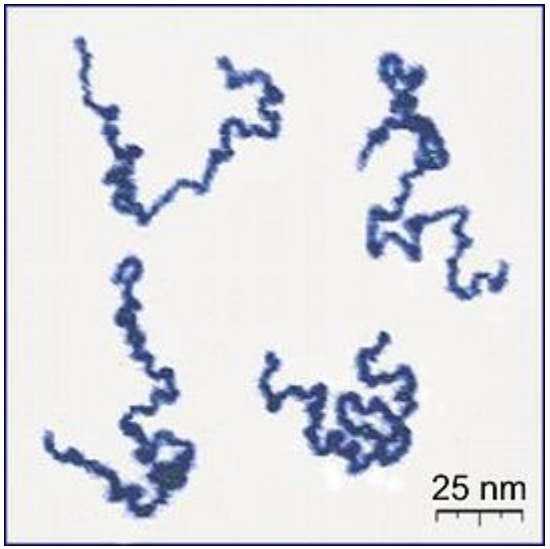
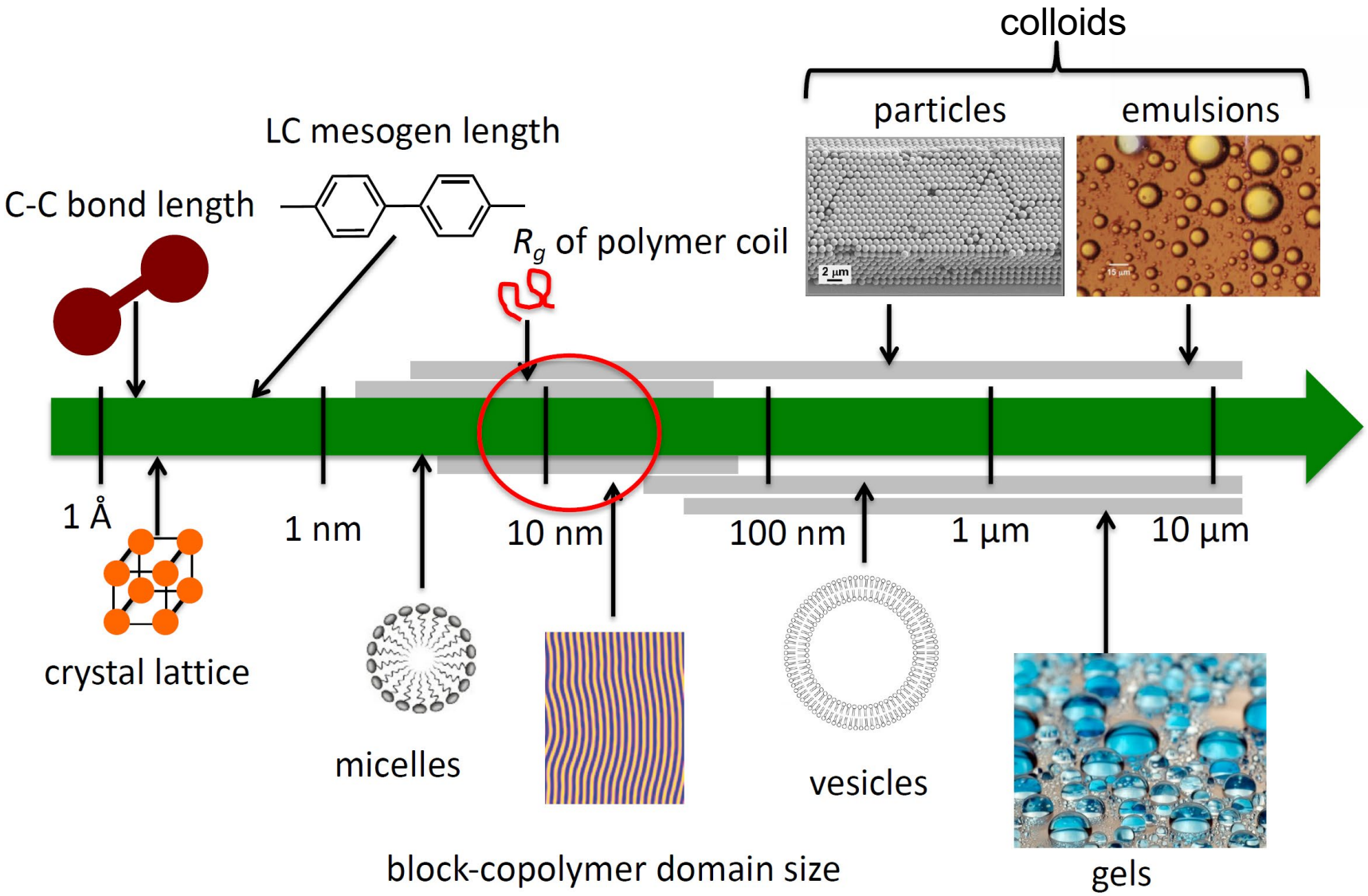
Polymer Structure in Solution



Appearance of real linear polymer chains as recorded using an atomic force microscope on a surface, under liquid medium.
Chain contour length for this polymer is ~204 nm; thickness is ~0.4 nm.

Roiter, Y.; Minko, S. (2005). "AFM Single Molecule Experiments at the Solid-Liquid Interface: In Situ Conformation of Adsorbed Flexible Polyelectrolyte Chains". Journal of the American Chemical Society. ***127*** *(45): 15688–15689.*

Introduction



Outline

How is the structure in solution?

