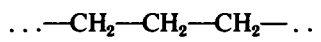
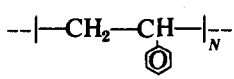
Introduction: Long Flexible Chains

Linear Polymers

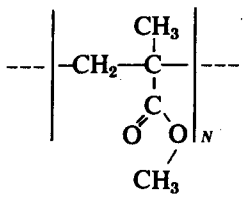
This book discusses the statistical properties of long, flexible objects, polymer chains being the fundamental example. The following is a short list of chains which are currently used in physical studies:



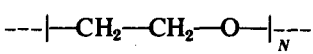
polyethylene



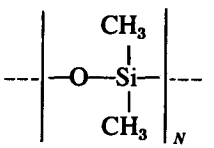
polystyrene



poly(methyl methacrylate)



poly(oxyethylene)



poly(dimethyl siloxane)

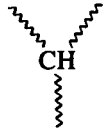
The number of repeat units, N, in one chain is often called the "degree of polymerization" (DP) and can be amazingly large. (For example, it is possible to reach $N > 10^5$ with polystyrene.) The fabrication of such long chains *without error* in a sequence of 10^5 operations is a remarkable chemical achievement. However, there are many difficulties. Two are particularly important for physical studies: polydispersity and branching.

Polydispersity

Most preparation schemes give chains with a very broad distribution of N values.[1] It is possible, however, to obtain relatively narrow distributions either by physical selection (via precipitations, gel permeation, chromatography, etc.[2]) or through special methods of synthesis, such as anionic polymerization.[3]

Branching

Many parasitic reactions occurring during the synthesis can lead to a chain which is not perfectly linear but which contains branch points. For example, industrial polyethylene has many three-functional branch points of the type



where the zigzag lines represent different chain portions.

When the fraction of branch points in the structure is not too small, these points can be detected by various physical methods, such as infrared spectroscopy. On the other hand, if a long chain has accidentally acquired one or two branch points, it is extremely hard to demonstrate their existence or absence (they show up mainly in certain mechanical studies on concentrated systems, discussed in Chapter VIII).

In some cases we encourage branching. For example, model molecules can be synthesized with the geometry of "stars" or "combs" (Fig. 0.1). More often, branching takes place statistically. It may lead either to tree-like molecules, or, at a higher level, to network structures (discussed in Chapter V). In summary, we can obtain chains that are strictly linear (when N is not too large); we can also insert on a chain a controlled number of branch points.

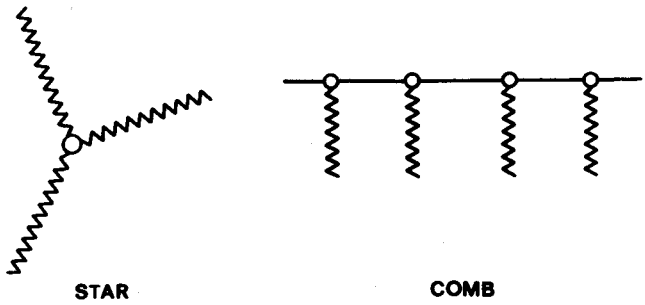


Figure 0.1.

Flexibility

Flexibility can be understood either in a static or in a dynamic sense.

Static flexibility

As a simple example, consider a carbon-carbon chain such as polyethylene. The angle θ between successive C—C bonds is essentially fixed, but when we build up successive units with the carbon atoms ($n-3$, $n-2$, $n-1$) fixed, and add carbon (n), we have one angle φ_n (Fig. 0.2). The energy between successive groups depends on the angle φ_n as shown on Fig. 0.3. There are three minima, corresponding to three principal conformations (called *trans* and *gauche*). In this figure we see two essential energy parameters: 1) the energy difference between minima $\Delta\epsilon$,* and 2) the energy barrier separating the minima ΔE.

For the moment, we focus on $\Delta\epsilon$. When $\Delta\epsilon$ is smaller than the thermal energy T,† we say that the chain is statically flexible. This has striking consequences if we look not at one monomer but at the whole chain. Because the relative weight of *gauche*/*trans* conformations is of order unity, the chain is not fully stretched. It appears rather as a *random coil* (Fig. 0.4).

Note the difference in magnification between Fig. 0.2 and Fig. 0.4. Fig. 0.2 deals with distances of order 1 Å. Fig. 0.4 deals with hundreds of Angströms.

The case of $\Delta\epsilon < T$ defines a limit of extreme flexibility. If we go to

*In polyethylene $\Delta\epsilon$ (as defined in the figure) is *positive:* the *trans* state is lower in energy than the *gauche* states.

†Recall that we use units where the Boltzmann constant is unity.

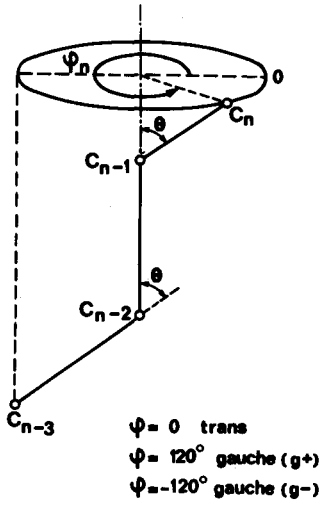


Figure 0.2.

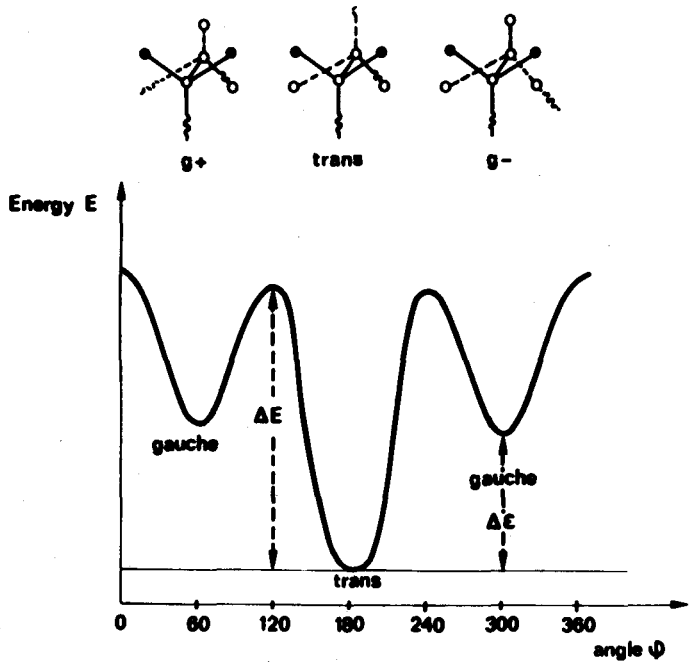


Figure 0.3.

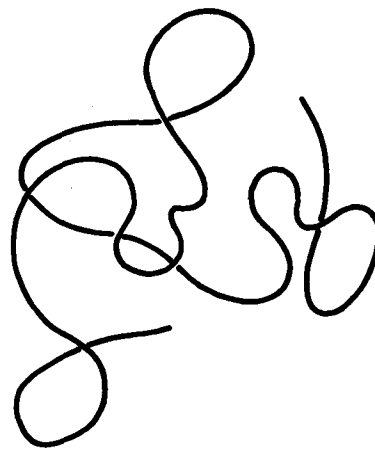


Figure 0.4.

slightly higher values of $\Delta\epsilon/T$, there will be a definite preference for the *trans* state; locally the chain will be rigid. However, if we look at it on a scale which is large enough, it will again appear as a flexible coil. This is illustrated in Fig. 0.5.

More generally, when we ignore details smaller than a certain characteristic length l_p, we see a continuous, flexible chain. The parameter l_p is called the *persistence length* of the chain[4] and can be calculated from the microscopic energies. For the polyethylene chain of Figs. 0.1 and 0.2 l_p is a rapidly increasing function of the energy difference $\Delta\epsilon$

$$l_p = l_0 \exp\left(\frac{\Delta\epsilon}{T}\right) \quad (\Delta\epsilon > 0)$$

where l_0 is of order a few Angströms.

