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Note: Wiki = Wikipedia
1) "Random Coil": Wiki
"*A random coil is a polymer conformation where the monomer subunits are oriented randomly while still being bonded to adjacent units. It is not one specific shape, but a statistical distribution of shapes for all the chains in a population of macromolecules. The conformation's name is derived from the idea that, **in the absence of specific, stabilizing interactions**, a polymer backbone will "sample" all possible conformations randomly. Many linear, unbranched homopolymers — in solution, or above their melting temperatures — assume (approximate) random coils. Even copolymers with monomers of unequal length will distribute in random coils if the subunits lack any specific interactions. The parts of branched polymers may also assume random coils.*

Below their melting temperatures, most thermoplastic polymers (polyethylene, nylon, etc.) have amorphous regions in which the chains approximate random coils, alternating with regions that are crystalline. The amorphous regions contribute elasticity and the crystalline regions contribute strength and rigidity. More complex polymers such as proteins, with various interacting chemical groups attached to their backbones, self-assemble into well-defined structures.

Random walk model --- The Gaussian chain:
*Consider a linear polymer to be a **freely jointed** chain with N subunits, each of length l, that occupy zero volume, so that no part of the chain excludes another from any location. One can regard the segments of each such chain in an ensemble as performing a random walk in three dimensions, **limited only by the constraint that each segment must be joined to its neighbors**. This is the ideal chain mathematical model. It is clear that the maximum, fully extended length L of the chain is N * l. If we assume that each possible chain conformation has an equal statistical weight, it can be shown that the probability P(r) of a polymer chain in the population to have distance r between the ends will obey a characteristic distribution described by the formula*

$$P(r) = 4\pi r^2 \left(\frac{3}{2\,\pi\langle r^2 \rangle} \right)^{3/2} e^{-\frac{3r^2}{2\langle r^2 \rangle}}$$

The average (root mean square) end-to-end distance for the chain, $\sqrt{\langle r^2 \rangle}$, turns out to be l times the square root of N — in other words, the average distance scales with N0.5.

Real polymers:
*A real polymer is not freely jointed. For example, A -C-C- single bond has a fixed tetrahedral angle of 109.5 degrees. The value of L is well-defined for, say, a fully extended polyethylene or nylon, but it is less than N x l because of the zig-zag backbone. There is, however, free rotation about many chain bonds. The model above can be enhanced. A longer, "effective" unit length can be defined such that the chain can be regarded as freely jointed, along with a smaller N, such that the constraint L = N x l is still obeyed. It, too, gives a Gaussian distribution. However, specific cases can also be precisely calculated. The average end-to-end distance for **freely-rotating (not freely-jointed)** polymethylene (polyethylene with each -C-C- considered as a subunit) is l times the square root of 2N, an increase by a factor of about 1.4. Unlike the zero volume assumed in a random walk calculation, all real polymers' segments occupy space because of the van der Waals radii of their atoms, including bulky substituent groups that interfere with bond rotations. This can also be taken into account in calculations. All such effects increase the mean end-to-end distance.*

Even with corrections for local constraints, the random walk model ignores steric interference between chains, and between distal parts of the same chain. A chain often cannot move from a given conformation to a closely related one by a small displacement because one part of it would have to pass through another part, or through a neighbor. We may still hope that the ideal-chain, random-coil model will be at least a qualitative indication of the shapes and dimensions of real polymers in solution, and in the amorphous state, as long as there are only weak physicochemical interactions between the monomers. This model, and the Flory-Huggins Solution Theory, apply only to ideal, dilute solutions in most case.

Stiffer polymers such as helical polypeptides and double-stranded DNA can be treated by the worm-like chain model".

2) "Van der Waals radius": Wiki
"*The van der Waals radius, r_w, of an atom is the radius of an imaginary hard sphere representing the distance of closest approach for another atom.*"

3) "Flory–Huggins solution theory": Wiki
"*Flory–Huggins solution theory is a lattice model of the thermodynamics of polymer solutions which takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the entropy of mixing. The result is an equation for the Gibbs free energy change ΔG for mixing a polymer with a solvent, which is*

$$\Delta G_m = RT \left[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} \right]$$

*The right-hand side is a function of the number of moles n_1 and volume fraction φ_1 of **solvent (component 1)**, the number of moles n_2 and volume fraction φ_2 of **polymer (component 2)**, with the introduction of a parameter χ to take account of the energy of interdispersing polymer and solvent molecules. R is the gas constant and T is the absolute temperature. The volume fraction is analogous to the mole fraction, but is weighted to take account of the relative sizes of the molecules*".

