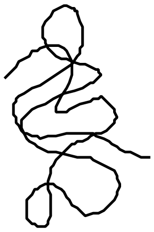
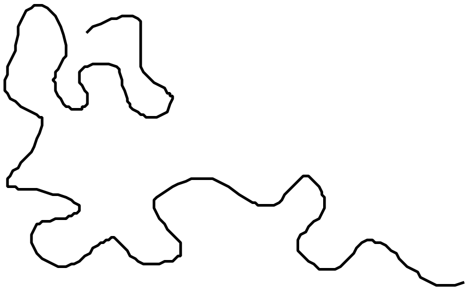
Chapter 1 Polymer Physics
The Isolated Polymer Chain

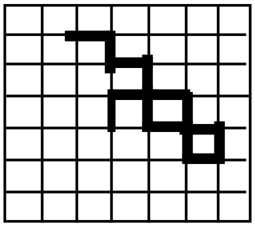
Random Walk model:

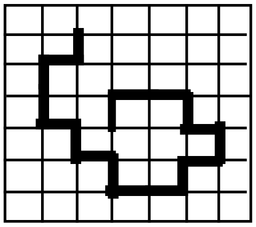
Brownian motion of a particle occurs in a close to random manner. If the path of a particle in a random (Brownian) walk is traced in time it will most likely cross itself several times (Left below in 2-d). If the walk does not penetrate itself a different type of path is formed, the self-avoiding walk (Right below in 2-d).





A random walk can be constructed more easily on a lattice where the number of choices in direction for each step are limited, and the step length is fixed, b (Left below). A lattice can also be used for a self-avoiding walk (Right).





A well know result of Brownian motion **for a random walk** is that the "average" distance traveled is proportional to the square root of the time allowed for the particle to travel in 3-d space. $<R> = k\ t^{1/2}$. This is a direct result of the distance traveled following a random distribution, i.e. for a random walk the choice of direction is completely random at each step. For a random distribution under the condition of a large (infinite) number of steps, and finite probability for each of the choices for direction **the probability** that the walk length (end to end distance) is x in units of b is given by the **Gaussian** distribution function (a special case of the Binomial Distribution),

$$P_G(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right] \qquad \text{1-d Gaussian}$$

$$P_G(R,n) = \frac{1}{\sqrt{2\pi n b^2}}\exp\left[-\frac{1}{2}\left(\frac{R}{b\sqrt{n}}\right)^2\right] \qquad \text{1-d Gaussian Walk of "n" steps}$$

Usually the probability of a walk of length between R and R + dR is needed for calculations and this is obtained by multiplication of the 1-d function by dR,

$$P_G(R,n)\,dR = \frac{1}{\sqrt{2\pi nb^2}} \exp\left[-\frac{1}{2}\left(\frac{R}{b\sqrt{n}}\right)^2\right] dR$$ 1-d Differential Probability

The 3-d Gaussian can be obtained by multiplying three probability functions similar to that above for each of the Cartesian coordinates on a 3-d lattice, and using n/3 steps for each direction. Also, a factor of $4\pi R^2\,dR$ is needed to consider a differential spherical surface

$$P_G(R,n)\,dR = 4\pi R^2 \left(\frac{2\pi}{3} nb^2\right)^{-3/2} \exp\left[-\frac{3}{2}\left(\frac{R}{b\sqrt{n}}\right)^2\right] dR$$ 3-d Gaussian Differential Probability

The Gaussian distribution describes a completely random choice of direction for each step of a walk. For such a condition the sum of all steps (taken as vectors on the lattice) is zero (eqn. 1.1 in Doi). This means that the average value of R (sum of step vectors divided by number of steps) is 0, <**R**> = 0. This is called **the first moment** of the distribution and is calculated from,

$$\langle R \rangle = \int_0^\infty R P_G(R,n)\,dR = 0$$

It is desirable to obtain a description of the average length of a random walk. This can be obtained using the second moment of the distribution, the mean square, <$\mathbf{R}^2$>, whose value is not zero.

$$\langle R^2 \rangle = \int_0^\infty R^2 P_G(R,n)\,dR = nb^2$$

This indicates that the average size of a random walk is proportional to the square-root of the number of steps (in parallel to the square root of time for a constant speed of motion).

