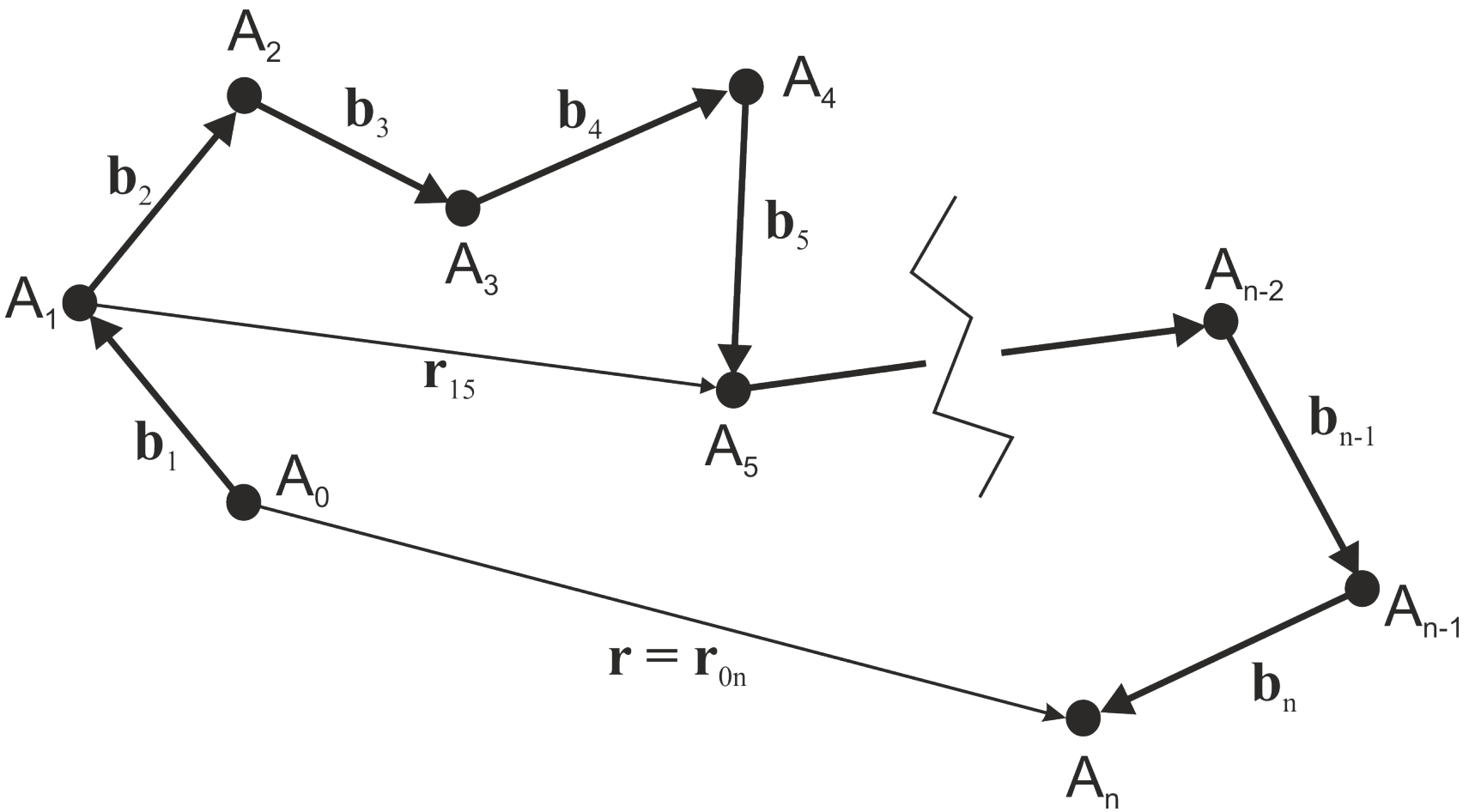
Class 3
Statistical-mechanical models of polymer chains.

November 3, 2026

Configuration and geometric characteristics of a linear polymer chain with n bonds



$\mathbf{b}_i$: bond vector from bead A_{i-1} to bead A_i.

Configuration and geometric characteristics of a linear polymer chain with n bonds

The end-to-end vector:

$$\mathbf{r} = \sum_{i=1}^{n} \mathbf{b}_i$$

The end-to-end distance:

$$r^2 = \|\mathbf{r}\|^2 = \mathbf{r} \bullet \mathbf{r} = \left(\sum_{i=1}^{n} \mathbf{b}_i \right) \bullet \left(\sum_{i=1}^{n} \mathbf{b}_i \right) =$$

$$\sum_{i=1}^{n} \sum_{j=1}^{n} \mathbf{b}_i \bullet \mathbf{b}_j = \sum_{i=1}^{n} b_i^2 + 2 \sum_{i=1}^{n} \sum_{j=1}^{i-1} \mathbf{b}_i \bullet \mathbf{b}_j$$

Configuration and geometric characteristics of a linear polymer chain with n bonds

The distance from bead i to bead j:

$$r_{ij}^2 = \sum_{k=i+1}^{j} b_k^2 + 2 \sum_{k=i+1}^{j} \sum_{l=i+1}^{k-1} \mathbf{b}_k \bullet \mathbf{b}_l$$

The radius of gyration:

$$s^2 = \frac{1}{n+1} \sum_{i=0}^{n} s_i^2$$

$$s_i^2 = \|\mathbf{r}_i - \mathbf{r}_C\|^2, \ \mathbf{r}_C = \frac{1}{n+1} \sum_{i=0}^{n} \mathbf{r}_i$$

$$s^2 = \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{i-1} r_{ij}^2$$

Configuration and geometric characteristics of a linear polymer chain with n bonds

End-to-end distribution for very long chains:

$$W(r) = \left(\frac{3}{2\pi\langle r^2\rangle}\right)^{\frac{3}{2}} \exp\left[-\frac{3}{2\langle r\rangle^2} r^2\right]$$

Heuristic derivation (Maxwell's argument):
The distributions of the coordinates of the end-to-end distance, $\mathbf{r} = (x, y, z)$, are independent of each other. On the other hand, the total distribution must be isotropic. Thus:

$$W(\mathbf{r}) = W(x, y, z) = w(x)w(y)w(z) = \phi(x^2 + y^2 + z^2)$$

The only function that fulfills such a condition is a Gaussian. Thus:

$$w(x) = c\exp(ax^2)$$
$$\phi(r^2) = c^3\exp(ar^2),\ r^2 = x^2 + y^2 + z^2$$

The freely jointed chain

Bonds rigid, bond angles fully flexible, no clashes.

$$\langle \mathbf{b}_i \bullet \mathbf{b_j} \rangle = 0$$
$$b_1 = b_2 = \ldots = b_n = b$$

The average end-to-end distance.

$$\langle r^2 \rangle_0 = \sum_{i=1}^{n} b_i^2 + 2 \sum_{i=1}^{n} \sum_{j=i+1}^{n} \langle \mathbf{b}_i \bullet \mathbf{b}_j \rangle = nb^2$$

We refer the end-to-end distance of other chain types to that of the random-flight chain by defining the characteristic ratio.

$$C_n = \frac{\langle r^2 \rangle_0}{nb^2}$$

The freely jointed chain

The average radius of gyration.

$$\langle r_{ij}^2 \rangle_0 = (j-i)b^2$$

$$\langle s^2 \rangle_0 = \frac{b^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=i+1}^{n} (j-i) =$$

$$\langle s^2 \rangle_0 = \frac{b^2}{(n+1)^2} \sum_{j=1}^{n} \sum_{k=1}^{j} k = \langle s^2 \rangle_0 = \frac{b^2}{(n+1)^2} \sum_{j=1}^{n} \frac{j(j+1)}{2} = \frac{1}{6} \frac{n(n+2)}{n+1} b^2$$

$$\frac{\langle s^2 \rangle_0}{nb^2} = \frac{1}{6} \frac{(n+2)}{(n+1)}$$

$$\frac{\langle s^2 \rangle_0}{nb^2} = \frac{1}{6}, \quad \langle s^2 \rangle_0 = \frac{\langle r^2 \rangle_0}{6}, \quad n \to \infty$$

The freely jointed chain

The distribution functions:

$$W_2(r) = \frac{1}{8\pi b^2 r}, \qquad 0 < \frac{r}{b} < 2$$

$$W_3(r) = \frac{1}{8\pi b^3}, \qquad 0 \leq \frac{r}{b} < 1$$
$$W_3(r) = \frac{1}{16\pi b^2 r}\left(3 - \frac{r}{b}\right), \qquad 1 \leq \frac{r}{b} < 3$$

$$W_4(r) = \frac{1}{64\pi b^3}\left(8 - 3\frac{r}{b}\right), \qquad 0 \leq \frac{r}{b} < 2$$
$$W_4(r) = \frac{1}{64\pi b^2 r}\left(4 - \frac{r}{b}\right)^2, \qquad 2 \leq \frac{r}{b} < 4$$

In general:

$$W_n(r) = \frac{n(n-1)}{8\pi r b^2} \sum_{t=0}^{\tau} \frac{(-1)^t}{t!(n-t)!)} \left[\frac{n - \frac{r}{l} - 2t}{2}\right]^{n-2}$$