4) "Worm-like chain": Wiki
"*The worm-like chain (WLC) model in polymer physics is used to describe the behavior of polymers that are semi-flexible: ==**fairly stiff with successive segments pointing in roughly the same direction, and with persistence length within a few orders of magnitude of the polymer length**==.*

*The WLC model assumes a continuously flexible isotropic rod. This is in contrast to the freely jointed chain model, which is only flexible between discrete freely hinged segments. The model is particularly suited for describing stiffer polymers, with successive segments displaying a sort of cooperativity: ==**nearby segments are roughly aligned**==. At room temperature, the polymer adopts a smoothly curved conformation; at T=0 K, the polymer adopts a rigid rod conformation.*

For a polymer of maximum length L_0, parametrize the path of the polymer as $s \in (0, L_0)$. Allow $\widehat{t(s)}$ to be the unit tangent vector to the chain at point s, and $\overrightarrow{r(s)}$ to be the position vector along the chain, as shown to the right. Then:

$$\hat{t}(s) \equiv \frac{\partial \vec{r}(s)}{\partial s} \text{ and the end-to-end distance } \vec{R} = \int_0^{L_0} \hat{t}(s)ds$$

The energy associated with the bending of the polymer can be written as:

$$E = \frac{1}{2}k_B T \int_0^{L_0} P \cdot \left(\frac{\partial^2 \vec{r}(s)}{\partial s^2}\right)^2 ds$$

where P is the polymer's characteristic persistence length, k_B is the Boltzmann constant, and T is the absolute temperature. At finite temperatures, the end-to end distance of the polymer will be significantly shorter than the maximum length L_0. This is caused by thermal fluctuations, which result in a coiled, random configuration of the undisturbed polymer."

5) "Kuhn length": Wiki
"The Kuhn length is a theoretical treatment, in which <u>a real polymer chain is considered as a collection of N Kuhn segments each with a Kuhn length b. **Each Kuhn segment can be thought of as if they are freely jointed** with each other. Each segment in a freely jointed chain can randomly orient in any direction without the influence of any forces, independent of the directions taken by other segments.</u> Instead of considering a real chain consisting of n bonds and with fixed bond angles, torsion angles, and bond lengths, Kuhn considered an equivalent ideal chain with N connected segments, now called <u>Kuhn segments</u>, that can orient in any random direction.

The length of a fully stretched chain is L=Nb for the Kuhn segment chain. In the simplest treatment, such a chain follows the random walk model, where each step taken in a random direction is independent of the directions taken in the previous steps, forming a random coil. The average end-to-end distance for a chain satisfying the random walk model is $<R_2> = N*b_2$.

Since the space occupied by a segment in the polymer chain cannot be taken by another segment, a self-avoiding random walk model can also be used. The Kuhn segment construction is useful in that it allows complicated polymers to be treated with simplified models as either a random walk or a self-avoiding walk, which can simplify the treatment considerably.

For worm-like chain, Kuhn length equals two times the persistence length."

6) "Persistence length":
(A) Wikipedia
"The persistence length is a basic mechanical property ==quantifying the bending stiffness of a polymer==. The molecule behaves like a flexible elastic rod. Informally, for pieces of the polymer that are shorter than the persistence length, the molecule behaves like a rigid rod, while for pieces of the polymer that are much longer than the persistence length, the properties can only be described statistically, like a three-dimensional random walk.

Formally, the persistence length, P, is defined as the length over which correlations in the direction of the tangent are lost (Hard to understand, refer to Part (B)). In a more chemical based manner, it can also be defined as the average sum of the projections of all bonds j ≥ i on bond i in an infinitely long chain.*

Let us define the angle θ between a vector that is tangent to the polymer at position 0 (zero) and a tangent vector at a distance L away from position 0, along the contour of the chain. It can be shown that the expectation value of the cosine of the angle falls off exponentially with distance

$$<cos\ \theta> = e^{-(L/P)}$$

*where P is the persistence length (==**The persistence length is the characteristic length scale of that exponential decay**==) and the angled brackets denote the average over all starting positions.*

The persistence length is considered to be one half of the Kuhn length, the length of hypothetical segments that the chain can be considered as freely joined. The persistence length equals the average projection of the end-to-end vector on the tangent to the chain contour at a chain end in the limit of infinite chain length.