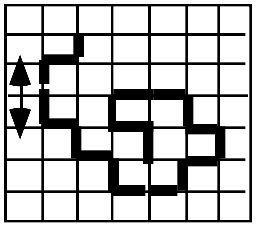
Dimensional Considerations

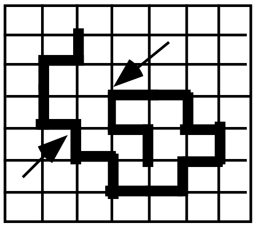
An expression for the "average" length of a rod yields <R> = kn, and the average diameter of a sphere or cube, <R> = $kn^{1/3}$. For a disk the average size is given by <R> = $kn^{1/2}$. A general expression for any object in terms of a "scaling-law" is <R> = $\alpha n^{1/df}$, where α is called the lacunarity and d_f is the mass-fractal dimension of the object. A rod is 1 dimensional and $d_f = 1$, a disk is 2 dimensional and $d_f = 2$ and a cube is 3 dimensional and $d_f = 3$. A linear polymer coil also follows a dimensional scaling law with $d_f = 2$ for a 2-d object.

Obviously polymers and plates are distinguishable structures despite the fact that both display 2-dimensional scaling. Other scaling dimensions are useful to distinguish between plates and Gaussian polymers for instance. One of these, the connectivity dimension is of particular use and reflects the relationship between a primitive path of minimum distance, R_{min}, and the number of total units in an object, n, $L_{min} = kn^{1/C}$, where C is the connectivity dimension. For a linear-polymer the path of minimum end to end distance is the chain's primitive path which is of length nb so, $L_{min} = kn^1$ and C = 1. For a plate, the path is the diameter and $L_{min} = kn^{12}$, so C = 2. For all **regular objects** (plate, rod, sphere) d_f = C. Thus, a Gaussian polymer coil and a plate have the same mass-fractal dimension but different connectivity dimensions. C ranges from 1 to 3 and is independent of d_f.

Random Walks as Models for Polymer Coils.

It can next be considered that the lattice model is adaptable to describing a polymer coil. For a Gaussian coil the average end to end distance is given by $n^{1/2}b$ as for the random walk. In polymer physics two common modifications to the Random Walk approach are usually considered and these are called **Short Range** and **Long Range Interactions**. Short-range interactions involve chain units close to each other ***in terms of the path of the random walk.*** Long-range interactions involve interactions which are "spatially" close but which involve chain units separated by ***long distances along the chain path***. Both short- and long-range interactions involve chain units which are spatially close to each other as shown below (short range LEFT, long range RIGHT).





Short Range Interactions:

Rotational-Isomeric-States and other chain stiffness/helicity issues and the fact that a real chain can never "fold back on to itself" fall under the category of "short-range" interactions. As might be expected such issues can be dealt with in terms of modification of the value of "b" to account for chain-stiffness (b would increase from a bond distance or mer-unit size for instance). This type of modification can be described in terms of an average length of persistence or a Persistence Length and has been describe by Flory in terms of the Characteristic ratio for real chains.

Doi demonstrates that short-range interactions do not modify the basic physics of a random walk in section 1.12 on pp. 4, for the condition that a chain is free to rotate to any site **except the preceding step**. The main point is that this type of exclusion on a short range (in terms of the path) does not need to be considered in calculations of the scaling behavior of random walks, i.e. the mass-fractal dimension of the chain (see above).

Doi (pp. 4) considers a polymer chain as composed of a series of bond vectors, $\mathbf{r}_i$. In this terminology the mean value for a vector $\mathbf{r}_{i+1}$ for a Gaussian chain is 0 since,

$$\langle r_{i+1} \rangle = \sum_{i=1}^{i=z} b_i$$

where z is the coordination number for the lattice and the average $<\mathbf{b}_{i+1}>$ includes all directions. On a lattice with z possible directions for the bond vector $\mathbf{r}_{i+1}$, introduction of a short range interaction which forbids a chain from doubling back on itself leads to (z-1) choices rather than z choices given that the previous bond vector $\mathbf{r}_i$ is fixed in position. This means that the average value of $\mathbf{r}_{i+1}$ is not 0 but favors a direction away from the previous bond, $\mathbf{r}_i$.

