



The following is an extended excerpt from Paul Flory's 1974 Nobel Lecture, delivered in Stockholm. It is a characteristically incisive account of the effects of excluded volume on the physical dimensions of a long macromolecular chain. Perhaps more than anyone else, Flory laid the foundation for the mathematical treatment of these effects within the framework of classical statistical mechanics.

Binny J Cherayil

Spatial Configuration of Macromolecular Chains

Nobel Lecture, December 11, 1974

Paul J Flory

The science of macromolecules has developed from primitive beginnings to a flourishing field of investigative activities within the comparatively brief span of some forty years. A wealth of knowledge has been acquired and new points of view have illumined various branches of the subject. These advances are the fruits of efforts of many dedicated investigators working in laboratories spread around the world. In a very real sense, I am before you on this occasion as their representative.

In these circumstances, the presentation of a lecture of a scope commensurate with the supreme honor the Royal Swedish Academy of Sciences has bestowed in granting me the Nobel Prize for Chemistry is an insuperable task. Rather than attempt to cover the field comprehensively in keeping with the generous citation by the Royal Academy of Sciences, I have chosen to dwell on a single theme. This theme is central to the growth of ideas and concepts concerning macromolecules and their properties. Implemented by methods that have emerged in recent years, researches along lines I shall attempt to highlight in this lecture give promise of far-reaching advances in our understanding of macromolecular substances – materials that are invaluable to mankind.

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Polymeric substances are distinguished at the molecular level from other materials by the concatenation of atoms or groups to form chains, often of great length. The importance of macromolecular substances, or polymers, is matched by their ubiquity. Examples too numerous to mention abound in biological systems. They comprise the structural materials of both plants and animals. Macromolecules elaborated through processes of evolution perform intricate regulatory and reproductive functions in living cells. Synthetic polymers in great variety are familiar in articles of commerce.

The chemical bonds in macromolecules differ in no discernible respect from those in “monomeric” compounds of low molecular weight. The same rules of valency apply; the lengths of the bonds, e.g., C-C, C-H, C-O, etc., are the same as the corresponding bonds in monomeric molecules within limits of experimental measurement. This seemingly trivial observation has two important implications: first, the chemistry of macromolecules is coextensive with that of low molecular substances; second, the chemical basis for the special properties of polymers that equip them for so many applications and functions, both in nature and in the artifacts of man, is not therefore to be sought in peculiarities of chemical bonding but rather in their macromolecular constitution, specifically, in the attributes of long molecular chains.

A portion of such a molecule is shown schematically in *Figure 1*. Consecutive bonds comprising the chain skeleton are joined at angles θ fixed within narrow limits. Rotations φ may occur about these skeletal bonds. Each such rotation is subject, however, to a potential determined by the character of the bond itself and by hindrances imposed by steric interactions between pendant atoms and groups. The number and variety of configurations (or conformations in the language of organic chemistry) that

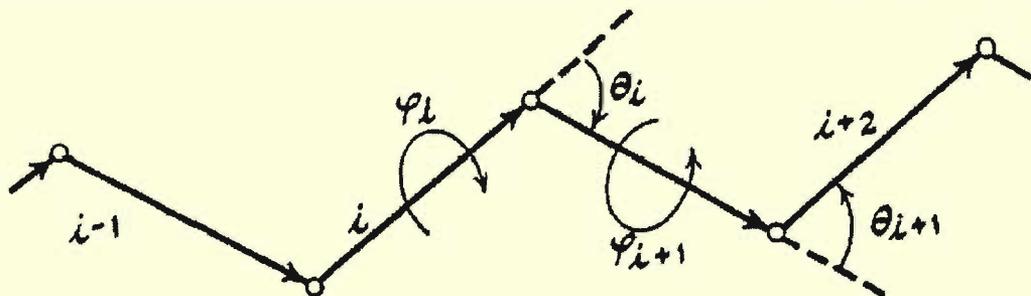


Figure 1. Representation of the skeletal bonds of a section of a chain molecule showing supplements of bond angles, and torsional rotations for bonds $i, i + 1$, etc.

may be generated by execution of rotations about each of the skeletal bonds of a long chain, comprising thousands of bonds in a typical polymer, is prodigious beyond comprehension.

Most of the properties that distinguish polymers from other substances are intimately related to the spatial configurations of their molecules, these configurations being available in profusion as noted. The phenomenon of rubber-like elasticity, the hydrodynamic and thermodynamic properties of polymer solutions, and various optical properties are but a few that reflect the spatial character of the random macromolecule. W Kuhn and E Guth and H Mark made the first attempts at mathematical description of the spatial configurations of random chains. The complexities of bond geometry and of bond rotations, poorly understood at the time, were circumvented by taking refuge in the analogy to unrestricted random flights, the theory of which had been fully developed by Lord Rayleigh. The skeletal bonds of the molecular chain were thus likened to the steps in a random walk in three dimensions, the steps being uncorrelated one to another. Restrictions imposed by bond angles and hindrances to rotation were dismissed on the grounds that they should not affect the form of the results.

