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Lecture: “Polymer Chains” by Ju Li.

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Polymer Chains

Ju Li

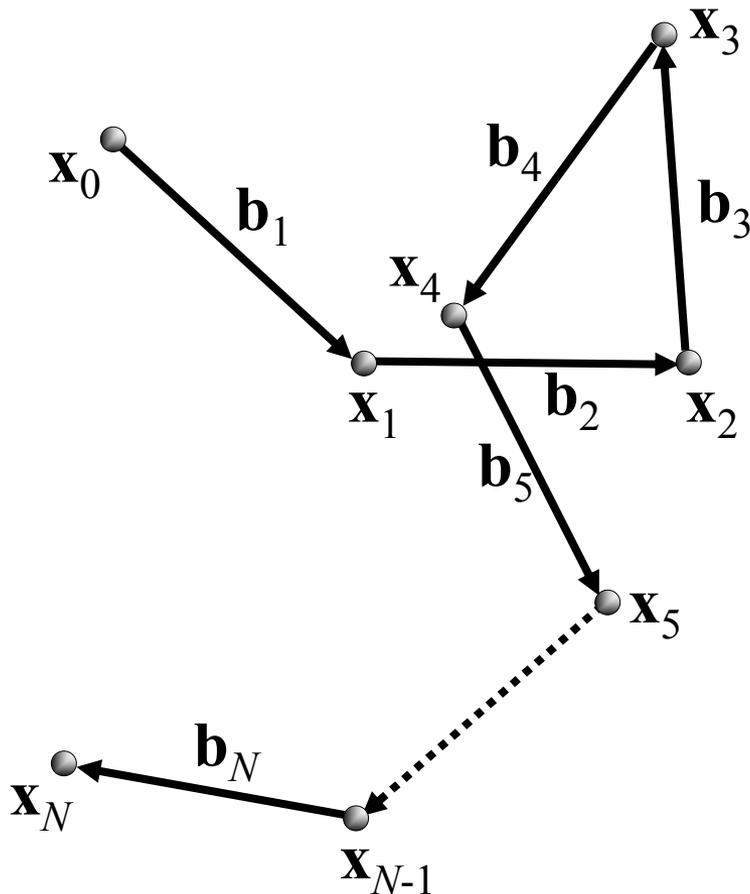


GEM4 Summer School 2006
Cell and Molecular Mechanics in BioMedicine
August 7–18, 2006, MIT, Cambridge, MA, USA

Outline

- Freely Jointed Chain
- Worm-Like Chain
- Persistence Length

Freely Jointed Chain (FJC)



degrees of freedom:
 $\{\mathbf{x}_i\}, i=0..N$

under constraints:

$$|\mathbf{x}_i - \mathbf{x}_{i-1}| = |\mathbf{b}_i| = b$$

b is called the Kuhn length

no energy penalty otherwise

In particular, the Kuhn segments can penetrate right through each other.

When it is not pulled...

Probability distribution of \mathbf{b}_i :

$$dP = \rho(\mathbf{b}_i) d^3 \mathbf{b}_i = \delta(b_i - b) db_i \cdot \frac{d\Omega}{4\pi}$$

$$\langle \mathbf{b}_i \rangle = 0, \quad \text{var}[\mathbf{b}_i] \equiv \langle |\mathbf{b}_i|^2 \rangle = b^2$$

\mathbf{b}_i and \mathbf{b}_{i+1} are uncorrelated.

Define end-to-end distance:

$$\mathbf{D} \equiv \mathbf{b}_1 + \mathbf{b}_2 + \dots + \mathbf{b}_N.$$

We can now apply central limit theorem:

$$\langle \mathbf{D} \rangle = 0, \quad \text{var}[\mathbf{D}] \equiv \langle |\mathbf{D}|^2 \rangle = Nb^2$$

Furthermore, we know distribution of \mathbf{D} must approach Gaussian

$$dP \rightarrow \left(\frac{3}{2\pi Nb^2} \right)^{\frac{3}{2}} \exp\left(-\frac{3|\mathbf{D}|^2}{2Nb^2} \right) d^3\mathbf{D}$$

The radius of gyration $R_g \propto \langle \mathbf{D} \cdot \mathbf{D} \rangle^{1/2}$ characterizes the spatial extent of the molecule $\propto N^{1/2}b$, which is much smaller than the contour length $L=Nb$.

