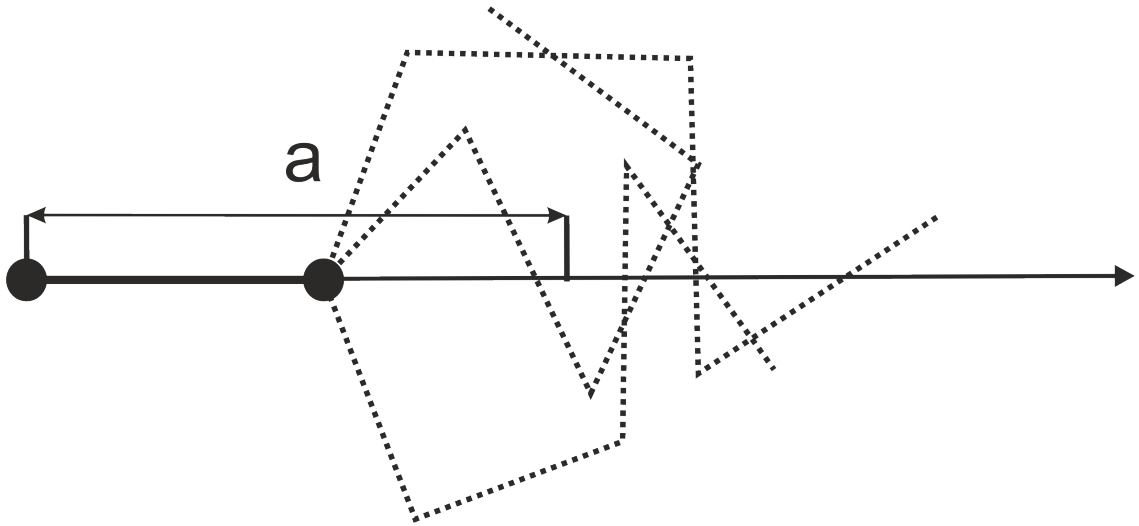
Class 4
Statistical-mechanical models of polymer chains, part 2

November 10, 2026

The persistence length



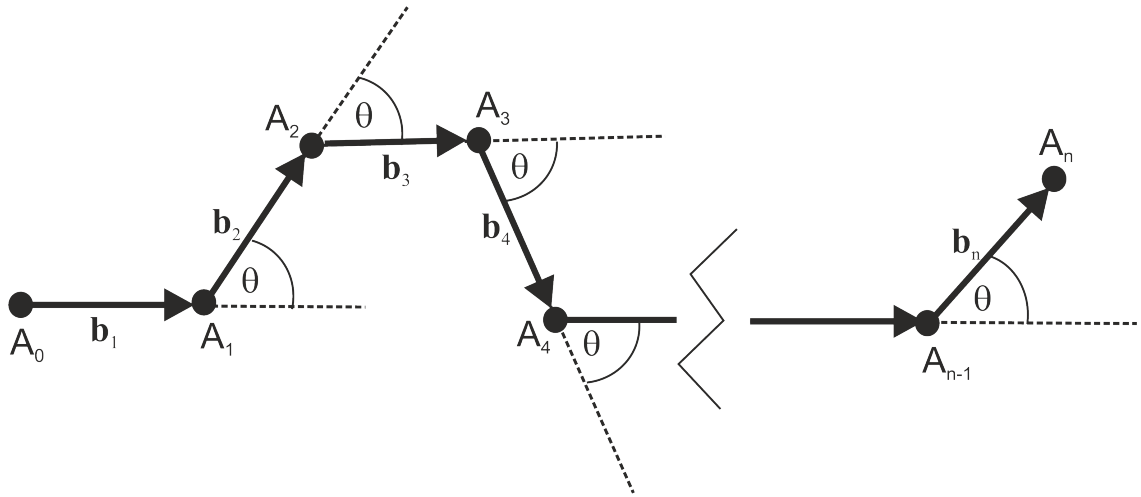
The persistence length is the limit of average sum of the projections of the bonds next to a given one onto it.

$$a = \lim_{n\to\infty} \frac{1}{b_1} \sum_{j=1}^{n} \langle \mathbf{b}_1 \bullet \mathbf{b}_j \rangle$$

For a freely-jointed chain the persistence length is b.

The persistence length

For a freely-rotating chain:



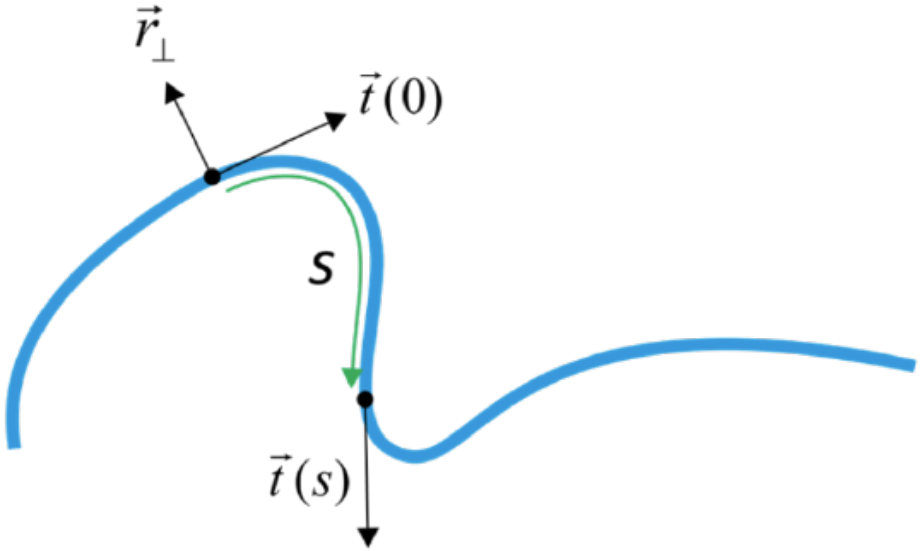
$$a = b \lim_{n\to\infty} \sum_{j=1}^{n} (\cos\theta)^{j-1} = b \lim_{n\to\infty} \frac{1-(\cos\theta)^n}{1-\cos\theta} = \left(\frac{b}{1-\cos\theta}\right)$$

Connection with the end-to-end distance and the characteristic ratio:

$$\langle r^2\rangle_0 = 2nba - nb^2$$

$$C_\infty = \left(\frac{\langle r^2\rangle_0}{nb^2}\right)_{n\to\infty} = \frac{2a}{l} - 1$$

The Kratky-Porod wormlike chain model

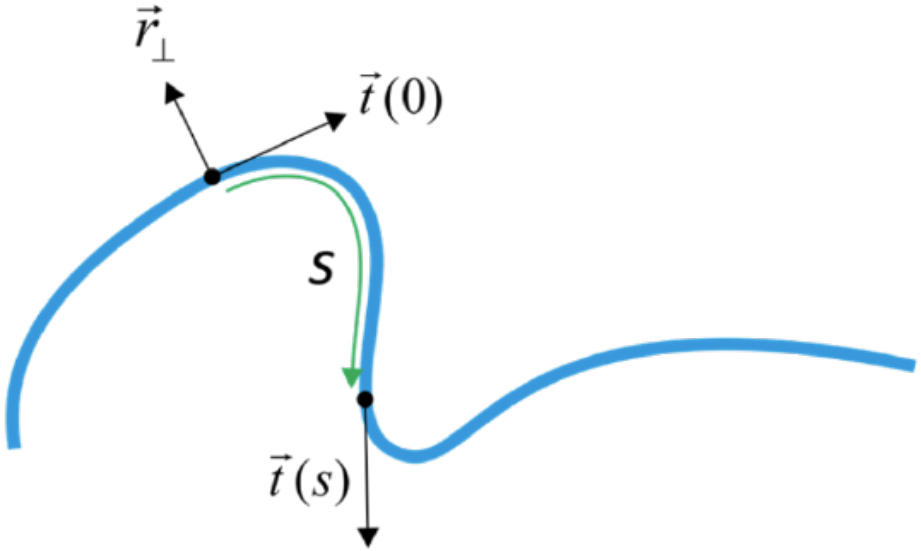


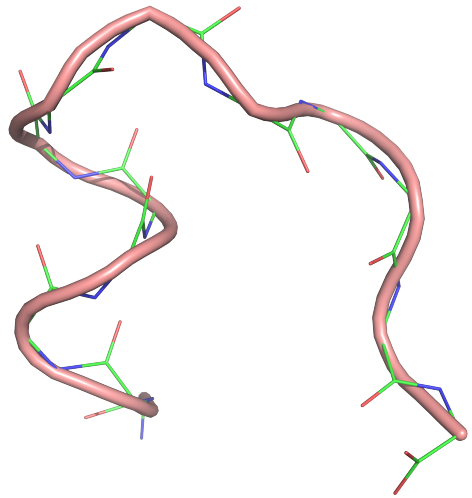


Freely rotating chain	Wormlike chain
bead index, i	position along chain, s
bond vector, $\mathbf{b}_i$	tangent vector, $\mathbf{t}(s)$
bond angle, θ_i	curvature, $\kappa(s)$
dihedral angle, ϕ	torsion, $\tau(s)$

A wormlike chain can be considered a limit of a freely-rotating chain in which the bond lengths approach zero and the bond angles approach $180°$ so that the persistence length is unchanged.