Since the average $<\mathbf{r}_{i+1}>_{SRI}$ for the short range interaction case includes all directions of $<\mathbf{r}_{i+1}>_{Gaussian}$ for the Gaussian case except $\mathbf{r}_i$,

$$<\mathbf{r}_{i+1}>_{Gaussian} = 0 = (z - 1) <\mathbf{r}_{i+1}>_{SRI} - \mathbf{r}_i \qquad \text{(Doi 1.10)}$$

and

$$<\mathbf{r}_{i+1}>_{SRI} = \mathbf{r}_i/(z-1)$$

For the Gaussian chain the mean square end to end distance is given by,

$$\langle R^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle r_i \cdot r_j \rangle$$

which for i not equal to j is $<\mathbf{r}_i><\mathbf{r}_j> = 0$ since there is not correlation in directions, and for i = j is $<\mathbf{r}_i^2> = nb^2$. For the SRI chain there is some correlation when i is not equal to j for instance when $j = i + 1$, $<\mathbf{r}_i><\mathbf{r}_j> = b^2/(z-1)$ as shown above. For $j = i + 2$, $<\mathbf{r}_i><\mathbf{r}_j> = b^2/(z-1)^2$, as shown by Doi on pp. 5. In general,

$$\langle r_i \cdot r_j \rangle = \frac{b^2}{(z-1)^{|n-m|}}$$

and

$$\langle R^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle r_i \cdot r_j \rangle \quad \sum_{i=1}^{n} \sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = nb^2 \frac{z}{z-2} = nb_{eff}^2$$

The second to the last equality is the result of the Sum of Geometric Progression Rule,
lim n->∞ of $a + ar + ar^2 + ... = a/(1-r)$
substituting $x=1/(z-1)$ results in $2/(1-x) - 1 = 2(z-1)/(z-2) - 1 = z/(z-2)$

The Gaussian chain model accounts for short-range interactions if the parameter b is allowed to have a modified definition.

Since short-range interactions involve ***the details of the lattice model*** and since these have no effect on the scaling-behavior of the chain or any of the physical understanding of the Gaussian chain, it should be easy to see that the Gaussian chain model is not tied to the lattice framework in any way. In fact, the original presentation above arrived at a Gaussian chain model by direct comparison with Brownian motion which does not depend on a lattice model.

The **Bead and Spring Model** for a chain is an alternative derivation which does not rely on a lattice. The Bead and Spring Model is useful for estimation of kinetic features of ideal coils such as the viscosity of Gaussian polymer chains. In this context it is referred to as **the Rouse Model** or the Rouse-Bueche-Zimm model. The Bead and Spring Model considers a chain composed of balls connected by Hookean springs. The length of the spring/bonds is allowed to elastically deform following a Gaussian distribution.

The Bead and Spring Model will be dealt with in detail in Chapter 4.

Spatial Distribution of Chain Segments.

The end to end distance is a useful parameter for describing an ideal chain for calculation of the **radius of gyration** and **hydrodynamic radius** of chains. The Radius of Gyration, R_g, is measured in static light, x-ray and neutron scattering experiments while the hydrodynamic radius, R_H, is measured in quasi-elastic light scattering and rheology experiments. It is also important to know a statistical description of the spatial distribution of chain segments within a polymer coil since in addition to R_g, a statistical spatial distribution is measured in scattering experiments especially in neutron scattering experiments.

Consider a chain of length N whose average end to end distance is $N^{1/2}$ b, where b is the effective step length for the chain which has no long-range interactions. For the n'th chain step, $g_n(\mathbf{r})$ is the average density of segments at a radial position **r** from step n. $\mathbf{R}_n$ is here the position vector for the segments of the chain. It is important to keep clear that $\mathbf{r}_n$ is a radial position relative to segment "n" while $\mathbf{R}_n$ is the segmental position relative to a coordinate system based at the first segment where n = 1. n can have values from 1 to N. Then,

$$g_n(r_n) = \sum_{m=1}^{N} \left\langle \delta\left(r - \left(R_m - R_n\right)\right)\right\rangle$$

where the del operator has a value of 1 when the position vector difference (**R**'s) is equal to **r**. $g_n(\mathbf{r})$ will have values between 0 for **r**'s larger than the chain to 1 for **r** = 0.

Since $g_n(\mathbf{r})$ only considers a single segment, "n", it must be averaged over all segments in order to obtain a statistical description of the spatial distribution of chain segments for the entire coil. This averaging results in the **pair correlation function**, g(**r**) for the coil,

$$g(r) = \frac{1}{N}\sum_{n=1}^{N} g_n(r) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle \delta\left(r - \left(R_m - R_n\right)\right)\right\rangle$$

The **pair correlation function**, g(**r**), is directly related to the intensity scattered by light, neutrons or x-rays from a polymer coil. The scattered intensity is measured as a function of scattering angle, θ, and is usually plotted against the reduced parameter, $q = |\mathbf{q}| = 4\pi/\lambda \sin(\theta/2)$, which is called the scattering vector. "q" is the inverse space vector and is related to the Bragg spacing, d, by $d = 2\pi/q$.