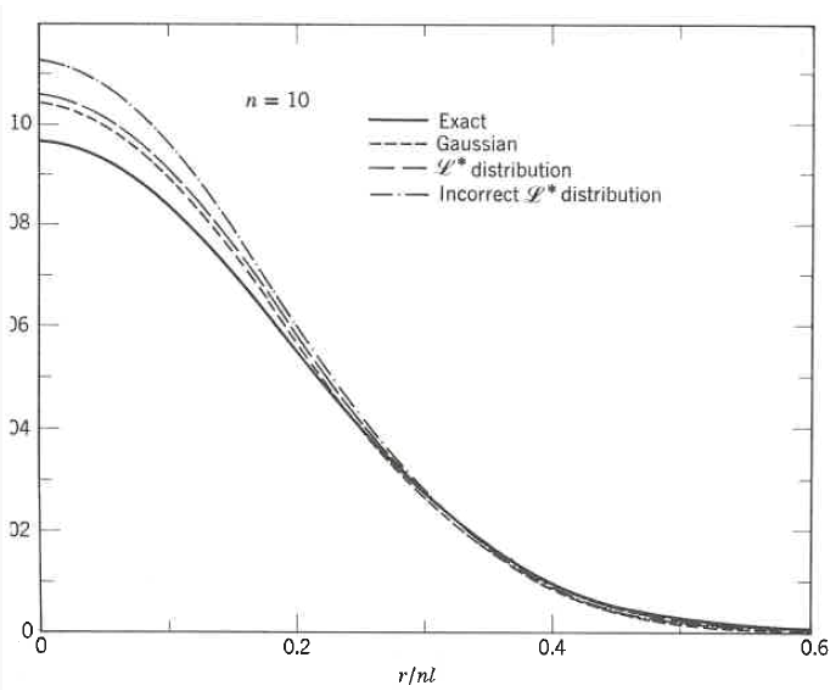
$$\frac{n - \frac{r}{b}}{2} \leq \tau < \frac{n - \frac{r}{b}}{2}$$

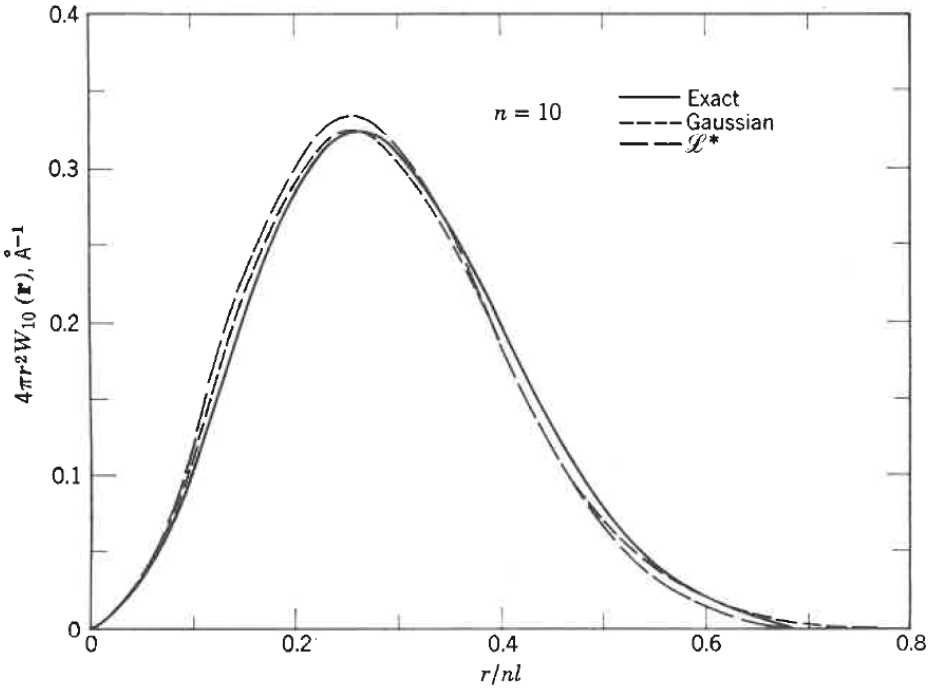
The freely jointed chain

Approximate expression for distribution:

$$W(r) = \left(\frac{3A}{nb^3}\right)\left[1 + \left(\frac{3}{5}\right)\left(\frac{r}{nb}\right)^2 + \left(\frac{99}{175}\right)\left(\frac{r}{nb}\right)^4 + \ldots\right] \times$$
$$\exp\left\{-\left(\frac{3}{2nb^2}\right)r^2\left[1 + \left(\frac{3}{10}\right)\left(\frac{r}{nb}\right)^2 + \left(\frac{33}{175}\right)\left(\frac{r}{nb}\right)^4 + \ldots\right]\right\}$$

