Polymer Physics

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PHY 558 - Physical Biology

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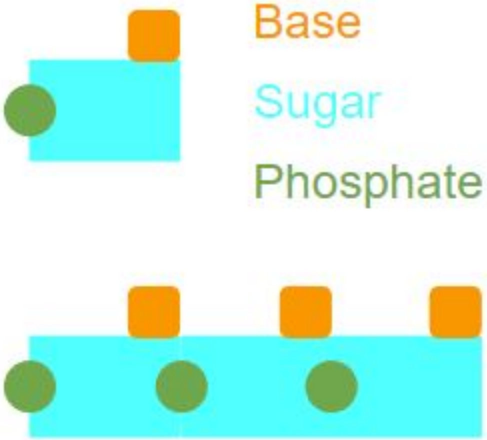
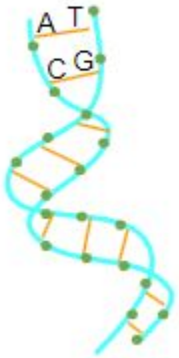
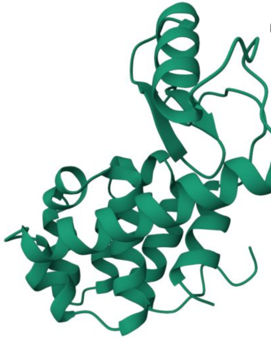
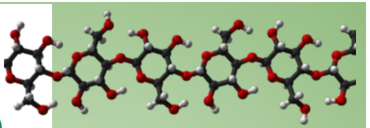
Polymers are chains of monomers





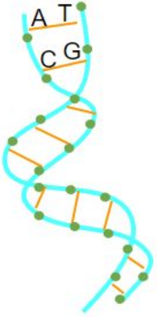
There are many types of polymers





Cellulose

Biopolymers



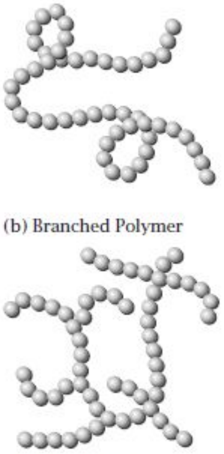
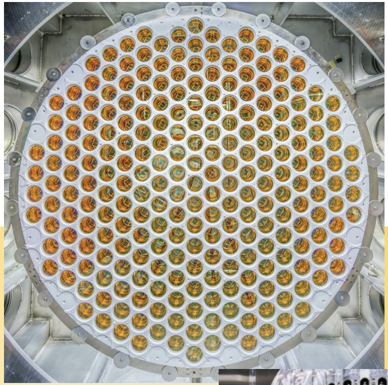
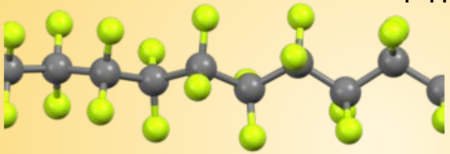


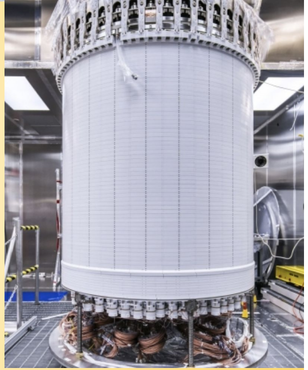
Figure 32.1 Polymers may be (a) linear or (b) branched chains of monomer units.

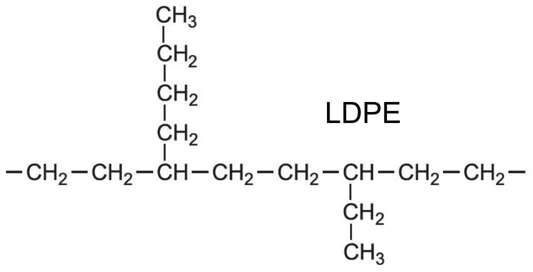
Synthetic polymers



PTFE







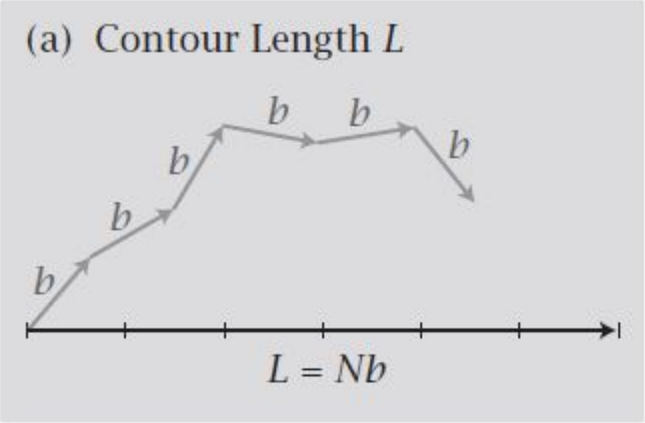
$-CH_2-CH_2-CH(CH_2CH_2CH_2CH_3)-CH_2-CH_2-CH(CH_2CH_3)-CH_2-CH_2-$

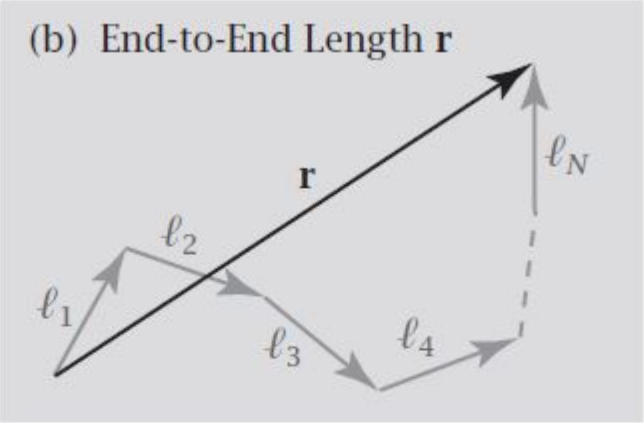
LDPE

MDF 33: Polymer Elasticity and Collapse

A polymer is a collection of N **vectors** of length b

Simplest possible case: ignore differences between monomers, movement, etc.





$$|\mathbf{r}| \leq L$$

$$\mathbf{r} = \sum_{i=1}^{N} \boldsymbol{\ell}_i.$$

$$r_x = \sum_{i=1}^{N} x_i,$$

$$x_i = b \cos \theta_i$$

Polymers can be modeled as random flights

Want to measure **average** properties of many polymers in solution.

Random flight: Angle of each bond is

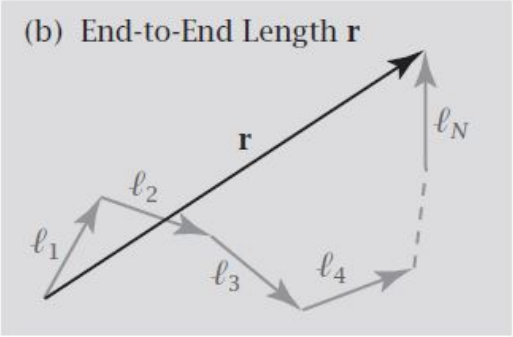
- Independent of neighbors (“freely jointed”)
- Randomly chosen

$$r_x = b \sum_{i=1}^{N} \cos \theta_i .$$

So, we can perform averages over the chain, e.g.

$$\langle r_x \rangle = \left\langle b \sum_{i=1}^{N} \cos \theta_i \right\rangle = b \sum_{i=1}^{N} \langle \cos \theta_i \rangle = 0,$$

Average end-to-end distances are all zero in this model


(b) End-to-End Length $\mathbf{r}$

When the mean is zero, use the second moment

First moment: <r> (mean). Second moment <r^2> (related to standard deviation).

$$\mathbf{r}\cdot\mathbf{r} = \left(\sum_{i=1}^{N} \boldsymbol{\ell}_i\right)^2 = \begin{array}{l} \boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_1 + \boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_2 + \boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_3 + \cdots + \boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_N + \\ \boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_1 + \boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_2 + \boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_3 + \cdots + \boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_N + \\ \quad\vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots \\ \boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_1 + \boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_2 + \boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_3 + \cdots + \boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_N. \end{array}$$

To find the second moment, take the average of this expression, <...>

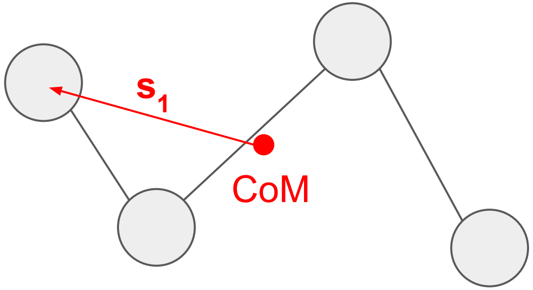
$\langle \boldsymbol{\ell}_i\cdot\boldsymbol{\ell}_i\rangle = b^2$ (length of the vector, N terms)