Contour length

End-to end radius

Radius of gyration

Hydrodynamic Radius

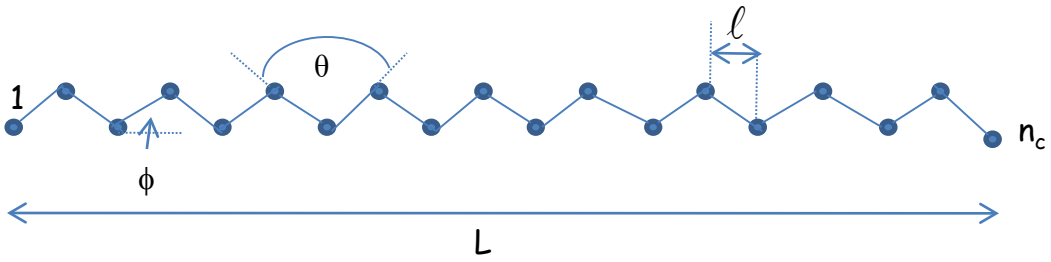
Model of the Random Coil

Schemes of Prefactors

Contour Length

Models developed by H. Staudinger, W. Kuhn and H. Mark

Considering: Polyethylene can be thought of as a sequence of connected ethylene units



all-trans conformation

n_c: number of atoms in the chain
n: number of bonds $n = n_c - 1$
ℓ_{eff}: effective bond length = $l \cos(\theta/2)$
Θ: bond angle
ϕ: half of the conformation angle

Contour length (physically maximum length) $L = n\ell \cos(\theta/2)$

Model of a Perfectly Flexible Chain – Random Coil

random walk in one -dimension:

n successive repeat units along a straight line

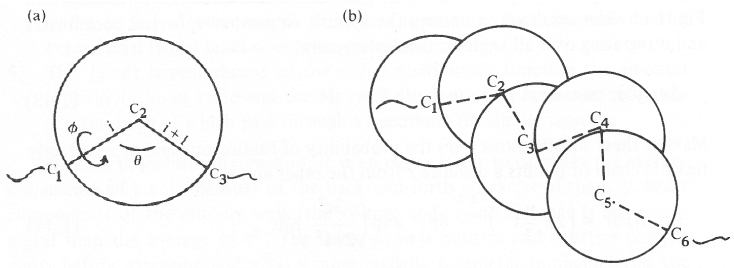


Figure 1.5 Placement of successive polymer segments connected by perfectly flexible joints. In (a), the ith and (i + 1)th bond can be moved through angles ϕ and θ so that carbon 3 can lie anywhere on the surface of a sphere. In (b), the pattern is illustrated for a longer portion of chain.

$$\overline{h^2} = \langle h^2 \rangle = n \cdot l^2$$

n: number of bonds along the backbone
ℓ: actual length of the backbone bond

$\overline{h^2} = \langle h^2 \rangle$ mean square end-to-end distance
with subscript 0 referrs to
unperturbed linear chain

assumptions:

1. the chain is perfectly flexible
2. it excludes a negligible volume

$$\langle h^2 \rangle = nl^2 + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left\langle \vec{l_i} \cdot \vec{l_j} \right\rangle$$

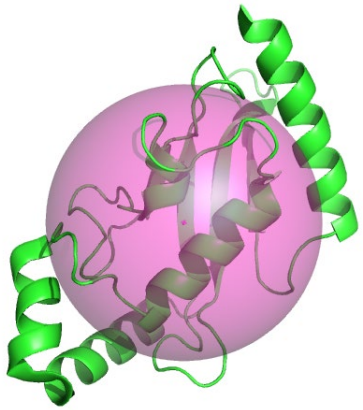
average of cross term:

$$\left\langle \vec{l_i} \cdot \overrightarrow{l_{i-1}} \right\rangle = l^2 \langle \cos\theta \rangle = 0$$

Radius of Gyration

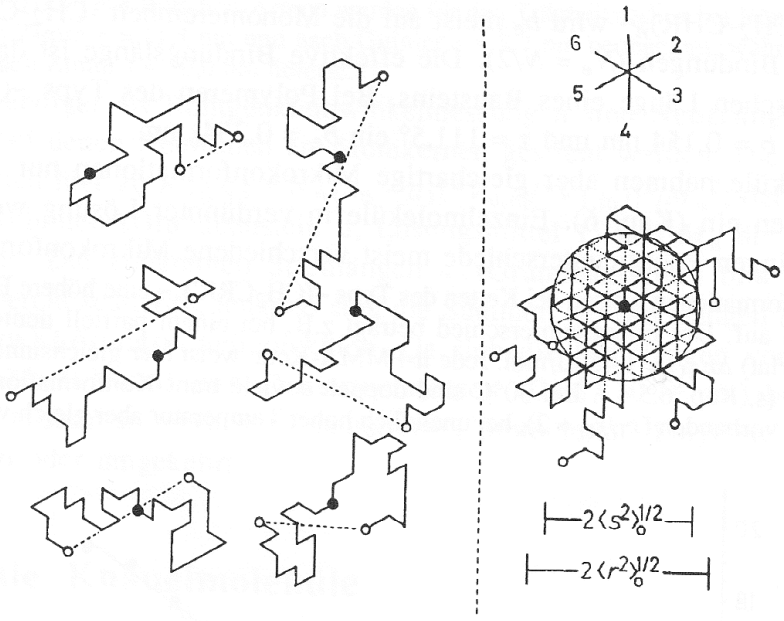
$\overline{h_0^2}$ is a measure for coil density and volume, cannot measured directly, but easily calculated from:

