta)} \approx -\frac{l}{\ln(1 - \theta^2/2)} \approx \frac{2l}{\theta^2}$$

Smaller bond angle leads to large persistence length

$$\langle R_{e2e}^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(|j-i|\ln(\cos\theta)\right) = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(-\frac{|i-j|l}{l_p}\right)$$

Convert sums to integrals over the contour length

$$\langle R_{e2e}^2 \rangle = 2l_p R_{\max} - 2l_p^2 \left[1 - \exp\left(-\frac{R_{\max}}{l_p}\right)\right]$$

Ideal Chain Limit	**Rod-like Limit**
$R_{\max} \gg l_p$	$R_{\max} \ll l_p$
$\langle R_{e2e}^2 \rangle \approx 2l_p R_{\max}$	$\langle R_{e2e}^2 \rangle \approx R_{\max}^2$

Radius of Gyration

- More general than end-to-end distance

Average distance of monomers from polymer center of mass

$$\mathbf{r}_{\text{cm}} = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i \qquad \langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle (\mathbf{r}_i - \mathbf{r}_{\text{cm}})^2 \rangle$$

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle (\mathbf{r}_i - \mathbf{r}_{\text{cm}})^2 \rangle = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=i}^{N} \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle$$

Convert sums to integrals over the contour length

$$\langle R_g^2 \rangle = \frac{1}{N^2} \int_0^N du \int_u^N dv \langle (\mathbf{r}(u) - \mathbf{r}(v))^2 \rangle$$

Ideal Linear Chain

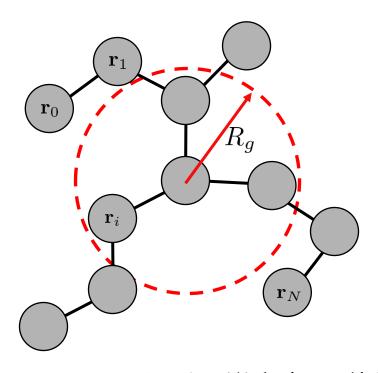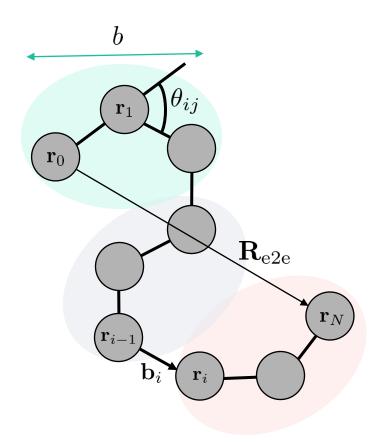$$\langle R_g^2 \rangle = \frac{Nl^2}{6} = \frac{\langle R_{\text{e2e}}^2 \rangle}{6}$$

Table 2.3 Mean-square radii of gyration of ideal polymers with N Kuhn monomers of length b: linear chain, ring, f-arm star with each arm containing N/f Kuhn monomers, and H-polymer with all linear sections containing $N/5$ Kuhn monomers

Ideal chains	Linear	Ring	f-arm star	H-polymer
$\langle R_g^2 \rangle$	$Nb^2/6$	$Nb^2/12$	$[(N/f)b^2/6]\,(3 - 2/f)$	$(Nb^2/6)\,89/625$

Equivalent Freely Jointed Chain

- Way to map non-freely-jointed chains onto freely-jointed model

Actual Chain

$$N : \ \text{\# bonds}$$

$$l : \ \text{bond length}$$

$$\langle R_{e2e}^2 \rangle = C_\infty N l^2$$

$$R_{\max} = N l$$

Equivalent FJ Chain

$$\hat{N} : \ \text{\# segments}$$

$$b : \ \text{Kuhn length}$$

$$\langle R_{e2e}^2 \rangle = \hat{N} b^2$$

$$R_{\max} = \hat{N} b$$

$$\hat{N} = \frac{R_{\max}^2}{C_\infty N l^2} \qquad b = \frac{C_\infty N l^2}{R_{\max}}$$