Whenever l_p is much smaller than the total length L of the chain, we can choose a magnification which is weak, so that the rigid portions (of size $\sim l_p$) are too small to be seen, but which is still strong enough to ensure that the whole chain is not reduced to a point. Then we may say that the molecule is still flexible at large scales. On the other hand, if l_p is larger than the overall chain length, the picture is a rigid rod at all scales.

We see that the essential parameter controlling global flexibility is the ratio

$$x = \frac{l_p}{L} \cong N^{-1} \exp\left(\frac{\Delta\epsilon}{T}\right)$$

Flexible behavior can be observed only at small x.

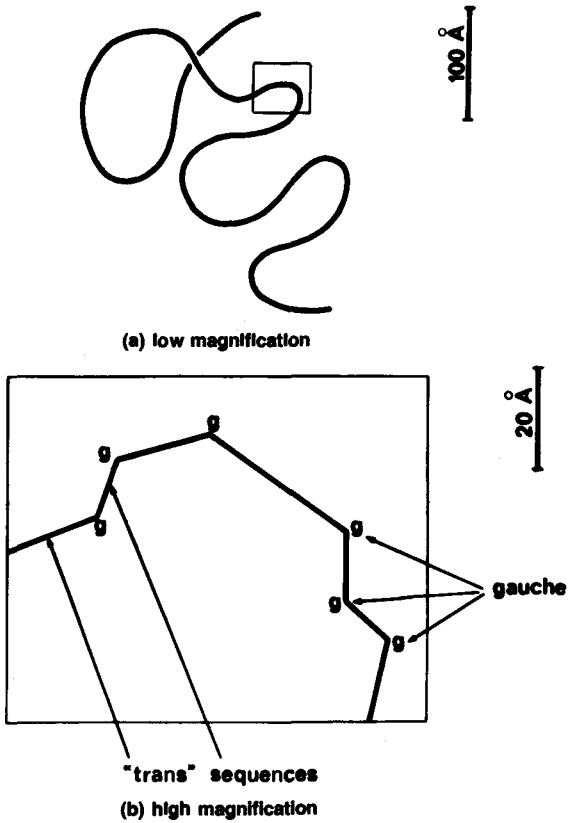


Figure 0.5.

Dynamic flexibility

Successive carbon–carbon links can be in one of two states: *trans* and *gauche*. One important question is related to the time τ_p required for a transition between these two states. This depends mainly on the height ΔE of the barrier separating them in the energy diagram of Fig. 0.3. If ΔE is not much larger than the thermal energy T, the barrier is not important, and the *trans–gauche* isomerization can take place in times $\tau \sim 10^{-11}$ sec. We say then that the chain is dynamically flexible. On the other hand, if the barrier ΔE is high, τ_p becomes exponentially long

$$\tau_p = \tau_0 \exp\left(\frac{\Delta E}{T}\right)$$

It is sometimes useful to call τ_p a persistence time.

Our discussion on spatial scales and static flexibility can be extended to temporal scales and dynamic flexibility. If we are interested in large scale motions of the molecule, involving frequencies ω smaller than $1/\tau_p$, we can still say that the chain is dynamically flexible.

One can find molecules which are flexible from a static point of view but which have high barriers ΔE (with certain flexible backbones carrying bulky side groups). This situation corresponds to a random coil which is essentially *frozen* in one conformation, like a piece of twisted wire. A molecule of this type in dilute solution could be called a "single chain glass," and should have some remarkable mechanical properties.

This book does not discuss any of these rigid molecules. It assumes both static and dynamic flexibility in the strongest form. Then l_p, for example, reduces to a monomer size [currently designated by (a)] and no other characteristic length is involved; this simplification will be helpful.

Global versus Local Properties

Fig. 0.5 illustrates a fundamental distinction between two aspects of polymer science:

(i) Strong magnification or local properties: conformations and motions of one monomer inside the chain, and their dependence on chemical substitutions in the side groups.

(ii) Weak magnification: global properties: dependence of physical properties observables on chain length, on concentration, and on a few basic interaction parameters.

The *local* features are essential whenever we want to choose an optimal polymer for a given practical application. If we want to improve the fabrication of rubbers, we need a good understanding of the local motions of a rubber chain—i.e., how they depend on temperature, the influence of steric constraints between neighboring monomers, and so forth. The experimental methods for local probing of a polymer chain are not very different from those used for small molecules (such as infrared and Raman measurements). Similarly, the theoretical methods are (or will become) related to those which are used for conventional liquids: molecular dynamics, Monte Carlo methods, etc.

The *global* point of view is completely different. Here we try to omit the details of the chain structure as much as possible and to extract simple, universal, features which will remain true for a large class of polymer chains. An example will make this statement more precise: Consider a dilute solution of separate coils in a good solvent. The radius of gyration of one coil R_G depends on the degree of polymerization, N, and we know from Flory that

$$R_G = (\text{constant})\ aN^{\nu} \tag{0.1}$$

where ν is close to 3/5. What is universal in this law is the exponent ν; it is the same for all coils (in three-dimensional solutions) provided that the solvent is good. What is nonuniversal here is the prefactor. It depends on the detailed monomer structure and on the solvent chosen. If we want to understand the properties of polymer coils in good solvents, the first step is to explain the existence and the value of the exponent ν. The second step is to account for the constant that multiplies a, and this involves delicate studies on local properties. In the present book we are concerned with the first step.

Eq. (0.1) is a good example of a *scaling* law. It tells us that if we double the chain length, the size is increased by a factor 2^{ν}. The theorist using such a scaling law can be compared with the chemist seeking comparisons in homologous series: finding the exact value of R_G for a given chain and solvent is extremely difficult. In a first stage, what we can and must do is to measure R_G for different values of N and compare them. This is the spirit of the present text.

A law such as $R(N)$ above holds only for large N, with flexible chains, and for good solvents. Later we make these statements more precise, but we see already that a scaling law is always defined only in a certain *limit*, which must be specified in each case.

Notation

If we compute a quantity exactly (within a certain model), including all numerical coefficients, we can use an equals sign—i.e., write $A = B$. If we state only a scaling law, ignoring all numerical coefficients but keeping all dimensional factors, we use the symbol, $\cong$ (e.g., $R \cong aN^{3/5}$). If we go to a further reduction and want to stress only the power law involved in $R(N)$, we use the symbol $\sim$ (e.g., $R \sim N^{3/5}$).

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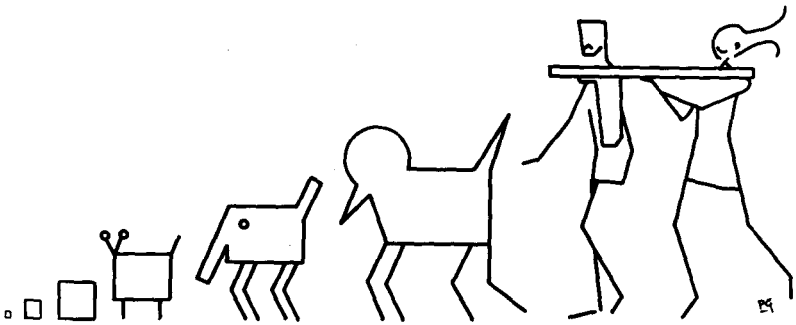
2. D. D. Bly, *Physical Methods of Macromolecular Chemistry*, B Carroll, Ed., Vol. 2, Marcel Dekker, New York, 1972.
3. P. Flory, *Principles of Polymer Chemistry*, Chap. V, Cornell University Press, Ithaca, N.Y., 1971.
4. T. Birshtein, O. Ptitsyn, *Conformations of Macromolecules*, John Wiley & Sons, New York, 1966.

Part A

STATIC CONFORMATIONS



Various animals attempting to follow a scaling law.