The Kratky-Porod wormlike chain model





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The Kratky-Porod wormlike chain model

$$a = \frac{b}{1-\cos\theta} = \frac{b}{1-\alpha}, \quad \alpha = \cos\theta$$

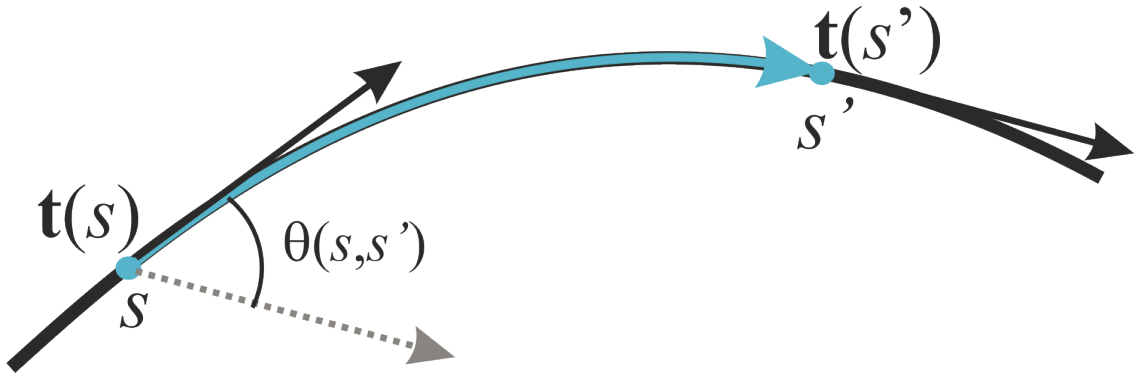
$$\alpha = 1 - \frac{b}{a}$$

$$\overline{X}_1 = b\frac{1-\alpha^n}{1-\alpha} = b\frac{1-\left(1-\frac{b}{a}\right)^n}{1-\left(1-\frac{b}{a}\right.} = a\left[1-\left(1-\frac{b}{a}\right)^n\right]$$

$$\lim_{b\to 0} a\left[1-\left(1-\frac{b}{a}\right)^n\right] = \lim_{b\to 0} a\left[1-\exp\left(-\frac{nb}{a}\right)\right]$$

$$\overline{X}_1 = a\left[1-\exp\left(-\frac{L}{a}\right)\right], \quad L = nb$$

The Kratky-Porod wormlike chain model



$$\overline{X}(s,s') = a\left[1 - \exp\left(-\frac{|s'-s|}{a}\right)\right]$$

The mean angle between two chain sections:

$$\langle \cos\theta(s,s')\rangle = \langle \mathbf{t}(s) \bullet \mathbf{t}(s')\rangle = \frac{\partial \overline{X}(s,s')}{\partial s'} = \exp\left(-\frac{|s'-s|}{a}\right)$$

Multiplicative property:

$$\langle \mathbf{t}(s) \bullet \mathbf{t}(s')\rangle = \langle \mathbf{t}(s) \bullet \mathbf{t}(l)\rangle\langle \mathbf{t}(l) \bullet \mathbf{t}(s')\rangle$$

The Kratky-Porod wormlike chain model

End-to-end distance:

$$d\langle r^2\rangle_0 = 2\langle \mathbf{r} \bullet d\mathbf{r}\rangle = 2\overline{X}_1 dL$$

$$\frac{\langle r^2\rangle_0}{L} = 2a\left[1 - \frac{a}{L}\left(1 - e^{-\frac{L}{a}}\right)\right]$$

$$\left(\frac{\langle r^2\rangle_0}{L}\right)_\infty = 2a$$

Thus, a is a measure of the extent of the "straight" section of the chain, hence the name "persistence length".

For real chain (note that $L < nb$):

$$C_\infty = \left(\frac{\langle r^2\rangle_0}{nb^2}\right) = \left(\frac{L}{nb}\right)\left(\frac{2a}{b}\right)$$

$$\frac{\langle r^2\rangle_0}{nb^2} = C_\infty\left[1 - \frac{a}{L}\left(1 - e^{-\frac{L}{a}}\right)\right]$$

The Kratky-Porod wormlike chain model

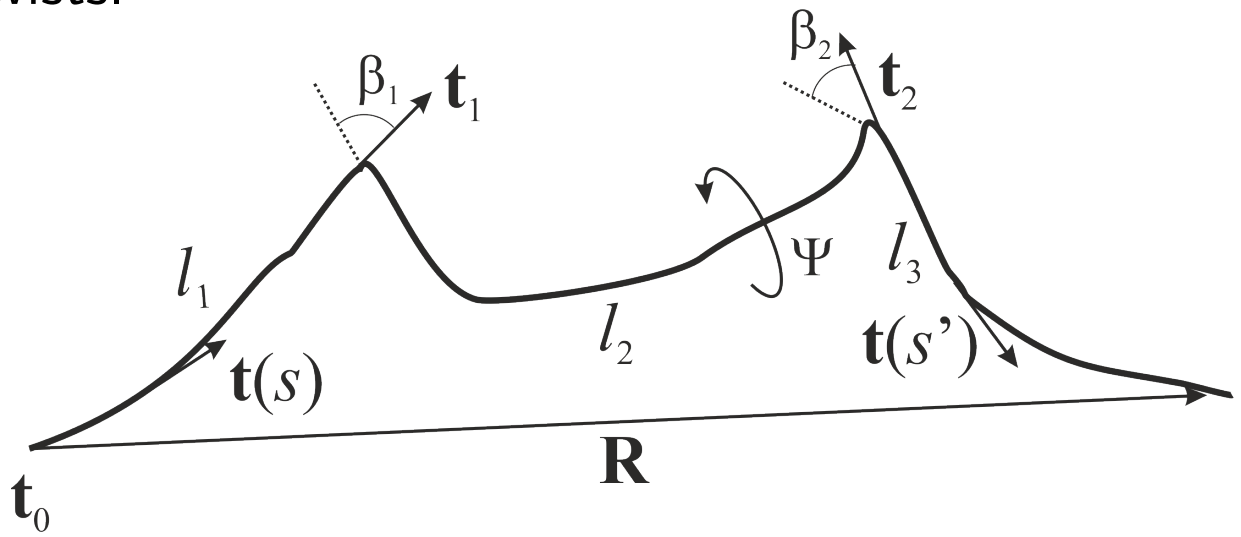
Radius of gyration:

$$\frac{\langle s^2\rangle_0}{L} = \left(\frac{a}{3}\right)\left\{1-\left(\frac{3a}{L}\right)\left[1-2\left(\frac{3a}{L}\right)+2\left(\frac{3a}{L}\right)^2-2\left(\frac{3a}{L}\right)^2 e^{-\frac{L}{a}}\right]\right\}$$

$$\frac{\langle s^2\rangle_0}{nb^2} = \left(\frac{\langle s^2\rangle_0}{nb^2}\right)_\infty \times$$
$$\left\{1-\left(\frac{3a}{L}\right)\left[1-2\left(\frac{3a}{L}\right)+2\left(\frac{3a}{L}\right)^2-2\left(\frac{3a}{L}\right)^2 e^{-\frac{L}{a}}\right]\right\}$$

The Kratky-Porod wormlike chain model

Bends and twists.



