THE VOLUME EXCLUSION EFFECT IN FLEXIBLE LONG CHAIN MOLECULES

A Thesis

Submitted to the Faculty

of

Purdue University

by

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In Partial Fulfillment of the
Requirements for the Degree

of

Doctor of Philosophy

June 1955

14515

PURDUE UNIVERSITY

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION

BY IRA JACOBS

ENTITLED THE VOLUME EXCLUSION EFFECT

IN FLEXIBLE LONG CHAIN MOLECULES

COMPLIES WITH THE UNIVERSITY REGULATIONS ON GRADUATION THESES

AND IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Dr. H. M. James for his indispensable aid, guidance, and encouragement throughout the course of this research.

The writer is grateful to the Purdue Research Foundation for financial support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Jacobs, Ira. Ph.D., Purdue University, June 1955.
The Volume Exclusion Effect in Flexible Long Chain Molecules.
Major Professor: Hubert M. James

A theoretical description of the volume exclusion effect in flexible long chain molecules is developed. A chain of impenetrable small beads is considered as a model of a macromolecule, and the statistical properties of this model are investigated in an attempt to explain a discrepancy between experiment and statistical theories neglecting volume exclusion.

Light scattering and viscosity measurements, quoted in Chapter I, indicate that the mean square chain extension, $\langle r^2 \rangle$, increases as $t^{1.2}$, where t is the number of links in the chain. Statistical theories considering only local hindrances give $\langle r^2 \rangle \sim t$.

A critical discussion of the literature on volume exclusion is given in Chapter II. Theories leading to the result $\langle r^2 \rangle \sim t$ in the limit of large t are criticized on one of the two following points:

i) The effect of volume exclusion can not be considered as a short-range correlation.

ii) Normalization of the transition weights in an analogous random-walk problem incorrectly weights the configurations of an actual chain.

Treatments leading to the result $\langle r^2 \rangle = t + \beta t^{\frac{1}{2}}$ are also criticized.

By relating the weights of configurations of t and t+1 links, a systematic formulation of the theory is developed in Chapter III. For mathematical convenience, volume exclusion due to the end beads is neglected. Integration over the co-ordinates of all but the end beads gives an integro-difference equation for $\Phi_0(t,\vec{r})$, the weight density of configurations of a chain of t links with extension $\vec{r}$. This equation contains a function, $\Phi_1(t,\vec{r}:\vec{r})$, the weight density of configurations in which another bead is at $\vec{r}$. Likewise, an integro-difference equation for Φ_1 is derived, containing a function Φ_2. In this way a system of t-1 equations can be obtained, which in principle can be used to calculate $\Phi_0(t,\vec{r})$. A method of successive approximations is proposed. Solutions are obtained in the absence of volume exclusion and in a first approximation, but the second-order calculation is not successfully completed. It is shown that the first-order result correctly excludes all configurations containing an interference (say, between beads i and j) such that there are no interferences between beads on opposite sides of either i or j, or between beads both of which lie between i and j.

In Chapter IV a limiting procedure is considered whereby the integro-difference equation for $\Phi_0(t,\vec{r})$ is replaced by a boundary value problem. Successive approximations to $\Phi_0(t,\vec{r})$ are defined by specifying successive approximations to $F(t,\vec{r}:\vec{r}) = \Phi_1(t,\vec{r}:\vec{r})/\Phi_0(t,\vec{r})$. The first-order calculation of James is shown to be formally valid

over a wider range of r values than he considers. It is shown that for values of $vt^{1/2} \geq 0.6$ to 2.0 the first order theory predicts $\langle r^2 \rangle \sim t^{1.25}$ in good agreement with experimental and Monte Carlo results. (The volume, v, excluded to all other beads by a single bead, is measured in units in which the rms link length is one.) For large values of $vt^{1/2}$, the first-order theory predicts $\langle r^2 \rangle \sim t^2$, but it is shown that the second-order calculation will give significant corrections in this range. The second-order calculation is considered in detail. Inadequate approximations can lead to either the first-order result or to the conclusion that volume exclusion is negligible in effect. Mathematical difficulties prevent any definite conclusion from being drawn.

In Chapter V it is shown how $\langle r^2 \rangle$ can be directly evaluated without explicitly determining $\Phi_s(t,\vec{r})$. The results are seen to be hypersensitive to the approximations made, and without extensive numerical computations, not considered here, the method is not useful.

The difficulty in further extending the calculation, due to the fact that the relative number of allowable configurations decreases exponentially with t, is discussed.