I

A Single Chain

I.1. The Notion of an Ideal Chain

I.1.1. Simple random walks

One of the simplest idealizations of a flexible polymer chain consists in replacing it by a random walk on a periodic lattice, as shown in Fig. I.1. The walk is a sucession of N steps, starting from one end (α) and reaching an arbitrary end point (ω). At each step, the next jump may proceed toward any of the nearest-neighbor sites, and the statistical weight for all these possibilities is the same. The length of one step will be called a.

This description was apparently initiated by Orr in 1947.[1] It is convenient from a pedagogical point of view: all chain properties are easy to visualize. For instance, the entropy $S(\mathbf{r})$ associated with all chain conformations starting from an origin ($\mathbf{r} = 0$) and ending at a lattice point $\mathbf{r}$, is simply related to the number of distinct walks $\mathfrak{N}_N(\mathbf{r})$ going from (0) to ($\mathbf{r}$) in N steps*

$$S(\mathbf{r}) = \ln[\mathfrak{N}_N(\mathbf{r})] \tag{I.1}$$

The main features of the number $\mathfrak{N}_N(\mathbf{r})$ are discussed now. First, the total number of walks is simple to compute; if each lattice site has z neighbors, the number of distinct possibilities at each step is z, and the total number is

*We always use units where Boltzmann's constant k_B is unity.

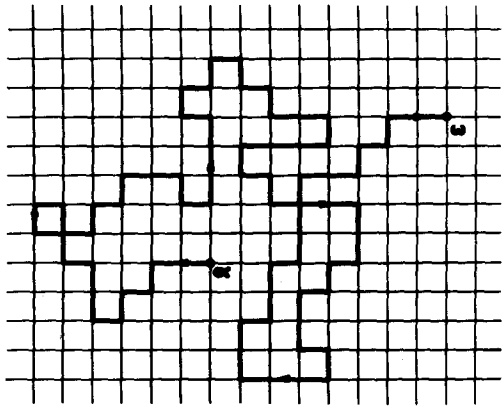


Figure I.1.

$$\sum_{(\mathbf{r})} \mathfrak{N}_N(\mathbf{r}) = z^N \tag{I.2}$$

(where $\sum_{\mathbf{r}}$ denotes a sum over lattice points)

The end-to-end vector $\mathbf{r}$ is the sum of N "jump vectors"

$$\mathbf{r} = \mathbf{a}_1 + \mathbf{a}_2 + \ldots + \mathbf{a}_N = \sum_n \mathbf{a}_n \tag{I.3}$$

where each of the $\mathbf{a}$ terms is a vector of length a with z possible orientations. Different $\mathbf{a}$ vectors have completely *independent* orientations, and this has many consequences:

(i) the average square end-to-end distance is *linear in N*

$$\langle \mathbf{r}^2 \rangle = \sum_{nm} \langle \mathbf{a}_n \cdot \mathbf{a}_m \rangle = \sum_n \langle \mathbf{a}_n^2 \rangle = Na^2 \; (= R_0^2) \tag{I.4}$$

since all cross-products vanish. Qualitatively, we shall say that a random walk has a size $R_0 \sim N^{1/2}\, a$.

(ii) the distribution function for $\mathbf{r}$, defined by

$$p\,(\mathbf{r}) = \mathfrak{N}_N\,(\mathbf{r})/(\sum_{\mathbf{r}} \mathfrak{N}_N\,(\mathbf{r})) \tag{I.5}$$

has a gaussian shape as soon as the number of independent jump vectors $\mathbf{a}_n$ is large ($N \gg 1$). For example, if we are in three dimensions

$$p\,(x,y,z) = \text{constant}\; N^{-1/2} \exp\left(\frac{-x^2}{2\langle x^2\rangle}\right) N^{-1/2} \exp\left(\frac{-y^2}{2\langle y^2\rangle}\right)$$

$$N^{-1/2} \exp\left(\frac{-z^2}{2\langle z^2\rangle}\right) \cong N^{-3/2} \exp\left(\frac{-3\,r^2}{2\,Na^2}\right) \quad \text{(I.6)}$$

The factors $N^{-1/2}$ arise from normalization conditions. We purposely do not write the complete numerical value of the constant in front of eq. (I.6); these constants would obscure our arguments. They can be found in standard textbooks on statistics.[2]

Eq. (I.6) gives a formula for the entropy of the chain at fixed elongation

$$S(\mathbf{r}) = S(0) - \frac{3\,r^2}{2\,R_0^2} \quad \text{(three dimensions)} \qquad \text{(I.7)}$$

The entropy decreases when the elongation increases. It is often convenient to rewrite eq. (I.7) in terms of free energy

$$F(\mathbf{r}) = E - TS$$

In the Orr model the energy E is a constant (independent of the chain conformation), and we have simply

$$F(\mathbf{r}) = F(0) + \frac{3\,Tr^2}{2\,R_0^2} \qquad \text{(I.8)}$$

This is a fundamental formula, giving the "spring constant" of an ideal chain. We return to it in eq. (I.11) and use it frequently.

I.1.2. More general models for ideal chains

The model in Fig. I.1 is crude but convenient. More accurately, it is possible to build up the chain by successive steps, taking into account all valence angles, the correct weights for *trans/gauche* conformations (or their generalization) and even statistical deviations from the ideal *trans* or *gauche* states. This type of calculation is described fully in the second book by P. Flory.[3]

The crucial approximation involved in this "progressive buildup" amounts to taking into account only the interactions between each unit (n) and its neighbor ($n+1$) [or possibly between (n) and ($n+1$, $n+2$, $n+p$)

with p fixed and finite]. Let us accept this for the moment. We can define the "backbone" of the chain by a sequence of vectors $\mathbf{b}_1 + \mathbf{b}_2 + \ldots + \mathbf{b}_N = \mathbf{r}$, each of the vectors $\mathbf{b}_i$ linking two consecutive monomers. In the Orr model these vectors are now correlated. For example, the average

$$\langle \mathbf{b}_n \cdot \mathbf{b}_m \rangle = \gamma_{nm} \tag{I.9}$$

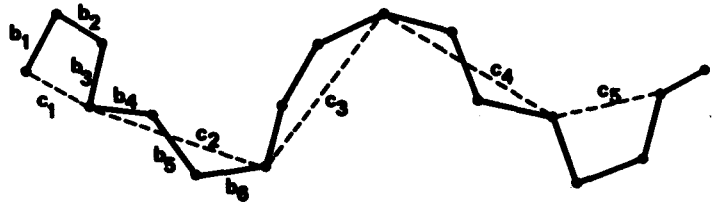
is nonzero even for $m \neq n$. It is, however, a decreasing function of the chemical interval $|m - n|$, and it decays exponentially at large $|n - m|$. Thus the correlations are of finite range. We now show that, in this case, the global properties are not affected seriously.

Let us put g consecutive vectors $\mathbf{b}$ into one *subunit*. In Fig. I.2 we show the case for $g = 3$. If g is much larger than the range of the correlations c_{nm}, the new vectors $\mathbf{c}$ will be uncorrelated, and we face the problem of N/g independent variables $\mathbf{c}_1, \mathbf{c}_2, \ldots$, leading again to gaussian statistics provided that N/g is large; this is what we call ideal chain behavior. The mean square end-to-end distance is linear in N

$$\langle r^2 \rangle = \frac{N}{g} \langle c^2 \rangle = Na^2 \tag{I.10}$$

where $a = (\langle c^2 \rangle / g)^{1/2}$ is now an effective length per monomer. Thus, whatever the microscopic structure of the chain, *if we take into account only the interactions between neighboring units on the chemical sequence, we always get an ideal chain if N is large enough.*

The single (but important) weak point in this approach is the neglect of interactions between monomers n and m with $|n - m|$ very large. Fig. I.3 shows an interaction which is omitted. When these "large loop interactions" are included, the chain is *not* gaussian. We discuss this extensively later in this chapter.