Scattered Intensity = K g(**q**) where K is a constant for a given system which includes the contrast and instrumental parameters. g(**q**) is the Fourier Transform of g(**r**),

$$g(q) = \int dr\, g(r) \exp\left(iq\cdot\ r\right) = \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle \exp\left[iq\cdot\left(R_m - R_n\right)\right]\right\rangle$$

For a Gaussian polymer coil the solution to this double summation is the Debye Equation for Polymer Coils which was first solved in 1946 by P. Debye.

$$g(q)_{Gaussian} = \frac{2}{Q^2}\left[Q - 1 + \exp(-Q)\right]$$

where $Q = q^2 N b^2/6 = q^2 R_g^{\ 2}$

The Debye function for polymer coils describes a decay of scattered intensity following a power-law of -2 at high-q and a constant value for intensity at low-q (below R_g).

<u>Radius of Gyration for an Ideal Chain.</u>

The exponential term in the summation for g(**q**) given above can be expanded using $e^{-x} = 1 - x/1! + x^2/2! - x^3/3! + \ldots x^n/n! + \ldots$ For x less than 1, i.e. at low-q, this can be truncated to the first three terms so the argument of the double summation becomes $[1 - iq\langle(\mathbf{R}_n - \mathbf{R}_m)\rangle \langle\cos\alpha\rangle - (1/2)\, q2 \langle(\mathbf{R}_n - \mathbf{R}_m)^2\rangle \langle\cos^2\alpha\rangle + \ldots]$ where α is the angle between **q** and $(\mathbf{R}_n - \mathbf{R}_m)$. Since cosine is an even function the term <cos α> = 0. Also, from math handbooks <cos^2 α> = 1/3. The argument of the double summation then becomes, [1 - (1/6) $\mathbf{q}^2$ <($\mathbf{R}_n$ - $\mathbf{R}_m$)^2>]. By performing the summation on the two terms independently, the summation for g(**q**) can be written,

$$g(q) = \frac{1}{N}\left[N^2 - \frac{1}{6}q^2\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle\left(R_n - R_m\right)^2\right\rangle\right]$$

The center of mass of the coil is given by,

$$R_G = \frac{1}{N}\sum_{n=1}^{N} R_n \ .$$

Using this center of mass, a radial term can be defined which describes a distance from $\mathbf{R}_G$ where all of the mass could be located and the particle would have the same inertia. This distance is the radius of gyration, R_g. R_g is defined by,

$$R_g^2 = \frac{1}{N}\sum_{n=1}^{N}\left\langle\left(R_n - R_G\right)^2\right\rangle$$

If the definition of R_G is substituted in the above expression,

$$R_g^2 = \frac{1}{N}\sum_{n=1}^{N}\left\langle\left(R_n - \frac{1}{N}\sum_{m=1}^{N}R_m\right)^2\right\rangle = \frac{1}{N}\sum_{n=1}^{N}\left\langle\frac{1}{2N}\sum_{m=1}^{N}\left(R_n - R_m\right)^2\right\rangle = \frac{1}{2N^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle\left(R_n - R_m\right)^2\right\rangle$$

The last expression can be substituted in to the expression for g(**q**) above to yield,

$$g(q) = N\left(1 - \frac{q^2R_g^2}{3} + \ldots\right) \quad g(0)e^{-\frac{q^2R_g^2}{3}}$$

The first two terms of the e^{-x} expansion above are 1 - x, so the expression in the brackets can be approximated by the latter term above which is known as Guinier's Law. Guinier's Law is a general expression for any object and describes an exponential decay in intensity with angle for angles where $qR_g \ll 1$.