$\langle \boldsymbol{\ell}_i\cdot\boldsymbol{\ell}_j\rangle = b^2\langle\cos\theta\rangle = 0$ (no correlations)

$$\Big< \mathbf{r}\cdot\mathbf{r} = \left(\sum_{i=1}^{N} \boldsymbol{\ell}_i\right)^2 = \begin{array}{l} \boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_1 + \cancel{\boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_2} + \cancel{\boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_3} + \cdots + \cancel{\boldsymbol{\ell}_1\cdot\boldsymbol{\ell}_N} + \\ \cancel{\boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_1} + \boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_2 + \cancel{\boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_3} + \cdots + \cancel{\boldsymbol{\ell}_2\cdot\boldsymbol{\ell}_N} + \\ \quad\vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots \\ \cancel{\boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_1} + \cancel{\boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_2} + \cancel{\boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_3} + \cdots + \boldsymbol{\ell}_N\cdot\boldsymbol{\ell}_N. \end{array} \Big>$$

$$\boxed{\langle r^2\rangle = Nb^2.}$$

The RMS end-to-end distance is related to other quantities



RMS e2e distance (random flight model): $\langle r^2\rangle^{1/2} = N^{1/2} b.$

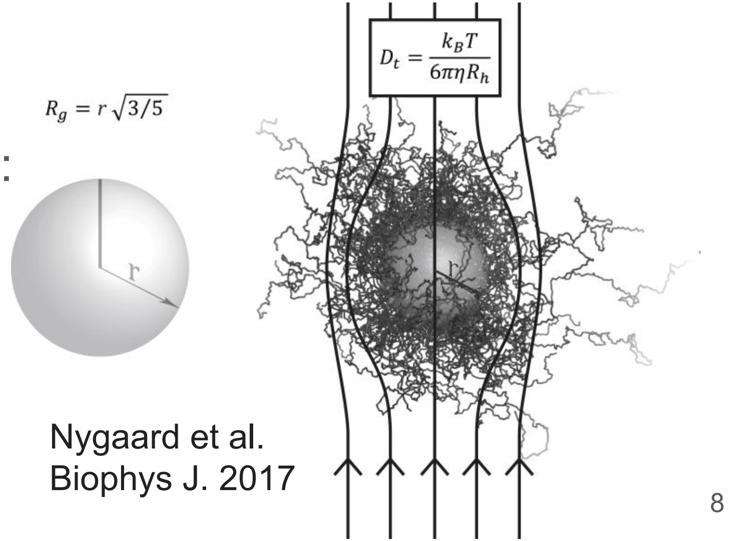
Radius of gyration: $R_g = [1/(N+1)]\,\langle \sum_{j=0}^{N} s_j^2 \rangle,$

Related to the moment of inertia I = M $R_g^{\ 2}$

For a long linear chain (rod), $R_g^{\ 2}$ = <r^2> / 6

Hydrodynamic radius from diffusion (Eqs. 17.42-3):

$$R_h = \frac{k_B T}{6\pi\eta D}$$



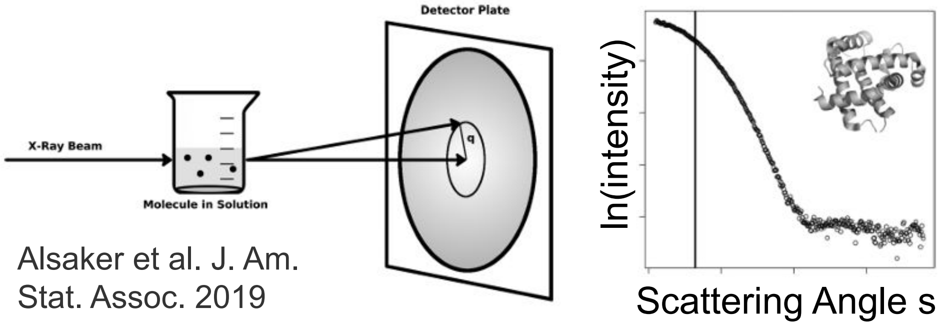
Nygaard et al.
Biophys J. 2017

R_g and R_h can be found experimentally

R_g found experimentally by e.g. small-angle x-ray scattering (SAXS)

R_h found experimentally (from D) by e.g. dynamic light scattering (DLS)

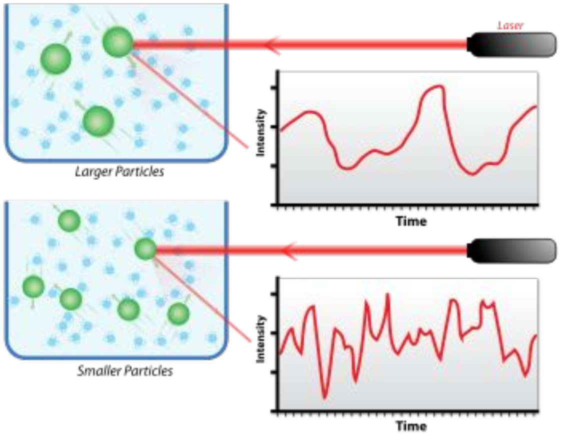
Shape factor $\rho = R_g / R_h$. Folded protein has $\rho \sim 0.78$, unfolded higher



Alsaker et al. J. Am. Stat. Assoc. 2019

$$\ln \mathcal{I}(s) = \ln \mathcal{I}(0) - \frac{1}{3}R_g^2 s^2 + \mathrm{O}\left(s^4\right);$$

SAXS



DLS

Real chain molecules have correlations

No correlations: $\langle \boldsymbol{\ell}_i \cdot \boldsymbol{\ell}_j \rangle = b^2 \langle \cos\theta \rangle = 0$ (all conformations have same energy)

For a straight rod, all angles the same θ = 0, so $\langle \boldsymbol{\ell}_i \cdot \boldsymbol{\ell}_j \rangle = b^2$ and $\langle r^2 \rangle = (Nb)^2 = L^2.$

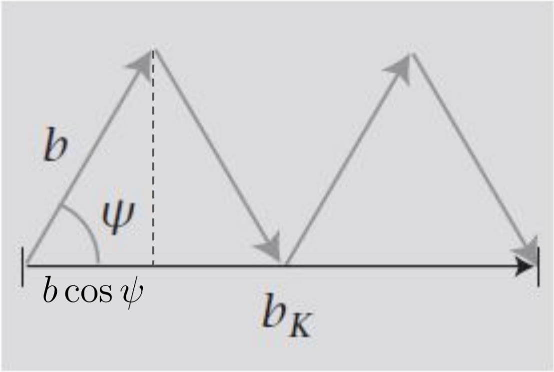
First nearest neighbors: $\langle \boldsymbol{\ell}_i \cdot \boldsymbol{\ell}_{i+1} \rangle = b^2 \gamma$, where $\gamma < 1$

$$< \mathbf{r}\cdot\mathbf{r} = \left(\sum_{i=1}^{N} \boldsymbol{\ell}_i \right)^2 = \begin{array}{l} \boldsymbol{\ell}_1 \cdot \boldsymbol{\ell}_1 + \boldsymbol{\ell}_1 \cdot \boldsymbol{\ell}_2 + \cancel{\boldsymbol{\ell}_1 \cdot \boldsymbol{\ell}_3} + \cdots + \cancel{\boldsymbol{\ell}_1 \cdot \boldsymbol{\ell}_N} + \\ \boldsymbol{\ell}_2 \cdot \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2 \cdot \boldsymbol{\ell}_2 + \boldsymbol{\ell}_2 \cdot \boldsymbol{\ell}_3 + \cdots + \cancel{\boldsymbol{\ell}_2 \cdot \boldsymbol{\ell}_N} + \\ \quad \vdots \qquad\qquad\qquad\qquad\qquad\qquad\qquad \vdots \\ \cancel{\boldsymbol{\ell}_N \cdot \boldsymbol{\ell}_1} + \cancel{\boldsymbol{\ell}_N \cdot \boldsymbol{\ell}_2} + \cancel{\boldsymbol{\ell}_N \cdot \boldsymbol{\ell}_3} + \cdots + \boldsymbol{\ell}_N \cdot \boldsymbol{\ell}_N . \end{array} >$$

$$\langle r^2 \rangle = N b^2 (1 + 2\gamma).$$

In general, $\langle r^2 \rangle \sim N.$ (rod is special)

The Kuhn model simplifies a real chain to a random flight

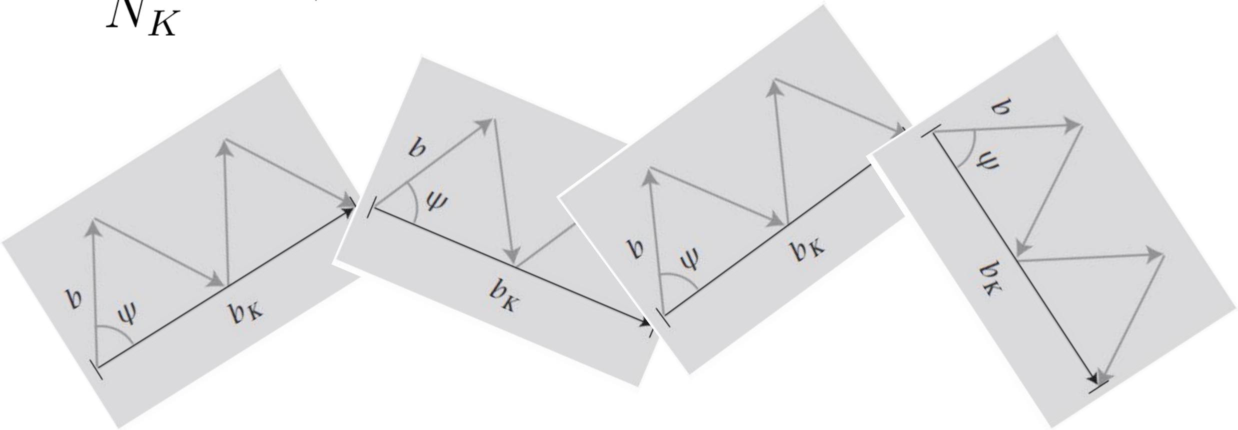


Polymer has “chunks” that orient randomly.