CHAPTER I

THE DISCREPANCY BETWEEN EARLY THEORY AND EXPERIMENT

1. Introduction

Since the early work of Kuhn (30) and Guth and Mark (20), considerable attention has been given to the application of statistical mechanics to the theoretical description of high polymers. We shall restrict our attention to linear polymers--that is, macromolecules in which the structural units are bonded to one another in linear sequence to form an unbranched chain. In particular, we shall consider here the configurations of these macromolecules in dilute solution, such that intermolecular interactions can be neglected. The main purpose of this work will be to obtain a statistical description of the configurations of flexible long chain molecules, giving for example the dependence of mean dimensions upon molecular weight. In an attempt to explain a discrepancy between the earlier theories and recent experimental results, we shall consider particularly the volume exclusion effect--that is, our model will take cognizance of the fact that no two parts of the chain can occupy the same position in space.

A brief description of pertinent experimental results will be given before we discuss the various theoretical models that have been used.

2. Light Scattering and Viscosity Studies

Light scattering from dilute solutions provides not only one of the most useful means for determining the molecular weight of high polymers, but also a means for determining the average dimensions of randomly coiled molecules in solution.

If the dimensions of the scattering molecule are small compared to the wavelength of the light, and if the solution is sufficiently dilute, then the excess scattering due to solute can be simply calculated by classical theory. If it is assumed that the scattering is due to induced dipoles and that the polarizing field is just the field of the incident radiation, undistorted by the presence of other scattering molecules, classical electromagnetic theory gives the following results. (5, 6, 11) If the incident radiation is unpolarized, then the scattering through an angle θ is proportional to $1+\cos^2\theta$, being symmetric about $\theta=\frac{\pi}{2}$. If the incident radiation is linearly polarized, then the scattered intensity is proportional to the square of the sine of the angle between the direction of polarization and the direction of scattering; consequently the scattering will be isotropic in the plane perpendicular to the direction of polarization.

For molecules with dimensions comparable to the wavelength of the light, it becomes necessary to consider the interference between light waves scattered from different

segments of the same molecule. It is clear that this will affect the angular distribution of the scattered intensity, and, from this angular distribution, information concerning the dimensions of the molecule can be obtained. Following the same procedure used in the theory of the scattering of X-rays by a gas, Debye (6, 7) evaluates the angular distribution due to interference, P (Θ), by means of the relation

$$P(\theta) \sim \left\langle \sum_m \sum_n \frac{\sin\left(\frac{2\pi}{\lambda} s r_{mn}\right)}{\frac{2\pi}{\lambda} s r_{mn}} \right\rangle, \tag{1.1}$$

where

$$s = 2 \sin \frac{\theta}{2}, \tag{1.2}$$

r_{mn} is the distance between segments m and n, and the average (indicated by the angular brackets) is over all configurations. If one assumes that r_{mn} is distributed normally with dispersion proportional to m-n, which is a consequence of the simple statistical models discussed in the next section, the average over all configurations and summation gives

$$P(\theta) = \frac{2}{u^2}\left[e^{-u} - (1-u)\right], \tag{1.3}$$

where

$$u = \frac{2\pi^2 s^2}{3\lambda^2} \langle r^2 \rangle \tag{1.4}$$

and $\langle r^2 \rangle$ is the mean square end to end separation of the chain. This result has also been obtained by Zimm (54), who in addition finds in the first approximation the effect of interactions between molecules. His result can be written

$$\frac{Kc}{I(\theta)} = \frac{1}{MP(\theta)} + 2A_2c, \qquad (1.5)$$

where M is the molecular weight, and c is the concentration by weight of the solute; $I(\theta)$ is the intensity scattered at an angle θ ; and A_2 is a parameter that depends upon the polymer-solvent interaction, being larger the better the solvent. K depends on the indices of refraction of solvent and solute, and upon the wavelength of the radiation. It also contains the angular dependence of the small particle scattering. Most experimental procedures (36, 42, 43, 55) use linearly polarized light and observe scattering in the plane perpendicular to the direction of polarization, so that there is no angular dependence of K. The experimental results are extrapolated to infinite dilution, and then the $(c/I)_{c=0}$ vs. $\sin^2\frac{\theta}{2}$ plot is extrapolated to $\theta = 0$. The molecular weight M is obtained from the intercept, and $\langle r^2 \rangle$ is determined from the initial slope. Although the calculation mentioned here involves an assumption of a distribution for r_{mn}, it will be shown in Appendix A that this procedure gives the mean square distance of the elementary scatterers from the center of gravity of the molecule, independent of the distribution.