Radius of gyration r_g (s): every particle is characterized by a radius of gyration. It is the distance from the mass center of an object with mass *m*, that gives an equivalent inertia (with mass *m*) if the object is spherical.



$$r_g^2 = \frac{\sum m_i \langle r_i^2 \rangle}{\sum m_i}$$

Elements (monomer i) of mass m_i in a distance r_i from center of mass s

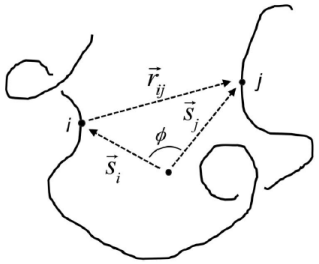


Relation of radius of gyration and end-to-end distance

For each linear chain an end-to-end distance h and a radius of gyration can be determined

Considering vectors of two monomers from center of mass, taking average of each term and summation up to N (number of monomers)

$$r_g^2 = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle r_{ij}^2 \rangle$$



statistical segment length b: $\langle r_{ij}^2 \rangle = |i - j| \, b^2$ $\overline{h_0^2} = Nb^2$ *see next slide*
Kuhn length

Summation over the monomers can be changed into integration over the contour of the chain:

$$\sum_{i=1}^{N} \rightarrow \int_0^N du \quad \text{and} \quad \sum_{j=1}^{N} \rightarrow \int_0^N dv$$

monomer indices into continuous coordinates

$$\Rightarrow r_g^2 = \frac{Nb^2}{6}$$

$$r_g^2 = \frac{\overline{h^2}}{6}$$

Distribution of the end-to-end vector

Example of a random walk in 1 dimension

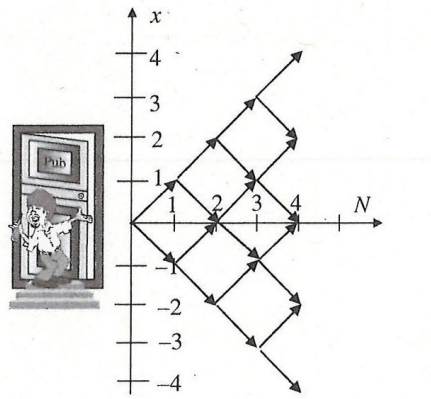


Fig. 2.9
A one-dimensional random walk of a drunk in an alley, showing all possible trajectories up to $N = 4$ steps.

Table 2.5 The number of trajectories $W(N, x)$ for one-dimensional random walks of N steps that start at the origin and end at position x

	$N=1$	$N=2$	$N=3$	$N=4$
$x=-4$	0	0	0	1
$x=-3$	0	0	1	0
$x=-2$	0	1	0	4
$x=-1$	1	0	3	0
$x=0$	0	2	0	6
$x=1$	1	0	3	0
$x=2$	0	1	0	4
$x=3$	0	0	1	0
$x=4$	0	0	0	1

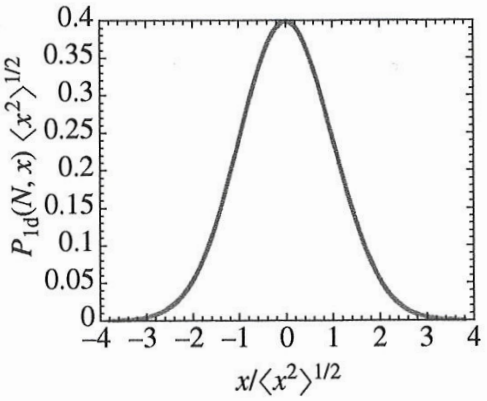


Fig. 2.10
Normalized one-dimensional Gaussian probability distribution function for occupying position x after random N steps from the origin ($x = 0$).

Distribution of the end-to-end vector

random walk in a 3-dimensional coordinate system: distribution of the end-to-end distance by Gaussian

How probable is it to have an end-to-end vector $\vec{h}$ after N steps of length b as random walk?

most probable vector position

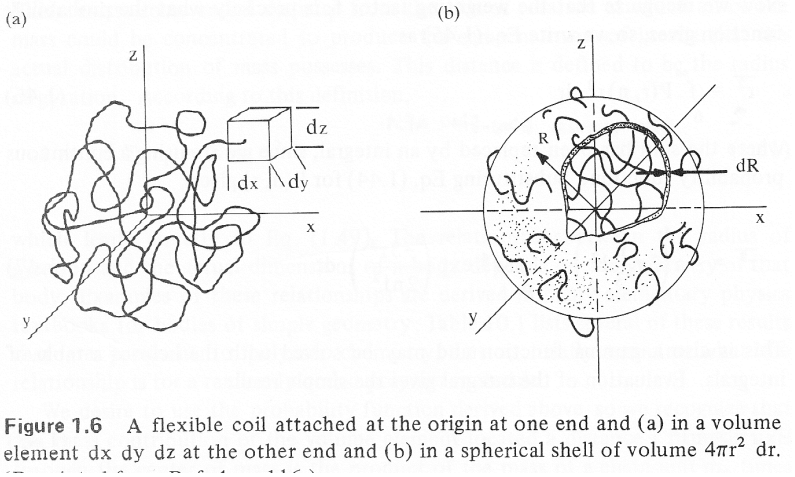


Figure 1.6 A flexible coil attached at the origin at one end and (a) in a volume element dx dy dz at the other end and (b) in a spherical shell of volume $4\pi r^2$ dr.