For a random flight chain consisting of n bonds each of length l , the mean-square of the distance r between the ends of the chain is given by the familiar relation

$$\langle r^2 \rangle = nl^2 \quad (1)$$

The angle brackets denote the average taken over all configurations. Kuhn argued that the consequences of fixed bond angles and hindrances to rotation could be accommodated by letting several bonds of the chain molecule be represented by one longer "equivalent" bond, or step, of the random flight. This would require n to be diminished and l to be increased in Eq. 1. Equivalently, one may preserve the identification of n and l with the actual molecular quantities and replace Eq. (1) with

$$\langle r^2 \rangle = Cnl^2 \quad (2)$$

where C is a constant for polymers of a given homologous series, i.e., for polymers differing in length but composed of identical monomeric units. The proportionality between $\langle r^2 \rangle$ and chain length expressed in Eq. (2) may be shown to hold for any random chain of finite flexibility, regardless of the structure, provided that the chain is of sufficient length, and that it is unperturbed by external forces *or by effects due to excluded volume*.



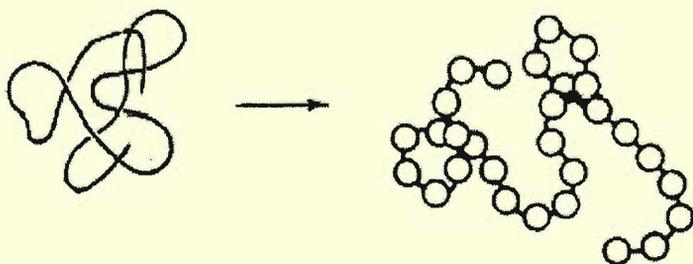


Figure 2. The effect of excluded volume. The configuration on the left represents the random coil in absence of volume exclusion, the chain being equivalent to a line in space. In the sketch on the right, the units of the chain occupy finite domains from which other units are excluded, with the result that the average size of the configuration is increased.

Excluded volume refers to the fact that a molecule is forbidden to adopt a configuration in which two of its parts, or segments, occupy the same space. Volume exclusion vitiates the analogy between the trajectory of a particle executing a random flight and the molecular chain, a material body. The particle may cross its own path at will, but self-intersections of the polymer chain are forbidden.

In this analogy of the trajectory traced by a particle undergoing a sequence of finite displacements, we consider only those trajectories that are free of intersections as being acceptable for the chain molecule. Directions of successive steps may or may not be correlated, i.e., restrictions on bond angles and rotational hindrances may or may not be operative; this is immaterial with respect to the matter immediately at hand. Obviously, the set of eligible configurations will occupy a larger domain, on the average, than those having one or more self-intersections. Hence, volume exclusion must cause $\langle r^2 \rangle$ to increase. The associated expansion of the spatial configuration is illustrated in *Figure 2*.

This much is readily evident. Assessment of the magnitude of the perturbation of the configuration and its dependence on chain length require a more penetrating examination. The problem has two interrelated parts: (i) the mutual exclusion of the space occupied by segments comprising the chain tends to disperse them over a larger volume, and (ii) the concomitant alteration of the chain configuration opposes expansion of the chain. Volume exclusion (i) is commonplace. It is prevalent in conventional dilute solutions and in real gases, molecules of which mutually exclude one another. In the polymer chain the same rules of exclusion apply, but treatment of the problem is complicated by its association with (ii).

Pursuing the analogies to dilute solutions and gases, we adopt a 'smoothed density' or 'mean field' model. The segments of the chain, x in number, are considered to pervade a volume V , the connections between them being ignored insofar as part (i) is concerned. The segment need not be defined explicitly; it may be identified with a repeating unit or some other approximately isometric portion of the chain. In any case, x will be proportional to the number n of bonds; in general $x \neq n$, however. For simplicity, we may consider the segment density ρ to be uniform throughout the volume V ; that is, $\rho = x/V$ within V and $\rho = 0$ outside of V . This volume should be proportional to $\langle r^2 \rangle^{3/2}$, where $\langle r^2 \rangle$ is the mean-square separation of the ends of the chain averaged over those configurations not disallowed by excluded volume interactions. Accordingly, we let

$$V = A \langle r^2 \rangle^{3/2} \quad (3)$$

where A is a numerical factor expected to be of the order of magnitude of unity.