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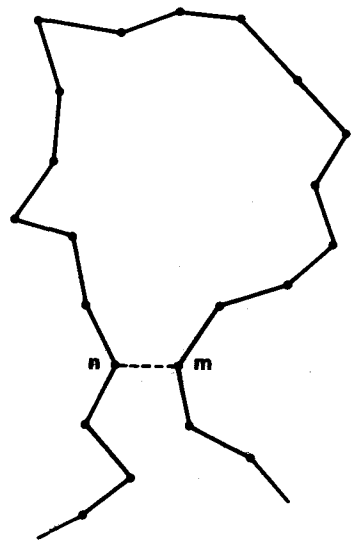

Figure I.3.

I.1.3. Ideal chains under external actions

It is of interest to study the response of a chain to external perturbations. With an ideal chain, this response is particularly easy to derive. We are concerned here with two main situations: pulling and squeezing.

PULLING A CHAIN AT BOTH ENDS (Fig. I.4)

We apply forces $\mathbf{f}$ and $-\mathbf{f}$ at both ends and ask for the average elongation $\langle \mathbf{r} \rangle_f$ of the chain. For an f that is not too large the answer is derived from the "spring constant equation" (I.8). The force $\mathbf{f}$ is $\partial F/\partial \mathbf{r}$ taken at $\mathbf{r} = \langle \mathbf{r} \rangle_f$, and thus

$$\langle \mathbf{r} \rangle_f = \mathbf{f} \frac{R_0^2}{3\,T} \tag{I.11}$$

Eq. (I.9) holds whenever $\langle \mathbf{r} \rangle$ is much smaller than Na (chain not fully stretched). This corresponds to $f \ll T/a$.

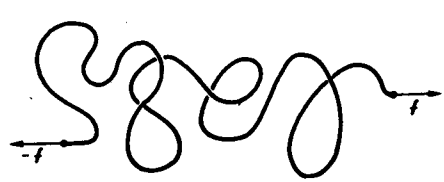

Figure I.4.

We rederive eq. (I.11) here through a scaling argument, which is good training for later problems. This derivation is based on the following points:

(*i*) Since the tension **f** is the same all along the chain, the elongation $\langle \mathbf{r} \rangle$ must be a linear function of N.

(*ii*) We expect $\langle \mathbf{r} \rangle$ to depend only on **f**, on temperature, and on the unperturbed size $R_0 = N^{1/2}\, a$. This leads to

$$|\langle \mathbf{r} \rangle| \cong R_0 \left(\frac{f R_0}{T}\right)^x$$

where x is fixed by requirement (i)—namely, $R_0^{(1+x)} \sim N$. Thus $x = 1$, and the elongation is a linear function of the force.

Eq. (I.11) is the basis of rubber elasticity, and we shall use it often.

Exercise: consider an ideal chain carrying charges $\pm e$ at both ends (e is one electron charge). What will be its relative elongation in a field $E = 30{,}000$V/cm?

Answer: we have $r/R_0 \cong R_0 eE/3\,T$. Take $N = 10^4$ and $a = 2$ Å (giving $R_0 = 200$ Å). The voltage drop on a length R_0 is $3.10^4 \times 2.10^{-6} = 0.06$ V. At room temperature $T = 1/40$ eV and thus $r/R_0 \sim 0.8$.

AN IDEAL CHAIN TRAPPED IN A TUBE

The chain is captured in a cylindrical tube of diameter $D \ll R_0$ (Fig. 1.5). On the other hand, we want $D \gg a$, so that the chain still retains some

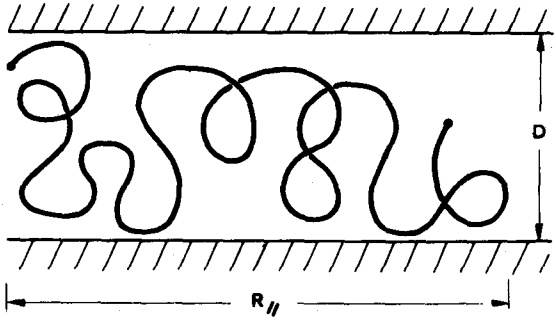

Figure I.5.

lateral wiggling. We assume that the tube walls repel the chain strongly (no trend towards adsorption).

We ask first, what is the length of tube ($R_\parallel$) occupied by the chain? The answer is $R_\parallel = R_0$; that is, confinement does not affect the components of the random walk parallel to the tube axis.

Second, we discuss the energy required to squeeze the chain, starting from a dilute solution in the same solvent and assuming that chain entropy is the only significant factor (no long-range van der Waals force in the tube). We try to estimate the reduction in entropy ΔS due to confinement:

(i) The leading term in ΔS will be a linear function of N.

(ii) ΔS is dimensionless and depends only on the length ratio R_0/D.

This leads to $\Delta S = -(R_0/D)^y \sim N^{y/2}$, and from (i) we must have $y = 2$. The corresponding free energy is

$$F \cong T\frac{R_0^2}{D^2} \tag{I.12}$$

The argument holds equally for a confinement in a slit or in a hollow sphere; only the coefficients differ. They have been computed first by Cassasa and co-workers[4,5] (see Chapter IX for more details).

WEAK ADSORPTION OF AN IDEAL CHAIN

The situation is represented in Fig. I.6. The chain sticks slightly to the wall and has large loops extending up to an average distance D. Exact calculations on this system have been performed in the past.[6,7,8] Here we present a simple scaling argument that relates D to the strength of the adsorption.[9] The starting point is a free energy per chain of the form

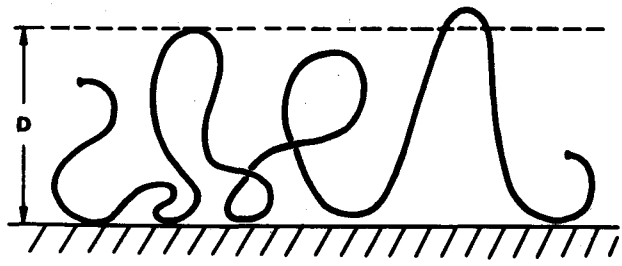

Figure I.6.

$$F \cong T\frac{R_0^2}{D^2} - T\delta f_b N \tag{I.13}$$

The first term is the confinement energy (eq. I.12), and the second term describes the contact interactions with the surface; $T\delta$ is the effective attraction seen by a monomer adsorbed at the surface (a balance between an attractive energy and a loss of entropy), and f_b is the fraction of bound monomers. Since the monomer density is spread over a thickness D, we expect

$$f_b \cong a/D \tag{I.14}$$

Inserting this in eq. (I.13) and minimizing the sum with respect to D, we reach a thickness

$$D \cong a\delta^{-1} \qquad (\delta \ll 1,\ D \ll R_0) \tag{I.15}$$

and a free energy of binding

$$F \cong -TN\delta^2 \tag{I.16}$$

The conditions required for the adsorption of *separate* chains are never realized in practice, but they provide a useful framework for future discussions of many chain adsorption.

I.1.4. Pair correlations inside an ideal chain

A pair correlation function $g(\mathbf{r})$ may be defined as follows. We pick one monomer at random in the chain, and we place it at the origin. Then we ask, what is the number density of other monomers at a distance $\mathbf{r}$ from the first, and we average the result over all choices of the first monomer.

The Fourier transform of $g(\mathbf{r})$

$$g(\mathbf{q}) = \int g(\mathbf{r})d\mathbf{r}e^{i\mathbf{q}\cdot\mathbf{r}}$$

is directly measured in many scattering experiments (light, X-rays, neutrons), $\mathbf{q}$ being the scattering wave vector. (In terms of wavelength λ and scattering angle θ we have $q = 4\pi\lambda^{-1}\sin\theta/2$.)

The function $g(\mathbf{r})$ has an integral which is just the total number of monomers per chain N

$$\int g(\mathbf{r})d\mathbf{r} = N = g(\mathbf{q} = 0)$$

The functions $g(\mathbf{r})$ and $g(\mathbf{q})$ obey simple scaling rules:

$$g(\mathbf{r}) = N\tilde{g}(r/R_0)$$

where $\tilde{g}$ is an universal function.

The structure of $g(\mathbf{q})$ for ideal chains was discussed first by Debye,[10] and thus we call $g(\mathbf{q})$ the *Debye function* $g_D(\mathbf{q})$.