Real chain: N monomers (length b)

Kuhn chain: N_K virtual bonds (length b_K)

$$b_K = \frac{N}{N_K} b\cos\psi$$



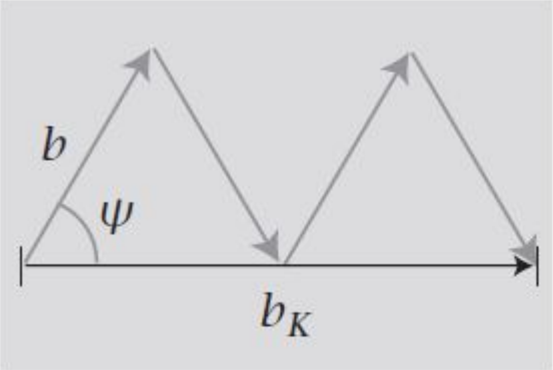
You can solve for the Kuhn parameters

We showed $b_K = \dfrac{N}{N_K} b \cos\psi$ (1)

We know $\langle r^2 \rangle \sim N. \longrightarrow \langle r^2 \rangle = C_N N b^2$

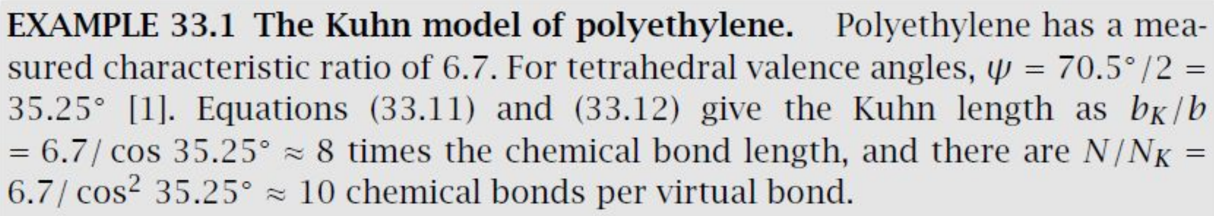
Kuhn model is random flight: $\langle r^2 \rangle = C_N N b^2 = N_K b_K^2.$ (2)

Two equations, two unknowns (N_K and b_K):



$$\frac{b_K}{b} = \frac{C_N}{\cos\psi}, \qquad \frac{N_K}{N} = \frac{\cos^2\psi}{C_N}.$$

C_N = characteristic ratio



EXAMPLE 33.1 The Kuhn model of polyethylene. Polyethylene has a measured characteristic ratio of 6.7. For tetrahedral valence angles, $\psi = 70.5°/2 = 35.25°$ [1]. Equations (33.11) and (33.12) give the Kuhn length as $b_K/b = 6.7/\cos 35.25° \approx 8$ times the chemical bond length, and there are $N/N_K = 6.7/\cos^2 35.25° \approx 10$ chemical bonds per virtual bond.

The persistence length gives a microscopic model

What if we can’t break the chain into random flight pieces?

Look at correlations: $g(s) = \frac{\langle \boldsymbol{\ell}_i \cdot \boldsymbol{\ell}_{i+s} \rangle}{b^2} = \langle \cos\theta(s) \rangle$

Common form is $g(s) = e^{-s/\xi_p}$;

Defines persistence length ξ_p.

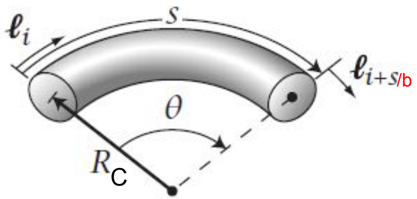
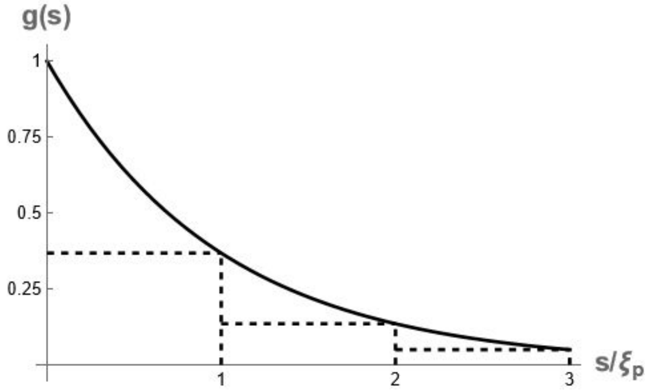


Figure 33.3 Relationship between the bond vectors $\boldsymbol{\ell}_i$ and $\boldsymbol{\ell}_{i+s}$, the angle θ between them, the radius of curvature R_C and the *contour length* s.



The persistence length is related to Hooke’s law bending

$$g(s) = \frac{\langle \boldsymbol{\ell}_i \cdot \boldsymbol{\ell}_{i+s} \rangle}{b^2} = \langle \cos\theta(s) \rangle = e^{-s/\xi_p};$$

Taylor expand the cosine for strong correlations $\langle \cos\theta \rangle \approx \left\langle 1 - \frac{\theta^2}{2} \right\rangle = 1 - \frac{\langle \theta^2 \rangle}{2}.$

Correlations come from energy differences. Simplest model: Hooke’s law

$$\varepsilon_{\text{bend}} = \left(\frac{k_b}{2s}\right)\theta^2.$$

Boltzmann distribution:

$$\langle \theta^2 \rangle = \frac{\displaystyle\int_0^{\pi} \theta^2 e^{-a\theta^2} \sin\theta \, d\theta}{\displaystyle\int_0^{\pi} e^{-a\theta^2} \sin\theta \, d\theta} \approx \frac{\displaystyle\int_0^{\infty} \theta^3 e^{-a\theta^2} d\theta}{\displaystyle\int_0^{\infty} \theta e^{-a\theta^2} d\theta} = \frac{1}{a} = \frac{2sRT}{k_b},$$

$$g(s) = 1 - \frac{1}{2}\left(\frac{2sRT}{k_b}\right) = 1 - \frac{s}{\xi_p} \approx e^{-s/\xi_p}$$

$$\boxed{\Longrightarrow \xi_p = \frac{k_b}{RT}.}$$

Example: Energy of DNA wrapping around histones

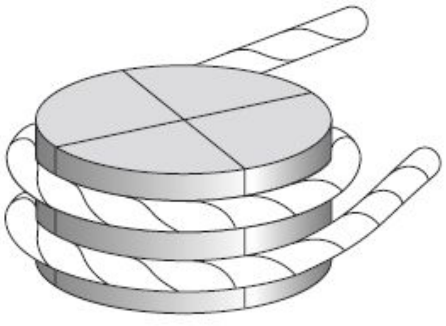


Figure 33.4 A chromosomal DNA molecule (the rope-like object) is wrapped around a histone protein (the post-like object). Because DNA is stiff, it costs energy to bend the DNA so tightly. Source: R Phillips, J Kondev, and J Theriot, *Physical Biology of the Cell*, Garland Science, New York, 2009.

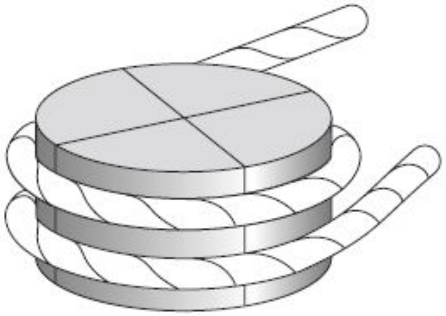
$$\varepsilon_{\text{bend}} = \left(\frac{k_b}{2s}\right)\theta^2. \qquad \xi_p = \frac{k_b}{RT}.$$

R_h = 45 Å

k_b = 300 Å kcal mol^{-1}

What is the energy required to bend the DNA around the histone?
What is the persistence length of the DNA molecule?

Solution: Energy of DNA wrapping around histones



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$$\varepsilon_{\text{bend}} = \left(\frac{k_b}{2s}\right)\theta^2. \qquad \xi_p = \frac{k_b}{RT}.$$

$R_h = 45$ Å

$k_b = 300$ Å kcal mol^{-1}

What is the energy required to bend the DNA around the histone?
What is the persistence length of the DNA molecule?