Stronger bond-bond correlation leads to larger b and smaller N̂

Mapping Wormlike Chain to FJC

Ideal Chain Limit

$$R_{\max} \gg l_p$$

$$\langle R_{\mathrm{e2e}}^2 \rangle \approx 2 l_p R_{\max}$$

- Locally very persistent
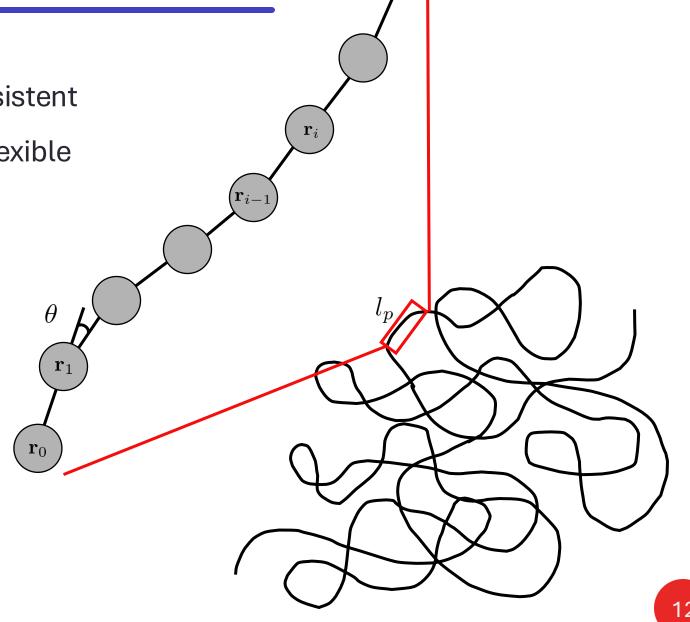- Globally looks flexible

$$b = \frac{C_\infty N l^2}{R_{\max}} = \frac{N l^2}{N l} \frac{1 + \cos\theta}{1 - \cos\theta} \approx \frac{4l}{\theta^2} = 2 l_p$$
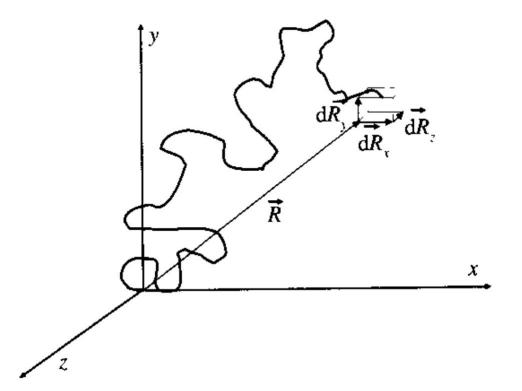
$$\langle R_{\mathrm{e2e}}^2 \rangle = b R_{\max}$$

$$\hat{N} = \frac{R_{\max}^2}{C_\infty N l^2} = \frac{N l}{2 l_p} = \frac{R_{\max}}{b}$$

Smaller bond angle means larger persistence length, which means larger Kuhn length and less effective freely jointed segments

$\mathbf{r}_N$

$\mathbf{r}_i$

$\mathbf{r}_{i-1}$

θ

$\mathbf{r}_1$

$\mathbf{r}_0$

l_p

End-to-End Vector Distribution

- Assume chain is long enough to be mapped onto FJC with N and b

- Bonds take a random walk in 3 independent dimensions (derive yourself!)

$$\mathcal{P}(\mathbf{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}\cdot\mathbf{R}}{2N b^2}\right)$$

- Distribution of end-to-end vectors is Gaussian! (central limit theorem)

- Any model with $\langle\boldsymbol{b}\rangle = 0$ and $\langle\boldsymbol{b}\cdot\boldsymbol{b}\rangle = b^2$ will result in Gaussian $P(\boldsymbol{R})$
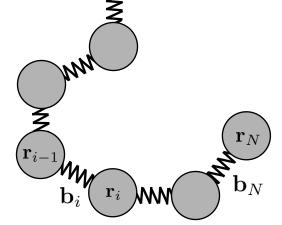
Gaussian Bonds

- Fixed bond length is inconvenient mathematically (see later)

- Choose Gaussian bonds

Single Bond

$$\mathcal{P}(\mathbf{b}) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{b}\cdot\mathbf{b}}{2b^2}\right)$$

Full Chain (bonds are independent)

$$\mathcal{P}(\mathbf{b}_1, \mathbf{b}_2, \ldots \mathbf{b}_N) = \left(\frac{3}{2\pi b^2}\right)^{3N/2} \exp\left(-\frac{3}{2b^2}\sum_{i=1}^{N}\mathbf{b}_i\cdot\mathbf{b}_i\right)$$