The double summation for R_g can be rewritten as follows,

$$\sum_{n=1}^{N}\sum_{m=1}^{N}\left\langle\left(R_n - R_m\right)^2\right\rangle = \sum_{n=1}^{N}\sum_{m=1}^{N}|n-m|b^2 = 2\sum_{n=m}^{N}\sum_{m=1}^{N}(n-m)b^2 = 2b^2\left[Z + 2(Z-1) + 3(Z-2)\ldots(Z-1)2 + Z\right]$$

where Z = N - 1. The last double summation can be justified by constructing an NxN matrix of m vs n with values of |n - m|. Such a matrix is symmetric about m = n (this is where the 2 prefactor comes from). The double summation at the end can be rewritten,

$$\sum_{p=1}^{Z}\left(Z+1-p\right)p = \left(Z+1\right)\sum_{p=1}^{Z}p - \sum_{p=1}^{Z}p^2 = \frac{Z(Z+1)(Z+2)}{6} \quad \frac{N^3}{6}$$

The latter steps involve the summation of power rule from math handbooks,

$$\sum_{u=1}^{n} u^p = \frac{n^{p+1}}{p+1} + \frac{n^p}{2} + \frac{pn^{p-1}}{12}$$ for p<3 (other terms needed for higher p's)

Using this result in the calculation for R_g gives,

$$R_g^2 = \frac{Nb^2}{6} = \frac{R^2_{RMSeted}}{6}$$

R_g is 1/√6 of the RMS end-to-end distance.

There are several advantages to using R_g rather than the end-to-end distance. For branched, ring or star chains the end-to-end distance has no meaning while the radius of gyration retains its meaning. Also, R_g is a natural measure for scattering experiments. Effects of polydispersity can be incorporated in the definition of R_g. Rg can be defined for any object, for example Rg for a sphere is √(3/5) of the sphere radius. Similar simple definitions are available for rods and ellipsoids.

Extensions of the Debye Equation for an Ideal Polymer Coil.

The Debye equation for polymer coils was given above,

$$g(q)_{Gaussian} = \frac{2N}{Q^2}\left[Q - 1 + \exp(-Q)\right]$$

where $Q = (qR_g)^2$. At low-q this function extrapolates to N (expansion of exp(-x) for small x is $1 - x + x^2/2$). At high-q the Debye function extrapolates to $2N/(qR_g)^2$ (at high-q, exp(-Q) goes to 0 and Q >>1). This high-q limit is a -2 slope power-law for intensity in q, so a log I vs log q plot will be a line with slope -2. In general, weak slopes in log-log plots of this type reflect the negative of the mass-fractal dimension of the object. The cutoff between this power-law behavior and the constant intensity behavior at low-q is governed by R_g.

Doi mentions an empirical function which approximates the Debye function, the so called Ornstein-Zernike scattering equation,

$$g(q) = \frac{N}{1 + {q^2R_g^2}/{2}}$$

As originally described the Ornstein-Zernike function used a term eta^2 for $R_g{}^2/2$. There is really no advantage to the use of the Ornstein-Zernike function and it can lead to errors in fit values. It is popularly used by theoreticians but rarely used by experimentalists.

Non-Ideal Chains (Long-Range Interactions).

Long range interactions can be described in terms of the volume excluded for a given chain segment by a chain segment a long primitive path distance away. In the sense of a Brownian, random walk this type interaction is commonly known as the ***Self-Avoiding Walk***.

The self-avoiding walk model is the normal description of a dilute polymer coil in solution.

That is, the ideal or Gaussian chain is, for polymers in solution, an extremely special condition which only exists at the critical point. Normal coils in solution are expanded in a self-avoiding walk.

Because of this the self-avoiding walk has special importance. However, it is also more complicated than a simple Gaussian description. The expanded coil is larger than the Gaussian coil since excluded volume is a type of self-repulsion for the coil.

In order to obtain a scaling law which describes the excluded volume coil, a perturbation on the ideal coil is considered. That is, the distribution function, $W_0(R)dR$ which describes the number of chains of length N which will have an end-to-end distance between R and dR must be modified by a probability, p(R) that these chains are self-avoiding, that is that they do not cross. Since $W_0(R)$ involves an exponential term (Gaussian term) it is desirable also to obtain p(R) in an exponential form. Once the probability function is obtained the derivative with respect to R of W(R) is taken to obtain the distance of maximum probability. Presumably this distance is proportional to $N^{1/2}b$ for the ideal chain and it is desired to find such a scaling law for the excluded volume chain.