most probable vector distance

Probability distribution function of the end-to-end vector

$$P(N,h)dh = 4\pi h^2 \, P\left(N,\vec{h}\right) dh$$

$$P\left(N,\vec{h}\right) = \left[\frac{3}{2\pi N b^2}\right]^{3/2} \exp\left(\frac{3\overrightarrow{|h^2|}}{2Nb}\right)$$

mean square value of h:

$$\overline{h^2} = \int_0^\infty h^2 P(N,h)dh = Nb^2$$

The real random coil

The dimensions of polymer molecules in solution deviate from those expected for perfectly flexible chains

1. The angle formed between successive bonds along the chain backbone (Θ) is not free to assume all values, but is fixed at a finite angle depending on the nature of the bond. For the tetrahedral angle associated with carbon-carbon single bonds $\Theta = 109.5°$.

2. The rotation of one carbon-carbon bond around another is subject to steric hindrance so that not all values of ϕ are equally probable.

3. Actual polymer repeat units occupy finite volumes and therefore exclude other segments from occupying the same space (excluded volume effect).

4. To obtain isolated polymer chains, a solvent must be present. The solvent might be selectively excluded or imbibed by the coil, depending on the free energy of interaction and thereby perturb the coil dimensions.

Geometric form of the coil

The shape of the coil changes continuously because of the flexibility of the chain and temperature (brown motion)

But it exists a most probable shape, the ellipsoid

The real random coil

1. Model of freely rotating chain: the bonding angle θ is fixed

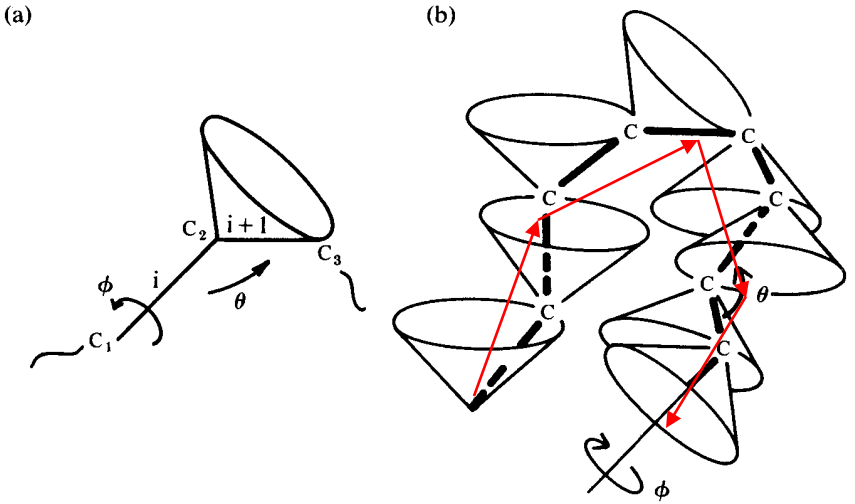
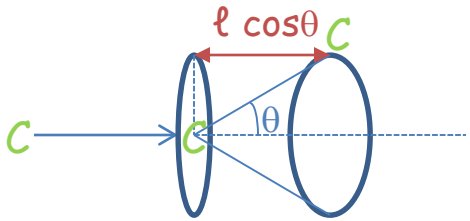


Figure 1.7 Placement of successive polymer segments connected at fixed bond angles. (a) Carbon 3 can lie anywhere on the rim of the cone. (b) This effect is illustrated for a longer portion of chain. [Panel (a) reprinted from Ref. 4, p. 118.]

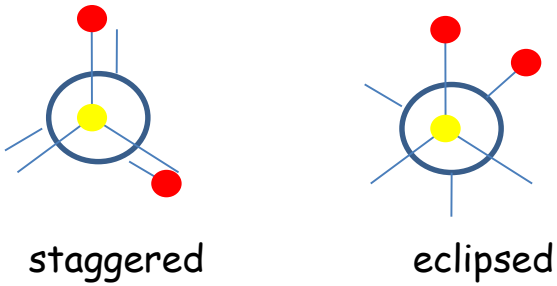


$\langle h^2 \rangle$ is larger than the freely jointed chain result if $\theta < 90°$ ($\cos\theta > 0$). Meaning: each link has some preference for heading in the same direction as the previous link, the chain will double back on itself less often

$$\langle h^2 \rangle = nl^2 \left\{ \frac{1 + cos\theta}{1 - cos\theta} \right\} \quad = Nb^2$$

The real random coil

2. Problem of hindered rotation: conformation angle ϕ



$$\langle h^2 \rangle = nl^2 \left\{ \frac{1 + cos\theta}{1 - cos\theta} \right\} \left\{ \frac{1 + \langle cos\phi \rangle}{1 - \langle cos\phi \rangle} \right\}$$