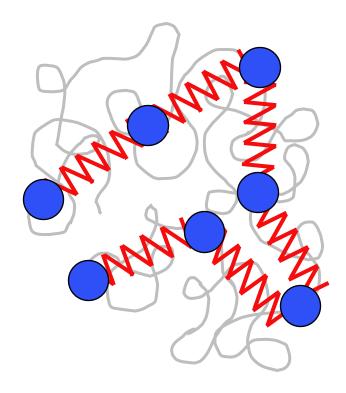**Recall** $\qquad P_\nu \propto \exp\left(-\beta H_\nu\right)$

$$H_\nu = \frac{3kT}{2b^2}\sum_{i=1}^{N}\mathbf{b}_i\cdot\mathbf{b}_i$$

Harmonic springs connected in serial

Spring Constant: $\quad \kappa = \dfrac{3kT}{b^2}$

A Case for Gaussian Bonds

- For long chains, one can divide into sub-chains that each have a Gaussian end-to-end vector distribution

- Overall chain will also have Gaussian end-to-end distribution
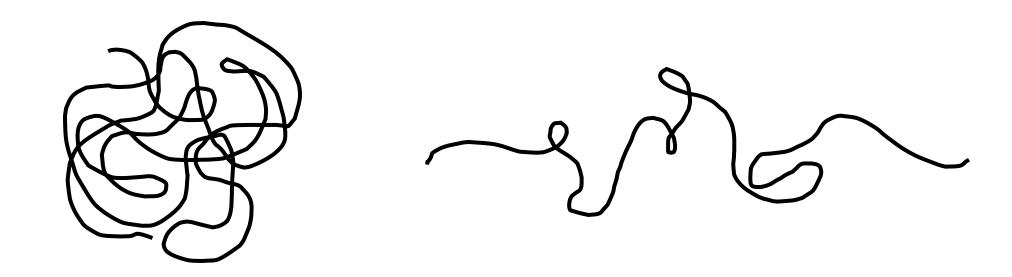
Sub-chains form a *super-bond* that is Gaussian!

$$b_{\text{eff}}^2 = Nb^2 = \langle R_{\text{e2e}}^2 \rangle_{\text{subchain}}$$

Entropic Spring Constant

- Spring constant is proportional to kT
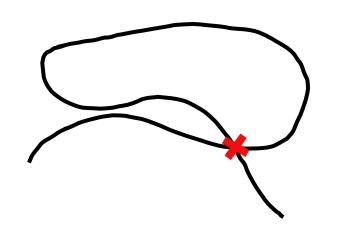
$$\kappa = \frac{3kT}{b^2}$$

- Origin of springiness of polymer is entropic

    - Stretching or compressing the chain from equilibrium necessarily *decreases* the available conformations, thus *decreasing* the entropy

Real Chains

- Consider contacts between monomers that are far apart on the chain

How frequent are contacts?

Probability of a given monomer contacting another monomer

$$\phi^* \approx \frac{Nb^3}{(N^{1/2}b)^3} \approx N^{-1/2} \ll 1$$
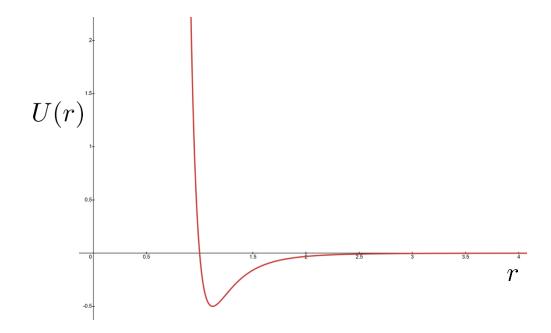
# of monomer-monomer contacts

$$N\phi^* \approx N^{1/2} \gg 1$$
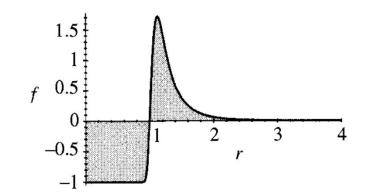
Effective Interactions and Excluded Volume