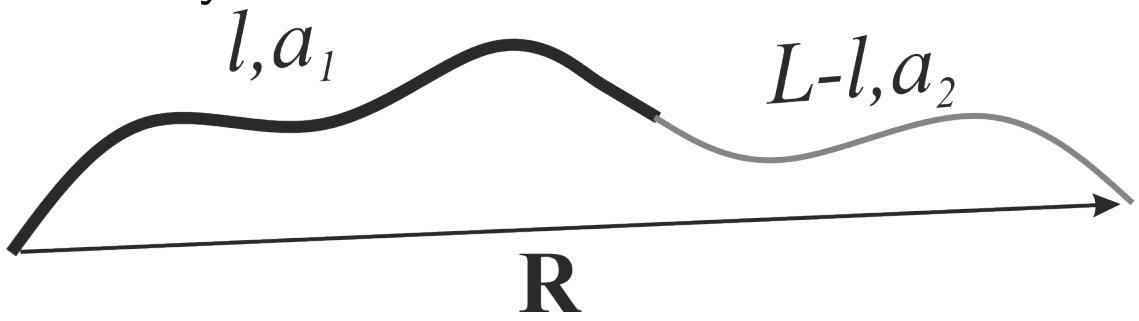
For 2 consecutive bends separated by a twist:

$$\langle R^2_{\beta_1,\psi,\beta_2}\rangle = 2aL\left\{1-\frac{a}{L}\left[\left(1-e^{-\frac{l_1}{a}}\right)+\left(1-e^{-\frac{l_2}{a}}\right)+\left(1-e^{-\frac{l_3}{a}}\right)\right.\right.$$
$$-\cos\beta_1\left(1-e^{-\frac{l_1}{a}}\right)\left(1-e^{-\frac{l_2}{a}}\right)-\cos\beta_2\left(1-e^{-\frac{l_2}{a}}\right)\left(1-e^{-\frac{l_3}{a}}\right)-$$
$$\left.\left.\left(\cos\beta_1\cos\beta_2-\sin\beta_1\sin\beta_2\sin\psi\right)e^{-\frac{l_2}{a}}\left(1-e^{-\frac{l_1}{a}}\right)\left(1-e^{-\frac{l_3}{a}}\right)\right]\right\}$$

Rivetti et al., *J. Mol. Biol.*, **1998** 280, 41-59.

The Kratky-Porod wormlike chain model

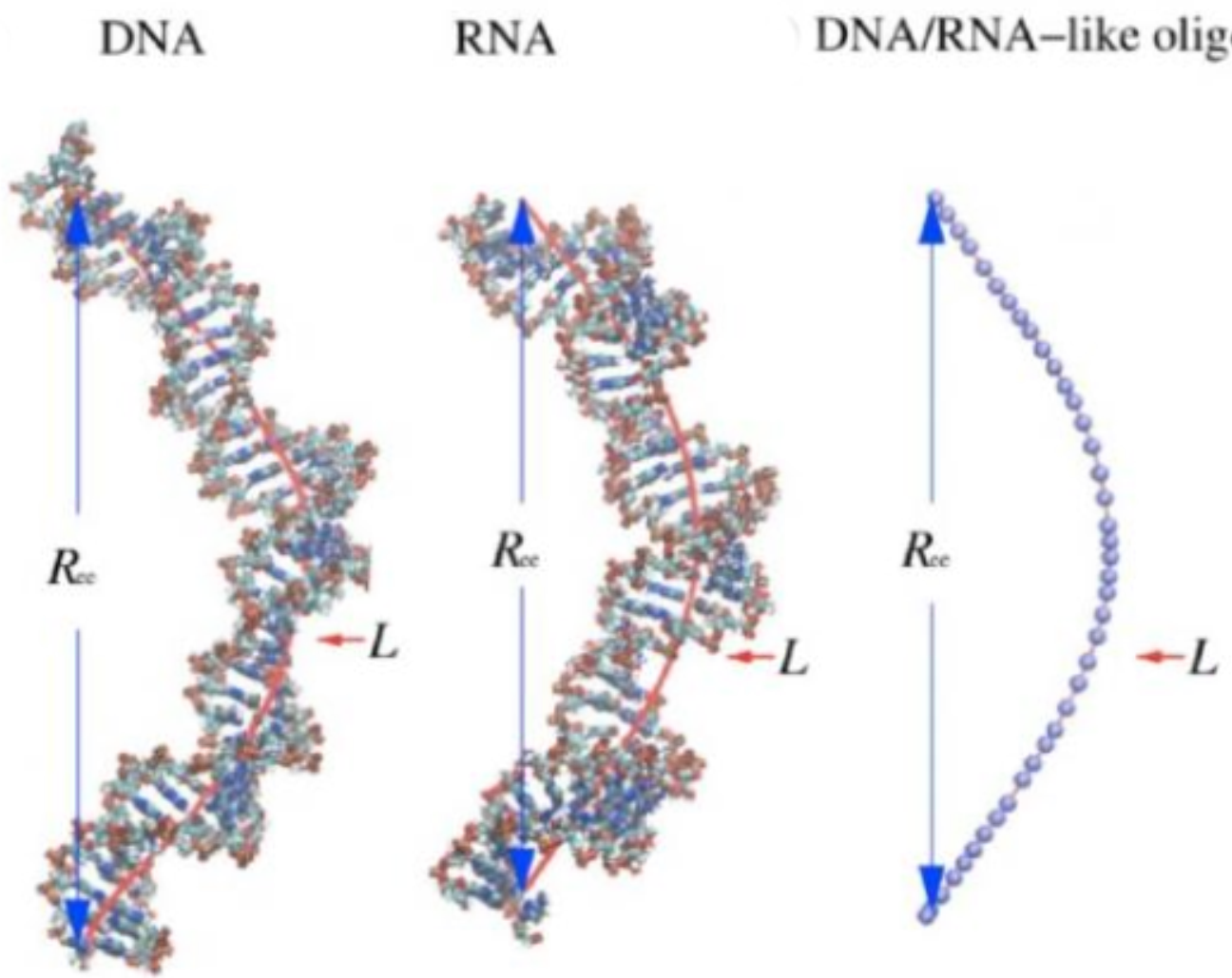
Variable chain flexibility



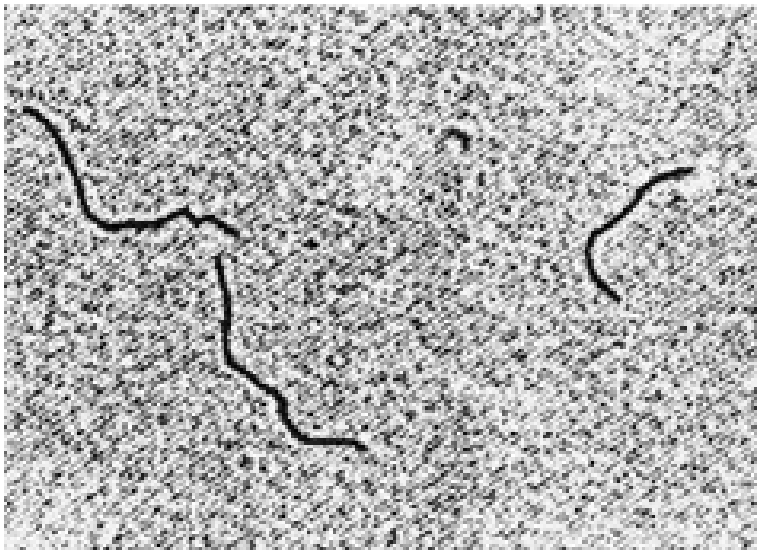
$$\langle R^2_{a_1 a_2} = 2a_1 l \left[1 - \frac{a_1}{l}\left(1 - e^{-\frac{l}{a_1}}\right)\right] + 2a_2(L-l)\left[1 - \frac{a_2}{l}\left(1 - e^{-\frac{L-l}{a_2}}\right)\right] + 2a_1 a_2 \left(1 - e^{-\frac{l}{a_1}}\right)\left(1 - e^{-\frac{L-l}{a_2}}\right)$$

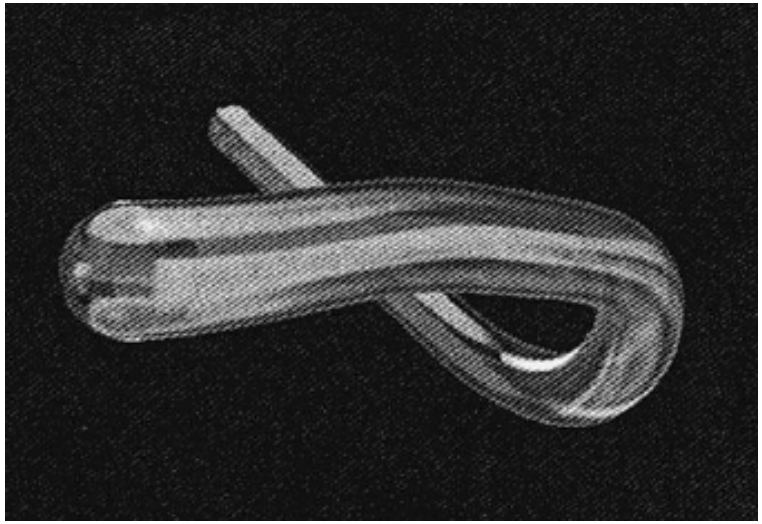
Rivetti et al., *J. Mol. Biol.*, **1998** 280, 41-59.