The freely jointed chain

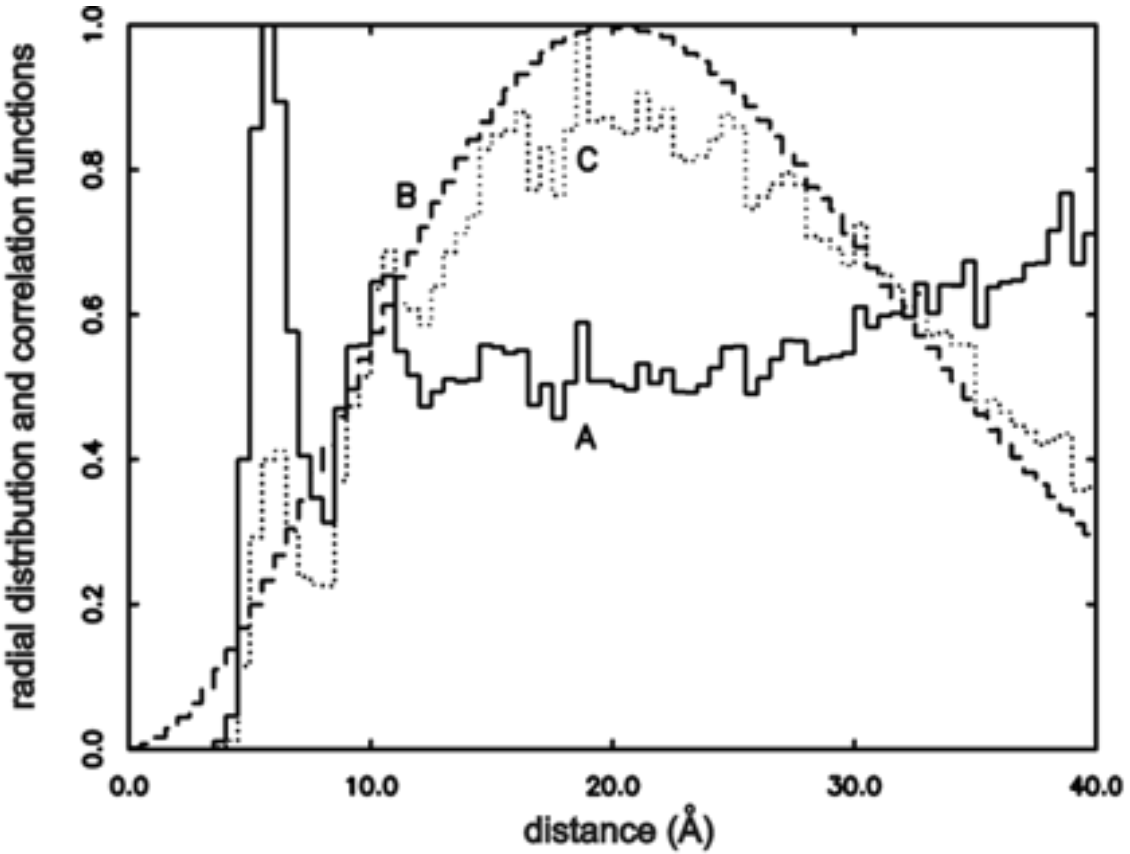




P. Flory, Statistical Mechanics of Chain Molecules, Wiley, 1969

The freely jointed chain

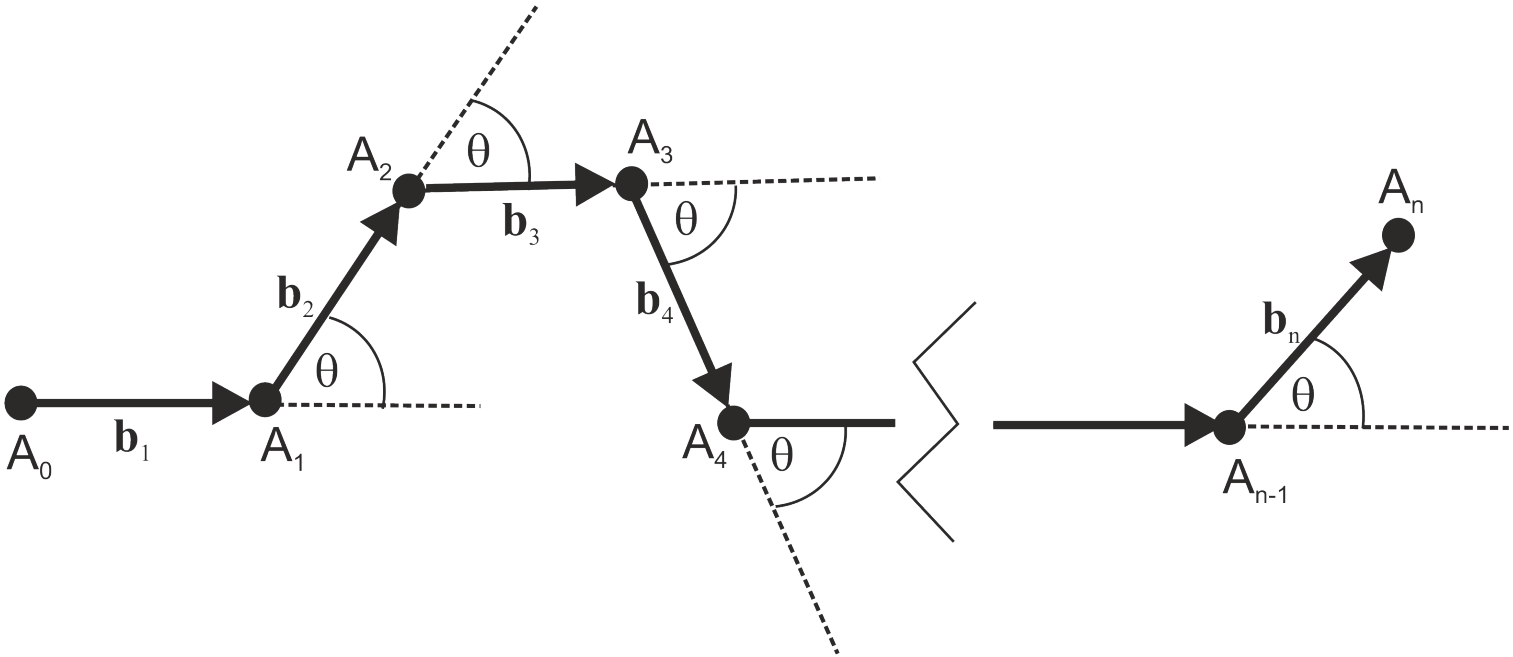
The "background" distribution must be taken into account when deriving statistical potentials from structural data.

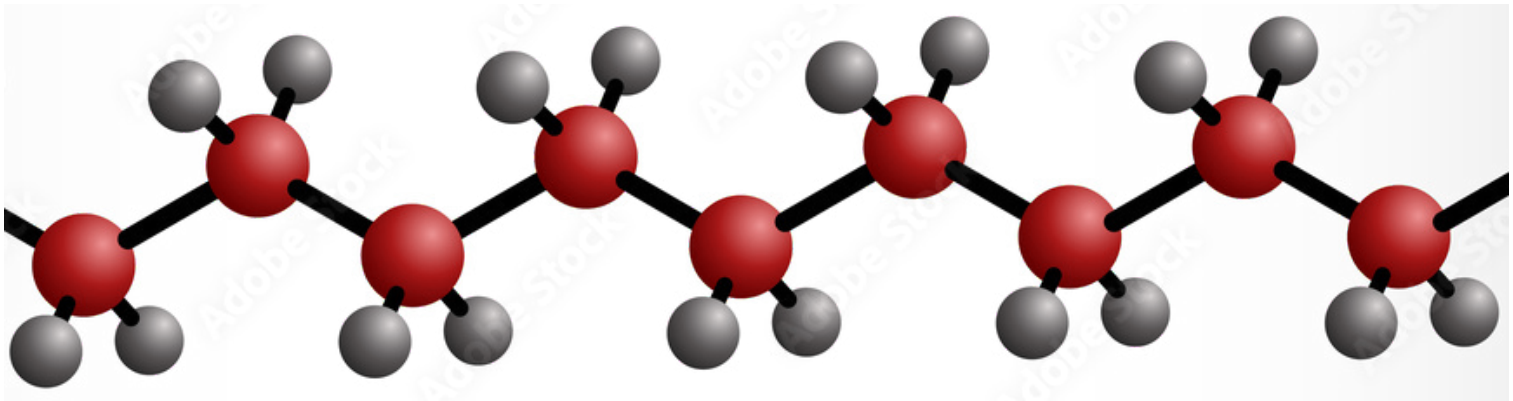


The pair-correlation function of Leu$\cdots$Leu pairs in protein structures (A), the reference distrubution function (B), and the radial distribution function (C).

Liwo et al., J. Comput. Chem., **1997**, 18, 849-873.

The freely rotating chain





$$\langle \mathbf{b}_i \bullet \mathbf{b}_{i+1} \rangle = \cos\theta$$

The freely rotating chain

The end-to-end distance:

$$\langle r^2 \rangle_0 = nb^2 + 2 \sum_{i=1}^{n} \sum_{j=i+1}^{n} \langle \mathbf{b}_i \bullet \mathbf{b}_j \rangle =$$

$$\langle \mathbf{b}_i \bullet \mathbf{b}_j \rangle = (\cos\theta)^{|j-i|}$$

$$nb^2 + 2b^2 \sum_{i=1}^{n} \sum_{j=i+1}^{n} (\cos\theta)^{j-i}$$

The characteristic ratio:

$$\frac{\langle r^2 \rangle_0}{nb^2} \equiv C_n = 1 + \frac{2}{n} \sum_{i=1}^{n} \sum_{j=i+1}^{n} (\cos\theta)^{j-i} =$$

$$1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k)(\cos\theta)^k = 1 + 2 \sum_{k=1}^{n-1} (\cos\theta)^k - \frac{2}{n} \sum_{k=1}^{n-1} k(\cos\theta)^k$$

The freely rotating chain

$$C_n = 1 + 2\sum_{k=1}^{n-1}(\cos\theta)^k - \frac{2}{n}\sum_{k=1}^{n-1} k(\cos\theta)^k$$

$$1 + 2\sum_{k=1}^{n-1}(\cos\theta)^k - \frac{2}{n}\cos\theta\frac{d}{d\cos\theta}\sum_{k=1}^{n-1}(\cos\theta)^k =$$

$$\frac{1+\cos\theta}{1-\cos\theta} - \frac{2\cos\theta}{n}\frac{[1-(\cos\theta)^n]}{(1-\cos\theta)^2}$$

For very long chains:

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}$$

The freely rotating chain

The radius of gyration:

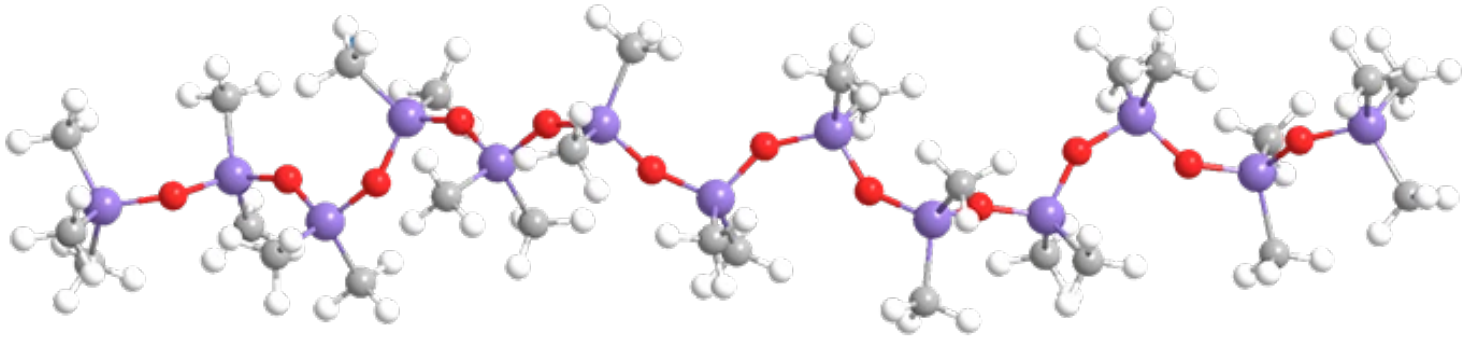
$$\frac{\langle s^2\rangle_0}{nb^2} = \frac{(n+2)(1+\cos\theta)}{6(n+1)(1-\cos\theta)} - \frac{\cos\theta}{(n+1)(1-cos\theta)^2} + \frac{2(\cos\theta)^2}{(n+1)^2(1-\cos\theta)^3} - \frac{2(\cos\theta)^3\left[1-\cos(\theta)^n\right]}{n(n+1)^2(1-\cos\theta)^4}$$

For large n:

$$\left(\frac{\langle s^2\rangle_0}{nb^2}\right)_\infty = \frac{1}{6}\frac{(1+\cos\theta)}{(1-\cos\theta)}$$