- Monomers have hard-core repulsion

- Monomers may also have attractive interactions depending on solvent

- Competition between repulsion and attraction determines excluded volume

Monomer-monomer interactions

Mayer f-function

$$f(r) = \exp\left[-\beta U(r)\right] - 1$$

Excluded volume

$$v = -\int \mathrm{d}\mathbf{r}\; f(r)$$
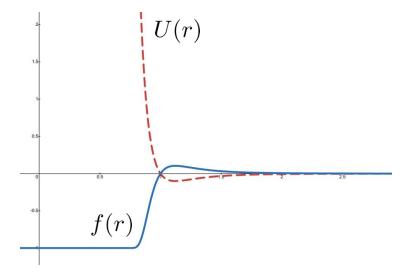
$v > 0$ Repulsive

$v < 0$ Attractive

$v = 0$ Balanced

Solvents

Good Solvent	**Theta Solvent**	**Poor Solvent**
• Effective monomer repulsion	• Repulsion and attraction balance	• Effective monomer attraction
• Chain swells (rel. to ideal)	• Chain behaves ideally	• Chain shrinks (rel. to ideal)

$$v = -4\pi \int \mathrm{d}r \; r^2 f(r) > 0$$

$$v = -4\pi \int \mathrm{d}r \; r^2 f(r) = 0$$

$$v = -4\pi \int \mathrm{d}r \; r^2 f(r) < 0$$

Flory Theory for Good Solvent

- Competition between energy and entropy
  - Swelling decreases entropy (less conformations)
  - Shrinking leads to more monomer contacts, increases energy

Free Energy of Stretching

$$F_{st} \sim \frac{kT}{Nb^2} R^2$$

Excluded Volume Energy

$$F_{ev} \sim NkTv\rho \sim kTv\frac{N^2}{R^3}$$

$$F = F_{st} + F_{ev} \approx kT \left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2} \right)$$

$$\frac{\partial F}{\partial R} = 0 \quad \rightarrow \quad R_F \approx v^{1/5}b^{2/5}N^{3/5}$$

Good Solvent Result

$$R \sim N^{3/5} > N^{1/2}$$

Note that v does not enter!

Thermal Blob

- Length beyond which excluded volume becomes unimportant

$$F_{\text{ev}} \sim vkT\frac{N^2}{R^3} \sim vkT\frac{N^{1/2}}{b^3}$$

Take subsection of chain with m monomers and size ξ^3

$$kT \sim vkT\frac{m^2}{\xi^3} \quad \rightarrow \quad \xi^3 \sim vm^2$$

Within this blob, the chain behaves ideally

$$\xi^2 \sim mb^2$$

Thermal Blob

$$\xi \sim \frac{b^4}{v} \qquad m \sim \left(\frac{b^3}{v}\right)^2$$

Stiffer and less repulsive chains have larger thermal blobs
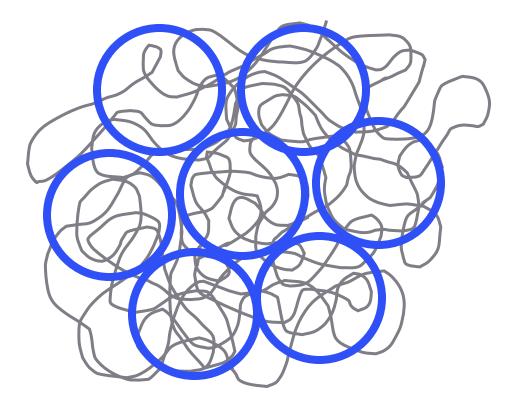
Poor Solvent

- Monomers attract causing the chain to collapse

Assume a dense packing of thermal blobs

$$R^3 \sim \xi^3 \left(\frac{N}{m}\right) \quad \rightarrow \quad R \sim \xi \left(\frac{N}{m}\right)^{1/3} \sim b^2 \frac{N^{1/3}}{|v|^{1/3}}$$