Applications of the wormlike chain model to DNA



Applications of the wormlike chain model to DNA

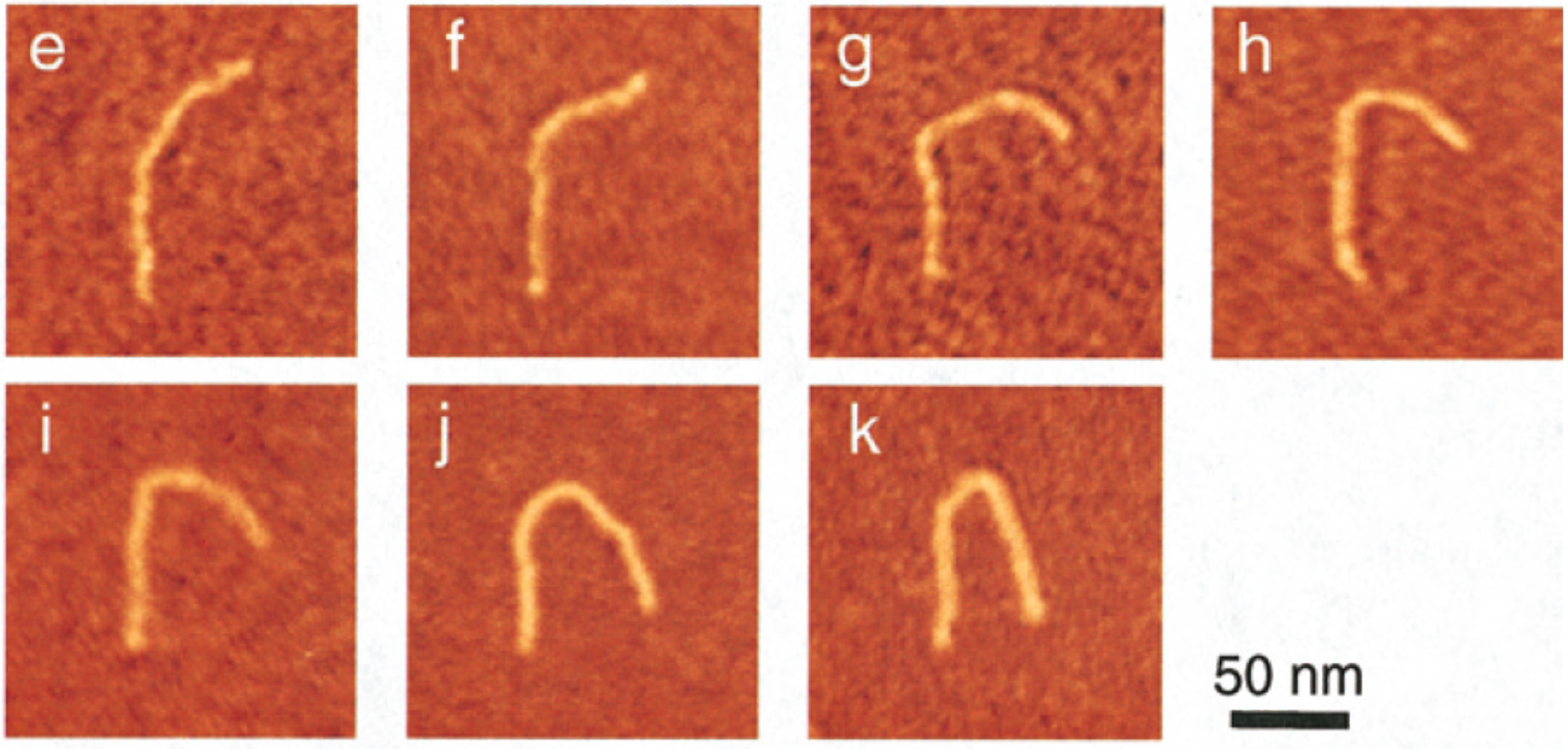




Electromicrographs of the artificial straight DNA [sequences (ATCTAATCTAACACAACACA)n] and a reconstructed 3D image of a sample DNA double strand. The persistence length determined using the wormlike chain model is about 82 bp (base pairs).

Bednar et al., *J. Mol. Biol.* **1995**, 254, 579-594.

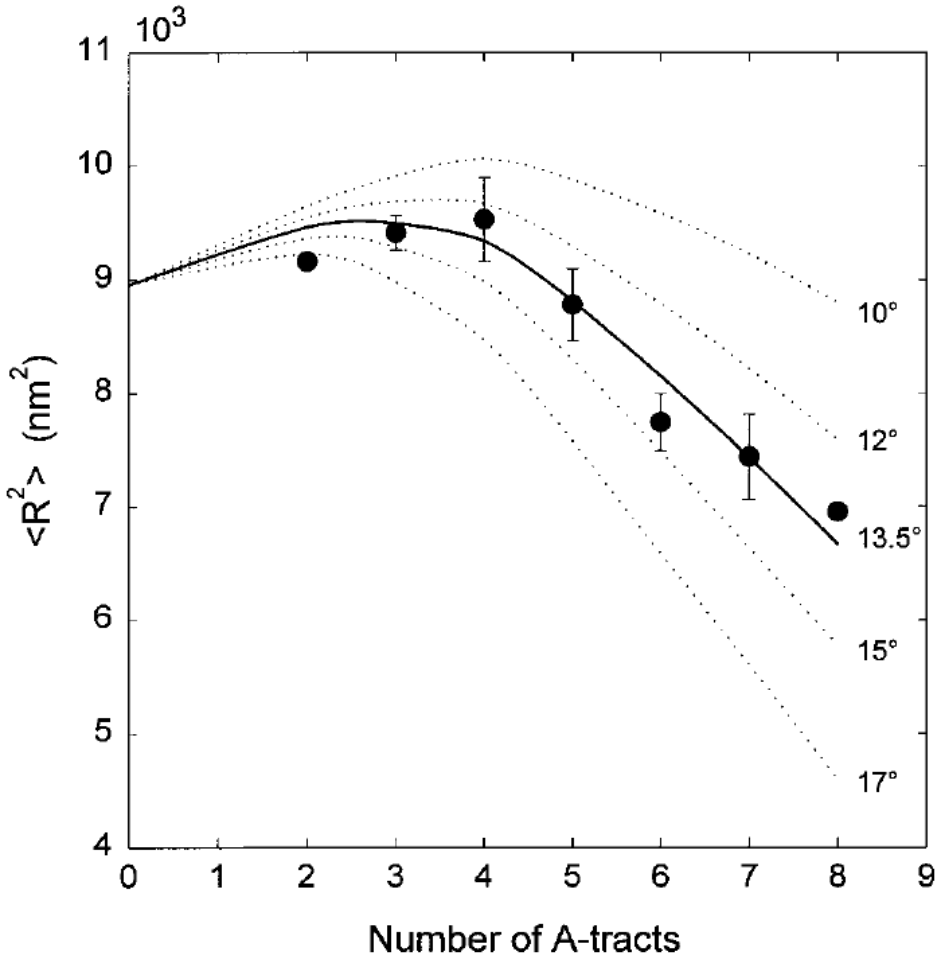
Applications of the wormlike chain model to DNA



Micrographs of DNA double strands containing 2–8 A-tracts (six adenine residues followed by a four base-pair GC-rich spacer) that generate bends.