$\theta = 2\pi \qquad s = 2\pi R_h$

$$\varepsilon_{\text{bend}} = \frac{\pi k_b}{R_h} = \frac{(3.14)\times(300\,\text{Å}\,\text{kcal}\,\text{mol}^{-1})}{45\,\text{Å}} = 21\,\text{kcal}\,\text{mol}^{-1}.$$

$$k_b = \xi_p RT = (\underline{500\,\text{Å}})(0.6\,\text{kcal}\,\text{mol}^{-1}) = 300\,\text{Å}\,\text{kcal}\,\text{mol}^{-1}.$$

Random-flight chain conformations are Gaussian

Back to random-flights. Ch 18: 1D random walk = Gaussian

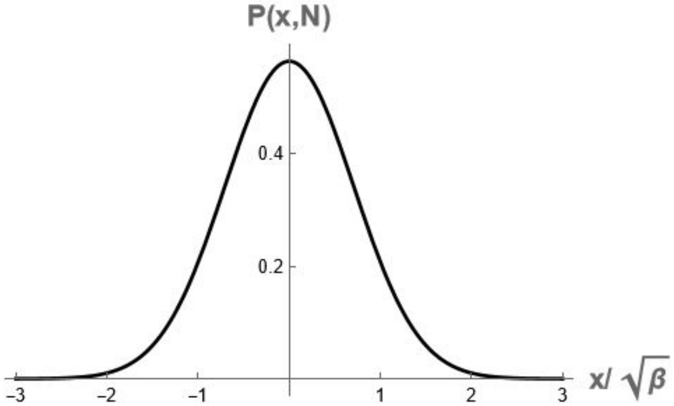
$$P(x,N) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta x^2} = \left(\frac{3}{2\pi N b^2}\right)^{1/2} e^{-3x^2/2Nb^2},$$

$$\beta = 3/(2Nb^2)$$

Figure 33.5 Example of a random-walk chain conformation.

x = end position

P(x,N) = probability of x given N steps



We can derive Hooke’s Law from the Gaussian

Random-flight = all conformations have the same energy = only entropy

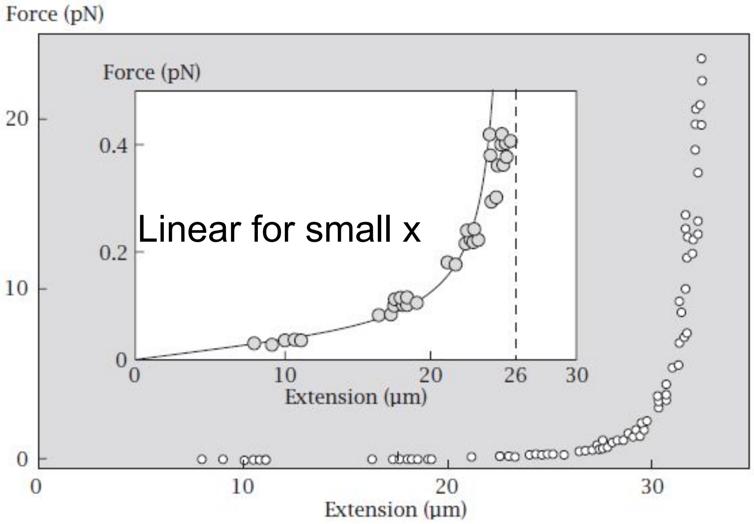
F = -TS, $S/R = \ln P(x,N)$ $P(x,N) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta x^2} = \left(\frac{3}{2\pi N b^2}\right)^{1/2} e^{-3x^2/2Nb^2},$

$$\frac{F}{RT} = -\frac{S}{R} = -\ln P(x,N) = \beta x^2 + \text{constant} = \frac{3x^2}{2Nb^2} + \text{constant}. \longrightarrow f_{\text{elastic}} = -\frac{dF}{dx} = -2RT\beta x = -\frac{3RTx}{Nb^2}.$$

How much can you pull?

$\langle r^2 \rangle^{1/2} = N^{1/2} b$

$L = Nb$



Linear for small x

The Gaussian distribution works in higher dimensions

That was all 1D. 3D is just 3 independent copies of 1D

$$\begin{aligned} P(x,y,z,N)\,dx\,dy\,dz &= P(x,N)P(y,N)P(z,N)\,dx\,dy\,dz \\ &= \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta(x^2+y^2+z^2)}\,dx\,dy\,dz. \end{aligned}$$

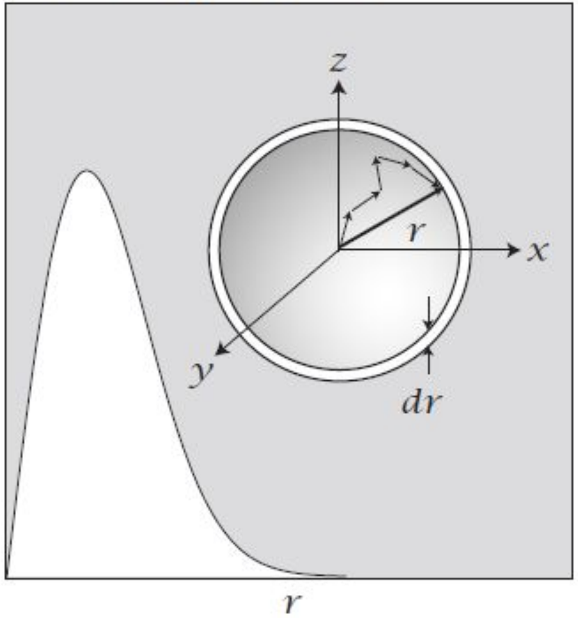
$$P(\mathbf{r},N) = P(x,y,z,N) = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta r^2}.$$

We should use polar coordinates

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P(x,y,z,N)\,dx\,dy\,dz = \int_0^{\infty} \underline{4\pi r^2 P(\mathbf{r},N)}\,dr = 1.$$

$$P(r,N) = 4\pi r^2 P(\mathbf{r},N).$$

$P(r,N) = 4\pi r^2 P(\mathbf{r},N)$



The Gaussian gives the likelihood of cyclization

As an application, what is the probability that the chain ends bond (within b)?

$$
\begin{aligned}
P_{\text{cyclization}} &= \int_0^b P(r,N)\,dr \\
&= \left(\frac{3}{2\pi N b^2}\right)^{3/2} \int_0^b e^{-3r^2/2Nb^2}\, 4\pi r^2\, dr.
\end{aligned}
$$

When N is big, r << $N^{1/2}$b, $e^{-3r^2/2Nb^2} \approx 1.$

$$P_{\text{cyclization}} = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \overbrace{\left(\frac{4}{3}\pi b^3\right)}^{\text{Volume of sphere}} = \left(\frac{6}{\pi}\right)^{1/2} N^{-3/2}.$$

Jacobson-Stockmayer theory, see Example 33.4

MDF 34: Polymers Resist Confinement and Deformation

(in brief)

Confining a polymer increases its free energy

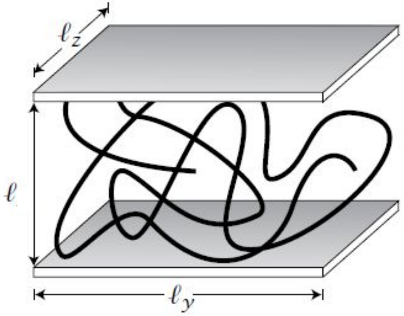
Chain conformations are described by a Gaussian, the solution to the diffusion eq

$$P(x,N) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta x^2} = \left(\frac{3}{2\pi N b^2}\right)^{1/2} e^{-3x^2/2Nb^2}, \longleftrightarrow \frac{\partial p}{\partial N} = \frac{b^2}{6}\frac{\partial^2 p}{\partial x^2}$$

Confined polymer = diffusion equation in a box

$$\left(\frac{\partial p}{\partial N}\right) = \frac{b^2}{6}\left(\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2}\right) = \frac{b^2}{6}\nabla^2 p.$$

With appropriate boundary conditions



V = box volume

Solve the PDE, integrate to find partition function q

$$\frac{F}{kT} = -\frac{S}{k} = -\ln q = -\ln\left(\frac{8V}{\pi^2}\right) + \frac{\pi^2 N b^2}{6\ell^2}.$$

$$F \propto \frac{R_g^2}{\ell^2}$$

MDF 32: Polymer Solutions

What have we left out so far?

We have only been dealing with the polymer chain itself.