Focusing on the limit $\mathbf{r} \ll R_0$, we can reach the form of $g(\mathbf{r})$ by a simple argument. In a sphere of radius r we have a certain number of monomers n, related to r by the random walk scaling law: $na^2 \sim r^2$. The function $g(\mathbf{r})$ scales like the density of monomers in the sphere:

$$g_D(\mathbf{r}) \cong n/r^3 \cong \frac{1}{a^2 r} \qquad (r \ll R_0) \tag{I.17}$$

The exact coefficient is displayed in Fig. I.7; for its complete derivation see Chapter IX. The Fourier transform of $1/r$ is $4\pi/q^2$, and the scattering function is

$$g_D(q) = \frac{12}{q^2 a^2} \qquad (qR_0 \gg 1) \tag{I.18}$$

It is not easy to measure this $g_D(q)$ on dilute chains directly; in light scattering q is too small, and in X-rays or neutron experiments the signals from dilute systems are weak. However, the result [eq. (I.18)] will be useful for more complicated systems.

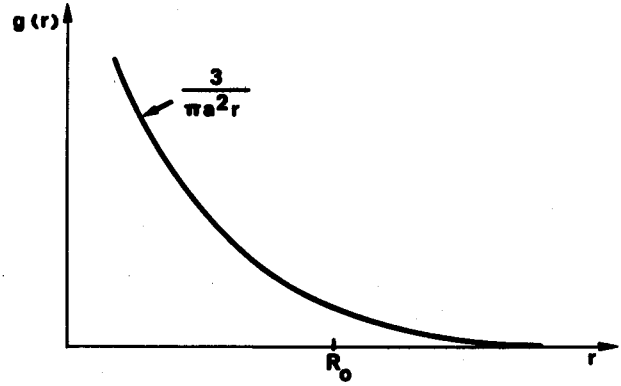

Figure I.7.
Pair correlation between all monomers in an ideal chain. The correlations decrease like $1/r$ at distances r, smaller than the chain size R_0. They fall off sharply for $r > R_0$.

I.1.5. Summary

Ideal chains are characterized by: 1) gaussian statistics; 2) size proportional to $N^{1/2}$; 3) large domain of linear relation between force and elongation; and 4) scattering law of the q^{-2} type. We now see how these properties are altered when we switch from ideal to real chains.

I.2. A "Real" Chain In a Good Solvent

I.2.1. The main experiments

The size of real chains in dilute solutions can be determined by various standard experimental methods:

(i) Measurements on scattered light intensity versus angle give us the radius of gyration R_G.[3]

(ii) More simply, a study of the viscosity η of dilute solutions measures a certain hydrodynamic radius R_η[11]

$$\eta = \eta_S \left[1 + 2.5 \frac{c}{N} \frac{4\pi}{3} R_\eta^3 \right] \qquad (c \to 0) \tag{I.19}$$

Here η_S is the solvent viscosity, and c is the concentration; we do not define it by weight but rather as *a number of monomers per unit volume*. Similarly c/N is the number of chains per cm^3. The numerical factors in eq. (I.15) correspond to a rigid sphere of radius R_η. On the experimental side this provides an excellent determination of R_η. However the interpretation of R_η is delicate. We return to this question in Chapter VI.

(iii) Photon beat measurements give us the diffusion coefficient D_0 for a single coil. This coefficient may be related to another effective radius R_D, defined through the Stokes relation for a sphere

$$D = \frac{T}{6\pi\eta_S R_D} \tag{I.20}$$

Summarizing a vast literature, we may say that the light scattering experiments (i) give a radius $R_G \sim N^{0.60}$ while the hydrodynamic studies (ii) and (iii) give a slightly weaker power $R \sim N^{0.55}$ or $N^{0.57}$. This discrepancy reflects some subtle corrections involved in dynamical experiments and is discussed in Chapter VI.

I.2.2. Numerical data on self-avoiding walks

We see that the direct data on coils are not quite conclusive. It is then helpful to return to theoretical calculations. There do exist rather accurate numerical studies on *real chains on a lattice*. The chain is still represented by a random walk as in Fig. (I.1), but the main difference is that now this walk can never intersect itself. We call it a *self-avoiding walk* (SAW).

The mathematical properties of simple random walks are trivial, but the mathematical properties of SAWs are complex. Two numerical methods have been used to study the SAWs:

(i) Exact counting of walks for finite N (typically up to $N \sim 10$) plus extrapolation methods allowing us to extend the results toward $N \to \infty$.[12]

(ii) Monte Carlo methods, where the computer generates a certain (manageable) fraction of all SAWs of N steps and performs averages on these.[13]

All these studies have been performed on three-dimensional lattices and in other dimensionalities, d. The case for $d = 1$ corresponds to chains along a line and is simple. The case for $d = 2$ may physically correspond to chains adsorbed at an interface. Higher dimensionalities ($d = 4, 5 \ldots$) are also of interest for the theorist, although they do not correspond to realizable systems. One important advance (during the past 10 years) has been to recognize the interest of discussing any statistical problem in arbitrary dimensions and to classify systems according to their behavior as a function of d. Thus, we shall often keep d as a parameter in our discussion of polymer chains.

The results of numerical studies on SAWs are usefully summarized in a recent review by McKenzie.[12] Our presentation, however, is slightly different since the physical meaning of the essential exponents has become more apparent in the recent years.

The total number of SAWs of N steps has the asymptotic form (at large N)

$$\mathfrak{N}_N\,(tot) = \text{constant}\ \tilde{z}^N\, N^{\gamma-1} \tag{I.21}$$

The first factor $\tilde{z}^N$ is reminiscent of the z^N which we had for ideal chains, but $\tilde{z}$ is somewhat smaller than z. For the three-dimensional simple cubic lattice, $z = 6$ and $\tilde{z} = 4.68$. The second factor, $N^{\gamma-1}$, is more unexpected and will be called the enhancement factor. The exponent γ *depends only on the dimensionality, d:*

$$\text{for all three-dimensional lattices } \gamma = \gamma_3 \cong 7/6 \tag{I.22a}$$

$$\text{for all two-dimensional lattices } \gamma = \gamma_2 \cong 4/3 \tag{I.22b}$$

We say that γ is a universal exponent; this is in contrast to $\tilde{z}$, which does depend not only on d but also on the particular lattice chosen (e.g., face-centered cubic/simple cubic). Note that for $d = 1$, $\mathfrak{N}_N\,(tot) = 2$, independently of N. Thus $\tilde{z}_1 = 1$ and $\gamma_1 = 1$.

The end-to-end distance r has a mean square average which we shall call R_F^2, and which scales as

$$R_F \cong a\, N^{\nu} \tag{I.23}$$

Here ν is another universal exponent ($\nu_3 \cong 3/5$, $\nu_2 \cong 3/4$, $\nu_1 = 1$).

The distribution law for $\mathbf{r}$ depends on $\mathbf{r}$ *only through the ratio* r/R_F

$$p_N(r) = \frac{1}{R_F{}^d}\, f_p\left(\frac{r}{R_F}\right) \quad (a \ll r \ll Na) \tag{I.24}$$

The prefactor $\dfrac{1}{R_F{}^d}$ is required to ensure the normalization

$$\int p_N(\mathbf{r})d\mathbf{r} = 1$$

The general structure of the reduced distribution $f_p(x)$ is shown in Fig. I.8 for $d = 3$. There is a very strong drop at large x

$$\lim_{x \to \infty} f_p(x) = \exp(-x^{\delta})\, f_1(x) \tag{I.25}$$

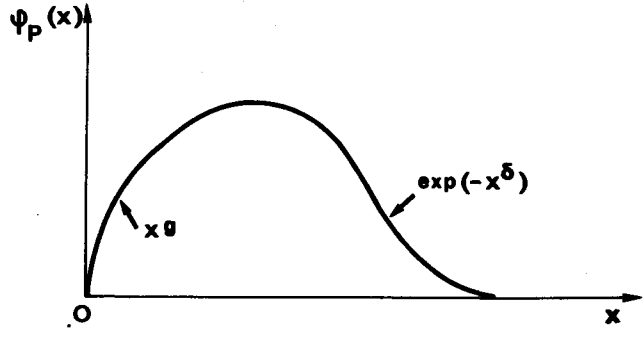

Figure I.8.