Rivetti et al., *J. Mol. Biol.*, **1998** 280, 41-59.

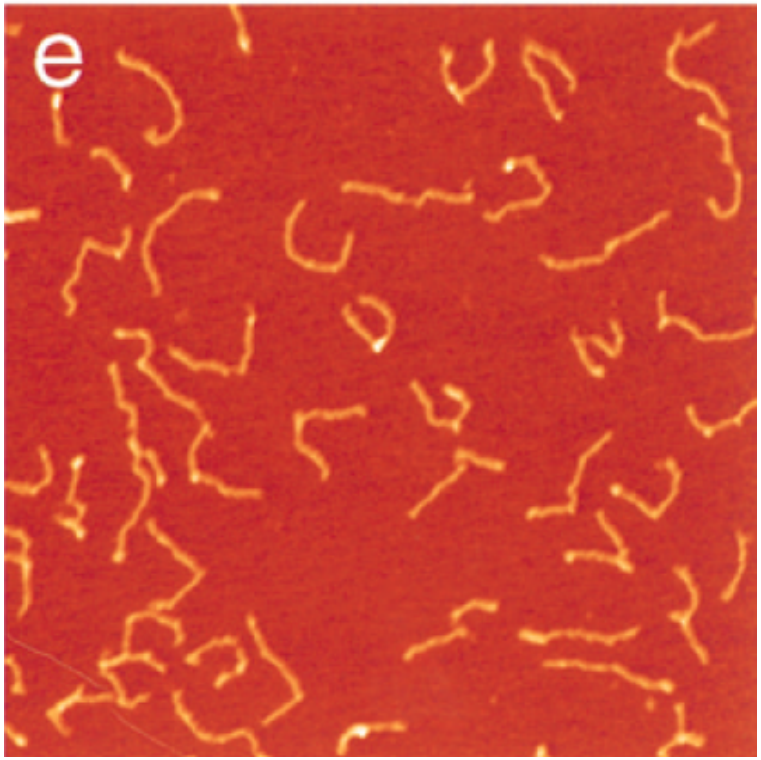
Applications of the wormlike chain model to DNA

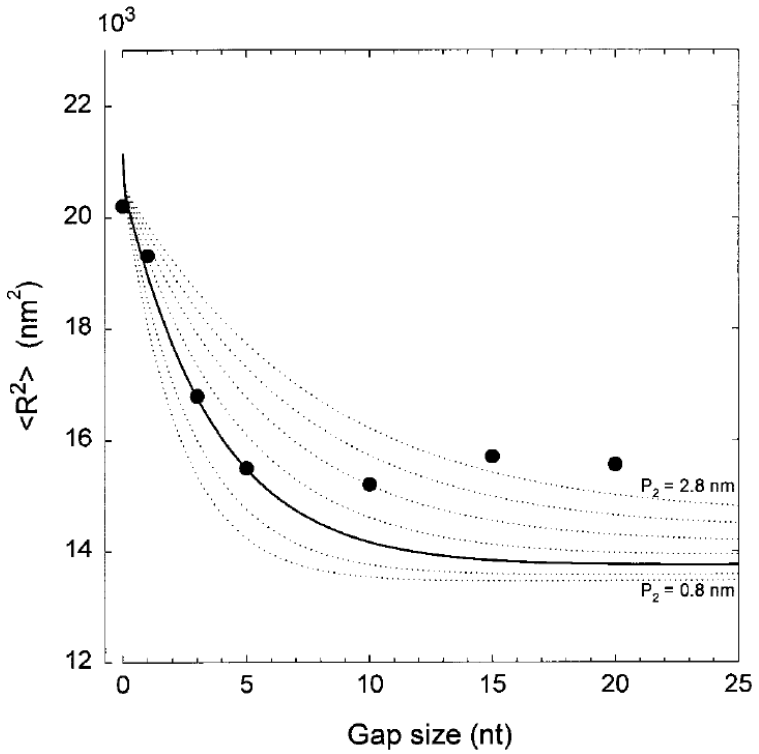


Dependence of the DNA end-to-end distance on the number of A-tracts. Curves represent the results of the calculations of the wormlike chain model with different bend angle β.

Rivetti et al., *J. Mol. Biol.*, **1998** 280, 41-59.

Applications of the wormlike chain model to DNA

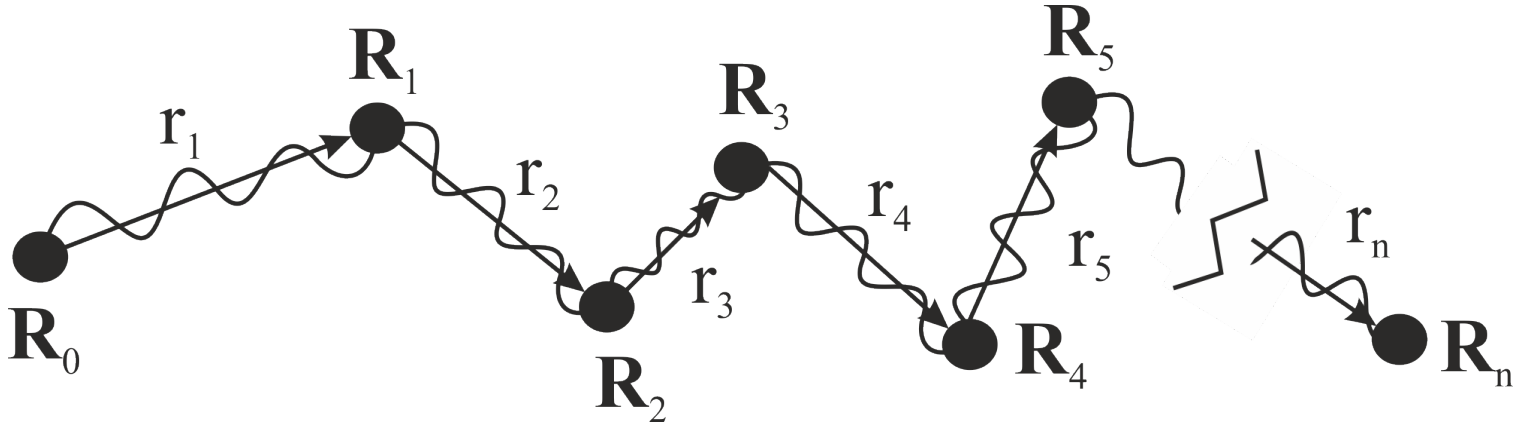




Electromicrographs of DNA double strands separated by single-strand gaps (regions of lower elasticity) and dependence of the DNA end-to-end distance on the number of gaps Curves represent the results of the calculations of the wormlike chain model with different single-strand persistence length.

Rivetti et al., *J. Mol. Biol.*, **1998** 280, 41-59.

Gaussian chain (Rouse model)



Each bond is a spring with equilibrium length 0. However, its *average* length is set at b (which may vary with bead index for heteropolymers). The distribution of bond vectors is expressed as

$$P(\mathbf{r}_i) = \left(\frac{3}{2\pi b^2}\right) \exp\left(-\frac{3\|\mathbf{r}_i\|^2}{2b^2}\right)$$

The cumulative distribution of bead positions is given by

$$P(\{\mathbf{R}_N\}) = \left(\frac{3}{2\pi b^2}\right)^{\frac{3N}{2}} \exp\left[-\sum_{i=0}^{n} \frac{3\|\mathbf{R}_{i+1} - \mathbf{R}_i\|^2}{2b^2}\right]$$

Gaussian chain (Rouse model)

The average potential energy at temperature T.

$$U_0 = \frac{3}{2b^2} k_B T \sum_{i=0}^{n} \|\mathbf{R}_{i+1} - \mathbf{R}_i\|^2$$