In reality, it's in solution

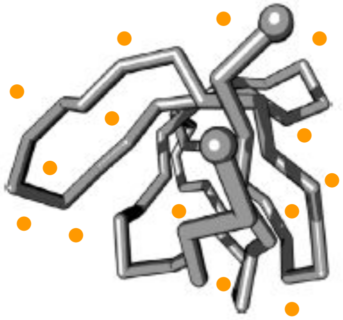
$$\langle r^2 \rangle = C_N N b^2$$

(C$_N$ = 1 for random flight)

$$P(\mathbf{r}, N) = P(x, y, z, N) = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta r^2}.$$

$$P(r, N) = 4\pi r^2 P(\mathbf{r}, N).$$

(Random flight)



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Review of mixing (Chs. 15, 25)

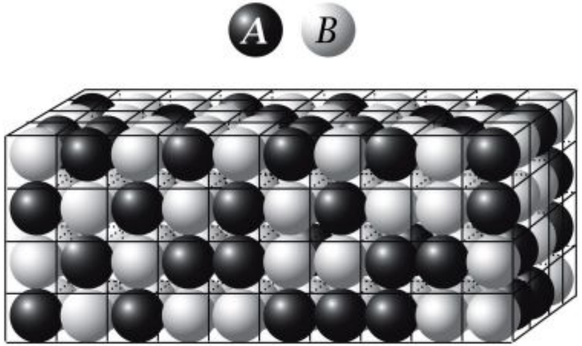
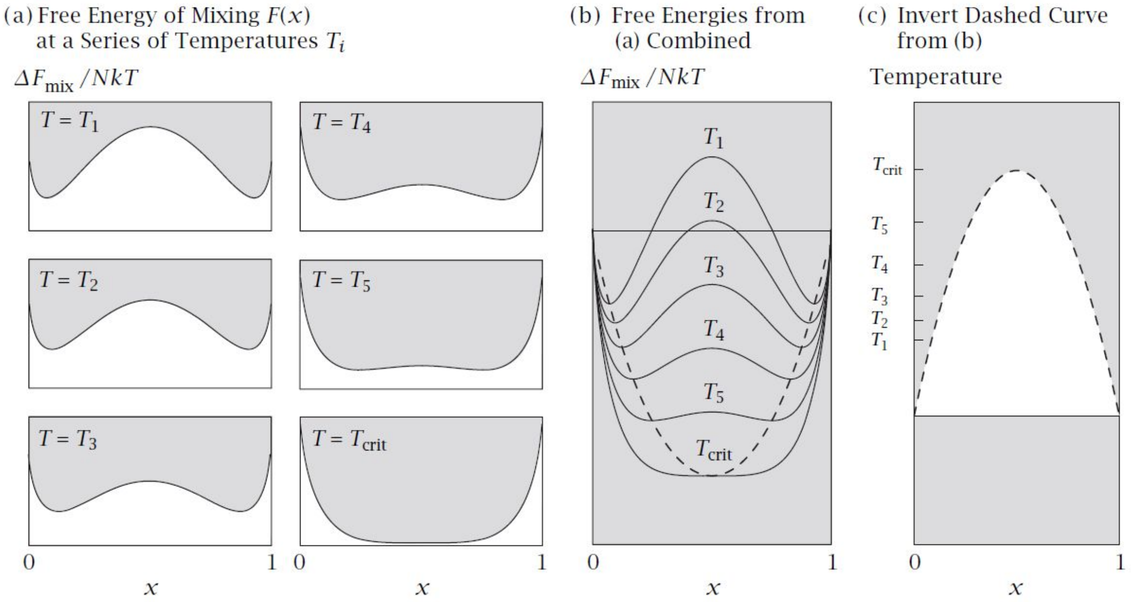


Figure 15.1 Molecular Driving Forces 2/e (© Garland Science 2011)



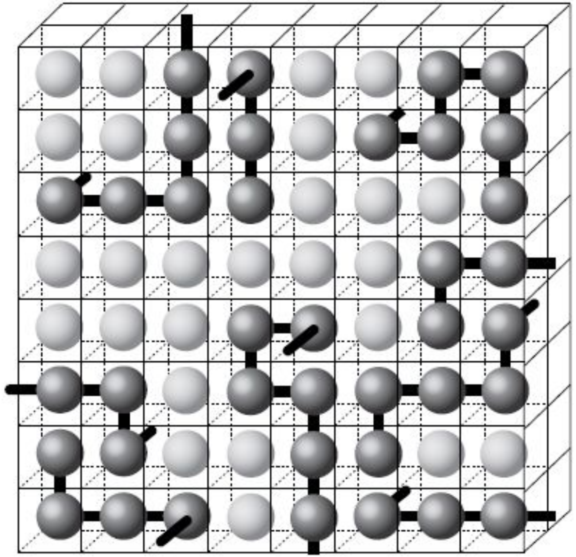
$$\frac{\Delta F_{\text{mix}}}{NkT} = x\ln x + (1-x)\ln(1-x) + \chi_{AB}x(1-x).$$

$$\chi_{AB} = \frac{z}{k_B T}\left(w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right)$$

Flory-Huggins theory is a lattice model

Each polymer takes N sites

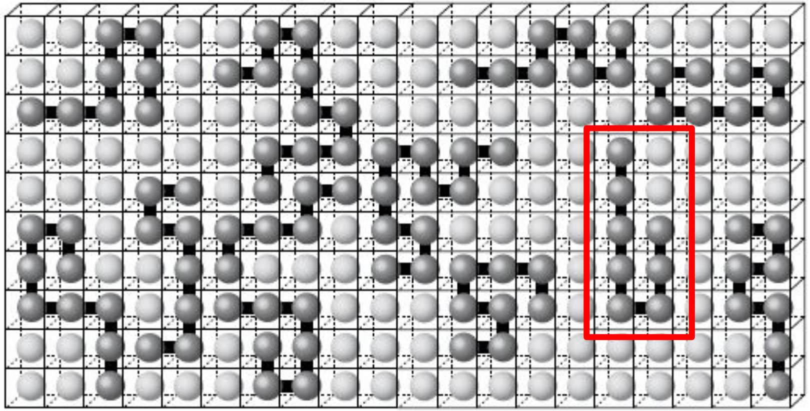
Total of M sites. We will need volume fractions



$$M = Nn_p + n_s.$$

$$\phi_s = \frac{n_s}{M} \quad \text{and} \quad \phi_p = \frac{Nn_p}{M}.$$

How do we find the entropy of mixing?



S ~ ln W. Naively: try to place one chain.

M options for start. Only z options for 2nd.

Only z-1 for the third, fourth…

$$\nu_1 = Mz(z-1)^{N-2} \approx M(z-1)^{N-1},$$

But this is wrong! We need to account for **excluded volume**

Flory: volume excluded to each segment is proportional to space already filled

$$\nu_1 = M\left[(z)\left(\frac{M-1}{M}\right)\right]\left[(z-1)\left(\frac{M-2}{M}\right)\right]\ldots\left[(z-1)\left(\frac{M-N+1}{M}\right)\right]$$

$$\approx \left(\frac{z-1}{M}\right)^{N-1}\frac{M!}{(M-N)!}.$$

Calculating the multiplicity of mixing

That was for one chain. Let's do the multiplicity of the whole mixture now

Place the first bead of each chain: $\nu_{\text{first}} = M(M-1)(M-2)\cdots(M-n_p+1) = \dfrac{M!}{(M-n_p)!}$.

To place the second bead, z~z-1 options, excluded volume fraction

Second bead of the next chain has excluded volume fraction $\dfrac{M - n_p - 1}{M}$

Each subsequent bead gets a factor of z-1 and a fraction from

$$\frac{M - n_p}{M} \quad \text{to} \quad \frac{M - Nn_p - 1}{M}$$

$$\nu_{\text{subsequent}} = \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{(M-n_p)!}{(M-Nn_p)!}.$$

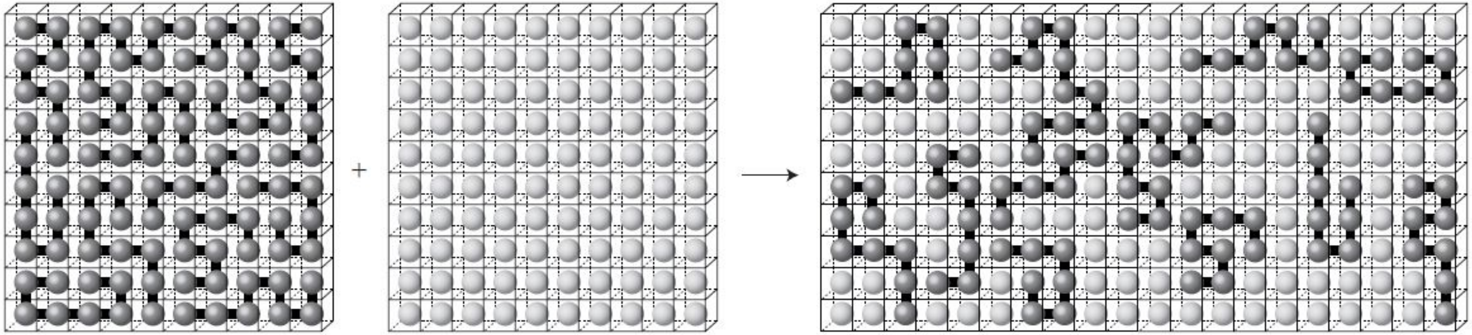
Calculating the Flory-Huggins entropy of mixing

$$W(n_p, n_s) = \frac{\nu_{\text{first}}\nu_{\text{subsequent}}}{n_p!}$$

Polymer chains are indistinguishable

$$= \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{M!}{(M-Nn_p)!n_p!}.$$

$$\frac{\Delta S_{\text{mix}}}{k} = \ln\left[\frac{W(n_p, n_s)}{W(0, n_s)W(n_p, 0)}\right]. \xrightarrow{\text{Algebra, Stirling approx}} \frac{\Delta S_{\text{mix}}}{Mk} = -\phi_s \ln \phi_s - \left(\frac{\phi_p}{N}\right) \ln \phi_p.$$