Suppose \mathbf{x}_0 is fixed, and \mathbf{x}_N is pulled with external force \mathbf{f} :

Gibbs free energy of the system:

$$G = F - \mathbf{f} \cdot \mathbf{D} = E - TS - \mathbf{f} \cdot \mathbf{D} = -TS - \mathbf{f} \cdot \mathbf{D}$$

$$F \equiv -k_B T \ln Z = \text{const} -$$

$$k_B T \ln \int d^3 \mathbf{b}_1 d^3 \mathbf{b}_2 \cdots d^3 \mathbf{b}_N \exp(-\beta \sum_{i=1}^N h(\mathbf{b}_i))$$

where $h(\mathbf{b}_i) \equiv \delta(|\mathbf{b}_i| - b)$
express the constraint condition.

$$G = -k_B T \ln Z e^{\beta \mathbf{f} \cdot \mathbf{D}} = -k_B T \ln Z e^{\beta \mathbf{f} \cdot (\mathbf{b}_1 + \mathbf{b}_2 + \dots + \mathbf{b}_N)}$$

$$= \text{const} - k_B T \ln \int d^3 \mathbf{b}_1 d^3 \mathbf{b}_2 \cdots d^3 \mathbf{b}_N \exp(-\beta \sum_{i=1}^N h'(\mathbf{b}_i))$$

$$\text{where } h'(\mathbf{b}_i) \equiv \delta(|\mathbf{b}_i| - b) - \mathbf{f} \cdot \mathbf{b}_i$$

The above is equivalent to N *biased* segments, still *independent* of each other.

Each *biased* segment is controlled by

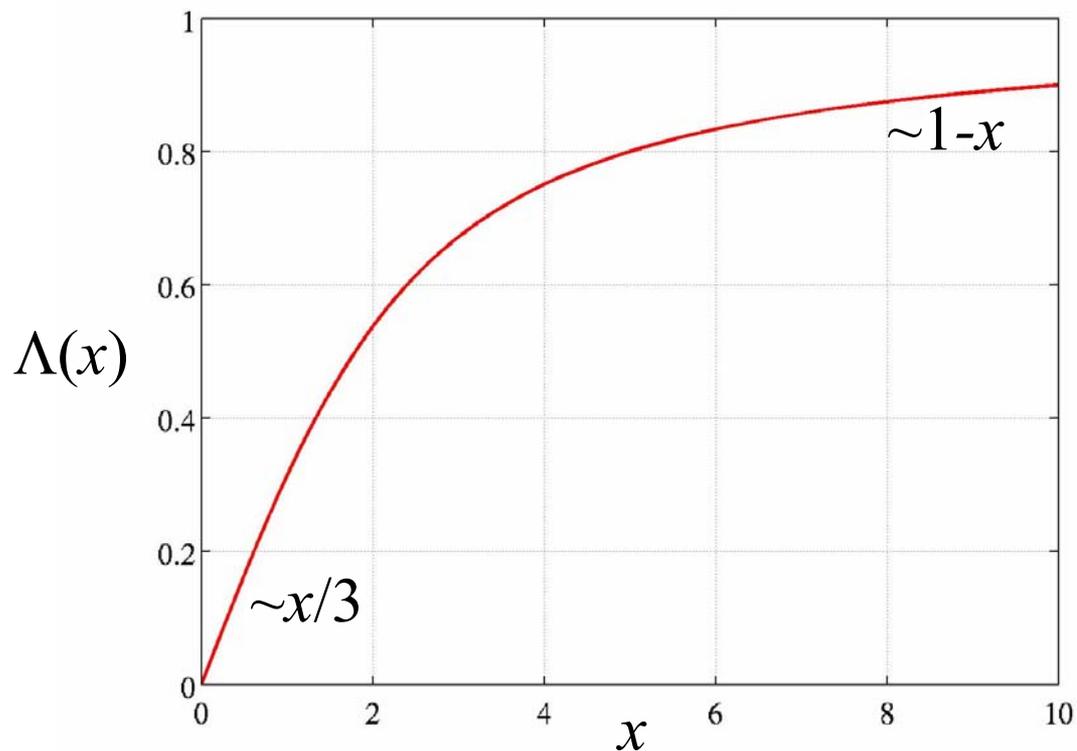
$$z_i \equiv \int d\Omega_i e^{\beta f b \cos \theta_i} = \int 2\pi e^{\beta f b \cos \theta_i} d \cos \theta_i = \frac{4\pi}{\beta f b} \sinh(\beta f b)$$

$$\langle \cos \theta_i \rangle = \frac{\partial \ln z_i}{\partial (\beta f b)} = \coth(\beta f b) - \frac{1}{\beta f b}.$$