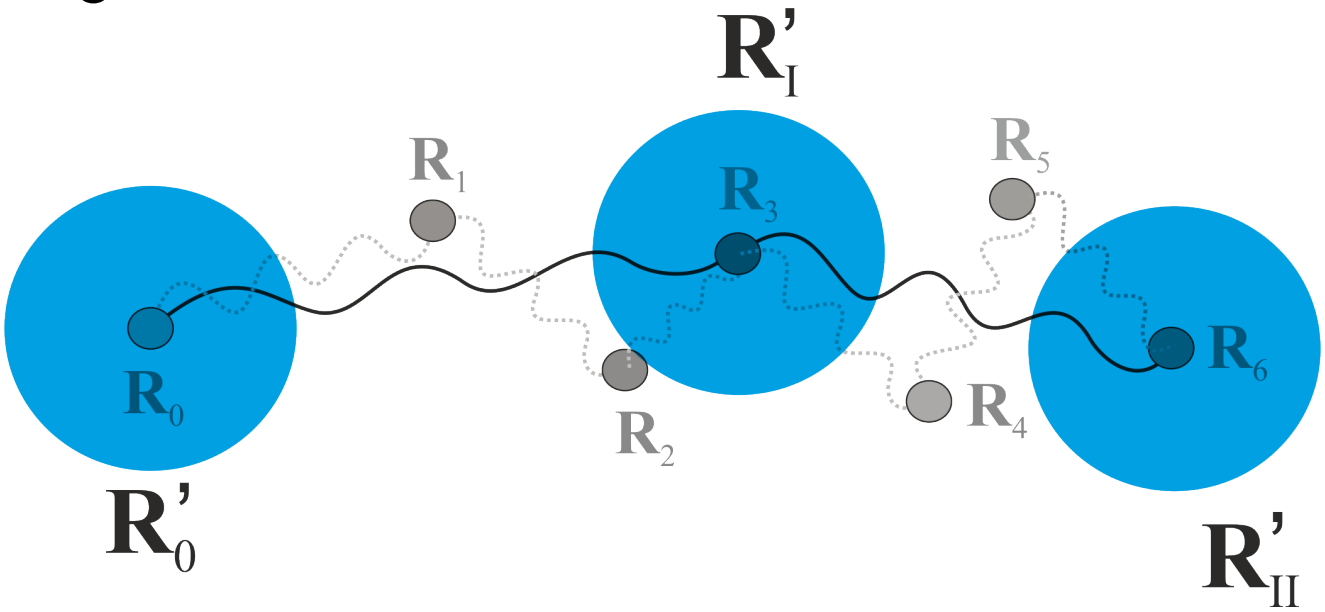
The distribution of the distances between beads and the mean distance are the same as for a freely jointed chain with bond length b.

$$P(\mathbf{R}_j - \mathbf{R}_i) = \left(\frac{3}{2\pi b^2 |j-i|} \right)^{\frac{3}{2}} \exp\left[-\frac{3\|\mathbf{R}_j - \mathbf{R}_i\|^2}{2|j-i|b^2} \right]$$

$$\langle \|\mathbf{R}_j - \mathbf{R}_i\|^2 \rangle = |j-i|b^2$$

Gaussian chain (Rouse model)

Coarse-graining the Gaussian chain.



If m original beads are merged into one and springs put every $m+1$ beads, the potential energy and distribution remain the same after rescaling b.

Gaussian chain (Rouse model)

$$U_0 = \frac{3}{2b^2} k_B T \sum_{i=0}^{n} \|\mathbf{R}_{i+1} - \mathbf{R}_i\|^2 = \frac{3}{2B^2} k_B T \sum_{I=0}^{n'} \|\mathbf{R}'_{i+1} - \mathbf{R}'_i\|^2$$

$$P(\mathbf{R}'_J - \mathbf{R}'_I) = \left(\frac{3}{2\pi B^2 |J-I|} \right)^{\frac{3}{2}} \exp\left[-\frac{3\|\mathbf{R}'_j - \mathbf{R}'_I\|^2}{2|J-I|B^2} \right]$$

$$\langle \|\mathbf{R}'_J - \mathbf{R}'_I\|^2 \rangle = |J-I|B^2$$

where $B = \sqrt{m}b$, $n' = n/m$.

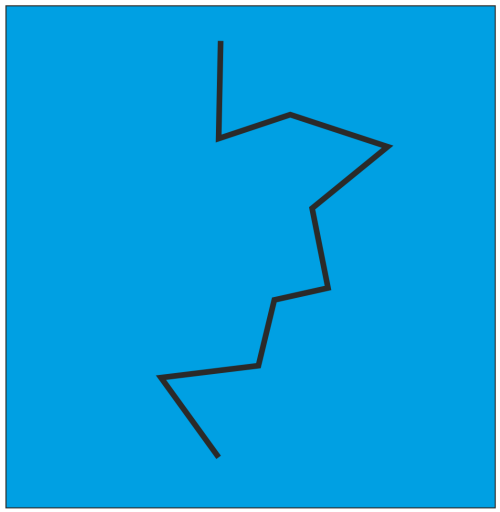
The Edwards continuous model

Replacing the bead index i with a continuous variable s in the Gaussian model, we get

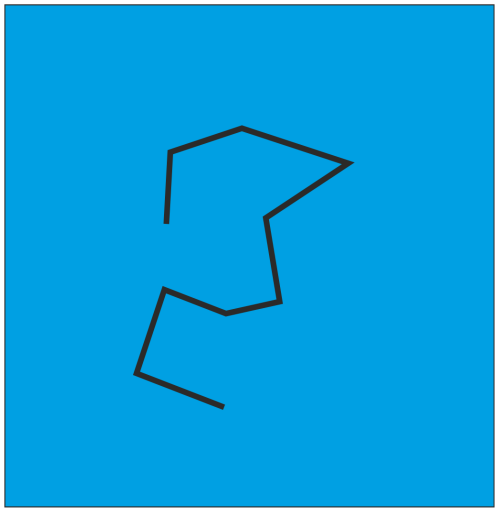
$$U_0 = H[\mathbf{R}(s)] = \frac{3}{2b^2} k_B T \int_0^L \left\| \frac{\partial \mathbf{R}}{\partial s} \right\|^2 ds$$