Distribution of the end-to-end distance r in a self-avoiding walk of N steps; x is equal to r/R_F, where R_F is the root mean square value.

where f_1 varies as a power of x. The exponent δ controls most of the chain properties for strong stretching and is given by:[14,15,16]

$$\delta = (1 - \nu)^{-1} \tag{I.26}$$

We present a simplified derivation of eq. (I.26) later in this chapter (see eq. (I.47) and the discussion following it).

At small x, f_p decreases sharply; it is exceptional for a self-avoiding walk to return close to its starting point

$$\lim_{x \to 0} f_p(x) = \text{constant } x^g \tag{I.27}$$

In three dimensions $g = g_3 \cong 1/3$. We relate g to other exponents below.

Let us consider the SAWs that return to a terminal site adjacent to the origin (Fig. I.9). In closing the $\alpha - \omega$ link we may say that each of these SAWs is associated with a closed polygon of $N + 1$ edges (and self-avoiding). The number of such polygons is of the form

$$\mathfrak{N}_N (r = a) \cong \tilde{z}^N \left(\frac{a}{R_F}\right)^d \tag{I.28}$$

The factor R_F^{-d} is natural since the terminal points ω of *all* SAWs of N steps are spread over a d-dimensional volume R_F^d. What is remarkable in eq. (I.28) is the absence of the enhancement factor $(N^{\gamma-1})$ which was present in $\mathfrak{N}_N$ (tot) [eq. (I.21)]. This absence also reflects the difficulty for a SAW to return near its starting point.

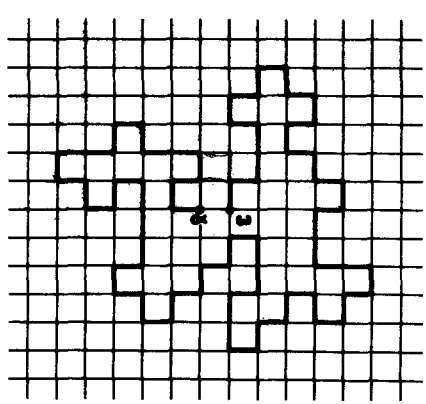

Figure I.9.

Eq. (I.28) is proved later by two independent methods (Chapters X and XI). If we accept it for the moment, we can predict simply what is the exponent g in eq. (I.27). The distribution function $p_N(\mathbf{r})$ taken for a terminal point adjacent to the origin ($r = a$) is from eqs. (I.24 and I.27)

$$p_N(a) \cong \frac{1}{R_F{}^d}\left(\frac{a}{R_F}\right)^g = \frac{1}{R_F{}^d}\, N^{-\nu g} \tag{I.29}$$

On the other hand, it is (by definition) related to $\mathfrak{N}_N(a)$ [eq. (I.28)]

$$p_N(a) = a^{-d}\,\frac{\mathfrak{N}_N(a)}{\mathfrak{N}_N(tot)} = \frac{1}{R_F{}^d}\, N^{1-\gamma}$$

Comparing this with eq. (I.29), we obtain:

$$g = \frac{\gamma - 1}{\nu} \tag{I.30}$$

a result first derived by des Cloiseaux.[17]

A REMARK ON HIGHER DIMENSIONALITIES

We have presented numerical data concerning $d = 3$, 2, and 1 (the latter being trivial). What would happen for larger d? The answer is simple: for $d > 4$, all exponents return to the ideal chain value ($\nu = 1/2$, $\gamma = 1$). This did not show up very clearly in the early numerical work but is a general theorem and is explained in Section I.3.2.

I.2.3. Correlations inside a swollen coil

Let us discuss briefly the changes in the pair correlation function $g(\mathbf{r})$ that occur when we incorporate the effects of excluded volume. First, $g(\mathbf{r})$ and its Fourier transform $g(\mathbf{q})$ follow simple scaling laws. For instance

$$g(\mathbf{q}) = N\tilde{g}(qR_F)$$

where $\tilde{g}(x)$ is a dimensionless function and $\tilde{g}(0) = 0$.

Second, we may still follow the approach of Chapter I and write $g(\mathbf{r}) = n/r^3$ (in three dimensions). However, now the number n of units inside the radius r is related to r by the excluded volume exponent $r^{3/5} \sim n$. This gives

$$n \sim \left(\frac{r}{a}\right)^{\frac{5}{3}}$$

$$g(r) \cong \frac{1}{r^{4/3}\, a^{5/3}} \quad (r < R_F)\ (d = 3) \tag{I.31a}$$

i.e., a more rapid decrease than for ideal coils. The Fourier transform is

$$g(q) \cong \frac{1}{(qa)^{5/3}} \quad (qR_F > 1)\ (d = 3) \tag{I.31b}$$

These power laws were derived first by S. F. Edwards.[18] They have been verified directly on dilute chains with X-rays.[19] They have also been checked by neutron scattering experiments on semi-dilute systems (see Section III.2.5).

I.2.4. Summary

Real chains in good solvents have the same universal features as self-avoiding walks on a lattice. These features are described by two "critical exponents," γ and ν. All other exponents of interest can be expressed in terms of these two. The exponent γ is related to chain entropy, and the exponent ν is related to chain size. A real chain has a size ($R_F \sim N^{\nu}$), which is much larger than an ideal chain ($R_0 \sim N^{1/2}$). For three dimensions the exponent ν is very close to 3/5.

I.3. The Flory Calculation of the Exponent ν

I.3.1. Principles

Long ago, Flory devised a simple and brilliant scheme for computing the exponent ν, which gives excellent values for all dimensionalities.[20] We briefly describe his method and the approximations involved. The starting point is a chain, with a certain unknown radius R and an internal monomer concentration

$$c_{int} \cong \frac{N}{R^d} \tag{I.32}$$

(Note that we present the argument for an arbitrary dimensionality d).

There is a certain repulsive energy in the chain due to monomer monomer interactions. If c is the local concentration of monomers, the repulsive energy per cm^3 is proportional to the number of pairs present—i.e., to c^2. We write it (per unit volume) as:

$$F_{rep} = \frac{1}{2} Tv\,(T) c^2 \tag{I.33}$$

where v has the dimension of a (d dimensional) volume and is positive. We call v the excluded volume parameter. [In the Flory notation $v = (1-2\chi)\, a^d$ where a^d is the monomer volume and χ is an interaction parameter. For good solvents $\chi < 1/2$ and $v > 0$.]

One essential approximation is to replace the average of c^2 (inside the coil) by the square of the average

$$\langle c^2 \rangle \to \langle c \rangle^2 \sim c_{int}{}^2 \tag{I.34}$$

Eq. (I.34) is typical of a *mean field* approach: all correlations between monomers are ignored. The overall repulsive energy after integration over a volume R^d, scales as:

$$F_{rep}|_{tot} \cong Tv(T) c_{int}{}^2\, R^d = Tv \frac{N^2}{R^d} \tag{I.35}$$

This tends to favor large values of R (i.e., to swell the chain). However if the distortion is too large, the chain entropy becomes too small, and this is unfavorable. Flory includes this through an elastic energy term derived from the ideal chain result [eq. (I.8)]

$$F_{el} \cong T \frac{R^2}{Na^2} \tag{I.36}$$

Eq. (I.36) is also a very strong approximation; as shown later, the spring constant of a real chain is much smaller than that suggested by eq. (I.36). However, let us accept eqs. (I.35) and (I.36) and add them:

$$\frac{F}{T} \cong v \frac{N^2}{R^d} + \frac{R^2}{Na^2} \tag{I.37}$$

Eq. (I.37) has a minimum for a well defined radius $R = R_F$. Omitting all numerical coefficients, we find

$$R_F{}^{d+2} \cong va^2 N^3 \tag{I.38}$$

or $R_F \sim N^\nu$ with*

*Eq. (I.39) was written by Flory for $d = 3$. For general d, it was first quoted by M. Fisher, *J. Phys. Soc. Japan* **26** (Suppl.) 44 (1969).

$$\nu = \frac{3}{d+2} \tag{I.39}$$

Eq. (I.39) is amazingly good; it gives the correct value for $d = 1$ ($\nu_1 = 1$). The values for $d = 2$ and $d = 3$ are within a percent of the most accurate numerical results.[12,21] For most practical applications the Flory formula can be considered exact.