The freely rotating chain

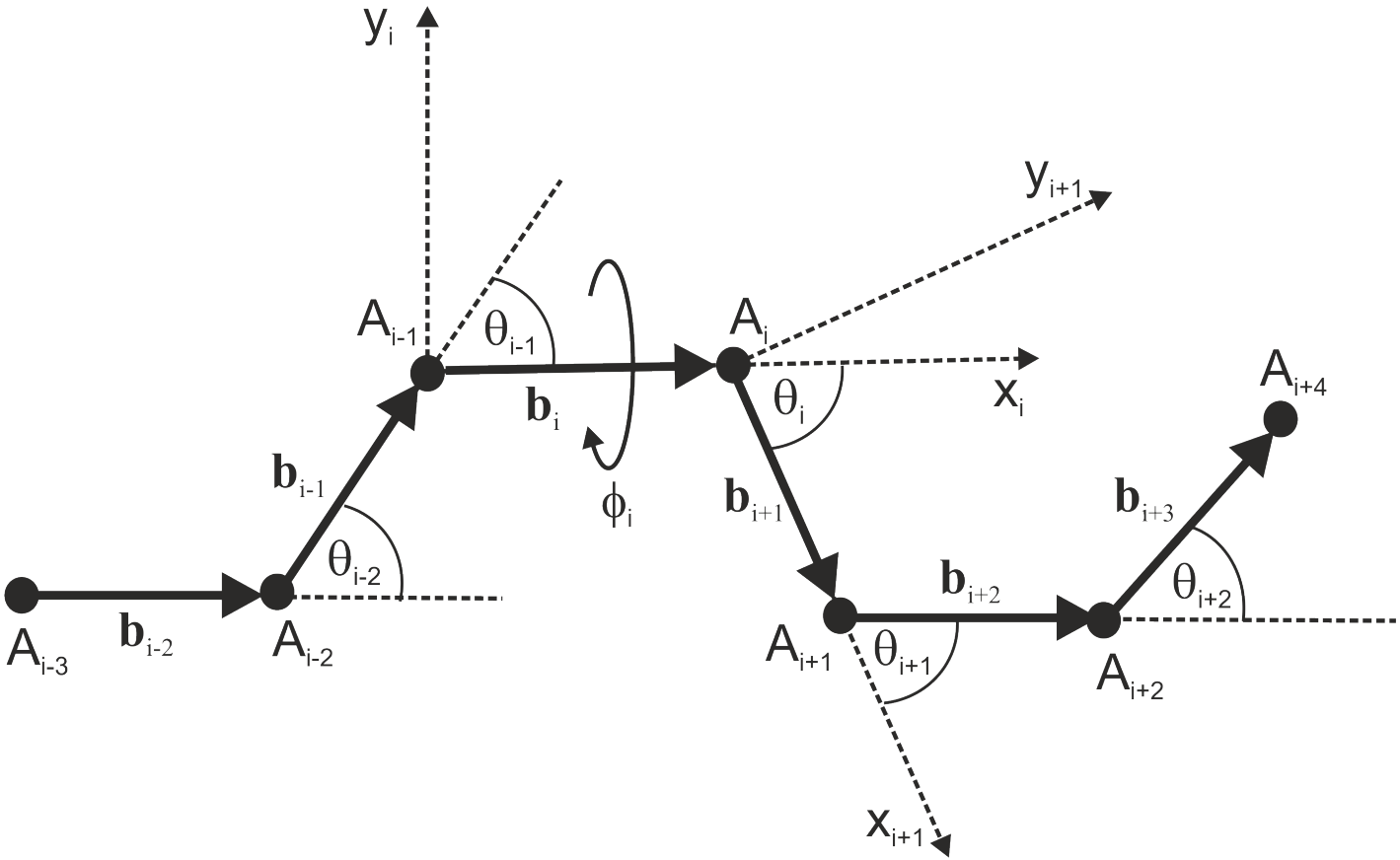
Two distinct bond angles (e.g., polymethylsiloxane)



$$\langle \mathbf{b}_i \bullet \mathbf{b}_{i+k} \rangle = \begin{cases} (\cos\theta_1 \cos\theta_2)^{\frac{k}{2}} & k \text{ even} \\ \begin{cases} (\cos\theta_1 \cos\theta_2)^{\frac{k-1}{2}} \cos\theta_1 \\ \text{or} \\ \cos\theta_2 (\cos\theta_1 \cos\theta_2)^{\frac{k-1}{2}} \end{cases} & k \text{ odd} \end{cases}$$

$$C_\infty = \frac{(1+\cos\theta_1)(1+\cos\theta_2)}{1-\cos\theta_1\cos\theta_2}$$

Neighbor correlations



Transforming coordinates from the frame of the $(i+1)$th to that of the ith bond.

$$\mathbf{v}^{(i)} = \mathbf{T}_i \mathbf{v}^{(i+1)}$$

$$\mathbf{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{bmatrix}$$

Neighbor correlations

The scalar products and bond vectors and their averages.

$$\mathbf{b}_i \bullet \mathbf{b}_j = \mathbf{b}_i^T (\mathbf{T}_i \dots \mathbf{T}_{j-1}) \mathbf{b}_j =$$

$$\mathbf{b}_j = b_j \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

$$b_i b_j \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} (\mathbf{T}_i \dots \mathbf{T}_{j-1}) \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = (\mathbf{T}_i \dots \mathbf{T}_{j-1})_{11}$$

$$\langle \mathbf{b}_j \bullet \mathbf{b}_j \rangle = b_i b_j \langle \mathbf{T}_i \dots \mathbf{T}_{j-1} \rangle_{11}$$

$$\langle \mathbf{T}_i \dots \mathbf{T}_{j-1} \rangle = \frac{\int \dots \int (\mathbf{T}_i \dots \mathbf{T}_{j-1}) \exp\left[-\frac{E\{\mathbf{b}\}}{RT}\right] d\{\mathbf{b}\}}{\int \dots \int \exp\left[-\frac{E\{\mathbf{b}\}}{RT}\right] d\{\mathbf{b}\}}$$

Neighbor correlations

Separable configurational energies: rotational potentials.

$$E\{\mathbf{b}\} = \sum_{i=2}^{n-2} E_i(\phi_i)$$

$$p(\phi_i)d\phi_i = z_i^{-1} \exp\left[-\frac{E(\phi_i)}{RT}\right] d\phi_i, \qquad z_i = \int_0^{2\pi} \exp\left[-\frac{E(\phi_i)}{RT}\right] d\phi_i$$

The average transformation matrix.

$$\langle \mathbf{T}_i \dots \mathbf{T}_{j-1} \rangle = \prod_{k=i}^{j-1} \langle \mathbf{T}_k \rangle, \quad \langle \mathbf{T}_k \rangle = \frac{\int_0^{2\pi} \mathbf{T}_k \exp\left[-\frac{E_k(\phi_k)}{RT}\right] d\phi_k}{\int_0^{2\pi} \exp\left[-\frac{E_k(\phi_k)}{RT}\right] d\phi_k}$$

For chains composed of same units $\langle \mathbf{T}_2 \rangle = \langle \mathbf{T}_3 \rangle \dots = \langle \mathbf{T}_{n-2} \rangle = \langle \mathbf{T} \rangle$.

Neighbor correlations

$$\langle r^2\rangle_0 = nb^2 + \sum_{i=1}^{n}\sum_{j=i+1}^{n} \mathbf{b}_i \bullet \mathbf{b}_j = \mathbf{b}^T \left[n\mathbf{I} + 2\sum_{i=1}^{n}\sum_{j=i+1}^{n} \langle \mathbf{T}\rangle^{j-i} \right] \mathbf{b}$$

$$= \mathbf{b}^T \left\{ n\mathbf{I} + \frac{2}{n}\left[\sum_{k=1}^{n-1} (n-k)\langle \mathbf{T}\rangle^k \right] \right\} \mathbf{b}, \quad \mathbf{b} = \begin{bmatrix} b \\ 0 \\ 0 \end{bmatrix}, \quad \mathbf{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sum_{k=1}^{n-1} \langle \mathbf{T}\rangle^k = (\langle \mathbf{T}\rangle - \langle \mathbf{T}\rangle^n)(\mathbf{I} - \langle \mathbf{T}\rangle)^{-1}$$

$$\frac{\langle r^2\rangle_0}{n} = \mathbf{b}^T \left[(\mathbf{I} + \langle \mathbf{T}\rangle)(\mathbf{I} - \langle \mathbf{T}\rangle)^{-1} - \frac{2}{n}\left(\mathbf{I} - \langle \mathbf{T}\rangle^n\right)(\mathbf{I} - \langle \mathbf{T}\rangle)^{-2} \right] \mathbf{b}$$

$$\left(\frac{\langle r^2\rangle_0}{n} \right)_{n\to\infty} = \mathbf{b}^T (\mathbf{I} + \langle \mathbf{T}\rangle)(\mathbf{I} - \langle \mathbf{T}\rangle)^{-1}\mathbf{b}$$

Neighbor correlations

The characteristic ratio:

$$C_n = \frac{\langle r^2 \rangle_0}{nb^2} = \left[(\mathbf{I} + \langle \mathbf{T} \rangle)(\mathbf{I} - \langle \mathbf{T} \rangle)^{-1} - \frac{2}{n} \left(\mathbf{I} - \langle \mathbf{T} \rangle^n \right) (\mathbf{I} - \langle \mathbf{T} \rangle)^{-2} \right]_{11}$$

$$C_\infty = \left[\mathbf{I} + \langle \mathbf{T} \rangle)(\mathbf{I} - \langle \mathbf{T} \rangle)^{-1} \right]_{11}$$

The radius of gyration:

$$\frac{\langle s^2 \rangle_0}{nb^2} = \frac{(n+2)}{6(n+1)} \left[(\mathbf{I} + \langle \mathbf{T} \rangle)(\mathbf{I} - \langle \mathbf{T} \rangle)^{-1} \right]_{11} - \frac{1}{n+1} \left[\langle \mathbf{T} \rangle (\mathbf{I} - \langle \mathbf{T} \rangle)^{-2} \right]_{11} +$$

$$\frac{2}{(n+1)^2} \left[\langle \mathbf{T} \rangle^2 (\mathbf{I} - \langle \mathbf{T} \rangle)^{-3} \right]_{11} - \frac{2}{n(n+1)^2} \left[\langle \mathbf{T} \rangle^3 (\mathbf{I} - \langle \mathbf{T} \rangle^n)(\mathbf{I} - \langle \mathbf{T} \rangle)^{-4} \right]_{11}$$

$$\left(\frac{\langle s^2 \rangle_0}{nb^2} \right)_{n \to \infty} = \frac{1}{6} \left[(\mathbf{I} + \langle \mathbf{T} \rangle)(\mathbf{I} - \langle \mathbf{T} \rangle)^{-1} \right]_{11}$$