Poor Solvent Result
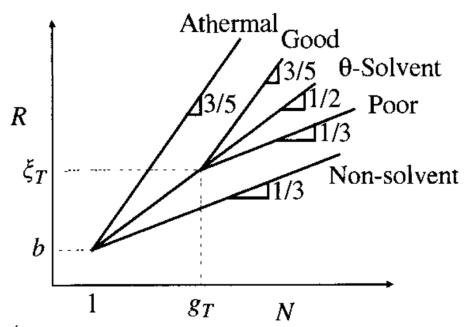
$$R \sim N^{1/3} < N^{1/2}$$
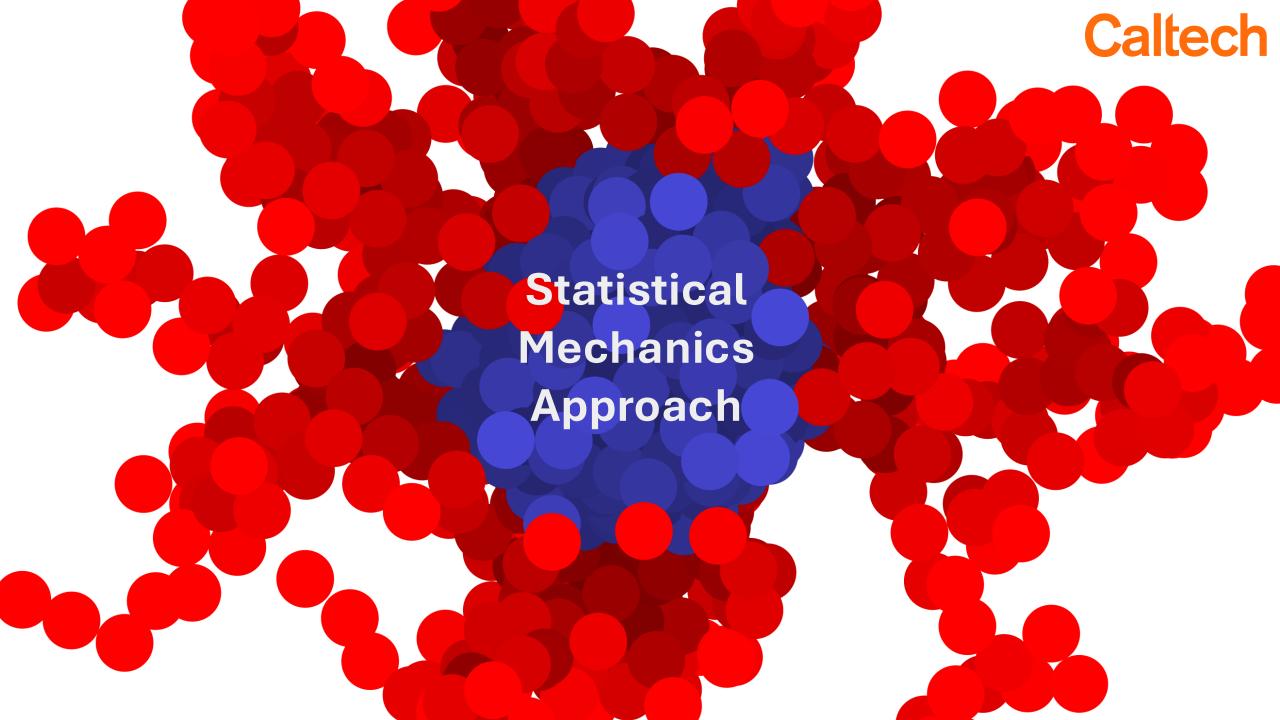
- Size ξ^3
- m monomers

Summary

- **Ideal chains**
  - Uncorrelated bonds, $R \sim N^{1/2} l$
  - Correlated bonds, $R \sim C_\infty N^{1/2} l$, with $(C_\infty > 1)$
  - Equivalent FJC, $R \sim \widehat{N} b \sim C_\infty N^{1/2} l$
  - Gaussian end-to-end distribution
    - Informs Gaussian bond potential (superbonds)

- **Real Chains**
  - Monomers feel other monomers
  - Excluded volume energy increases with N, $F_{\mathrm{ev}} \sim N^{1/2}$
    - Thermal blob, chain behaves ideally for $F_{\mathrm{ev}} \sim kT$
  - Good, Theta and Poor solvents
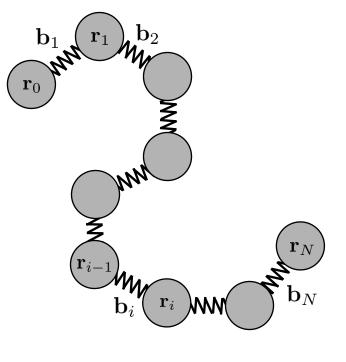

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Statistical Mechanics Approach