I.3.2. Chains are ideal above four dimensions

Eq. (I.39) tells us that $\nu = 1/2$ for $d = 4$. This is precisely the ideal chain exponent. We can understand this better if we return to the repulsive energy [eq. (I.35)]. We expect $R > R_0$, and thus the repulsive energy is at most of order

$$F_{rep.\ max} \cong vT \frac{N^2}{R_0^d} \cong T \frac{v}{a^d} N^{2-d/2} \tag{I.40}$$

while the elastic energy [eq. (I.30)] is at least of order T. We see then that the ratio

$$\frac{F_{rep}}{F_{el}} \leqslant N^{2-d/2} \tag{I.41}$$

For dimensionalities of $d > 4$ we conclude that repulsions between monomers represent only a weak perturbation; the local concentration in an ideal chain is so low that excluded volume effects become negligible.

The idea of calculating the effects of repulsions by *perturbation* methods (treating the excluded volume v as infinitesimally small) is relatively old.[22] When this is done, to first order in v, one finds*

$$\frac{R - R_0}{R_0} \cong \frac{F_{rep.\ max}}{T} = (\text{constant})\ \zeta + 0\ (\zeta^2)$$

$$\zeta \cong \frac{v}{a^d} N^{2-d/2} \tag{I.42}$$

Thus the real, dimensionless, expansion parameter is ζ. When ζ is small, the chain is ideal. When ζ is large, the chain shows strong excluded volume effects. (For intermediate ζ values a precise interpolation formula

*For the most simplified models R/R_0 is a function of ζ only. This point will be discussed more in Chapter XI.

has been worked out by Domb and Barrett.[23]) Note that for the usual case $d = 3$, the parameter

$$\zeta \cong \frac{v}{a^3} N^{1/2} \tag{I.42'}$$

is always large for large N; eq. (I.42) has a very limited range of validity. The self-consistent method of Flory is clearly much more powerful, but the characteristic parameter ζ will be of frequent use in this book.

I.3.3. Why is the Flory method successful?

It is important to realize that the self-consistent calculation of eqs. (I.35, I.36) benefits from a remarkable cancellation of two errors:

(i) The repulsive energy is enormously overestimated when correlations are omitted.

(ii) The elastic energy is also largely overestimated; if we think for example of the end-to-end elongation of the chain, since the distribution function $p_N(r)$ [eq. (I.19)] is a function of (r/R_F) only, this implies that the entropy at fixed r is also a function of r/R_F only. Finally the elastic energy should be written Tr^2/R_F^2 rather than $Tr2/R_0^2$. Again this brings in a large reduction.

As often happens in self-consistent field calculations (e.g., in the Hartree theory of atoms) the two errors (*i*) and (*ii*) cancel each other to a large extent. Many post-Flory attempts, which tried to improve on one term, (*i*) or (*ii*), leaving the other unaltered, led to results that were poorer than eq. (I.39).

In fact, another problem exists in chain statistics, where the self-consistent method does not benefit from the same cancellations. This is the case of a charged chain (polyelectrolyte) for which a self-consistent approach was attempted very early.[24,25] Here the neglect of correlations is not too serious because most of the repulsion comes from very distant monomers. Thus point (i) is improved, but point (ii) remains weak; the net result is a formula for ν in charged systems which gives incorrect values for $3 < d < 6$.[26] We return to this problem in Chapter XI.

I.4. Constrained Chains

We now turn to a discussion of real chains in good solvents, when external constraints are applied. The basic situations are listed in Section I.1. in connection with ideal chains. We shall see that all exponents are modified strongly by excluded volume effects, and that most of them can

be related directly to the exponent ν. To simplify the notation, we set $\nu = 3/5$ (the Flory value) for three-dimensional systems.

I.4.1. A chain under traction (Fig. I.4)

The external energy due to the force f, when the end-to-end distance is $\mathbf{r}$, is simply $-\mathbf{f}\cdot\mathbf{r}$. Thus, we may write a partition function for the chain in the form

$$Z = \int d\mathbf{r}\, p_N(\mathbf{r}) \exp(\mathbf{f}\cdot\mathbf{r}/T) \tag{I.43}$$

and using the results from Section (I.2) on $p_N(\mathbf{r})$, we can compute all averages involving $\mathbf{r}$.[12] Here, however, we use a simpler approach due to Pincus.[27] The only characteristic lengths entering into eq. (I.43) are: 1) the Flory radius, $R_F \cong aN^{3/5}$, and 2) the length $\xi_p = T/f$.

Let us now consider the elongation $\mathbf{r}(\mathbf{f})$. We may write

$$|\langle \mathbf{r} \rangle| = R_F\, \varphi_r\left(\frac{R_F}{\xi_p}\right) = R_F\, \varphi_r(x) \tag{I.44}$$

where φ_r is a dimensionless function. For small f we expect $|\langle \mathbf{r} \rangle|$ to be linear in x, and thus $\varphi_r(x \to 0) \cong x$

$$|\langle \mathbf{r} \rangle| \cong \frac{R_F^2}{T} f \qquad (fR_F < T) \tag{I.45}$$

Note that $\langle \mathbf{r} \rangle$ is not linear in N at small f. This means that the tension f is transmitted not only through the backbone (as in the ideal case) but also through contacts between certain pairs of monomers (n, m) (with $|n-m|$ large).

Consider now the limit of large tensions ($x \gg 1$). What happens here can be idealized as shown in Fig. I.10. The chain breaks up into a series

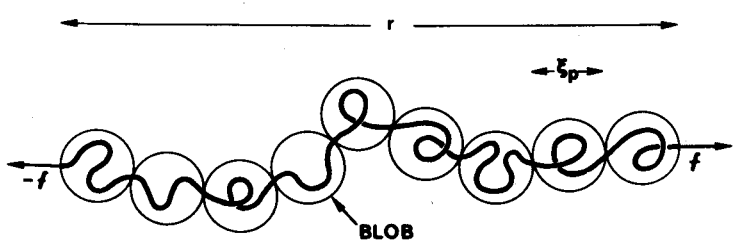

Figure I.10.

of "blobs" each of size ξ_p. Inside a blob (i.e., for spatial scales $r < \xi_p$) the force f (measured by the dimensionless number fr/T) is a weak perturbation. Thus, each blob retains the local correlations of a Flory chain, but at larger scales $r > \xi_p$ we have a string of independent blobs.

The number of monomers per blob, g_p, is related to ξ_p by the Flory law of real chains [eq. (I.39)], giving

$$\xi_p \cong a\, g_p^{3/5}$$

or

$$g_p = \left(\frac{T}{af}\right)^{5/3} \tag{I.46}$$

and the total number of blobs is N/g_p. The chain elongation is then

$$|\langle \mathbf{r} \rangle| \cong \frac{N}{g_p}\xi_p \cong Na\left(\frac{fa}{T}\right)^{2/3} \qquad \left(\frac{fa}{T} \ll 1\right) \tag{I.47}$$

Eq. (I.47) deserves some discussion. We see that a real chain has an elastic response which is significantly more nonlinear than an ideal chain. This appears on the plot of $\varphi(x)$ shown qualitatively in Fig. I.11.

The high f limit could have been obtained directly on the scaling form [eq. (I.44)] by imposing the restriction that $|\langle \mathbf{r} \rangle|$ becomes linear in N at high f. The reason for this linearity is that at high f, separate blobs do not interact; thus, we return to an ideal string of blobs.