$W_0(R)$ is the Gaussian probability $P(\mathbf{R},N)4\pi R^2dR$ times the total number of chain conformations possible for chains of N steps, Z^N,

$$W_0(R)dR = Z^N 4\pi R^2 \left(\frac{2\pi}{3} Nb^2\right)^{-3/2} \exp\left[-\frac{3}{2}\left(\frac{R}{b\sqrt{N}}\right)^2\right] dR$$

of this number the fraction which follow self-avoidance is $p(R) = (1 - V_C/R^3)^{N(N-1)/2}$ where V_C is the volume of one segment of the chain so $(1- V_C/R^3)$ is the probability of the chain avoiding one segment, and this is raised to the total number of possible combinations of two segment pairs, N(N-1)/2!. This function for p(R) can be expressed as an exponential,

$$p(R) = \exp\left[\frac{1}{2} N(N-1)\ln\left(1-\frac{V_C}{R^3}\right)\right] = \exp\left(-\frac{N^2V_C}{2R^3}\right)$$

where the second equality uses the fact that for small x, ln(1-x) = -x, and that for large N, (N-1)=>N. W(R)dR for the excluded volume chain can be estimated by $W_0(R)p(R)dR$ and since both are expressed as exponentials the powers sum leading to,

$$W(R)dR = W_0(R)p(R)dR = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_C}{2R^3}\right)$$

The derivative of $W_0(R)$ will equal 0 at $R^*_0 = (2Nb^2/3)^{1/2}$. This is proportional to $N^{1/2}b$ as expected. Setting the derivative of W(R) to 0 yields,

$$-\frac{3R^{*2}}{2Nb^2} + \frac{3N^2V_C}{4R^{*3}} + 1 = 0$$

Rearranging and substituting R^*_0 yields,

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16}\frac{V_C}{b^3}\sqrt{N}$$

For large N the R ratio is large and the cubic term can be ignored with respect to the 5'th power term. This yields,

$$R^* \quad R_0^* \left(\frac{N^{1/2} V_C}{b^3} \right)^{1/5} = kN^{3/5}$$

This ***critical result*** was first noted by Flory and Krigbaum and its development is termed Flory-Krigbaum theory.

Solvation Effects:

Long-range interactions are potentially of variable degree. That is a polystyrene chain will dissolve in toluene or THF but it is expected that toluene, being a better solvent, will have a different solvation behavior than THF, i.e. the chain conformation in the two solvents might be expected to be different. Another way to look at this is that the excluded volume, discussed above, could be of a hard or soft core type, that is, rather than complete exclusion at a specified distance, there might be a potential gradient which describes the long-range excluded volume. The result of some simple calculations can show an extremely surprising result. No matter how good a "good"-solvent is, the chain scaling follows the law given above. ***For dilute solutions of polymer chains there are only three discrete states, Gaussian, Expanded, and Collapsed!!*** This result is by no means self-evident from a chemical perspective.

In order to show that the goodness of solvation for good solvents does not effect the chain scaling, consider the interaction energies for solvent, s, and polymer, p, sites on a lattice; ε_{pp}, ε_{ps}, ε_{ss}, and the number of contacts for a given conformation of a polymer chain; N_{pp}, N_{ps}, N_{ss}. The overall system energy is given by a sum of the components for a single chain system in a configuration "i", $E_i = -N_{pp}\ \varepsilon_{pp} - N_{ps}\ \varepsilon_{ps} - N_{ss}\ \varepsilon_{ss}$. The average energy for all configurations with end to end distance "R" is $\bar{E}(R)$. The probability of an excluded volume chain W(R), given above, needs to be modified by a Boltzman distribution function which describes the thermal distribution based on these interaction energies to give the probability of an excluded volume chain with specific interaction energies, P(R),

$$P(R) = kW(R) \exp\left[\frac{-\bar{E}(R)}{kT} \right]$$

The details of $\bar{E}(R)$ can be calculated. First, an average change in energy per lattice site for solvation of a given solvent/polymer system can be given by $\Delta\varepsilon = 1/2(\varepsilon_{pp} + \varepsilon_{ss}) - \varepsilon_{ps}$. The volume fraction of polymer cells is given by $\varphi = NV_c/R^3$. The average probability that a given lattice site contains a polymer segment is φ. The probability that a site neighboring a given site contains a polymer segment is φ times the coordination number, z. For PP interactions this probability must be divided by 2 since this will involve two indistinguishable arrangements by exchanging the two P sites. The average number of PP sites is this probability times the number of segments, N,

$$\bar{N}_{pp} \quad \frac{1}{2} zN\varphi$$

The average number of SP sites is $(1-\varphi)$, the probability of a solvent in any site, times z, times the number of P segments, N,