Neighbor correlations

$$\langle \mathbf{T}_i \rangle = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \langle \cos\phi_i \rangle & -\cos\theta_i \langle \cos\phi_i \rangle & \langle \sin\phi_i \rangle \\ \sin\theta_i \langle \sin\phi_i \rangle & -\cos\theta_i \langle \sin\phi_i \rangle & -\langle \cos\phi_i \rangle \end{bmatrix}$$

$$\langle \cos\phi_i \rangle = \frac{1}{z_i} \int_0^{2\pi} \cos\phi_i \exp\left[-\frac{E(\phi_i)}{RT} \right] d\phi_i$$

$$\langle \sin\phi_i \rangle = \frac{1}{z_i} \int_0^{2\pi} \sin\phi_i \exp\left[-\frac{E(\phi_i)}{RT} \right] d\phi_i$$

$$z_i = \int_0^{2\pi} \exp\left[-\frac{E(\phi_i)}{RT} \right] d\phi_i$$

Neighbor correlations

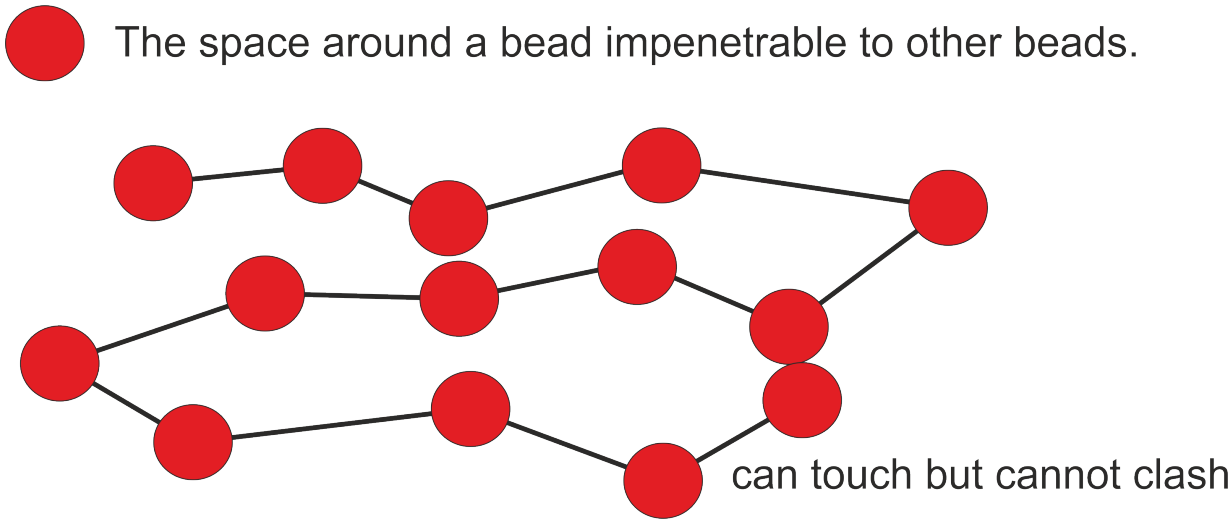
$$\theta_1 = \theta_2 = \ldots = \theta_{n-1} = \theta$$
$$\langle \cos\phi_2 \rangle = \langle \cos\phi_3 \rangle = \ldots = \langle \cos\phi_{n-1} \rangle \langle \cos\phi \rangle$$
$$\langle \sin\phi_2 \rangle = \langle \sin\phi_3 \rangle = \ldots = \langle \sin\phi_{n-1} \rangle = \langle \sin\phi \rangle$$
$$\langle \mathbf{T}_2 \rangle = \langle \mathbf{T}_3 \rangle = \ldots = \langle \mathbf{T}_{n-1} \rangle = \langle \mathbf{T} \rangle$$

The characteristic ratio and radius of gyration for very long chains:

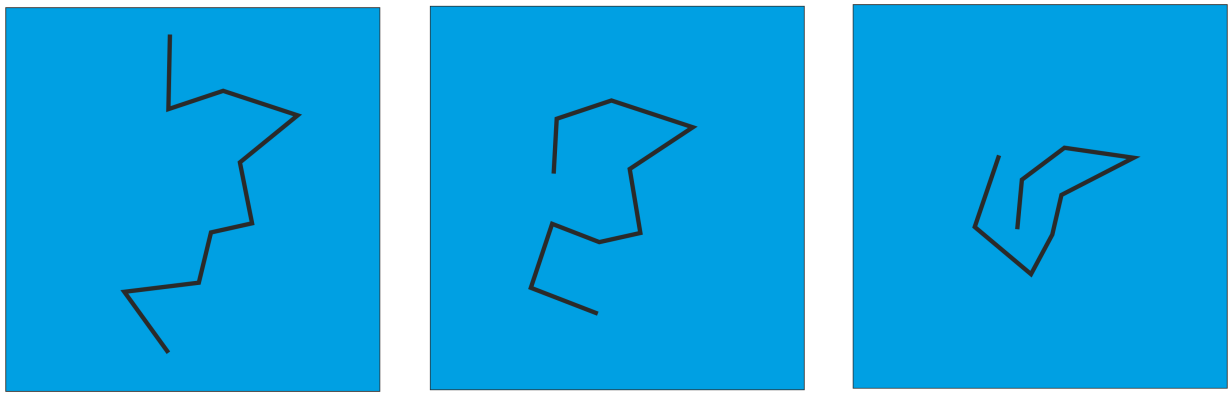
$$C_\infty = \left(\frac{1+\cos\theta}{1-\cos\theta} \right) \left(\frac{1+\langle \cos\phi \rangle}{1-\langle \cos\phi \rangle} \right)$$
$$\left(\frac{\langle s^2 \rangle_0}{nb^2} \right)_{n\to\infty} = \frac{1}{6} \left(\frac{1+\cos\theta}{1-\cos\theta} \right) \left(\frac{1+\langle \cos\phi \rangle}{1-\langle \cos\phi \rangle} \right)$$

Long-range interactions and solvent

Excluded volume



Solvent contribution to exlcuded volume:



Long-range interactions and solvent

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, solubitilty 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:

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

Measurements of polymer-chain dimensions

- Viscosity of polymer soution.
- Sedimentation velocity.
- Diffusion coefficients.
- Force measurements.
- Light scattering.
- Small angle X-ray scattering (SAXS).

Measurements of polymer-chain dimensions

Intrinsic viscosity.

$$[\eta] = \lim_{c \to 0} \left[\frac{(\eta_{rel} - 1)}{c} \right]$$

$$\eta_{rel} = \frac{\eta_{\text{solution}}}{\eta_{\text{pure solvent}}}, \quad c : \text{polymer concentration}$$

$$[\eta] = \frac{\Phi \langle r^2 \rangle^{\frac{3}{2}}}{M}, \quad \Phi : \text{ a constant}, \quad M : \text{ molecular mass}$$

At the Θ point, for a given series of homologs:

$$[\eta]_\Theta = K M^{\frac{1}{2}}$$

$$\left(\frac{\langle r^2 \rangle_0}{M} \right)_\infty = \left(\frac{K}{\Phi} \right)^{\frac{2}{3}}$$

The characteristic ratio:

$$C_\infty = \left(\frac{\langle r^2 \rangle_0}{M} \right)_\infty \left(\frac{M_b}{b^2} \right), \quad M_b : \text{ bead mass}$$

Measurements of polymer-chain dimensions

Characteristic Ratios for Representative Polymer Chains at the Limit of High Chain Length

Polymer	Structural unit	Solvent	Temp, °C	$K \times 10^4 = ([\eta]_\Theta / M^{1/2}) \times 10^4$ deciliters g^{-1} (g mol wt)$^{-1/2}$	$C_\infty = (\langle r^2 \rangle_0 / nl^2)_\infty$
Polymethylene	$-CH_2-$	Dodecanol-1	138	30.7[a], 31.6[b]	6.7
		Diphenylmethane	142	31.5[a], 32.3[c]	6.8
		α-Cl-Naphthalene*	140	30.5[d]	6.6
Polystyrene, atactic	$-CH_2-CH(C_6H_5)-$	Cyclohexane	34.8	8.2[e], 8.4[f], 8.7[g]	10.2
		$Cl-(CH_2)_{11}-H$	32.8	7.8[g]	10.0
		Diethyl malonate	35.9	7.7[g]	9.9
Polypropylene, atactic	$-CH_2-CH(CH_3)-$	α-Cl–Naphthalene	74	18.2[h]	7.0
		Cyclohexane	92	17.2[h]	6.8
		Diphenyl ether	153	12.0[h]	5.3
Polypropylene, isotactic	$-CH_2-CH(CH_3)-$	Diphenyl ether	145	13.2[h]	5.7
Poly(*n*-pentene-1), isotactic	$-CH_2-CH(C_3H_7)-$	Isoamyl acetate	31.5	14.1[i]	10.0
		2-Pentanol	62.4	12.1[j]	9.0
Polyisobutylene	$-CH_2-C(CH_3)_2-$	Benzene	24	10.7[k]	6.6