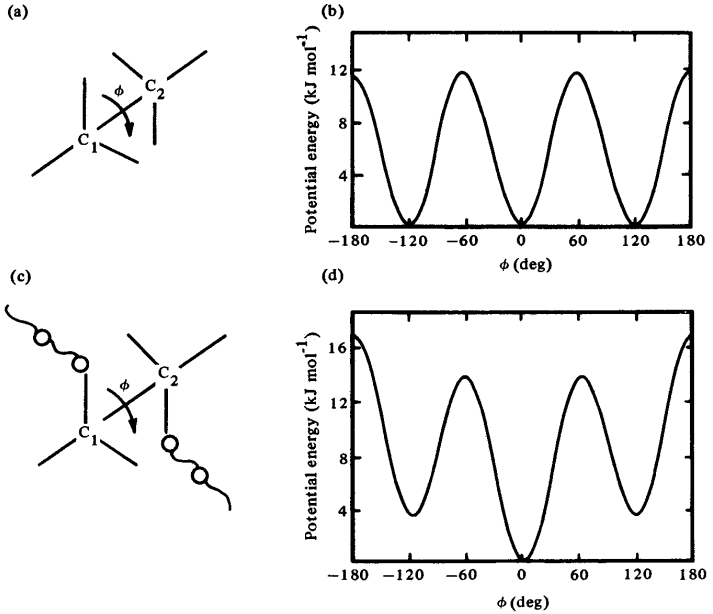
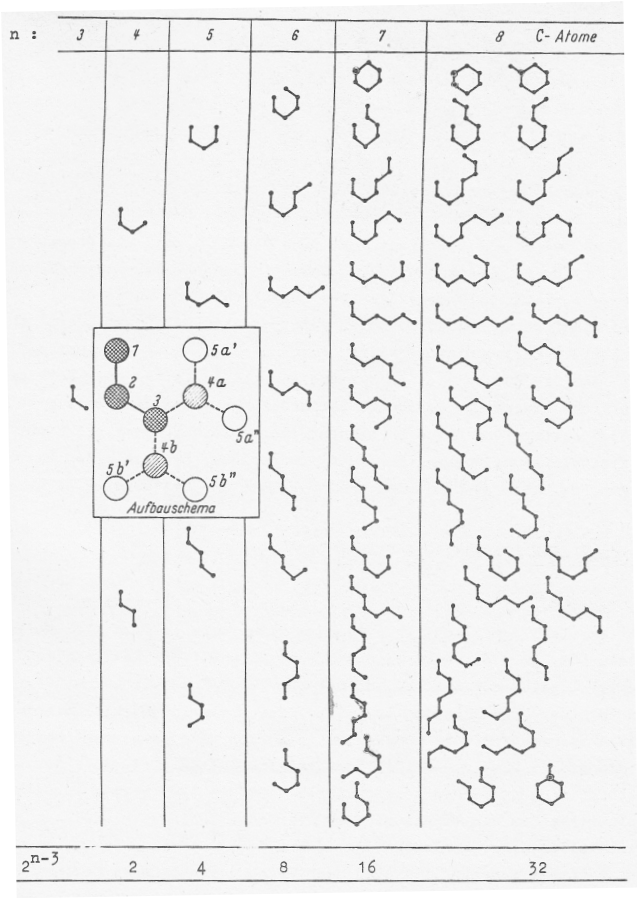


Figure 1.8 Hindered rotation around a carbon–carbon bond. (a) The definition of ϕ (from $\phi = 0$) in terms of the ethane molecule. (b) The potential energy as a function of ϕ. (c) Here ϕ is shown (from $\phi = 0$) for a carbon–carbon bond along a polyethylene backbone. (d) The potential energy for case (c) shown as a function of ϕ. [Panels (b) and (d) reprinted with permission from W. J. Taylor, *J. Chem. Phys.* 16:257 (1948).]



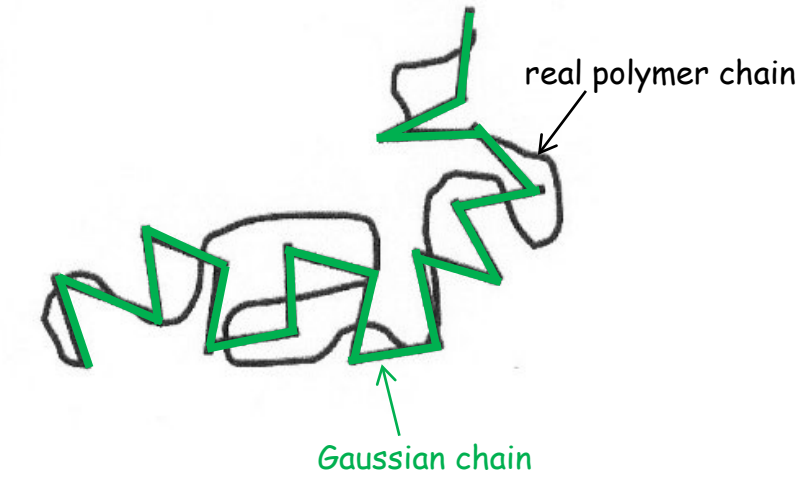
Characteristic Ratio and Statistical Segment Length

Characteristic ratio $$C_n \equiv \frac{\langle h^2 \rangle_0}{nl^2}$$

with **n** number of chemical bond along the polymer backbone
and ℓ actual length of the backbone bond
(1.5Å for C-C)

Theorem: Taking the limit n → ∞ and considering „phantom“ chains that can double back on themselves, then $\langle h^2 \rangle = Cn\ell^2$, where C is a numerical constant that depends only on local constraints and not on n.