$$\bar{N}_{ps} \quad zN(1-\varphi)$$

The average number of SS sites is the number of SS sites in a system with no polymer, N^0_{ss}, minus the other two numbers for PP and SP given above. The expression for $\bar{E}(R)$ can be written as terms linear in φ and those independent of φ,

$$\bar{E}(R) \quad -\bar{N}_{pp}\varepsilon_{pp} - \bar{N}_{ss}\varepsilon_{ss} - \bar{N}_{ps}\varepsilon_{ps} = -\left(\frac{zN\varphi}{2}\varepsilon_{pp} + zN\varepsilon_{ps} - \varphi zN\varepsilon_{ps} + N^0_{ss}\varepsilon_{ss} - \frac{zN\varphi}{2}\varepsilon_{ss} - zN\varepsilon_{ss} + zN\varphi\varepsilon_{ss}\right)$$

$$= -\frac{zN\varphi}{2}\left[\varepsilon_{pp} - 2\varepsilon_{ps} + \varepsilon_{ss}\right] - \left[zN\varepsilon_{ps} + N^0_{ss}\varepsilon_{ss} - zN\varepsilon_{ss}\right] = -\frac{zN^2V_c}{R^3}\Delta\varepsilon + \text{ Terms independent of R}$$

This expression can be used in the first equation of this section to yield,

$$P(R) = CR^2 \exp\left(\frac{-3R^2}{2Nb^2} - \frac{N^2V_c}{2R^3} + \frac{zN^2V_c\Delta\varepsilon}{R^3kT} + \text{Terms independent of R}\right)$$

Here the chi parameter, χ, can be defined as $\chi = z\Delta\varepsilon/kT$, and substituted in the above expression,

$$P(R) = CR^2 \exp\left(\frac{-3R^2}{2Nb^2} - \frac{N^2V_c(1-2\chi)}{2R^3}\right)$$

which has the same functional form as the original "long-range" interaction expression with V_C being replaced by $V_C\,(1-2\chi) = V$, the excluded volume as a function of goodness of solvent!

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16}\frac{V}{b^3}\sqrt{N} = \frac{9\sqrt{6}}{16}\frac{V_c(1-2\chi)}{b^3}\sqrt{N} = \text{(alternatively)}\frac{9\sqrt{6}}{16}\frac{V_c}{b_{eff}^3}\sqrt{N}$$

This means that the goodness of solvent can be isolated as having an effect on chain persistence rather than on chain scaling, the 5/3 dimension of an expanded coil (the normal condition for a solvated chain) is retained regardless of the goodness of solvent. Solvation effects, goodness of solvent, effect local chain rigidity or flexibility and not chain scaling!

<u>Changes in Solvent Goodness with Temperature.</u>

A polymer chain in a good solvent at some temperature T will have an excluded volume parameter, $V = V_c\,(1 - 2\,z\Delta\varepsilon/(kT))$, the second term in the brackets being smaller than 1 the coil will show expanded scaling with a mass-fractal dimension of 5/3 and some effective persistence length, $b_{eff} = b/(1 - 2\,z\Delta\varepsilon/(kT))^{1/2}$, which is larger than that for a Gaussian coil since $1/(1 - 2\,z\Delta\varepsilon/(kT))^{1/2}$ is larger than 1. As the temperature is dropped within the good solvent regime the coil decreases in size while retaining good solvent scaling, mass-fractal dimension of 5/3, through changes in the local persistence. This will be a continuous change until $2\,z\Delta\varepsilon/(kT)$ approaches 1 with decreasing temperature. At a very narrow (and specialized) temperature $2\,z\Delta\varepsilon/(kT)$ will be exactly equal to 1 and the coil will not display excluded volume at all! At this unique temperature the coil in dilute solution will be Gaussian. This temperature is called the theta temperature, θ, and has a unique value for any polymer/solvent pair. The θ-temperature is also sometimes called the Flory Temperature.