Discrete Gaussian Chain Model

$$\mathbf{r}^{N+1} = (\mathbf{r}_0, \mathbf{r}_1, \ldots \mathbf{r}_N)$$

Configurational Partition Function

$$Z_0 = \int d\mathbf{r}^{N+1} \, \exp\left[-\beta U_0(\mathbf{r}^{N+1})\right] = \int d\mathbf{r}^{N+1} \, \exp\left[-\frac{3}{2b^2}\sum_{i=1}^{N}|\mathbf{r}_i - \mathbf{r}_{i-1}|^2\right]$$

$$= V \int d\mathbf{b}^N \exp\left[-\frac{3}{2b^2}\sum_{i=1}^{N}\mathbf{b}_i \cdot \mathbf{b}_i\right] = V\left(\int d\mathbf{b} \exp\left[-\frac{3}{2b^2}\mathbf{b}\cdot\mathbf{b}\right]\right)^N$$

Full Probability Distribution

$$P(\mathbf{r}_0, \mathbf{b}^N) = \frac{1}{V}\prod_{i=1}^{N}\frac{\exp\left[-\beta h(\mathbf{b}\cdot\mathbf{b})\right]}{\int d\mathbf{b}_i \exp\left[-\beta h(\mathbf{b}_i \cdot \mathbf{b}_i)\right]} \qquad h(x) = \frac{3kT}{2b^2}x^2 \qquad$$ *N* independent harmonic springs

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Chapman-Kolmogorov Equation

- Bond propagation is a stochastic process

- Build up probability recursively

Probability of finding bead j at position $\boldsymbol{r}$

$$p(\mathbf{r}, j)$$

Normalized transition probability

$$\Phi(\mathbf{b}) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\frac{3}{2b^2}\mathbf{b}\cdot\mathbf{b}\right]$$

$$p(\mathbf{r}, j) = \int d\mathbf{b}\, \Phi(\mathbf{b})p(\mathbf{r} - \mathbf{b}, j - 1)$$

Fourier transform (convolution theorem)

$$\hat{p}(\mathbf{k}, j) = \hat{\Phi}(\mathbf{k})\hat{p}(\mathbf{k}, j - 1)$$

$$\hat{p}(\mathbf{k}, N) = \left[\hat{\Phi}(\mathbf{k})\right]^N \hat{p}(\mathbf{k}, 0) = \exp\left(-\frac{Nb^2}{6}\mathbf{k}\cdot\mathbf{k}\right)\hat{p}(\mathbf{k}, 0)$$

Fix bead 0 at the origin

$$\boxed{\hat{p}(\mathbf{R}, N) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \exp\left(-\frac{3}{2Nb^2}\mathbf{R}\cdot\mathbf{R}\right)}$$
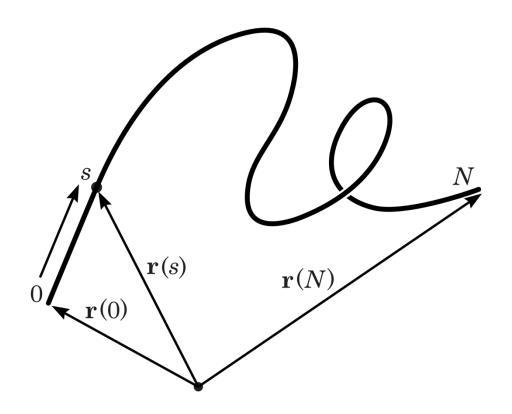
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Continuous Gaussian Chain

- Chain is a space curve $\boldsymbol{r}(s)$ with $s \in [0, N]$
  - s is the location of a segment on the backbone
  - $\boldsymbol{r}(s)$ is the location of that segment in space

$$\beta U[\mathbf{r}] = \frac{3}{2b^2} \int_0^N ds \left| \frac{d\mathbf{r}(s)}{ds} \right|^2$$

[] functional

Continuous chain results in a PDE
for the probability distribution

$$\frac{\partial}{\partial s} p(\mathbf{r}, s) = \frac{b^2}{6} \nabla^2 p(\mathbf{r}, s)$$

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Solving the Fokker-Planck Equation