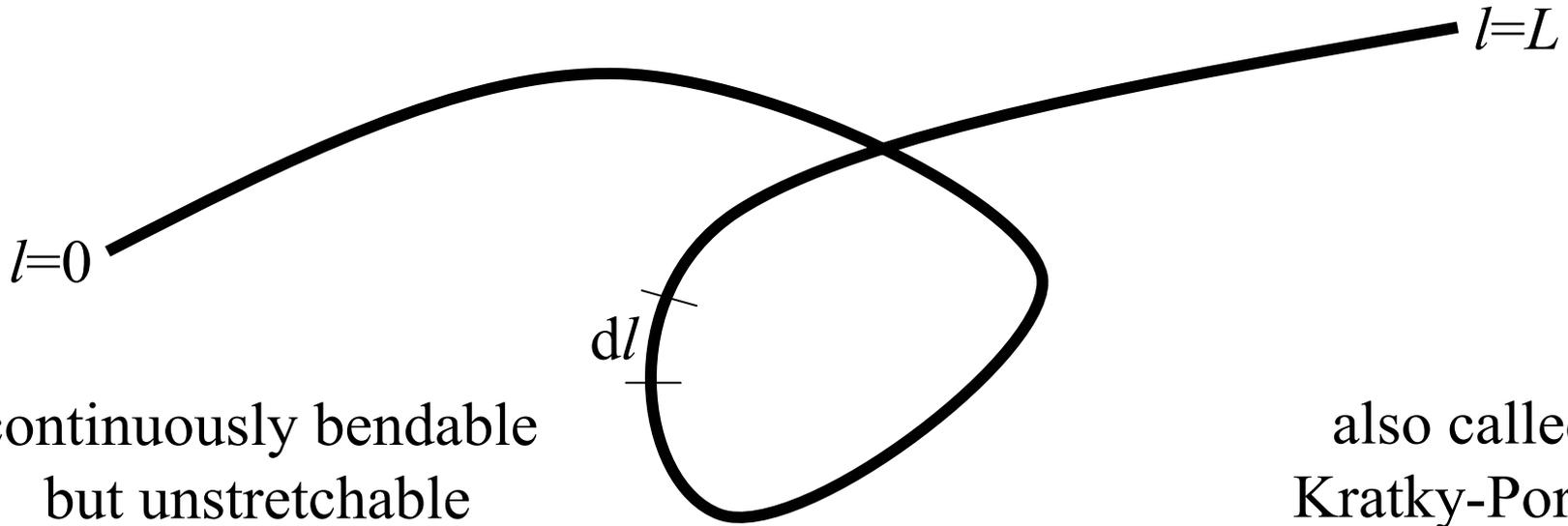
$$X = \langle \mathbf{D} \cdot \hat{\mathbf{f}} \rangle = N \langle b \cos \theta_i \rangle = Nb \left(\coth(\beta fb) - \frac{1}{\beta fb} \right)$$

$$\frac{X}{L} = \Lambda \left(\frac{fb}{k_B T} \right)$$

Langevin function $\Lambda(x) \equiv \coth(x) - x^{-1}$



Worm-Like Chain (WLC)