The larger the value of C_n, the more the local constraints have caused the chain to extend in one direction.
C_n depends on n, but it approaches a constant value at large n: C_∞



$$\langle h^2 \rangle_0 = C_\infty n\ell^2 = Nb^2$$

N: number of monomers or repeat unit
b: statistical segment length which is a new effective step length

Persistence Length and Kuhn Length

Persistence Length [a] or [l_p] represents the tendency of the chain to continue to point in a particular direction as one moves along the backbone. It measures how far we have to travel along a chain before it will, on average, bend 90°.
When [a] > L, where L = nl is the contour length of the chain, such a molecule is called a rigid rod.

The Kuhn Length [L_K] is defined as twice the persistence length and tells us how far we have to go along the chain contour before it will, on average, reverse direction completely.

for flexible chain: $L_K \equiv 2\,a = C_\infty \ell$

→ C_∞ is the number of backbone bonds needed for the chain to easily bend 180°.

mean-square unperturbed end-to-end distance of a flexible chain:

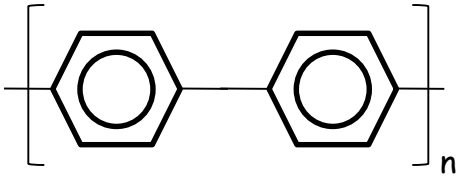
$$\overline{h_0^2} = C_\infty n l^2 = 2anl = L_K L = Nb^2$$

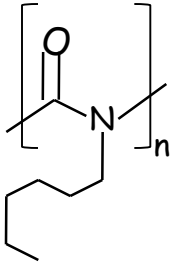
n: number of chemical bonds along the polymer backbone
l: actual length of backbone bond
L: contour length
N: number of monomers or repeat units
b: statistical segment length
a: persistence length

Worm Like Chains and Persistence Length

For many polymers, the backbone does not consist of a string of single bonds with facile rotations, but rather some combination of bonds that tend to make the backbone continue in one direction

Ex. Poly(p – phenylene) (aromatic rings in backbone) or poly(n-hexyl isocyanate) with large side-groups





Description of the chain dimension "rigid rods" with the scheme of Kratky and Porod: worm-like chain
Transforming the freely rotating chain continuously in a worm-like chain by taking a special limit, where the number of bonds n go to infinity, but the length of each bond, l, will go to zero, while maintaining the contour length L = nl constant.

$$\langle h^2 \rangle = 2aL - 2a^2\left(1 - exp\left[\frac{-L}{a}\right]\right) \text{ as } \ell \rightarrow 0$$

The real random coil

3. Excluded Volume and 4. Solvent Interaction

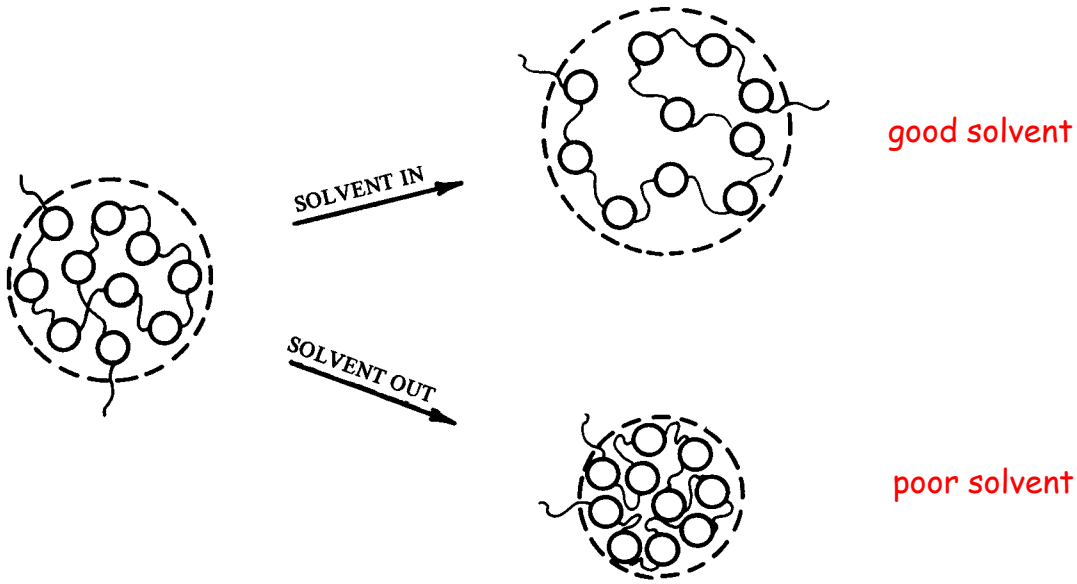


Figure 1.9 The spherical domain of a polymer molecule either expanding by imbibing solvent or contracting by excluding solvent.

Under Θ (theta) conditions, the poorness of the solvent exactly compensates for the excluded volume effect = pseudoideal state

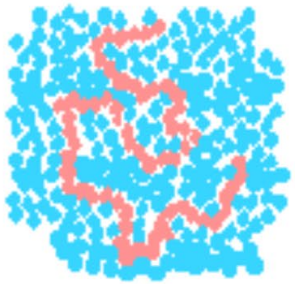
→ Equations of the ideal random coil are valid

Solvent Quality – Influence on h

Good solvent

Solute – solvent interactions are favored such that the chain is swollen

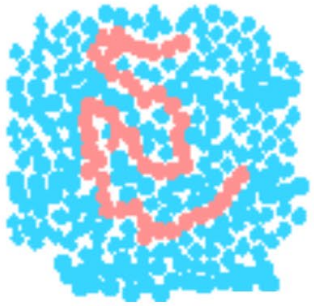
$\chi < 0.5$



Theta solvent

The interactions between different solute molecules are equal to those between solutes and solvents.