It is necessary to draw a distinction between $\langle r^2 \rangle$ for the chain perturbed by the effects of excluded volume and $\langle r^2 \rangle_0$ for the unperturbed chain in the absence of such effects. If α denotes the factor by which a linear dimension of the configuration is altered, then

$$\langle r^2 \rangle = \alpha \langle r^2 \rangle_0 \quad (4)$$

Equation (2), having been derived without regard for excluded volume interactions, should be replaced by (2')

$$\langle r^2 \rangle_0 = Cn l^2 \quad (2')$$

where C reaches a constant value with increase in n for any series of finitely flexible chains.

The smoothed density within the domain of a linear macromolecule having a molecular weight of 100,000 or greater (i.e., $n > 1000$) is low, only on the order of one percent or less of the space being occupied by chain segments. For a random dispersion of the segments over the volume V , encounters in which segments overlap are rare in the sense that few of them are thus involved. However, the expectation that such a dispersion is entirely free of overlaps between any pair of segments is very small for a long chain. The attrition of configurations due to excluded volume is therefore severe.

In light of the low segment density, it suffices to consider only binary encounters.



Hence, if β is the volume excluded by a segment, the probability that an arbitrary distribution of their centers within the volume V is free of conflicts between any pair of segments is

$$P_{(i)} \approx \prod_{i=1}^x (1 - i\beta/V) \approx \exp(-\beta x^2 / 2V). \quad (5)$$

Introduction of Eq. (3) and (4) gives

$$P_{(i)} = \exp(-\beta x^2 / 2A \langle r^2 \rangle_0^{3/2} \alpha^3) \quad (6)$$

or, in terms of the conventional parameter z defined by

$$z = (3/2\pi)^{3/2} (\langle r^2 \rangle_0 / x)^{-3/2} x^{1/2} \beta, \quad (7)$$

$$P_{(i)} = \exp(-2^{1/2} (\pi/3)^{3/2} A^{-1} z \alpha^{-3}) \quad (8)$$

Since $\langle r^2 \rangle_0$ is proportional to x for long chains (see Eq. (2')), z depends on the square root of the chain length for a given series of polymer homologs.

We require also the possibility $P_{(ii)}$ of a set of configurations having the average density corresponding to the dilation α^3 relative to the probability of a set of configurations for which the density of segments corresponds to $\alpha^3 = 1$. For the former, the mean-square separation of the ends of the chain is $\langle r^2 \rangle$; for the latter it is $\langle r^2 \rangle_0$. The distribution of chain vectors \mathbf{r} for the unperturbed chain is approximately Gaussian. That is to say, the probability that \mathbf{r} falls in the range \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ is

$$W(\mathbf{r})d\mathbf{r} = \text{Const} \exp(-3r^2/2\langle r^2 \rangle_0) d\mathbf{r}, \quad (9)$$

where $d\mathbf{r}$ denotes the element of volume. The required factor is the ratio of the probabilities for the dilated and the undilated set of configurations. These probabilities, obtained by taking the products of $W(\mathbf{r})d\mathbf{r}$ over the respective set of configurations, are expressed by $W(\mathbf{r})$ according to Eq. (9) with r^2 therein replaced by the respective mean values, $\langle r^2 \rangle$ and $\langle r^2 \rangle_0$, for the perturbed and unperturbed sets. Bearing in mind that the volume element $d\mathbf{r}$ is dilated as well, we thus obtain

$$\begin{aligned} P_{(ii)} &= [(d\mathbf{r})/(d\mathbf{r})_0] \exp[-3(\langle r^2 \rangle - \langle r^2 \rangle_0)/2\langle r^2 \rangle_0] \\ &= \alpha^3 \exp[-(3/2)(\alpha^2 - 1)]. \end{aligned} \quad (10)$$



$$P_{(i)} P_{(ii)} = \alpha^3 \exp[-2^{1/2} (\pi/3)^{3/2} A^{-1} z \alpha^{-3} - (3/2)(\alpha^2 - 1)] \quad (11)$$

The combined probability of the state defined by the dilation α^3 is

$$\alpha^5 - \alpha^3 = 2^{1/2} (\pi/3)^{3/2} A^{-1} z \quad (12)$$

Recalling that z is proportional to $x^{1/2}$ (according to Eq.(7)), one may express this result alternatively as follows

$$\alpha^5 - A^3 = Bx^{1/2}\beta, \quad (12')$$

where $B = (\langle r^2 \rangle_0/x)^{-3/2} (2A)^{-1}$ is a constant for a given series of polymer homologs.

Treatments carried out with various refinements affirm the essential validity of the result expressed by Eq. (12) or 12'). They show conclusively that the form of the result should hold in the limit of large values of $(\beta x^{1/2})$, i.e., for large excluded volume and/or high chain length, and hence for $\alpha \gg 1$. In this limit, $(\alpha^5 - \alpha^3)/z = 1.67$ according to Fujita and Norisuye. For $\alpha \sim 1.4$, however, this ratio decreases, reaching a value of 1.276 at $\alpha = 1$.