continuously bendable
but unstretchable

also called
Kratky-Porod
model

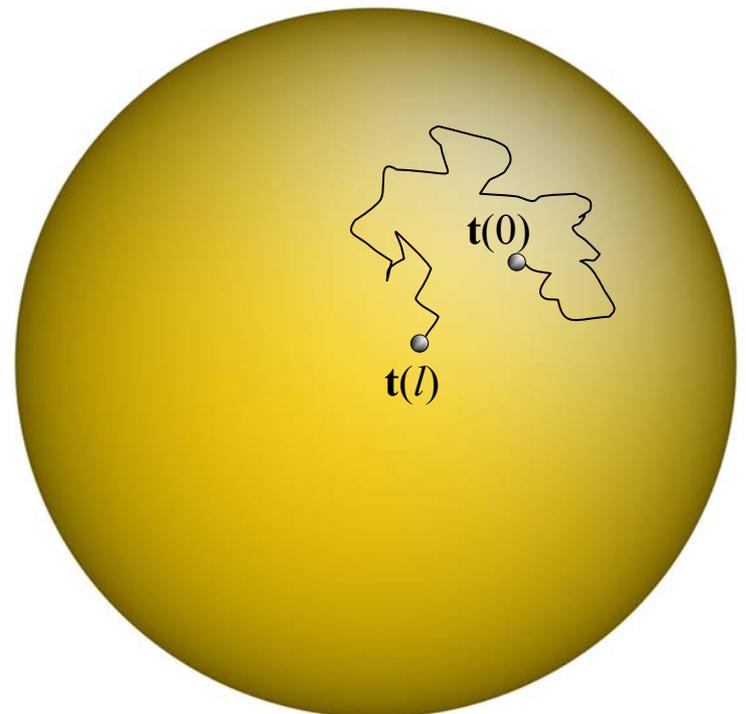
Bending energy penalty: $E[\mathbf{x}(l)] = \int_0^L dl \left(\frac{\kappa C^2}{2} \right)$

curvature $C = \frac{1}{R} = \left| \frac{d^2 \mathbf{x}}{dl^2} \right|$, $\kappa = \frac{Y \pi r^4}{4}$ for solid cylinder

$$\mathbf{t} \equiv \frac{d\mathbf{x}}{dl}, \quad |\mathbf{t}| = 1, \quad C = \left| \frac{d\mathbf{t}}{dl} \right|, \quad E[\mathbf{t}(l)] = \int_0^L \frac{\kappa d\mathbf{t} \cdot d\mathbf{t}}{2dl}$$

$$Z \approx \int \overset{\text{over solid angle } 4\pi}{d\mathbf{t}(\Delta L) d\mathbf{t}(2\Delta L) \dots d\mathbf{t}(L)} \exp\left(-\beta \sum \frac{\kappa \Delta\mathbf{t} \cdot \Delta\mathbf{t}}{2\Delta L}\right)$$

The above path integral can be shown to be equivalent to diffusion of a free particle constrained on a spherical shell (quantum propagator in imaginary time), with diffusivity identified as $1/2\beta\kappa$ (“time” is l).



orientation space

So, $\langle |\mathbf{t}(l) - \mathbf{t}(0)|^2 \rangle \approx \frac{2l}{\beta\kappa}$ when l is small.

$$\langle \mathbf{t}(l) \cdot \mathbf{t}(0) \rangle \approx 1 - \frac{l}{\beta\kappa} \approx \exp\left(-\frac{l}{\beta\kappa}\right)$$

The exponential decay form turns out to be valid in both short- and long- l limit.

Let us define persistence length $p = \beta\kappa = \frac{\kappa}{k_B T}$

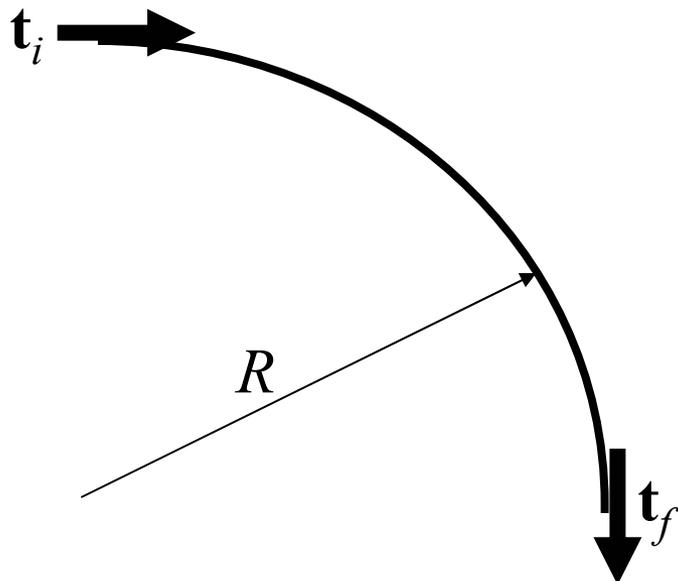
$$\langle \mathbf{t}(l) \cdot \mathbf{t}(0) \rangle \approx \exp\left(-\frac{l}{p}\right)$$

The above *orientation correlation* function is similar to velocity auto-correlation function in Brownian motion.