P. Flory, Statistical Mechanics of Chain Molecules, Wiley, 1969

Measurements of polymer-chain dimensions

Poly(vinyl acetate), atactic	$-CH_2-CH(OCOCH_3)-$	Ethyl *n*-butyl ketone	29	9.3[l]	9.2
		i-Pentanone–hexane	25	8.8[l]	8.9
		i-Pentanone–heptane	25	8.8[m]	8.9
Poly(isopropyl acrylate), atactic	$-CH_2-CH(COOC_3H_7)$	Benzene*	25		9.7 ± 0.8[n]†
isotactic	$-CH_2-CH(COOC_3H_7)$	Bromobenzene*	60		7.1 ± 0.6[n]†
syndiotactic	$-CH_2-CH(COOC_3H_7)$	Bromobenzene*	60		7.2 ± 1.0[n]†
Poly(methyl methacrylate), atactic	$-CH_2-C(CH_3)(COOCH_3)-$	Various solvents	4–70	4.8 ± 0.5[o,p]	6.9 ± 0.5
isotactic	$-CH_2-C(CH_3)(COOCH_3)-$	Acetonitrile	27.6	7.5[q]	9.3
		n-Butyl chloride	26.5	7.7[r]	9.5
		Butanone–isopropanol	25	7.2[r]	9.1
syndiotactic	$-CH_2-C(CH_3)(COOCH_3)-$	*n*-Butyl chloride	35	5.1[r]	7.2
		Butanone–isopropanol	8	4.4[r]	6.5

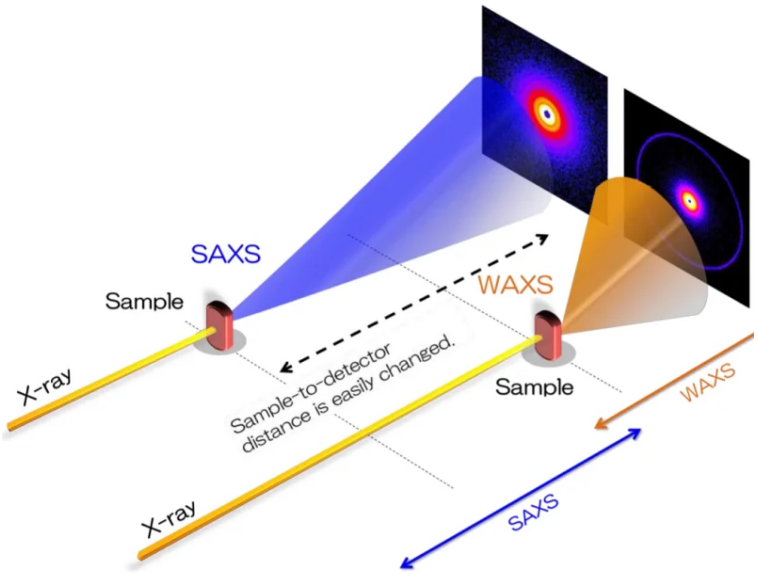
P. Flory, Statistical Mechanics of Chain Molecules, Wiley, 1969

Measurements of polymer-chain dimensions

Polymer	Structural unit	Solvent	Temp, °C	$K \times 10^4 = ([\eta]_\Theta / M^{1/2}) \times 10^4$ deciliters g^{-1} (g mol wt)$^{-1/2}$	$C_\infty = (\langle r^2 \rangle_0 / nl^2)_\infty$
Polyoxyethylene	—O—CH_2—CH_2—	Aqueous K_2SO_4	35	11.5 ± 1.5[s]	4.0
		Aqueous $MgSO_4$	45	11.5 ± 1.5[s]	
Poly-dimethylsiloxane	CH_3 | —O—Si— | CH_3	Butanone	20	7.8[t]	6.2
		$C_8F_{18} + C_2Cl_4F_2$	22.5	10.6[t]	7.6
		Various solvents	2–90	7.0–7.8[u]	5.7–6.2
Polyhexamethylene adipamide	—$NH(CH_2)_6NH$— —$CO(CH_2)_4CO$—	HCOOH, KCl, H_2O	25	19.2[v]	5.9
L-Polypeptides‡	—NHCH—CO— | CH_2R'	Various solvents*	25–100		8.5–9.5[w]‡
Polyphosphate	—O—$\tilde{P}O_2$—	Aq LiBr	25	7.5[x] (Li salt)	7.1
		Aq NaBr	25	5.2[y] (Na salt)	6.6

P. Flory, Statistical Mechanics of Chain Molecules, Wiley, 1969

Small-angle X-ray scattering (SAXS)

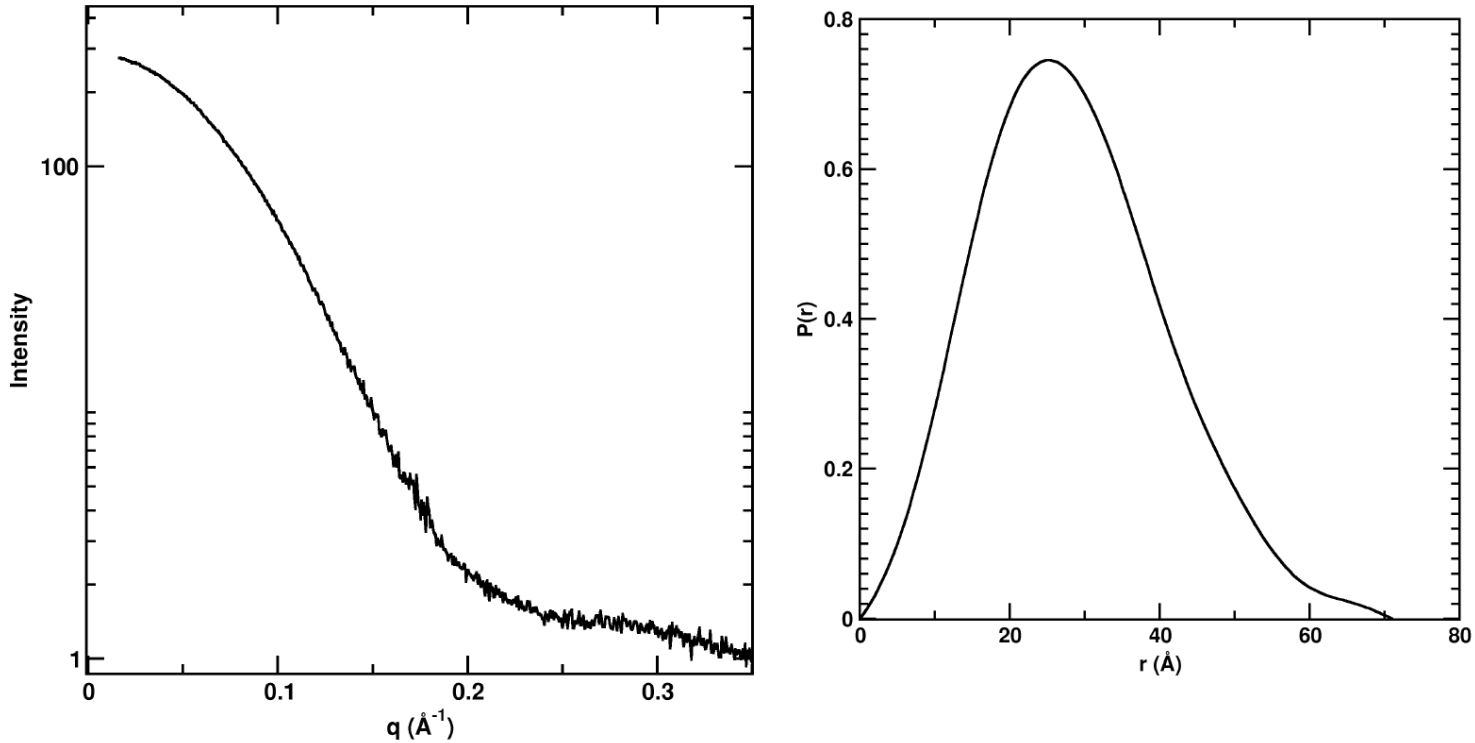




The scattering intensity and distance distribution:

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr \quad p(r) = \frac{1}{2\pi^2} \int_0^\infty qrI(q) \sin(qr) dq$$

Small-angle X-ray scattering (SAXS)

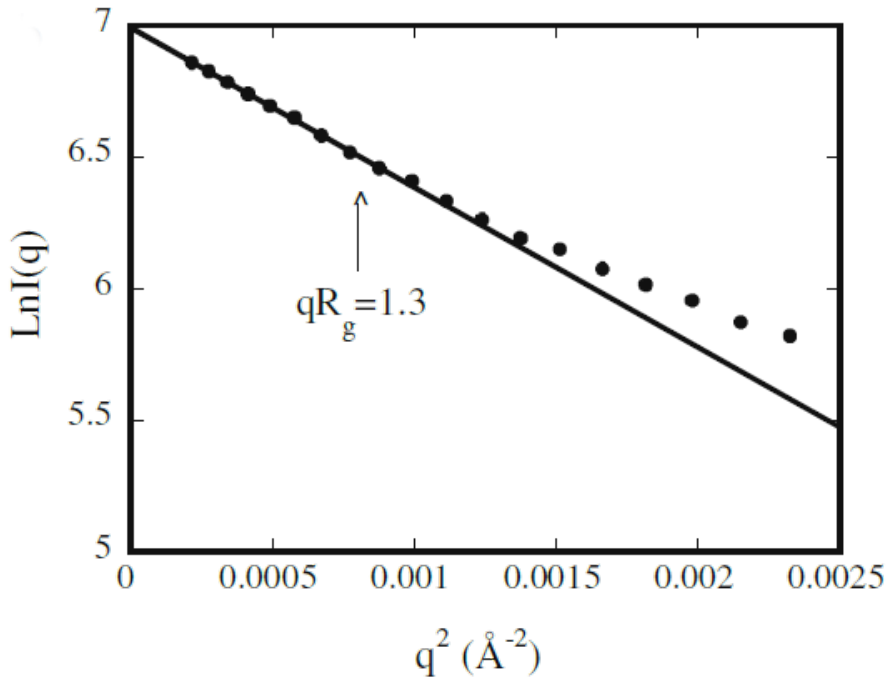


Plots of scattering intensity, $I(q)$, and distance distribution, $p(r)$, for the contact-dependent growth inhibition toxin-immunity complex from *E. coli* (PDB: 6CP8; CASP13 target H0957).