- Fix chain end at origin

Fundamental Solution (Green's Function)

$$\frac{\partial}{\partial s}p(\mathbf{r},s) = \frac{b^2}{6}\nabla^2 p(\mathbf{r},s)$$

$$p(\mathbf{r},0) = \delta(\mathbf{r})$$

$$p(\mathbf{r},s) = \left(\frac{3}{2\pi s b^2}\right)^{3/2}\exp\left(-\frac{3r^2}{2sb^2}\right)$$

- Compute segment density distribution

Probability that chain of s segments originating at origin ends at $\boldsymbol{r}$

$$\hat{\rho}(\mathbf{r},s) = \int d\mathbf{R}\ p(\mathbf{r},s)p(\mathbf{R}-\mathbf{r},N-s)$$

Probability that chain of $N-s$ segments originating at $\boldsymbol{r}$ ends at $\boldsymbol{R}$

$$\rho(\mathbf{r}) = \int_0^N ds\ \hat{\rho}(\mathbf{r},s)$$

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Chain with Fixed End

$$\rho(r) = \frac{3}{2\pi b^2 r} \left[1 - \mathrm{erf}\left(\sqrt{\frac{3}{2N}} \frac{r}{b} \right) \right]$$

Two-Point Green's Function

$$G(\mathbf{r}, \mathbf{r}', N)$$

Conditional probability that the chain-end is located at $\mathbf{r}$ given that the other chain end is located at $\mathbf{r}'$

$$G(\mathbf{r} - \mathbf{r}', N) = p(\mathbf{r} - \mathbf{r}', N)$$

Often-times reduces to symmetric case

$$\left(\frac{\partial}{\partial s} - \frac{b^2}{6} \nabla^2 \right) G(\mathbf{r}, \mathbf{r}', s) = \delta(\mathbf{r} - \mathbf{r}') \delta(s)$$

Gaussian Chain in External Potential

$$Z = \int \mathcal{D}\mathbf{r} \, \exp\left[-\beta U_0[\mathbf{r}] - \beta U_1[\mathbf{r}]\right] = \int \mathcal{D}\mathbf{r} \, \exp\left[-\frac{3}{2b^2}\int ds \left|\frac{d\mathbf{r}(s)}{ds}\right|^2 - \int_0^N ds \int d\mathbf{r}' \, w(\mathbf{r}')\delta(\mathbf{r}' - \mathbf{r}(s))\right]$$

Segment density is conjugate to external chemical potential field

$$\frac{\partial}{\partial s}q(\mathbf{r}, s) = \left(\frac{b^2}{6}\nabla^2 - w(\mathbf{r})\right)q(\mathbf{r}, s) = \mathcal{L}q(\mathbf{r}, s)$$

$$Q[w] = \frac{1}{V}\int d\mathbf{r} \, q(\mathbf{r}, N; [w])$$ Chain partition function

Density of chain in external field

$$\rho(\mathbf{r}) = \frac{\delta \beta F}{\delta w} = -\frac{1}{Q[w]}\frac{\delta Q[w]}{\delta w} = \frac{1}{VQ[w]}\int_0^N ds \, q(\mathbf{r}, N - s; [w])q(\mathbf{r}, s; [w])$$

Ground-State Dominance

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \left(\frac{b^2}{6} \nabla^2 - w(\mathbf{r}) \right) q(\mathbf{r}, s) = \mathcal{L} q(\mathbf{r}, s)$$

Self-adjoint Sturm-Liouville operator

Full Solution

$$\mathcal{L} \psi_k(\mathbf{r}) = -\Lambda_k \psi_k(\mathbf{r}), \quad k = 0, 1, 2, \ldots \infty$$

$$q(\mathbf{r}, s) = \sum_{k=0}^{\infty} q_k \psi_k(\mathbf{r}) \exp\left(-s\Lambda_k \right)$$

$$Q[w] = \frac{1}{V} \int d\mathbf{r} \, q(\mathbf{r}, N) = \frac{1}{V} \sum_{k=0}^{\infty} q_k^2 \exp(-N\Lambda_k) \sim \frac{q_0^2}{V} \exp(-N\Lambda_0)$$

Very large N means terms
decay rapidly

Truncate (GSD)

$$\rho(\mathbf{r}) \sim \frac{N q_0^2}{V Q[w]} \exp(-N\Lambda_0) [\psi_0(\mathbf{r})]^2 \sim N[\psi_0(\mathbf{r})]^2$$

GSD Condition

$$\exp[-N(\Lambda_1 - \Lambda_0)] \ll 1$$