Two segments on the same polymer chain can be considered to be strongly correlated in orientation if they are separated by less than the persistence length p .

But this correlation dies rather quickly for segments separated by chain length $> p$.

Consider a quarter-circle:



The initial tangent \mathbf{t}_i and the final tangent \mathbf{t}_f can be considered an example of orientation decorrelation.

But, this quarter-circle could be very expensive to make if R is too small.

What is the right price?

$$\frac{\pi R}{2} \cdot \frac{\kappa}{2R^2} \sim k_B T \rightarrow \frac{\kappa}{R} \sim k_B T \rightarrow R \sim \frac{\kappa}{k_B T} \rightarrow R \sim p$$

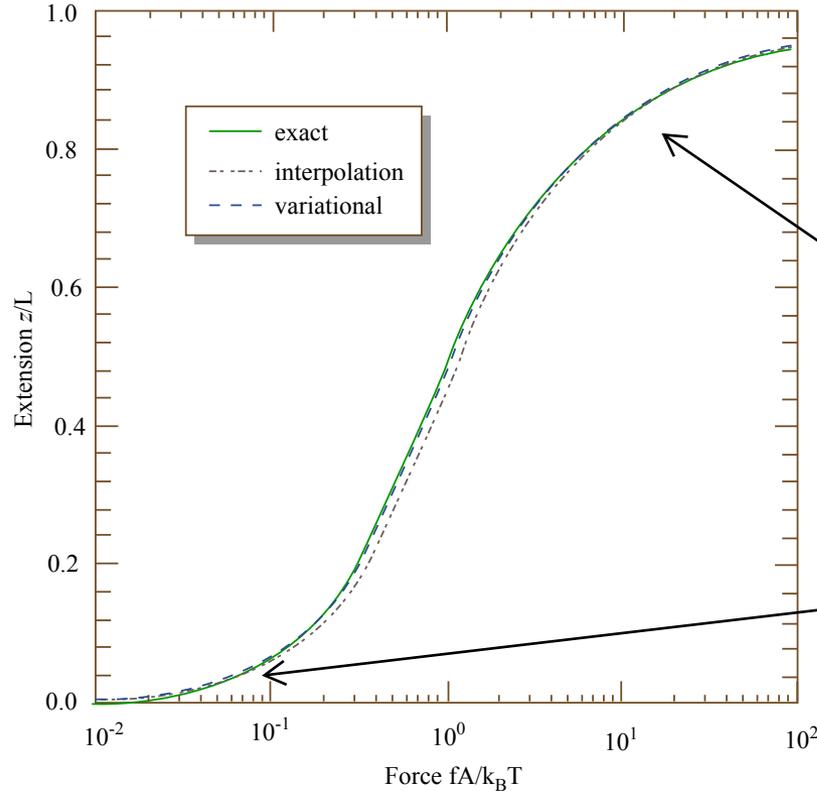
You can afford to make a loop of $R > p$.

The force-extension behavior of WLC-Kratky-Porod model does not admit simple closed-form solution like the Langevin function.

The problem can be mapped to a charged quantum particle confined on a unit sphere, biased by an electric field \rightarrow a Sturm-Liouville eigenfunction problem seeking the lowest eigenvalue. Requires diagonalization of a small matrix, after converting to spherical harmonic basis.

Interpolation form:

$$\frac{fp}{k_B T} = \frac{X}{L} - \frac{1}{4} + \frac{1}{4 \left(1 - \frac{X}{L}\right)^2}$$



Comparison of three different calculations of the WLC extension z/L as a function of $fA/k_B T$. The solid line shows the numerical exact result; the dashed line shows the variational solution; the dot-dashed line shows the interpolation formula. All three expressions are asymptotically equal for large and small $fA/k_B T$.

Good thing about this interpolation form is that both limits are asymptotically correct.

Figure by MIT OpenCourseWare. After Marko and Siggia, 1995.

Marko and Siggia,
Macromolecules
28 (1995) 8759.