The persistence length can be also expressed using the bending stiffness Bs, the Young's modulus E and knowing the section of the polymer chain. $P = Bs/(k_BT)$.

(B) Examples from Wikipedia! (Important for understanding)
*The persistence length of a long object (such as a polymer) is a measure of the flexibility of that object. Imagine a long cord that is slightly flexible. At short distance scales, the cord will basically be rigid. If you look at the direction the cord is pointing at two points that are very close together, the cord will likely be pointing in the same direction at those two points (i.e. the angles of the tangent vectors are highly correlated). If you choose two points on the this flexible cord (imagine a piece of cooked spaghetti that you've just tossed on your plate) that are very far apart, however, the tangent to the cords at those locations will likely be pointing in different directions (i.e. the angles will be uncorrelated). ==**If you plot out how correlated the tangent angles at two different points are as a function of the distance between the two points, you'll get a plot that starts out at 1 (perfect correlation) at a distance of zero and drops exponentially as distance increases. The persistence length is the characteristic length scale of that exponential decay**==.*"

7) "Ideal chain": Wiki
"An ideal chain (or freely-jointed chain) is the simplest model to describe polymers, such as nucleic acids and proteins. It only assumes a polymer as a random walk and neglects any kind of interactions among monomers.

In this model, monomers are rigid rods of a fixed length l, and their orientation is completely independent of the orientations and positions of neighbouring monomers, to the extent that two monomers can co-exist at the same place. In some cases, the monomer has a physical interpretation, such as an amino acid in a polypeptide. In other cases, a monomer is simply a segment of the polymer that can be modeled as behaving as a discrete, freely jointed unit. If so, l is the Kuhn length.

Applicable for the case of a polymer in solution whose monomers form an ideal mix with the solvent (in which case, the interactions between monomer and monomer, solvent molecule and solvent molecule, and between monomer and solvent are identical, and the system's energy can be considered constant, validating the hypotheses of the model)

Other fluctuating polymer models that consider **no interaction between monomers and no excluded volume,** like the worm-like chain model, are all asymptotically convergent toward this model at the thermodynamic limit.

7.1 "Central limit theorem (CLT)": Wiki
"In probability theory, the central limit theorem (CLT) establishes that, in some situations, when independent random variables are added, their properly normalized sum tends toward a normal distribution even if the original variables themselves are not normally distributed."
Consider the example of tossing a coin for many times.

8) "Radius of gyration": Wiki
Preface:
In mechanics, "*radius of gyration is defined as the radial distance to a point which would have a moment of inertia the same as the body's actual distribution of mass, if the total mass of the body were concentrated.*

Mathematically, the radius of gyration is the root mean square distance of the object's parts from either its center of mass or a given axis, depending on the relevant application. It is actually the perpendicular distance from point mass to the axis of rotation. One can represent a trajectory of a moving point as a body. Then radius of gyration can be used to characterize the typical distance travelled by this point."

"In polymer physics*, the radius of gyration is used to describe the dimensions of a polymer chain. The radius of gyration of a particular molecule at a given time is defined as:*

$$R_g^2 \overset{\text{def}}{=} \frac{1}{N} \sum_{k=1}^{N} \left(\mathbf{r}_k - \mathbf{r}_{\text{mean}} \right)^2$$

where r_{mean} is the mean position of the monomers. As detailed below, the radius of gyration is also proportional to the root mean square distance between the monomers:

$$R_g^2 \overset{\text{def}}{=} \frac{1}{2N^2} \sum_{i,j} \left(\mathbf{r}_i - \mathbf{r}_j \right)^2$$

*As a third method, the radius of gyration can also be computed by summing the principal moments of the gyration tensor. Since the chain conformations of a polymer sample are quasi infinite in number and constantly change over time, the "radius of gyration" discussed in polymer physics must usually be understood as a mean **over all polymer molecules of the sample** and **over time**. That is, the radius of gyration which is measured as an average over time or ensemble:*

$$R_g^2 \overset{\text{def}}{=} \frac{1}{N} \left\langle \sum_{k=1}^{N} \left(\mathbf{r}_k - \mathbf{r}_{\text{mean}} \right)^2 \right\rangle$$

An entropically governed polymer chain follows a random walk in three dimensions. The radius of gyration for this case is given by

$$R_g = \frac{1}{\sqrt{6}} \sqrt{N} \, a$$

Note that although aN represents the contour length of the polymer, a is strongly dependent of polymer stiffness and can vary over orders of magnitude. N is reduced accordingly.