$$P[\mathbf{R}(s)] = \exp\left[-\frac{H[\mathbf{R}(s)]}{k_B T} \right]$$

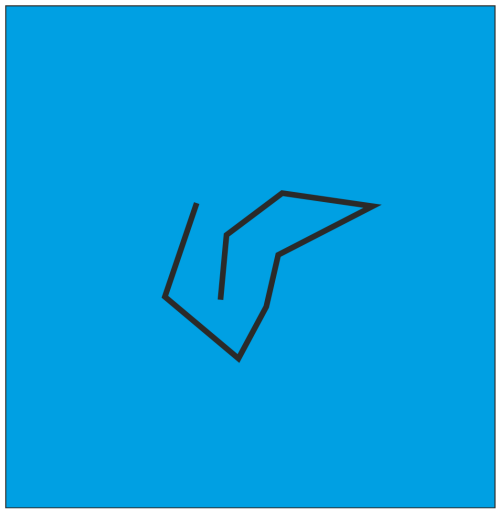
Excluded volume effect



good solvent



Θ solvent



poor solvent

Excluded volume effect

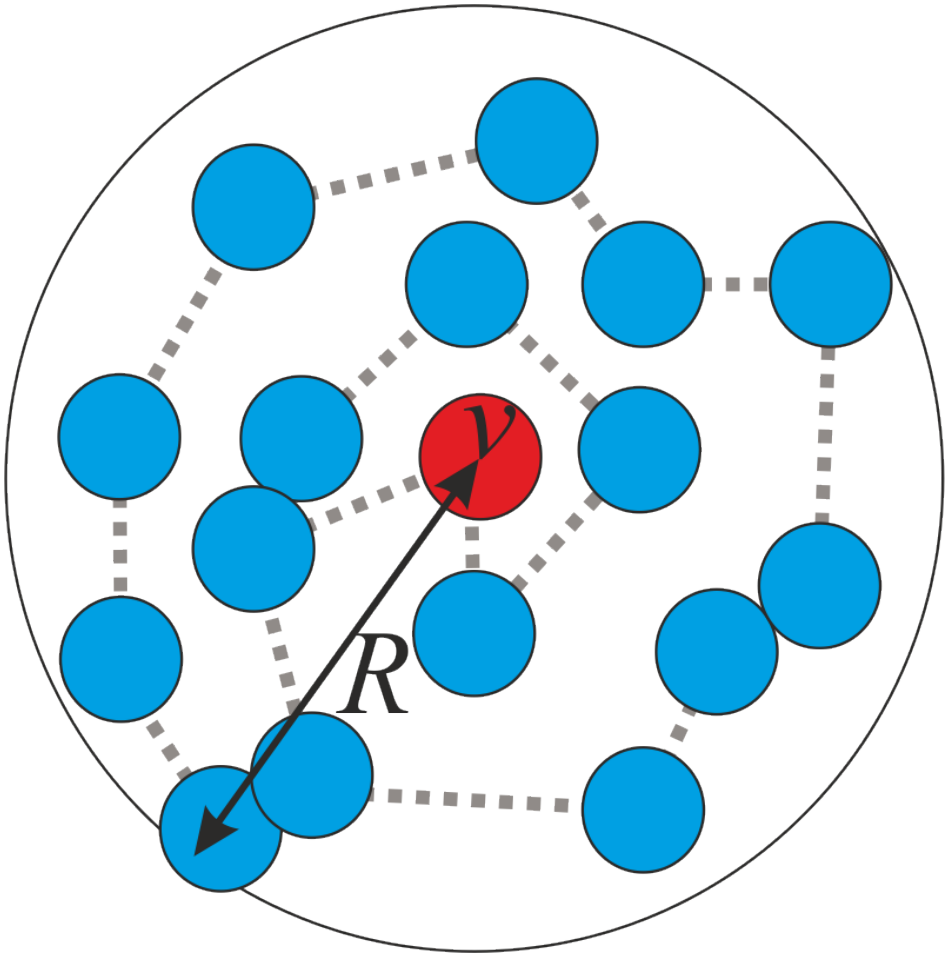
The excluded volume is that of the space around a bead impenetrable to other beads; it contains the solvation co-volume.

- Good solvent: polymer – solvent interactions are stronger than those between polymer units; chains swollen, solubility high.
- Θ solvent: polymer – solvent interactions are as strong as those between polymer units; chain dimensions comparable with those of ideal chains; solubility high.
- Poor solvent: polymer – solvent interactions are weaker than those between polymer units; chains collapsed, solubility low.

Measure of excluded volume:

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0$$

Flory's derivation of the dependence of end-to-end distance on chain length (N) for a good solvent



v: the excluded volume around the selected bead.
R: The radius of the system.

Flory's derivation of the dependence of end-to-end distance on chain length (N) for a good solvent

We consider the free energy of a freely-jointed chain confined to end-to-end distance R. From the distribution we get (note that for the freely-jointed chain $\langle R^2 \rangle = Nb^2$)

$$W(R) = \left(\frac{3}{2\pi N b^2} \right)^{\frac{3}{2}} \exp \left[-\frac{3}{2Nb^2} R^2 \right]$$

$$F(R) = -k_B T \ln W(R) = -\frac{3}{2} k_B T \ln \left(\frac{3}{2\pi N b^2} \right) + k_B T \frac{3R^2}{2Nb^2}$$

This free energy is entirely due to entropic elasticity.
In what follows we ignore the first term independent of R.

Flory's derivation of the dependence of end-to-end distance on chain length (N) for a good solvent

The average concentration of beads for an N-bead chain that occupies a ball with radius R is

$$\bar{c} = \frac{N}{V} = \frac{N}{R^3} \quad (\text{we ignore the shape of the container})$$

Each bead experiences the interaction energy proportional to the excluded volume and to the mean square of the concentration. The interaction energy of the whole chain is additionally proportional to the total volume of the system (proportional to R^3)

$$E_{int} = \frac{1}{2} k_B T R^3 v \overline{c^2} \approx \frac{1}{2} k_B T R^3 v \bar{c}^2 = \frac{1}{2} k_B T \frac{v N^2}{R^3}$$

The correlations between monomers are ignored, $\overline{c^2} \approx \bar{c}^2$.

Flory's derivation of the dependence of end-to-end distance on chain length (N) for a good solvent

The total free energy of an N-bead chain:

$$F = F_G + E_{int} = k_B T \left[\frac{3R^2}{2Nb^2} + \frac{1}{2} \frac{vN^2}{R^3} \right]$$

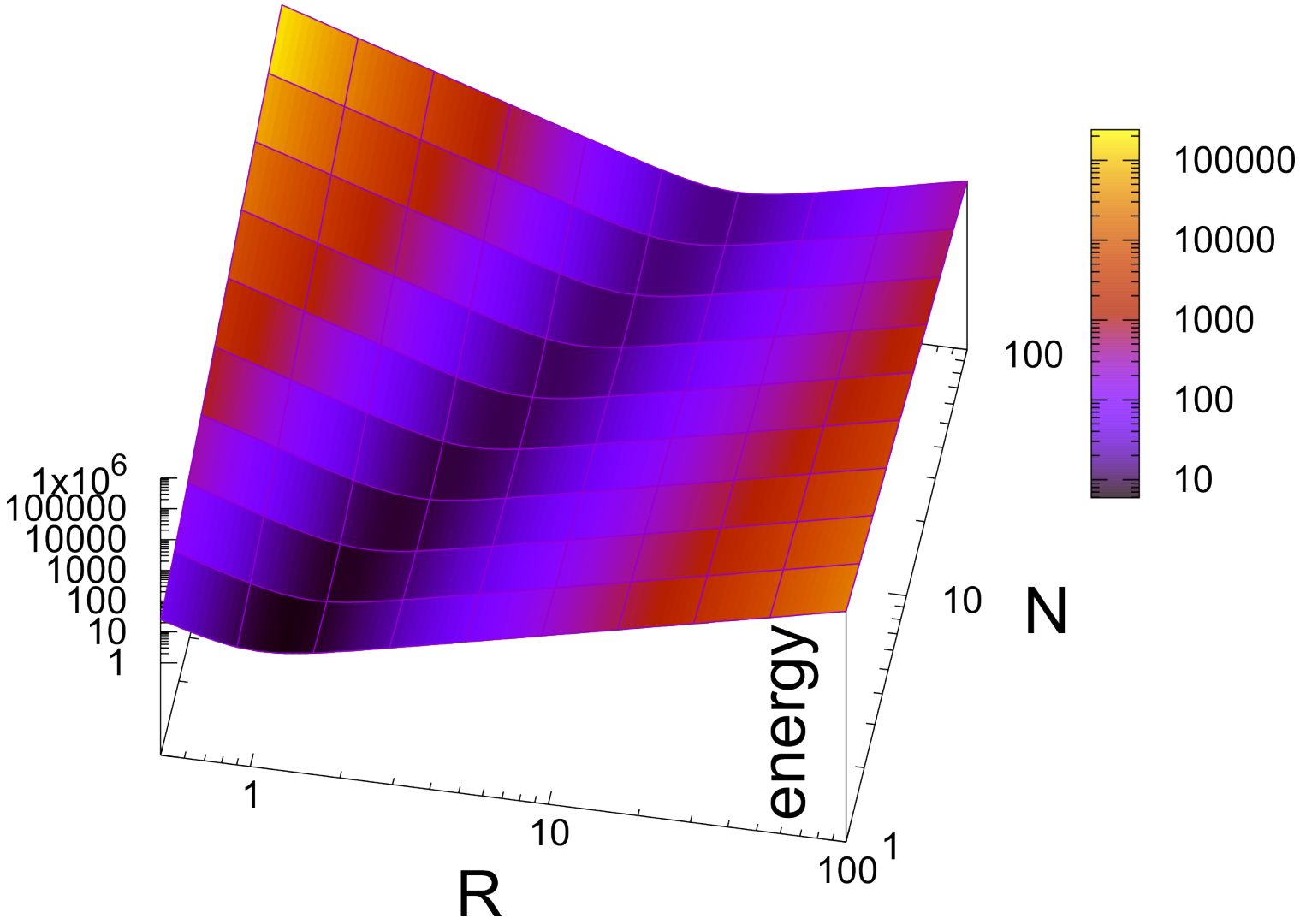
Free energy minimum:

$$\frac{\partial F}{\partial R} = k_B \left(\frac{3R}{Nb^2} - \frac{3vN^2}{2R^4} \right)$$