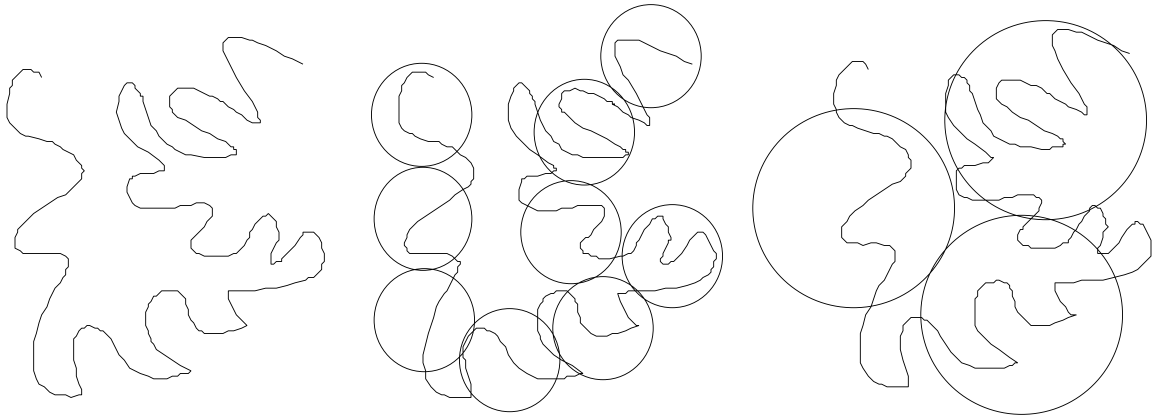
At the Flory-Temperature the mass-fractal dimension of the coil becomes uniquely 2 and the parameter "b" can be uniquely observed. If the polymer solution is cooled below the theta-temperature the polymer coil collapses into a "globule" which is a highly compact state related to precipitation from solution. It is difficult to obtain sufficient thermal control to access Gaussian scaling in solution (±0.1°C is needed). Figure 1.6 on pp. 16 of Doi shows the coil-to-globule transition for dilute solutions of polystyrene whose theta temperature is close to 34.6°C in cyclohexane. Notice the abrupt collapse of expanded coils and the tenuous position of the Gaussian state close to the middle of this rapid collapse in temperature.

The Globule state is of little interest to polymer scientists. It is of dominant importance to protein physicists and other biophysicists since this is the use state for most biopolymers. Because of the latter the coil-to-globule transition has received extended treatment in the past 5 to 8 years by polymer theorists.

Blobs, Renormalized Groups and Chain Scaling.

The modern treatment of polymer coils involves adaptation of a number of concepts which are native to other areas of physics such as critical phenomena, liquid crystals and superconductors. The parallels involve statistical summations of directional vectors in thermally equilibrated systems.

From the above discussion it should be clear that variation of the step size, b, is necessary to describe chain structure. For instance, a group of mer units can be considered as a sub-unit for a chain. Consider three cases below. In the first the chemical unit, b, is considered as the basic unit and the end-to-end distance is $<R^2>^{1/2} = n^{1/2}$ b. In the second, the chain is composed of groups of mers which are themselves Gaussian so that the rms end-to-end distance, L, for a group of k mers is given by $L = k^{1/2}$ b. The chain's end-to-end distance is described by $<R^2>^{1/2} = (n/k)^{1/2}$ L. In the third case k is a larger number and the same equations apply.



This technique of redefining the chain by considering groupings of subunits is a basic feature of a technique termed **renormalization** of the chain. The basic features of the chain are not changed by renormalization. R_g and $<R^2>^{1/2}$ for the coil are not changed by renormalization.

As the concentration of a polymer solution is increased it is possible to obtain conditions where there is a change in coil scaling with size of observation (size of the circles in the diagram above).

If the circle size in the above diagram is set to the size scale of this transition, the subunit of the chain is called a **blob**. Through the use of renormalization and blobs much of the complicated scaling features observed in high polymers can be simplified into universal laws. This will be discussed in detail in Chapter 2.

It should be noted that the original work on polymer coil conformation in the 1940's and 1950's involved measurement of R_g and the end to end distance as a function of the molecular weight and solvent conditions. The familiar Mark-Houwink equation is typical of the characterization of polymers prior to Mandelbrot's seminal work on fractal systems and dimensional analysis of statistical systems. The Mark-Houwink equation describes the intrinsic viscosity of a polymer solution in terms of two parameters, K and a, where a is a scaling coefficient for molecular weight,

$$[\eta] = KM^{a}$$

The intrinsic viscosity is proportional to the rms end-to-end distance for a coil, so the parameter "a" should be proportional to $1/d_f$ where d_f is the mass-fractal dimension. In polymer physics this scaling relationship has been explicitly described for the rms end-to-end distance using the scaling exponent ν,

$$\langle R^2 \rangle^{1/2} = n^{\nu} b$$

ν is equal to $1/d_f$ in a more universal lexicon, although rarely used in polymer physics.