$\chi = 0.5$



Poor solvent

The solute – solute interactions are favored such that the chain is contracted.

$\chi > 0.5$

Influence of solvent quality (interaction parameter χ) on end – to – end distance h

$$\sqrt{\langle h^2 \rangle} \approx N^{\nu}$$

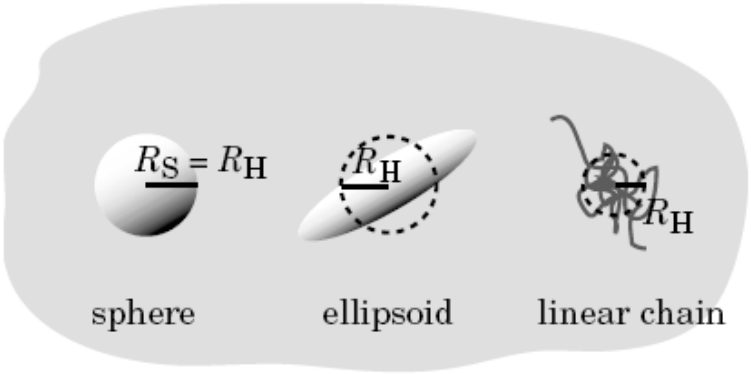
good solvent	$\nu = 0.588$
theta solvent	$\nu = 0.5$
poor solvent	$\nu = \frac{1}{3}$

Hydrodynamic Radius

The hydrodynamic radius of a polymer includes the solvent molecules which surround it and which move with it during diffusion. Thus it is the size of a hypothetical hard sphere that diffuses in the same fashion as that of the particle being measured.

$$R_H = \frac{k_B T}{6\pi\eta_s D}$$ hydrodynamic radius

K_B : Boltzmann's constant
T : Temperature
η_s : Viscosity
D : Diffusion coefficient



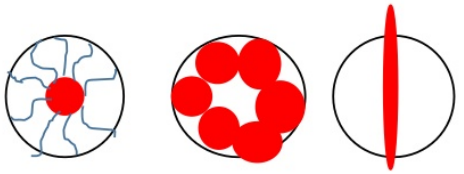


Figure 3.13. For the center-of-mass motion, an ellipsoid with a hydrodynamic radius R_H receives the same friction as a sphere of radius R_H does. Likewise, a linear chain with a hydrodynamic radius R_H diffuses with the same diffusion coefficient as the sphere of radius R_H.

For a linear chain molecule, R_H is proportional to R_G and h; therefore $R_H \propto N^{\nu}$

ν = ~ 0.59 for a good solvent
ν = ½ for a theta solvent

Relationship between Different Radii

R_H is quite small compared with the end-to-end distance h.

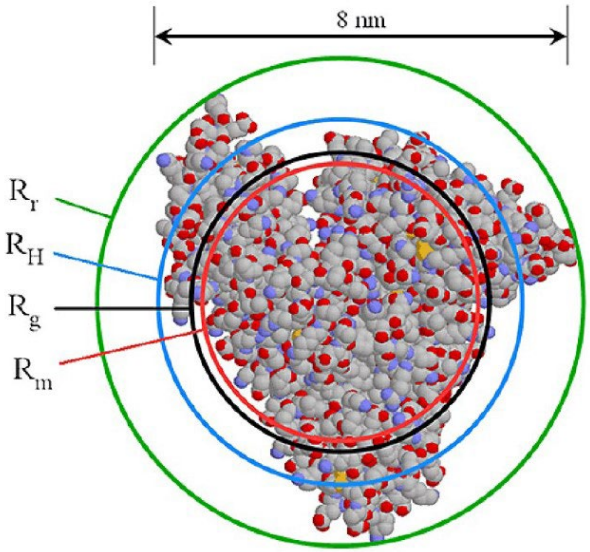
R_H is also smaller than R_g.

For a chain with a Gaussian conformation (ideal coil) is

$$R_H/h = (3\pi/2)^{1/2}/8 \cong 0.271$$

and $$R_H/R_g = (3/8)\pi^{1/2} \cong 0.665$$

Thus **$R_H < R_g < h$ for a Gaussian coil**



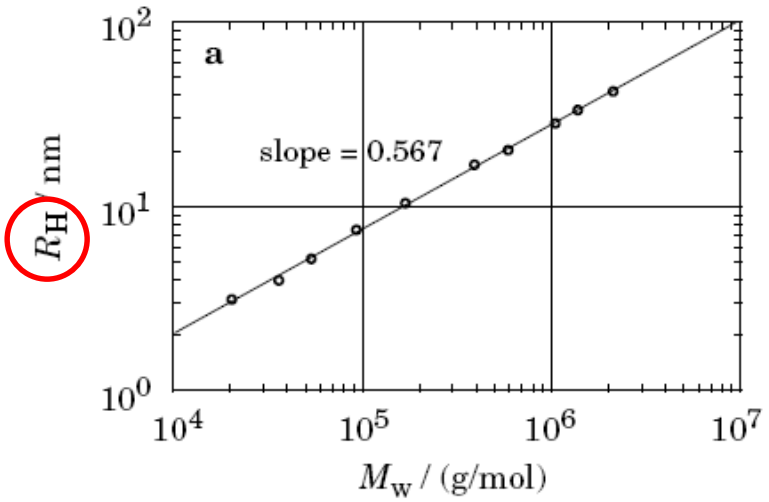
Radius of rotation, hydrodynamic radius, radius of gyration and mass radius which is the radius of a sphere with the same partial specific volume as the protein Bovine serum albumin
https://www.s21.co.kr/news_proc/news_contents.jsp?ncd=4182