Calculating the energy of mixing

$$zn_s = 2m_{ss} + m_{sp}$$

$$zNn_p = 2m_{pp} + m_{sp}.$$

Total energy: $U = m_{ss}w_{ss} + m_{pp}w_{pp} + m_{sp}w_{sp}.$

Mean field (Bragg-Williams, see Ch 15) approx: $m_{sp} \approx (zn_s Nn_p)/M$

Algebra…

$$\frac{U}{kT} = \left(\frac{zw_{ss}}{2kT}\right)n_s + \left(\frac{zw_{pp}}{2kT}\right)Nn_p + \boxed{\chi_{sp}\frac{n_s n_p N}{M},} \quad \Delta U_{\text{mix}} \text{ part}$$

$$\chi_{sp} = \frac{z}{kT}\left(w_{sp} - \frac{w_{ss} + w_{pp}}{2}\right)$$

$$\frac{\Delta U_{\text{mix}}}{Mk_BT} = \chi_{sp}\phi_s\phi_p$$

Calculating the free energy of mixing

$$\frac{\Delta F_{\mathrm{mix}}}{Mk_BT} = \frac{\Delta U_{\mathrm{mix}}}{Mk_BT} - \frac{\Delta S_{\mathrm{mix}}}{Mk_B}$$

$$\frac{\Delta U_{\mathrm{mix}}}{Mk_BT} = \chi_{sp}\phi_s\phi_p$$

$$\frac{\Delta S_{\mathrm{mix}}}{Mk} = -\phi_s \ln \phi_s - \left(\frac{\phi_p}{N}\right) \ln \phi_p .$$

Generalize: two polymers A and B in solution

$$\boxed{\frac{\Delta F_{\mathrm{mix}}}{MkT} = \left(\frac{\phi}{N_A}\right) \ln \phi + \left(\frac{1-\phi}{N_B}\right) \ln(1-\phi) + \chi_{AB}\phi(1-\phi).}$$

Compare: $\frac{\Delta F_{\mathrm{mix}}}{NkT} = x \ln x + (1-x)\ln(1-x) + \chi_{AB}x(1-x).$ w/ $\phi_B = 1 - \phi_A = 1 - \phi$

Analyzing the phase separation of a polymer mixture

Recall Ch. 25, we now need some derivatives

$$\Delta F_{\text{mix}}/(Mk_BT) = F = \frac{\phi}{N_A}\ln\phi + \frac{(1-\phi)}{N_B}\ln(1-\phi) + \chi_{AB}\phi(1-\phi)\ .$$

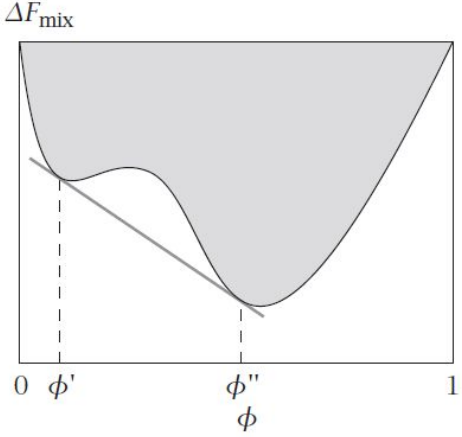
$$\frac{\partial F}{\partial \phi} = \frac{1}{N_A}[\ln\phi + 1] - \frac{1}{N_B}(\ln(1-\phi)+1) + \chi_{AB}(1-2\phi)\ ,$$

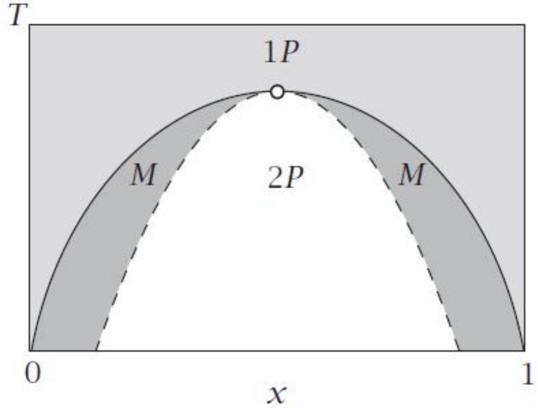
$$\frac{\partial^2 F}{\partial \phi^2} = \frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi_{AB}\ ,$$

$$\frac{\partial^3 F}{\partial \phi^3} = -\frac{1}{N_A\phi^2} + \frac{1}{N_B(1-\phi)^2}\ .$$

Coexistence (why?): $\left(\frac{\partial \Delta F_{\text{mix}}}{\partial \phi}\right)' = \left(\frac{\partial \Delta F_{\text{mix}}}{\partial \phi}\right)''$,

Critical point (why?): $\frac{\partial^2}{\partial \phi^2}\left(\frac{\Delta F_{\text{mix}}}{MkT}\right) = \frac{\partial^3}{\partial \phi^3}\left(\frac{\Delta F_{\text{mix}}}{MkT}\right) = 0.$





Finding the critical point

Set third derivative to zero: $\frac{\partial^3 F}{\partial \phi^3} = -\frac{1}{N_A\phi^2} + \frac{1}{N_B(1-\phi)^2} \longrightarrow \left(\frac{\phi_c}{1-\phi_c}\right)^2 = \frac{N_B}{N_A}$

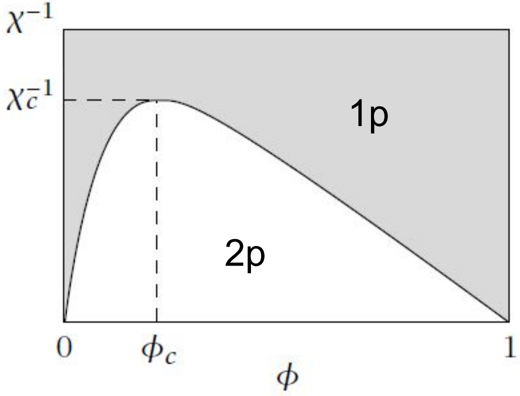
Algebra… $\phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A}+\sqrt{N_B}}$

We also want the critical temperature (from χ). Use 2nd derivative = 0

$$\frac{\partial^2 F}{\partial \phi^2} = \frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi_{AB}$$

Algebra… $\chi_c = \frac{(\sqrt{N_A}+\sqrt{N_B})^2}{2N_AN_B}$

Check: Critical χ is symmetric under A↔B



Special cases: polymer + polymer, polymer + small mol.

$$\phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}} \qquad \chi_c = \frac{(\sqrt{N_A} + \sqrt{N_B})^2}{2N_A N_B}$$

Polymer + small molecule: N = N_A >> 1. Taylor expand χ:

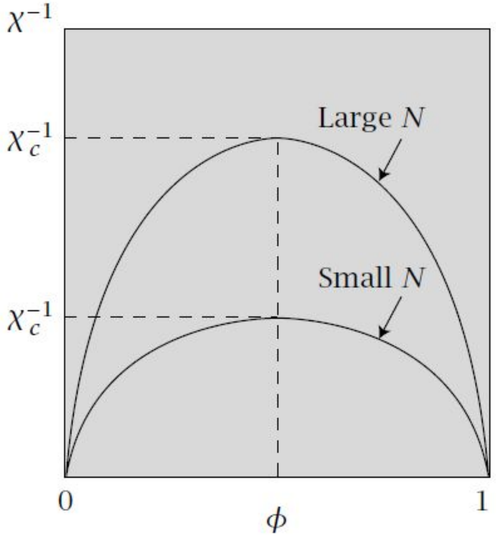
$$\phi_c = \frac{1}{1+N^{1/2}}. \qquad \chi_c \approx \frac{1}{2} + \frac{1}{\sqrt{N}}$$

Note: Eq 32.29 is wrong

Two polymers with same N:

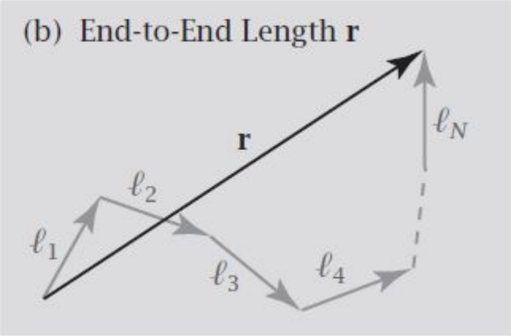
$$\phi_c = \frac{1}{2} \qquad \chi_c = \frac{2}{N}.$$