Small-angle X-ray scattering (SAXS)

The Guinier relationship.

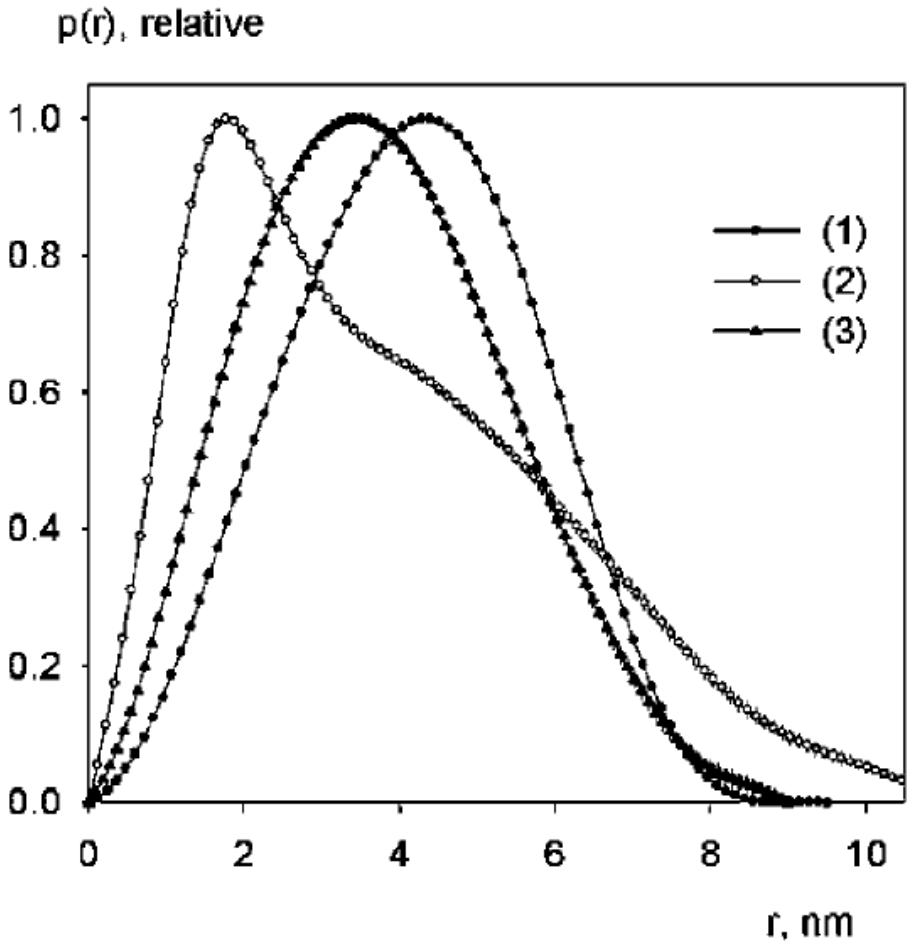
$$\ln I(q) = \ln I(0) - \frac{R_g^2}{3} q^2$$



The Guinier plot for NADPH oxidase activator p67$^{\mathrm{phox}}$.

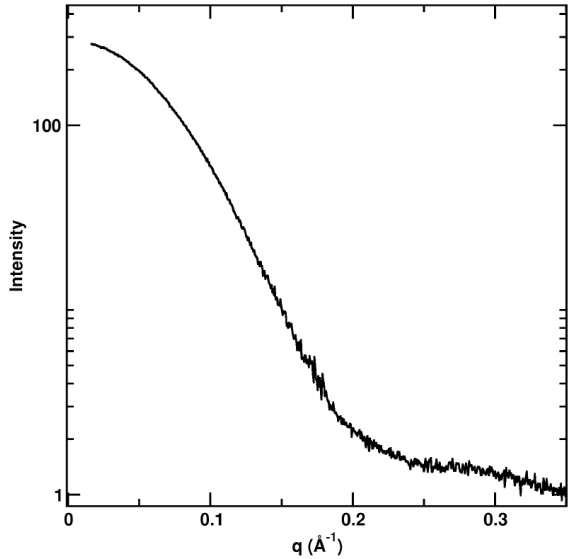
Durand et al., *J. Struct. Biol.*, **2010**, 169, 45-54.

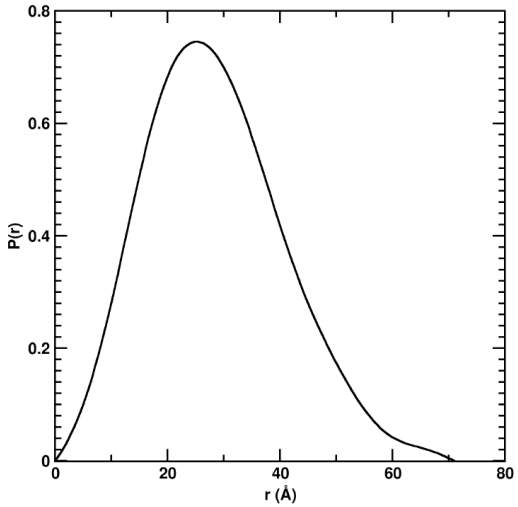
Small-angle X-ray scattering (SAXS)

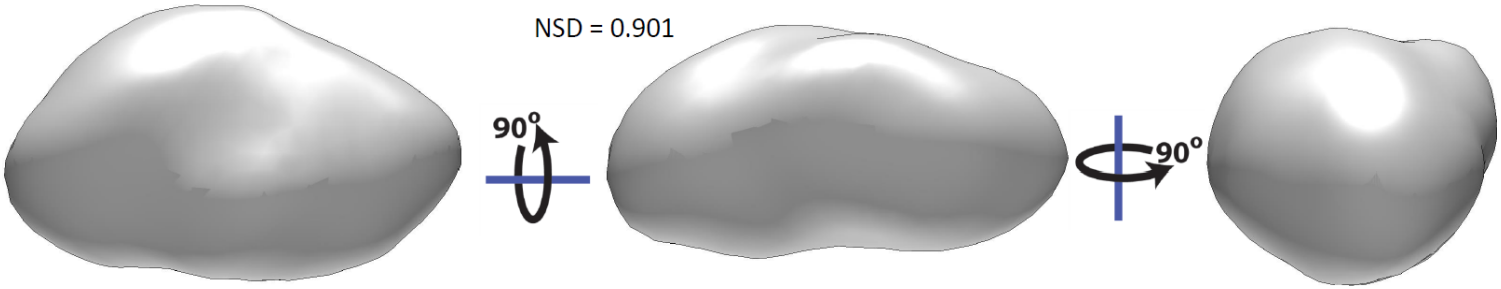


Distance distributions of (1) urate oxidase (hollow globular), (2) Z1Z2 domain of the N-terminus of titin (elongated), (3) bovine serum albumin (flattened).
Koch et al., *Quart. Rev. Biophys.*, **2003**, 36, 147-227.