One reason that the radius of gyration is an interesting property is that it can be determined experimentally with static light scattering as well as with small angle neutron- and x-ray scattering. This allows theoretical polymer physicists to check their models against reality. The hydrodynamic radius is numerically similar, and can be measured with Dynamic Light Scattering (DLS)."

8.1 "Contour length": Wiki
"*The contour length of a polymer chain is its length at maximum physically possible extension. Contour length is equal to the product of the number of segments of polymer molecule(N) and its length(l).*"

9) "Polymer Physics": Wiki
(I) Models
"Models of polymer chains are split into two types: "ideal" models, and "real" models. Ideal chain models assume that there are no interactions between chain monomers. This assumption is valid for certain polymeric systems, where the positive and negative interactions between the monomer effectively cancel out. Ideal chain models provide a good starting point for investigation of more complex systems and are better suited for equations with more parameters.

(A) Ideal chains

- The **freely-jointed chain** is the simplest model of a polymer. In this model, fixed length polymer segments are linearly connected, and all bond and torsion angles are equiprobable. The polymer can therefore be described by a simple random walk and ideal chain.

- The **freely-rotating chain** improves the freely-jointed chain model by taking into account that polymer segments make a fixed bond angle to neighbouring units because of specific chemical bonding. Under this fixed angle, the segments are still free to rotate and all torsion angles are equally likely.

- The **hindered rotation model** assumes that the torsion angle is hindered by a potential energy. This makes the probability of each torsion angle proportional to a Boltzmann factor $P(\theta) \propto \exp(-U(\theta)/kT)$: where $U(\theta)$ is the potential determining the probability of each value of θ.

- In the **rotational isomeric** state model, the allowed torsion angles are determined by the positions of the minima in the rotational potential energy. Bond lengths and bond angles are constant.

- The **Worm-like chain** is a more complex model. It takes the persistence length into account. Polymers are not completely flexible; bending them requires energy. At the length scale below persistence length, the polymer behaves more or less like a rigid rod.

(B) Real chains
Interactions between chain monomers can be modelled as excluded volume. This causes a reduction in the conformational possibilities of the chain, and leads to a self-avoiding random walk.

10) "Reptation": Wiki

Reptation is the thermal motion of very long linear, entangled macromolecules in polymer melts or concentrated polymer solutions.

Entanglements with other polymer chains restrict polymer chain motion to a thin virtual tube passing through the restrictions. Without breaking polymer chains to allow the restricted chain to pass through it, the chain must be pulled or flow through the restrictions. The mechanism for movement of the chain through these restrictions is called reptation.

11) Bead-Spring Model

http://polymerdatabase.com/polymer%20physics/BeadSpring.html

In this model, "*the high-molecular weight polymer is **described as N + 1 beads connected by N massless (harmonic) springs** (see Figure below). Each bead may represent a subchain that contains several repeat units. In many cases, a simple harmonic potential is assumed, that is, the virtual springs follow Hooke's law of elasticity, which implies they are infinitley extendable with a linear elastic response. The potential energy of such a chain can be calculated from the positions of each bead in space, r_i, or from the relative distance between the beads, l_i:*

$$H_l (\{l_i\}) = C_l \sum_{i=1}^{N} (l_i - l_0)^2 / 2$$

$$= C_l \sum_{i=1}^{N} (|r_i - r_{i-1}| - l_0)^2 / 2$$

where one typically chooses the constants C_l, l_0 and l_{max} in relation to the parameters ε, σ of the Lennard-Jones potential between the effective beads (if one allows only finite extension of the beads).
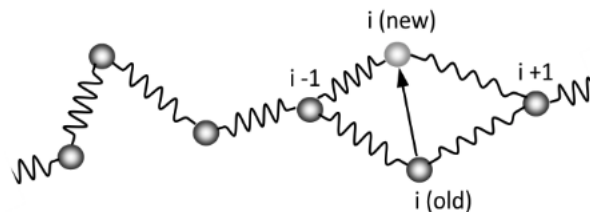
The simplest case is a Gaussian probably distribution of the beads, that is, it is assumed that the beads show ideal chain behavior. For this case, the spring constant reads

$$C_l = 3\, k_B T / \langle l_0^2 \rangle$$

where $\langle l_{02} \rangle$ is the mean squared end-to-end distance of two beads to a polymer in its relaxed state."