Eq. (I.47) allows us to derive the exponent δ defined in connection with the strongly stretched limit [eq. (I.25)]. At large r the probability distribu-

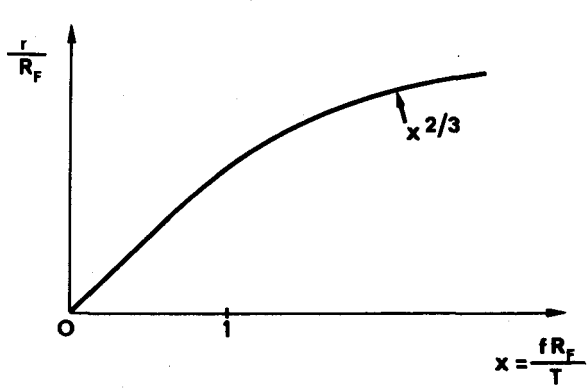

Figure I.11.

tion is essentially proportional to $\exp -(r/R_F)^{\delta}$, and the entropy for fixed elongation $S(\mathbf{r})$ has the form

$$S(\mathbf{r}) = \text{constant} + \ln p_N(\mathbf{r})$$
$$= \text{constant}\,(-)\left(\frac{r}{R_F}\right)^{\delta} \tag{I.48}$$

The corresponding elastic free energy is $-TS$, and the overall energy is

$$F_{tot} = T\left(\frac{r}{R_F}\right)^{\delta} - fr$$

The physically realized elongation corresponds to the minimum of F:*

$$f \cong \frac{T}{R_F}\left(\frac{r}{R_F}\right)^{\delta-1} \tag{I.49}$$

Comparing eq. (I.49) with (I.47) we see that $\delta = 5/2$ (when $\nu = 3/5$). Keeping a more general value of ν would lead to eq. (I.26).

Apart from the longitudinal elongation $\langle \mathbf{r} \rangle$ (parallel to f) it is of interest to ascertain the lateral spread of the chain $r_\perp$ in strong elongation. The projection of the string of blobs on a plane normal to $\mathbf{f}$ is an ideal string, and thus

$$\langle r_\perp^2 \rangle \cong \frac{N}{g_p}\,\xi_p^2 \cong Na^2\left(\frac{T}{fa}\right)^{1/3} \qquad (fR_F > T) \tag{I.50}$$

Thus the chain not only elongates but also shrinks in its lateral dimensions.

No experimental verifications of the laws [eqs. (I.47, I.50)] seem to be available at present. For the future, studies on strong distortions in flows of dilute solutions, and also in gels, may become relevant.

I.4.2. Squeezing a real chain in a tube

In one dimension, excluded volume effects are very strong. Thus it is of interest to consider a chain trapped in a thin tube of diameter $D \ll R_F$ (but D still larger than a). Situations of this sort may become available in the future. What is the length of tube $R_\parallel$ occupied by the chain? What is the energy required to squeeze the chain in?

Let us start with the length $R_\parallel$; it must have the scaling form

*The mathematically inclined reader will recognize that this describes a saddle point integration in Eq. (I.43).

$$R_{\parallel} = R_F \, \Phi_{\parallel} (R_F/D) \tag{I.51}$$

where $\Phi_{\parallel}(x) \to 1$ for $x \to 0$ (thick tube) and $\Phi_{\parallel}(x) \to x^m$ when $x \to \infty$ (thin tube). To determine the exponent m, we notice that for a thin tube we have a one-dimensional problem, and $R_{\parallel}$ must therefore be a *linear* function of N. Since $R_F \sim N^{\nu_3}$ this requirement means that

$$\begin{aligned} N^{\nu_3(+m)} &\cong N \\ m &= \nu_3^{-1} - 1 = 2/3 \end{aligned} \tag{I.52}$$

Thus the formula for the length of the chain is[28]

$$R_{\parallel} \cong Na \left(\frac{a}{D}\right)^{2/3} \qquad (a \ll D \ll R_F) \tag{I.53}$$

Note that $R_{\parallel}$ is larger than R_F. The chain is extended by squeezing, and this behavior is very different from an ideal chain. Further, the concentration inside the chain is interesting. It scales according to:

$$c_{int} \cong \frac{N}{D^2 R_{\parallel}} \sim \frac{1}{a^3} \left(\frac{a}{D}\right)^{4/3} \tag{I.54}$$

and is independent of N.

Another derivation of eq. (I.53) is based on a "blob" picture. The chain behaves as a sequence of blobs of diameter D. Inside each blob the effects of the boundaries are weak. The number g_D of monomers per blob is still given by the three-dimensional law: $g_D^{3/5} = D/a$. Successive blobs act as hard spheres and pack into a regular one-dimensional array. Thus $R_{\parallel} = N/g_D D$ in agreement with eq. (I.53).

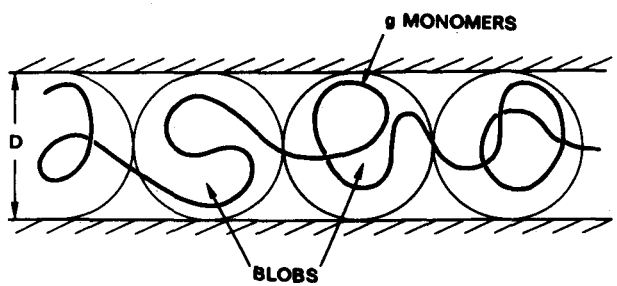

Figure I.12.

Let us now turn to the *confinement energy*. In the strong confinement limit ($D < R_F$) we see from Fig. I.12 that the energy must be linear in N; doubling N simply doubles the number of blobs. On the other hand, the energy must be of the form

$$F_{conf} \cong T\,\varphi_F\left(\frac{R_F}{D}\right) \cong T\,\varphi_F\,(x)$$

$$\lim_{x\to\infty} F_{conf} \cong Tx^n \tag{I.55}$$

Thus R_F^n must be linear in N, and $n = 5/3$.

$$F_{conf} = TN\left(\frac{a}{D}\right)^{5/3} \tag{I.56}$$

Note first the difference in behavior from the ideal chain [eq. (I.12)]. The confinement energy (at given D and N) is larger for the real chain. Note also the analogy between eq. (I.56) and the energy for strong elongation of a chain in free space [eq. (I.48)] $1/T\,(F_{conf}) \cong (R_\parallel/R_F)^{5/2}$. Thus $R_\parallel$ plays the role of the total elongation $\langle \mathbf{r} \rangle$ in the Pincus problem.

GENERALIZATIONS

This analysis can be extended to chains that are squeezed in slits and to other geometries provided that the confining object is characterized by a single length D. One such case has been recently studied by numerical methods.[29,30] This corresponds to a two-dimensional lattice, where we allow the chains to explore only a finite strip of width D. Then a similar argument suggests $R_\parallel \sim Na\,(a/D)^{1/3}$; this dependence on N and especially on D seems well confirmed by the data.

I.4.3. Weak adsorption of a single chain

This situation is again described by Fig. I.6. To determine the thickness of the adsorption layer D, we write, instead of eq. (I.13), an energy per chain of the form

$$F = TN\left(\frac{a}{D}\right)^{5/3} - T\delta f_b N \tag{I.57}$$

where the first term is the confinement energy in a slit of thickness D and

has the scaling structure of eq. (I.56), while the second term is unaltered ($f_b \sim a/D$). After minimization we find

$$D \sim a\delta^{-3/2} \tag{I.58}$$

$$F_{ads} \sim NT\delta^{5/2} \tag{I.59}$$

These equations should apply for $1 \gg \delta \gg N^{-2/5}$ (the latter inequality corresponding to $D < R_F$).

Monte Carlo studies on chains near an adsorbing surface have been carried out,[31,32] but the small δ limit is not very well known.

On the physical side, there are many complications. As mentioned, single-chain adsorption is never observed. One always reaches a situation where many chains compete for the same portion of surface. Furthermore the single-chain problem may be modified by the existence of *long range van der Waals forces* between the surface and each monomer. The corresponding potential decreases relatively slowly (as D^{-3}) and the attraction energy may not be cast into the form used in eq. (I.57).

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