Small-angle X-ray scattering (SAXS)

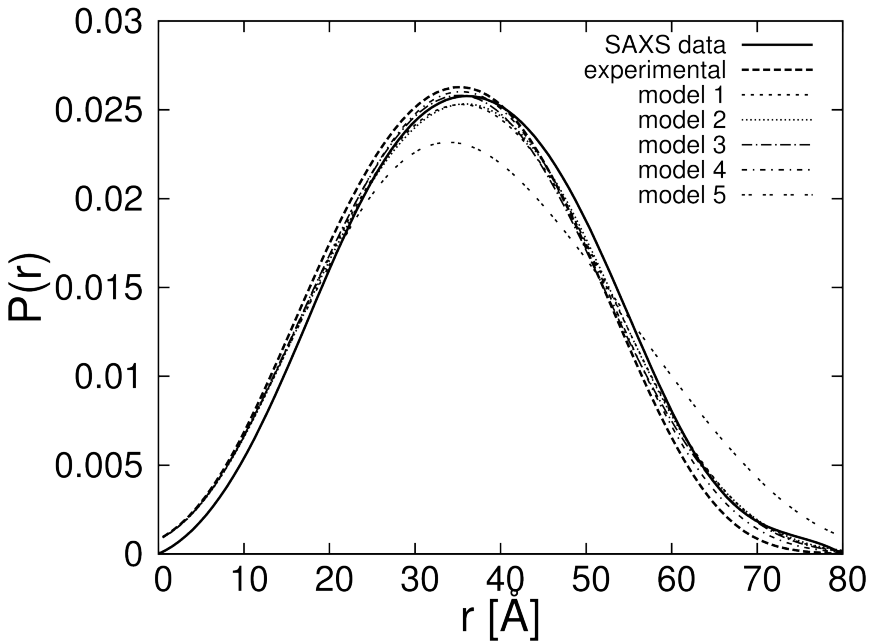


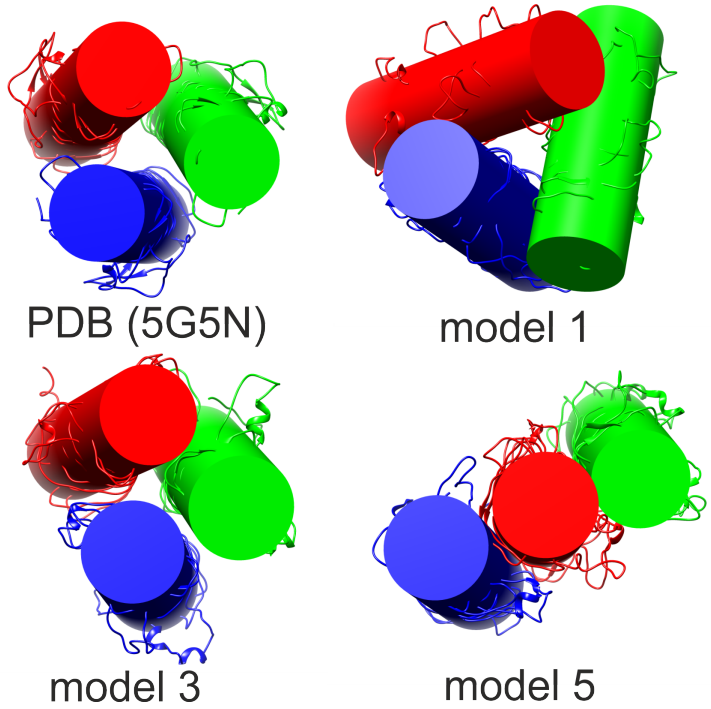




The shape of the the contact-dependent growth inhibition toxin-immunity complex from *E. coli* (PDB: 6CP8; CASP13 target H0957) calculated with the CRYSOL program.

Small-angle X-ray scattering (SAXS)

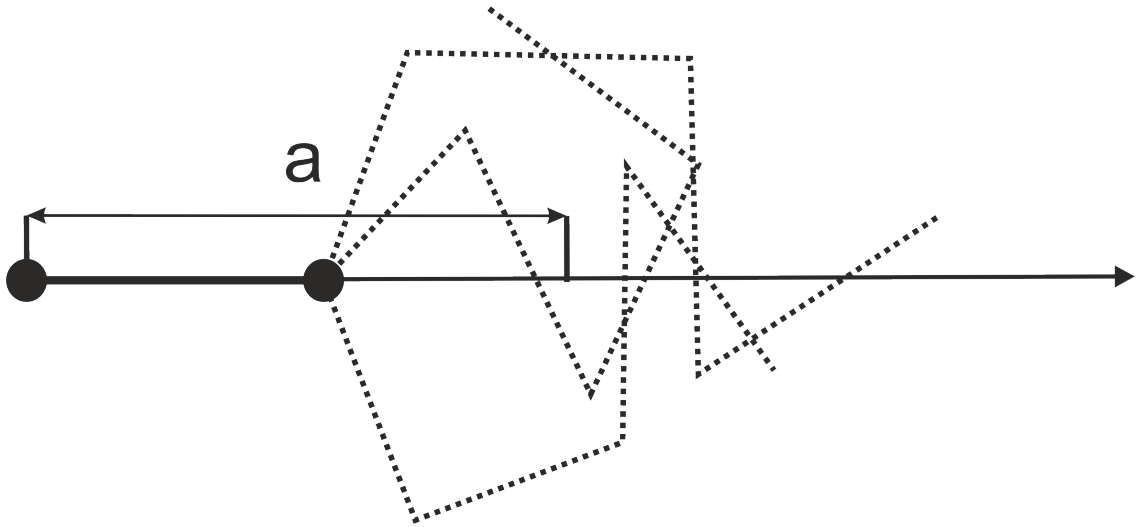




SAXS-data assisted modeling of the structure of snake adenovirus 1 hexon-interlacing LH3 protein (CASP12 target T909; PDB: 5G5N).

Karczyńska et al., *Proteins*, **2018**, 86, 228-239.

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.

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

The persistence length

For a freely-jointed chain the persistence length is 1.
For a freely-rotating chain:

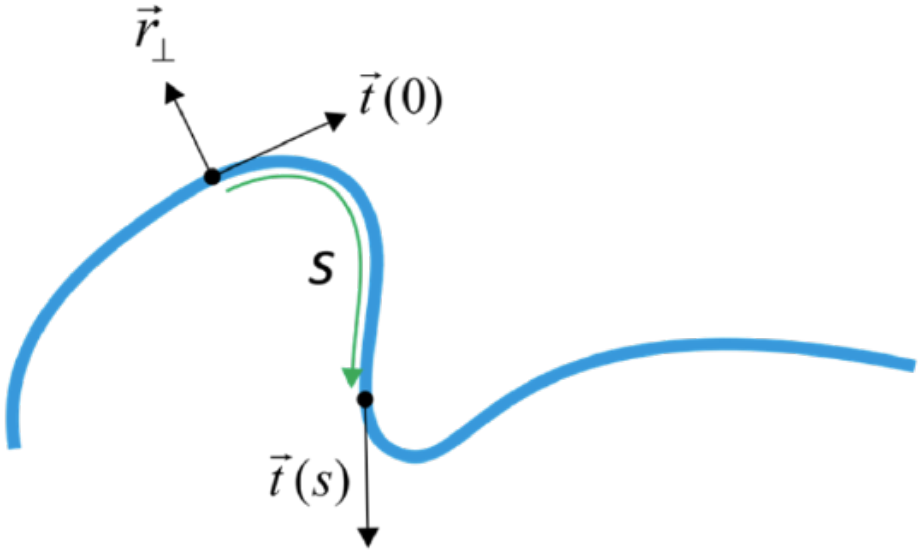
$$a = b \lim_{n\to\infty} \sum_{j=1}^{n} (\cos\theta)^{j-1} = b \lim_{n\to\infty} \frac{1-(\cos\theta)^n}{1-\cos\theta} = \left(\frac{b}{1-\cos\theta}\right)$$

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

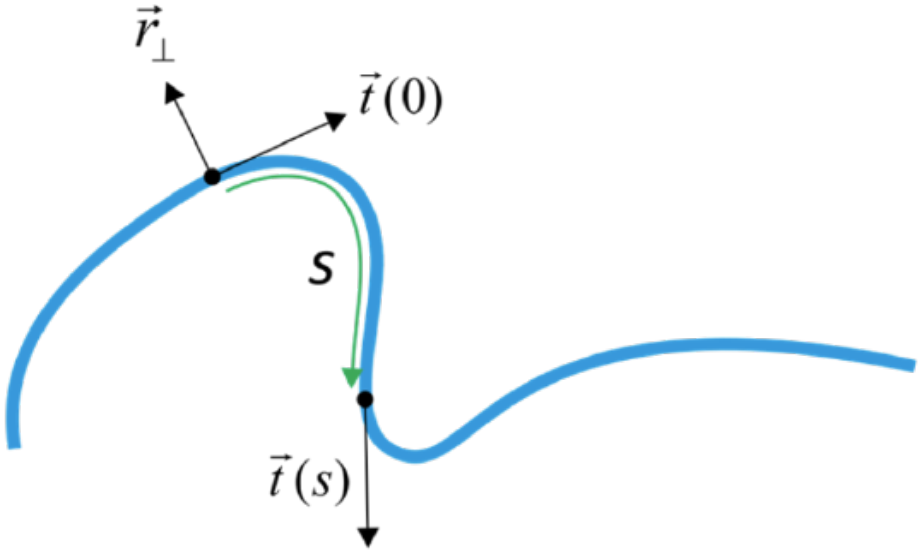


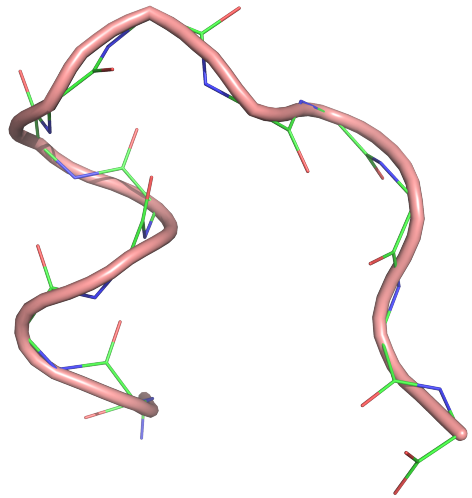


Freely rotating chain	Wormlike chain
bead index, i	position along chain, s
bond vector, $\mathbf{b}_i$	tangent vector, $\mathbf{t}(s)$
bond angle, θ_i	curvature, $\kappa(s)$
dihedral angle, ϕ	torsion, $\tau(s)$

A wormlike chain is 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

End-to-end distance:

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

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

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

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:

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

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