The concept of persistence length is also applicable to Freely Jointed Chain model, if we make the following calibration.

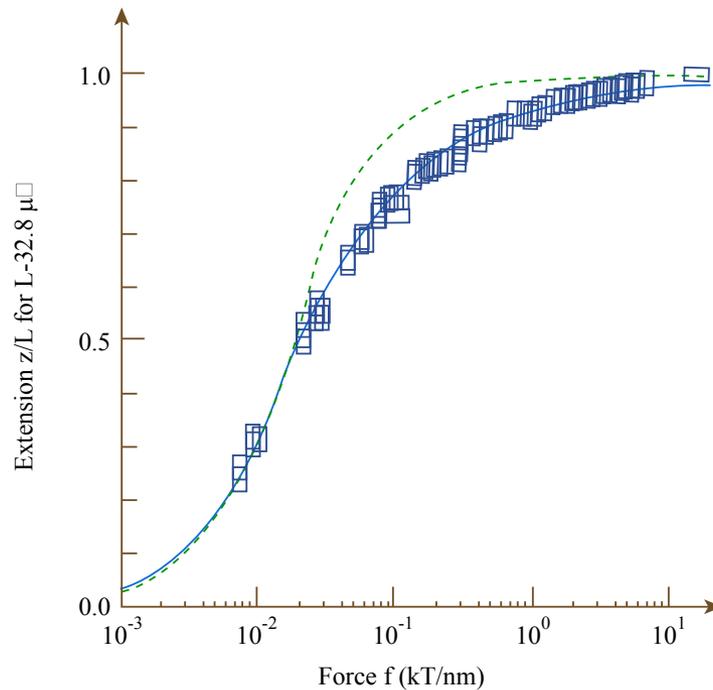
$$\begin{aligned}\langle \mathbf{D} \cdot \mathbf{D} \rangle &= \left\langle \int_0^L dl \mathbf{t}(l) \cdot \int_0^L dl' \mathbf{t}(l') \right\rangle \\ &= \int_0^L dl dl' \langle \mathbf{t}(l) \cdot \mathbf{t}(l') \rangle \\ &\approx L \int_{-\infty}^{\infty} g(l) dl\end{aligned}$$

We know $g(0) = 1$. If we claim $g(l)$ is "equivalent" to $\exp(-l/p)$, then $\langle \mathbf{D} \cdot \mathbf{D} \rangle = 2Lp$.

However, we know in FJC model, $\langle \mathbf{D} \cdot \mathbf{D} \rangle = Nb^2 = Lb$.

So the equivalent persistence length in FJC model is $p = \frac{b}{2}$.

How well does it actually work?



Fit of numerical exact solution of WLC force-extension curve to experimental data of Smith et al. (97004 bp DNA, 10 mM Na⁺). The best parameters for a global least squares fit are $L = 32.8 \mu\text{m}$ and $A = 53 \text{ nm}$. The FJC result for $b = 2A = 100 \text{ nm}$ (dashed curve) approximates the data well in the linear low- f regime but scales incorrectly at large f and provides a qualitatively poorer fit.

In the low-stretch regime:

$$f \rightarrow \frac{3k_{\text{B}}T}{2p} \frac{X}{L} \quad (\text{WLC})$$
$$= \frac{3k_{\text{B}}T}{b} \frac{X}{L} \quad (\text{FJC})$$

Figure by MIT OpenCourseWare. After Marko and Siggia, 1995.

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Self-Avoiding Random Walk (SAW)

Experiments show that R_g grows more quickly than $N^{1/2}$. Flory suggested this is due to excluded volume of the polymer chain. He predicted that:

$$\begin{aligned} R_g &\sim N^{3/(2+d)} = N^{0.6} \text{ (in 3 dimensions)} \\ &= N^{0.75} \text{ (in 2 dimensions)} \end{aligned}$$

Self-avoiding random walker moves on a lattice and never re-visits a site if it has been visited before.

The more precise result in 3D is $R_g \sim N^{0.588 \pm 0.001}$

Reading List

Doi, Introduction to Polymer Physics
(Oxford University Press, Oxford, 1996).

Doi and Edwards,
The Theory of Polymer Dynamics
(Clarendon Press, New York, 1986).

Boal, Mechanics of the Cell
(Cambridge University Press, New York, 2002).