Table 3.1 Various Measures of the Chain Dimension $R_F = h$

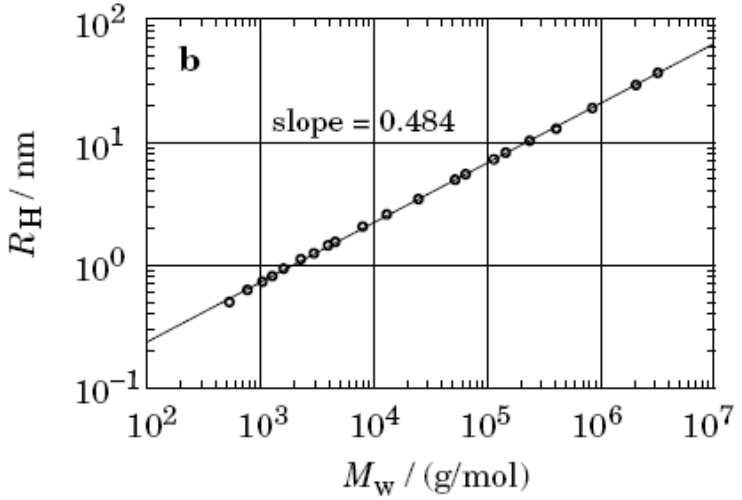
Polymer Chain	R_H/R_g	R_H/R_F	R_F/R_g
Ideal/theta solvent*	0.665 $(=(3/8)\pi^{1/2})$	0.271 $(=(3\pi/2)^{1/2}/8)$	2.45 $(=6^{1/2})$
Real (good solvent)	0.640	0.255	2.51
Rod-like	$3^{1/2}/(\ln(L/b)-\gamma)$**	$1/[2(\ln(L/b)-\gamma)]$**	3.46 $(=12^{1/2})$

*Chains with an ideal-chain conformation.
**Depends on the rod length L and rod diameter b. $\gamma \cong 0.3$.

Molar mass dependence of the Radii



Exp. of a good solvent:
polystyrene in 2-fluorotoluene at 42,6°C



Exp. of a theta solvent:
Poly(α-methylstyrene) in cyclohexane at 30,5°C

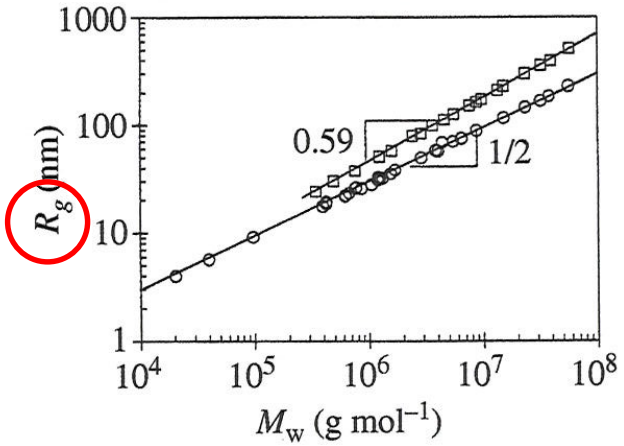


Fig. 3.6
Molar mass dependence of the radius of gyration from light scattering in dilute solutions for polystyrenes in a θ-solvent (cyclohexane at $\theta = 34.5\,°C$, circles) and in a good solvent (benzene at 25 °C, squares). Data are compiled in L. J. Fetters, *et al.*, *J. Phys. Chem. Ref. Data*, **23**, 619 (1994).

Summary

1. A single chain can adopt an almost infinite number of possible conformations; only an average size can be described. For any chain with some degree of conformational freedom the average size will grow as the square root of the degree of polymerization: this is the classic result for a random walk. Furthermore, the distribution of chain sizes is approximately Gaussian.

2. The concept of a theta solvent emerges as a central feature of polymer solutions. It has 4 equivalent operational definitions:
(a) the temperature where $A_2 = 0$
(b) the temperature where the interaction parameter $\chi = ½$
(c) the temperature at which an infinite molecular weight fraction would just precipitate
(the limit of the critical temperature T_c as $M \rightarrow \infty$)
(d) **a solvent in which $R_g \sim M^{1/2}$**

Physically, a theta solvent is one in which the polymer-solvent interactions are rather unfavorable, so that the chain shrinks to its random-walk dimensions. This contraction cancels the effect of the excluded volume interactions, which otherwise swell the chain to self-avoiding conformations: $R_g \sim M^{3/5}$

3.The prefactor that relates size to molecular weight is a measure of local flexibility.
Chemical structures for which the chain orientation can reverse direction in about 20 backbone bonds or less are called «flexibel»; much stiffer polymers are termed «semiflexible».
Four interchangeable schemes for quantifying the prefactors are the characteristic ratio, the statistical segment length, the persistencelength, and the Kuhn length.

4.The radius of gyration is the most common employed measure of size; it can be defined for any chemical structure and it is directly measurable.