1p hard to get for big N



MDF 33 (again): Polymer Collapse in Solution

Review: Random-flight model



$$\langle r^2 \rangle = Nb^2.$$

$$P(\mathbf{r}, N) = P(x, y, z, N) = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta r^2}.$$

$$P(r, N) = 4\pi r^2 P(\mathbf{r}, N).$$

No energy difference between conformations

(Elastic) Free energy:

$$\frac{F}{RT} = -\frac{S}{R} = -\ln\left[4\pi r^2 P(\mathbf{r}, N)\right] = \beta r^2 - 2\ln r + \text{constant}.$$

Most probable radius:

$$\left[\frac{d}{dr}\left(\frac{F}{RT}\right)\right]_{r=R_0} = 2\beta R_0 - \frac{2}{R_0} = 0$$

$$\Longrightarrow R_0^2 = \frac{1}{\beta} = \frac{2Nb^2}{3}.$$

Solvation forces also affect the free energy

Let's find the most probable radius in solution, not necessarily random flight

$$\left(\frac{d}{dr}\left[F_{\text{elastic}}(r)+F_{\text{solvation}}(r)\right]\right)_{r=R}=0.$$

Look at one chain in the Flory model, find S, U, F

$$\nu_1=\cancel{M}\left[\cancel{(z)}\left(\frac{M-1}{M}\right)\right]\left[\cancel{(z-1)}\left(\frac{M-2}{M}\right)\right]\ldots\left[\cancel{(z-1)}\left(\frac{M-N+1}{M}\right)\right]$$

CoM position irrelevant

Constant (no ρ, r)

$$\frac{S}{k}=\ln \nu_1=\ln\frac{M!}{(M-N)!M^N}.$$

Algebra…

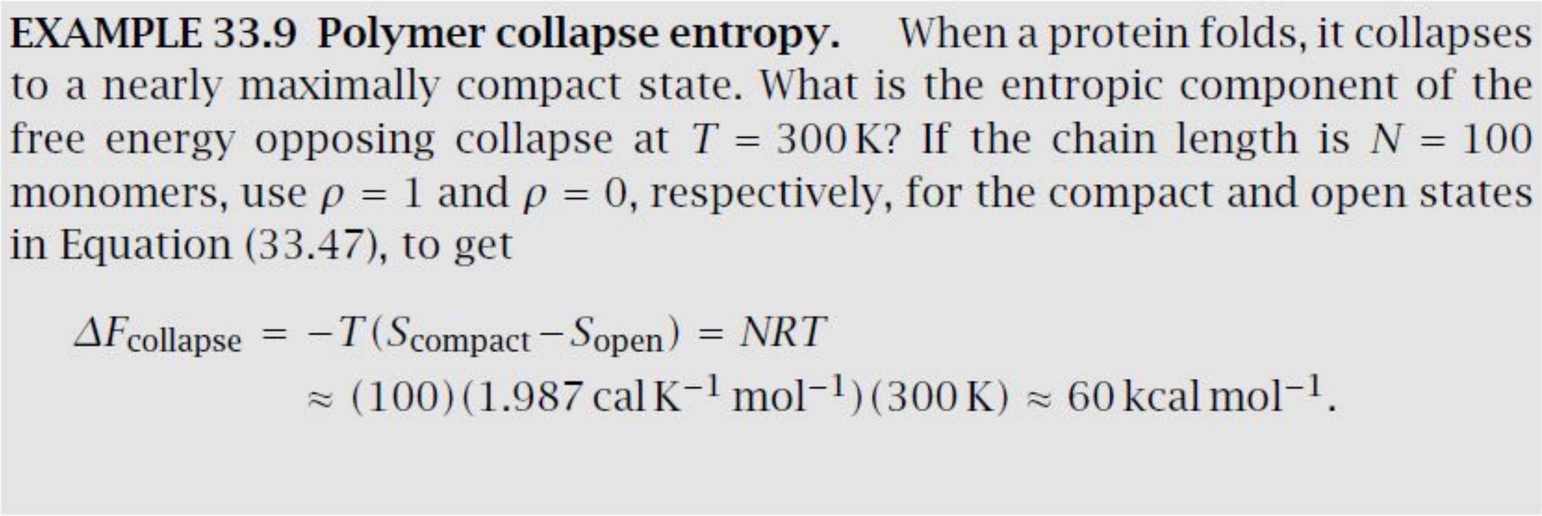
$$\boxed{\frac{S}{Nk}=-\left(\frac{1-\rho}{\rho}\right)\ln(1-\rho)-1.}$$

$$\rho=N/M$$

Quick example: Polymer collapse entropy

$$\frac{S}{Nk} = -\left(\frac{1-\rho}{\rho}\right)\ln(1-\rho) - 1.$$

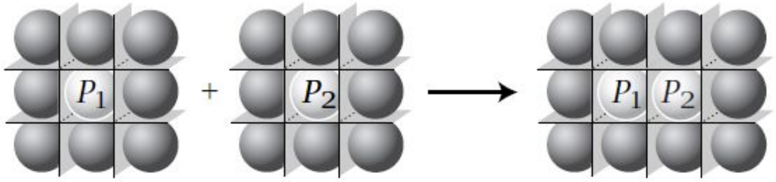
$$S \to 0 \text{ as } \rho \to 0 \text{ and } S \to -Nk \text{ as } \rho \to 1.$$



EXAMPLE 33.9 Polymer collapse entropy. When a protein folds, it collapses to a nearly maximally compact state. What is the entropic component of the free energy opposing collapse at $T = 300\,\text{K}$? If the chain length is $N = 100$ monomers, use $\rho = 1$ and $\rho = 0$, respectively, for the compact and open states in Equation (33.47), to get

$$\begin{aligned}\Delta F_{\text{collapse}} &= -T(S_{\text{compact}} - S_{\text{open}}) = NRT \\ &\approx (100)(1.987\,\text{cal}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K}) \approx 60\,\text{kcal}\,\text{mol}^{-1}.\end{aligned}$$

Calculating the solvation free energy



For one contact: $\Delta g = -2\left(w_{sp} - \frac{w_{ss}+w_{pp}}{2}\right) = -\frac{2}{z}\chi RT.$

Mean field: $\boxed{U = \frac{N\rho z}{2}\Delta g = -NRT\rho\chi.}$

$$\frac{F_{\text{solvation}}}{NRT} = \frac{U}{NRT} - \frac{S}{NR} = \left(\frac{1-\rho}{\rho}\right)\ln(1-\rho) + 1 - \rho\chi.$$

Taylor expand for good solvent: $\boxed{\frac{F_{\text{solvation}}}{RT} = N\rho\left(\frac{1}{2}-\chi\right).}$

Finding the most probable radius

Flory assumption:

$$\rho = \frac{N}{M} = \frac{Nv}{r^3},$$

$$\frac{F_{\text{elastic}}}{RT} + \frac{F_{\text{solvation}}}{RT} = \beta r^2 - 2\ln r + \frac{N^2 v}{r^3}\left(\frac{1}{2} - \chi\right) + \text{constant}.$$

Maximize (algebra):

$$\boxed{\left(\frac{R}{R_0}\right)^5 - \left(\frac{R}{R_0}\right)^3 = \left(\frac{3}{2}\right)^{5/2} \frac{v}{b^3}\left(\frac{1}{2} - \chi\right)\sqrt{N}.}$$

Polymers are random-flights in θ solvents

$$\left(\frac{R}{R_0}\right)^5 - \left(\frac{R}{R_0}\right)^3 = \left(\frac{3}{2}\right)^{5/2} \frac{v}{b^3} \left(\frac{1}{2} - \chi\right) \sqrt{N}.$$

Theta solvent: $\chi = 1/2$

$$\left(\frac{R}{R_0}\right)^2 = 1 \quad \Longrightarrow \quad R^2 = R_0^2 = \frac{2Nb^2}{3},$$

Random flight model can be experimentally realized

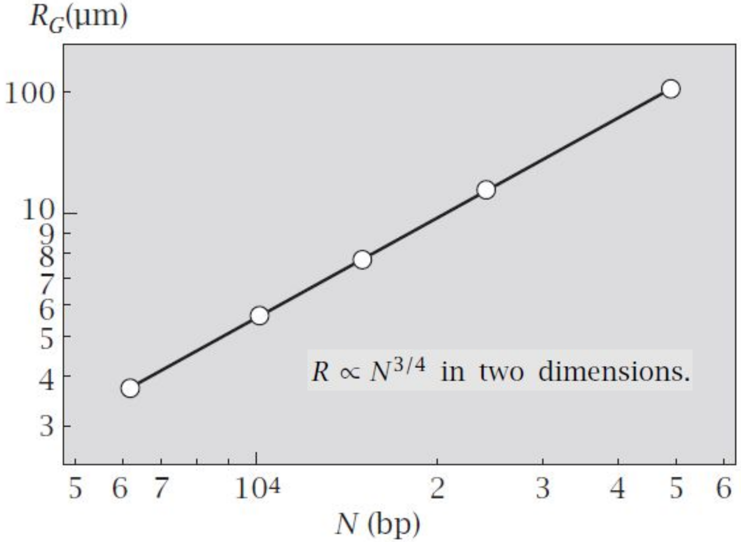
Good solvents expand polymers

$$\left(\frac{R}{R_0}\right)^5 - \left(\frac{R}{R_0}\right)^3 = \left(\frac{3}{2}\right)^{5/2} \frac{v}{b^3}\left(\frac{1}{2}-\chi\right)\sqrt{N}.$$

Good solvent: $\chi < 1/2$, RHS > 0. If N is large,

$$\left(\frac{R}{R_0}\right)^5 \approx \left(\frac{3}{2}\right)^{5/2} \frac{v}{b^3}\left(\frac{1}{2}-\chi\right)\sqrt{N} \quad \Longrightarrow \quad R^5 \propto R_0^5\, N^{1/2} \propto N^3$$

$$\Longrightarrow \quad R \propto N^{0.6}.$$



Same argument works in 2D, but $\rho \propto r^{-2}$ (see Ex 33.10)

Polymers collapse in poor solvents

$$\cancel{\left(\frac{R}{R_0}\right)^5 - \left(\frac{R}{R_0}\right)^3} = \left(\frac{3}{2}\right)^{5/2} \frac{v}{b^3} \left(\frac{1}{2} - \chi\right) \sqrt{N}.$$

Poor solvent: $\chi > 1/2$, RHS < 0. But, expanding the log assumed good solvent.