$$R_{min} = \left(\frac{vb^2}{2} \right)^{\frac{1}{5}} N^{\frac{3}{5}}$$

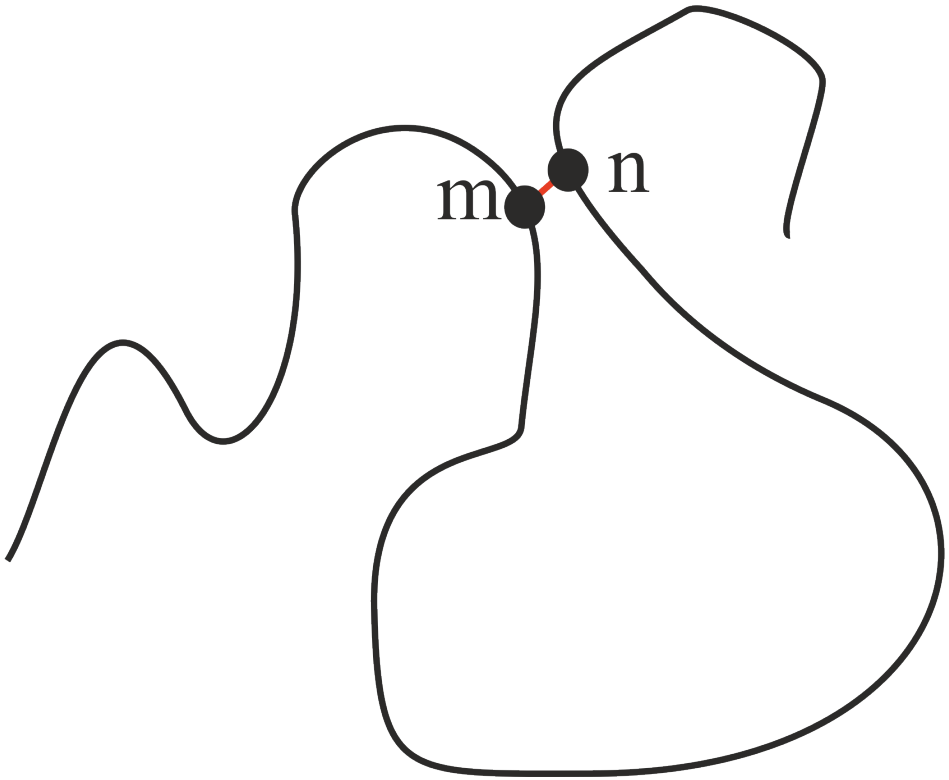
Thus, for good solvents (effectively repulsive interactions between beads dominate) $R \propto N^{\frac{3}{5}}$ (Flory's prediction). The exponent at N is termed the Flory exponent, ν. More accurate calculations yield $\nu = 0.588 \pm 0.001$.

Flory's derivation of the dependence of end-to-end distance on chain length (N) for a good solvent



The surface of F in R and N (full logarithmic scale); arbitrary units.

Dependence of excluded volume parameter on temperature



Interaction energy between segments m and n:

$$U_{mn} = k_B T v(\mathbf{R}_n - \mathbf{R}_m) = v k_B T \delta(\mathbf{R}_n - \mathbf{R}_m)$$

$$\delta(\mathbf{x}) = \begin{cases} \infty & \mathbf{x} \neq \mathbf{0} \\ 0 & \text{otherwise} \end{cases}$$

$$\int \delta(\mathbf{x}) d^n \mathbf{x} = 1$$

Dependence of excluded volume parameter on temperature

$$U_1 = \frac{1}{2} v k_B T \int_0^N \left[\int_0^N \delta(\mathbf{R}_n - \mathbf{R}_m) dm \right] dn$$

$$c(\mathbf{r}) = \sum^n \delta(\mathbf{r} - \mathbf{R}_n) = \int_0^N \delta(\mathbf{r} - \mathbf{R}_n) dn$$

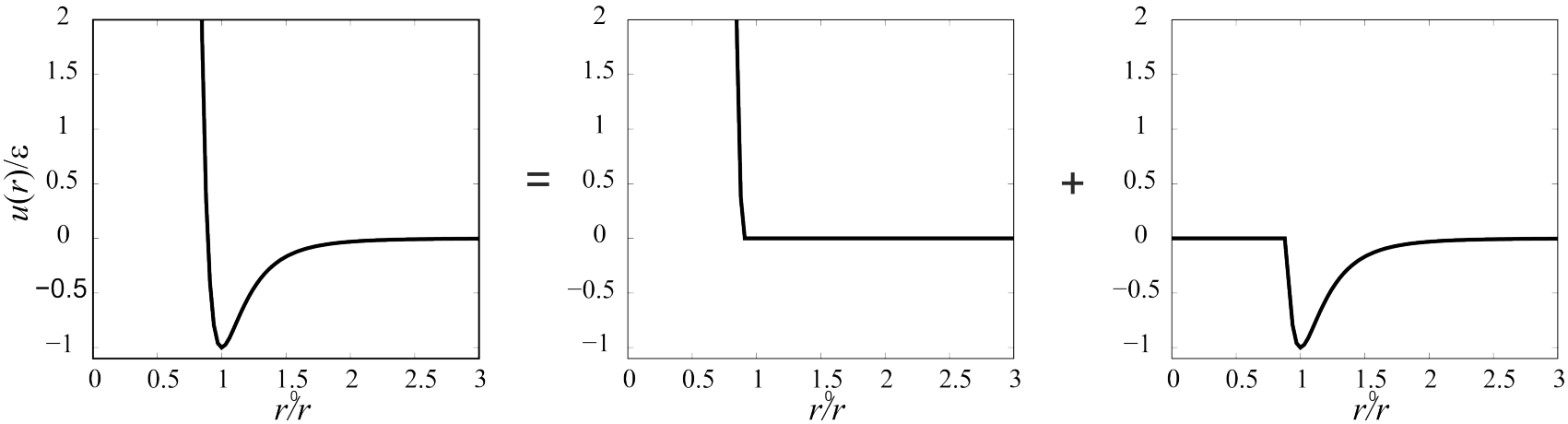
$$U_1 = \int \frac{1}{2} v k_b T c(\mathbf{r})^2 d\mathbf{r}$$

Dependence of excluded volume parameter on temperature

This is the second virial term in energy expansion; thus v can be expressed by

$$v = \int_0^\infty \left[1 - \exp\left(-\frac{u(r)}{k_B T}\right)\right] 4\pi r^2 dr$$

$$u(r) = u_{hard}(r) + u_{attr}(r)$$



for $u(r) = \epsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$.

Dependence of excluded volume parameter on temperature

$$v = \int_0^\infty \left[1 - \exp\left(-\frac{u_{hard}(r)}{k_B T}\right) \exp\left(-\frac{u_{attr}(r)}{k_B T}\right)\right] 4\pi r^2 dr \approx$$

$$\int_0^\infty \left[1 - \exp\left(-\frac{u_{hard}(r)}{k_B T}\right)\left(1 - \frac{u_{attr}(r)}{k_B T}\right)\right] 4\pi r^2 dr = A - \frac{B}{T}$$

Because at $T = \Theta$ the excluded volume is 0,

$$v = v^{(0)}\left(1 - \frac{\Theta}{T}\right), \quad \Theta = \frac{B}{A}$$

For $T < \Theta$, $v < 0$ (attractive forces take over, poor solvent), resulting in chain collapse or tight filling the space by beads. Thus

$$N \propto R^3 \Rightarrow R \propto N^{\frac{1}{3}}$$

Summary of the dependence of end-to-end distance on chain length

$$R \propto N^{\nu}$$

Flory regime	$v > 0$	$T > T_\Theta$	$\nu_F = \frac{3}{5}$
Θ regime	$v = 0$	$T = T_\Theta$	$\nu_\Theta = \frac{1}{2}$
compact regime	$v < 0$	$T < T_\Theta$	$\nu_c = \frac{1}{3}$

Generally, in d dimensions:

Flory regime	$2 \leq d \leq 4$	$v > 0$	$T > T_\Theta$	$\nu_F = \frac{3}{d+2}$
Flory regime	$d > 4$	$v > 0$	$T > T_\Theta$	$\nu_G = \frac{1}{2}$
Θ regime	$2 \leq d \leq 3$	$v = 0$	$T = T_\Theta$	$\nu_\Theta = \frac{2}{d+1}$
Θ regime	$d > 3$	$v = 0$	$T = T_\Theta$	$\nu_G = \frac{1}{2}$
compact regime	$\forall d$	$v < 0$	$T < T_\Theta$	$\nu_c = \frac{1}{d}$