The general utility of the foregoing result derived from the most elementary considerations is thus substantiated by the elaboration and refinement of the analysis, the quantitative inaccuracy of Eqs. (12) and (12') in the range $1.0 < \alpha \leq 1.4$ notwithstanding. The relationship between α and the parameter z prescribed in these equations, especially as refined by Fujita and Niroisuye, appears to be well supported by experiment.

The principal conclusions to be drawn from the foregoing results are the following: the expansion of the configuration due to volume exclusion increases with the chain length without limit for $\beta > 0$; for very large values of $\beta x^{1/2}$ relative to $(\langle r^2 \rangle_0/x)^{3/2}$ it should increase as the 1/10 power of the chain length. The sustained increase of the perturbation with chain length reflects the fact that interactions between segments that are remote in sequence along the chain are dominant in affecting the dimensions of the chain. It is on this account that the excluded volume effect is often referred to as a long-range interaction.

The analysis of the spatial configurations of macromolecular chains presented above is addressed primarily to an isolated molecule, as it exists, for example, in a dilute



solution. On theoretical grounds, the results obtained should be equally applicable to the molecules as they occur in an amorphous polymer, even in total absence of a diluent. This assertion follows unambiguously from the statistical thermodynamics of mixing of polymer chains, including their mixtures with low molecular diluents. It has evoked much skepticism, however, and opinions to the contrary have been widespread. These opposing views stem primarily from qualitative arguments to the effect that difficulties inherent in the packing of long chains of consecutively connected segments to space-filling density can only be resolved either by alignment of the chains in bundle arrays, or by segregation of individual molecules in the form of compact globules. In either circumstance, the chain configuration would be altered drastically.

Whereas dense packing of polymer chains may appear to be a distressing task, a thorough examination of the problem leads to the firm conclusion that macromolecular chains whose structures offer sufficient flexibility are capable of meeting the challenge without departure or deviation from their intrinsic proclivities. In brief, the number of configurations the chains may assume is sufficiently great to guarantee numerous combinations of arrangements in which the condition of mutual exclusion of space is met throughout the system as a whole. Moreover, the task of packing chain molecules is not made easier by partial ordering of the chains or by segregating them. Any state of organization short of complete abandonment of disorder in favor of creation of a crystalline phase offers no advantage, in a statistical-thermodynamic sense.

Theoretical arguments aside, experimental evidence is compelling in showing the chains to occur in random configurations in amorphous polymers, and further that these configurations correspond quantitatively with those of the unperturbed state discussed above. The evidence comes from a variety of sources: from investigations on rubber elasticity, chemical cyclization equilibria, thermodynamics of solutions, and, most recently, from neutron scattering studies on protonated polymers in deuterated hosts (or vice versa). The investigations last mentioned go further. They confirm the prediction made twenty-five years ago that the excluded volume perturbation should be annulled in the bulk amorphous state. The excluded volume effect is therefore an aberration of the dilute solution, which, unfortunately, is the medium preferred for physicochemical characterization of macromolecules.

Knowledge gained through investigations, theoretical and experimental, on the spatial configuration and associated properties of random macromolecular chains acquires



added significance and importance from its direct, quantitative applicability to the amorphous state. In a somewhat less quantitative sense, this knowledge applies to the inter-crystalline regions of semi-crystalline polymers as well. It is the special properties of polymeric materials in amorphous phases that render them uniquely suited to many of the functions they perform both in biological systems and in technological applications. These properties are intimately related to the nature of the spatial configurations of the constituent molecules.

Investigation of the conformations and spatial configurations of macromolecular chains is motivated therefore by considerations that go much beyond its appeal as a stimulating intellectual exercise. Acquisition of a thorough understanding of the subject must be regarded as indispensable to the comprehension of rational connections between chemical constitution and those properties that render polymers essential to living organisms and to the needs of man.

Excerpts from Flory's Nobel Banquet Speech

Perhaps I may be permitted to reflect briefly on Alfred Nobel the man vis-à-vis the prizes that bear his name. Lest it seems presumptuous of me to comment on that great but little appreciated man, may I remind you that I too am a chemist. In fact, my researches have touched upon one of the principal ingredients of his epochal discoveries and inventions. I refer to nitrocellulose. To be sure, our interests in this substance differed: his of a scope leading to developments warranting world-wide fame, mine obscure by comparison. Be this as it may, nitrocellulose is a duly respected member of the family of macromolecules, and I take pride in laying claim to scientific kinship to Alfred Nobel through an interest in this substance, however tenuous the connection may be.