Keep next order term,

$$\mathrm{LHS} \rightarrow \propto -\frac{N^{3/2}}{R^3}$$

Solve:

$$R \propto N^{1/3}$$

Take home messages: What have you learned?

Polymers have novel properties.

You can model them as beads on a string or a vector walk.

E2E distance for random-flight (experimentally R_g, R_h): $\langle r^2 \rangle = Nb^2.$

Kuhn model simplifies some real chains to random-flights.

Random-flight chains are Gaussian.

Polymers resist confinement: $F \propto \frac{R_g^2}{\ell^2}$

Excluded volume contributes to conformation S (Flory-Huggins).

Mixing F looks like usual, but ϕ and N.

Polymer-polymer usually immiscible; polymer-small molecule has asymmetric phase diagram.

Polymers are random-flights in θ solvents ($R \propto N^{1/2}$), expand in good solvents ($R \propto N^{3/5}$), and collapse in poor solvents ($R \propto N^{1/3}$).

EXTRA: Theoretical modeling of polymerization processes

Binding polynomial approach to polymerization

First, assume only one monomer adds or leaves at a time (MDF 28, aggregation):

$$u_1 + u_n \underset{r}{\overset{k}{\rightleftharpoons}} u_{n+1}$$

Steady-state: each reaction is in equilibrium

$$u_n = \frac{k}{r} u_1 u_{n-1} = \left(\frac{k}{r}\right)^{n-1} u_1^n$$

Problem: becomes badly divergent if k > r. All monomers in one chain

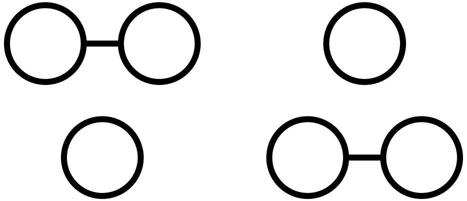
Can we make a more realistic model by fixing our first assumption?

More realistic: Any bond can form or break

$$u_i + u_j \underset{2r}{\overset{2k}{\rightleftharpoons}} u_{i+j} \qquad\qquad 2u_n \underset{r}{\overset{k}{\rightleftharpoons}} u_{2n}$$

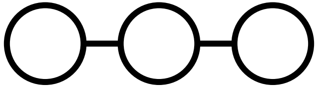
All reactions are one of the above, assuming indistinguishable monomers

Why the factors of 2 in some place but not others?

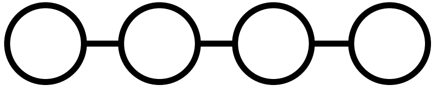


Two distinguishable ways to join, 2k

One way to join, k



Two bonds to split, 2r



One bond to split, r

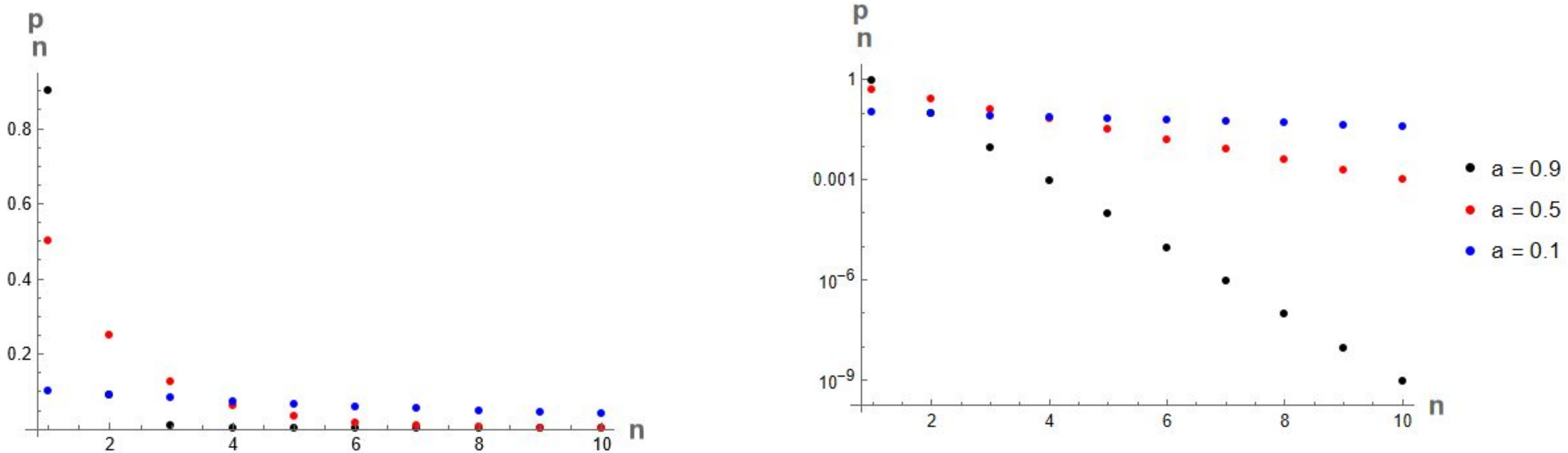
Random polymerization follows the Flory distribution

Can we set all reactions to equilibrium simultaneously? Guess (correct):

$$u_n = Ua(1-a)^{n-1}$$

$$ku_iu_j = ru_{i+j} \longrightarrow a = \frac{1}{1+kU/r}$$

Flory distribution $p_n = a\,(1-a)^{n-1}$, properly normalized pmf



Various calculations with the Flory distribution

$$u_n = Ua(1-a)^{n-1}$$

Average chain length: $\langle n \rangle = \frac{1}{a}$

Distribution peak (d/dn = 0): n = 1 (monotonically decreasing)

Total number of chains: U

Initial number of monomers (sum of n u_n, conserved, could start here): U/a

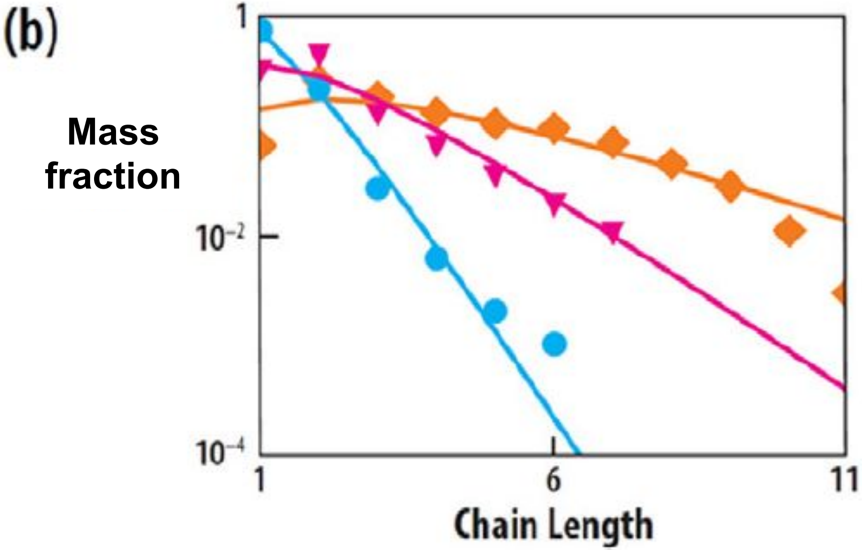
Distribution by weight (n u_n instead of u_n): $F_n = na^2(1-a)^{n-1}$

Peak of the weight distribution: $n_{\mathrm{mode}} = -\frac{1}{\ln(1-a)} \approx \frac{1}{a}$

The Flory mass distribution matches experimental data

$$F_n = na^2(1-a)^{n-1}$$

$$n_{\mathrm{mode}} = -\frac{1}{\ln(1-a)} \approx \frac{1}{a}$$



Mass fraction

Guseva et al.
PNAS 2017