In practice, even with careful fractionation, the solute will contain a distribution of molecules with different degrees of polymerization. If c_i is the concentration by

weight of molecules with molecular weight M_i, then the M calculated by the above procedure will be the weight average molecular weight, $\bar{M}_w$, defined by the relation

$$\bar{M}_w = \frac{1}{c} \sum c_i M_i . \tag{1.6}$$

The $\langle r^2 \rangle$ determined by the above procedure will be averaged somewhat differently, and to obtain the weight average, some knowledge must be had of the distribution of degrees of polymerization. Shultz (43) uses measurements in solvents where $A_2 = 0$ to obtain the dispersion of this distribution, but we shall not go into the detail of his procedure.

The measurements of Zimm (55) and Outer, Carr, Zimm (36) were designed to show the effect of temperature and solvent upon molecular dimensions. The molecule is considerably more extended in a good solvent than it is in a poor solvent. In good solvents there is a slight tendency for the molecule to become smaller with increasing temperature, indicating that the chain is extended by interaction energies considerably larger than kT. In the case of poor solvents, however, there is a positive temperature coefficient.

For the problem here considered, we are not directly interested in these effects, but rather in the dependence of $\langle r^2 \rangle$ upon M at a fixed temperature in a good solvent. For this purpose we quote Shultz's (43) results on light scattering by polyvinylacetate in methyl ethyl ketone. By a least square fit on a log-log plot, he finds $\langle r^2 \rangle / M$ proportional to $M^{0.46}$ over a range of molecular weight from

0.87×10^6 to 3.46×10^6 gm. On the basis of their measurements on polymethylmethacrylate in acetone, benzene, and chloroform, Schultz, Cantow, and Meyerhoff (42) conclude that $\langle r^2 \rangle / M$ is proportional to $M^{a.2}$. Their measurements were over approximately the same molecular weight range, and the values of $\langle r^2 \rangle^{1/2}$ ranged from 600 to 3000Å.

Light scattering methods are essentially limited to the above range. Another means of determining average polymer dimensions is by measurement of the intrinsic viscosity of a polymer in solution. The intrinsic viscosity is defined as the fractional increase in viscosity per unit concentration, in the limit as the concentration goes to zero, that is,

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{solution} - \eta_{solvent}}{c \eta_{solvent}} \right). \qquad (1.7)$$

We shall not discuss any of the viscosity theories (8, 27), but shall mention a semi-empirical method by which viscosity measurements can be used to calculate $\langle r^2 \rangle$. If the polymer is considered as a sphere (radius R_{eff}) that is impenetrable to the solvent, it can be shown (8) that $[\eta] \sim R_{eff}^3 / M$. Assuming $R_{eff}^2 \sim \langle r^2 \rangle$, one has (11, 14, 43)

$$[\eta] = \frac{\Phi \langle r^2 \rangle^{3/2}}{M}, \qquad (1.8)$$

where Φ should be a constant independent of solute or solvent, provided that the solute is a polymer of the random coil type. With $\langle r^2 \rangle$ and M obtained from light scattering

data on many polymers over an extensive molecular weight range, the $\bar{\Phi}$ calculated from Eq. (1.8) is essentially constant. For $[\eta]$ in 100 cm^3/gm, M in gm./mole, and r in cm., $\bar{\Phi} = (2.1 \pm 0.2)\ 10^{21}$.

As a check on Eq. (1.8), the viscosity data of Schultz, Cantow, and Meyerhoff (42), which is given in Table 1, will be considered. (Except for columns marked EMP, this data is taken from Tables V and VII of the SCM paper.) K R designates values of $\langle r^2 \rangle^{1/2}$ calculated from the Kirkwood-Riseman (27) theory, and DB designates values calculated from the Debye-Bueche (8) theory. EMP designates values calculated using Eq. (1.8) with $\bar{\Phi} = 2.1 \times 10^{21}$. It is to be noted that these last values in all cases lie between the values predicted by the two theories. SCM plot $\langle r^2 \rangle^{1/2}$ against M for both the KR and DB theories and obtain parallel lines on a log-log plot. Their results are

$[\eta] \sim M^{0.72}$ and $\langle r^2 \rangle^{1/2} \sim M^{0.58}$ in acetone,

$[\eta] \sim M^{0.76}$ and $\langle r^2 \rangle^{1/2} \sim M^{0.59}$ in benzene,

and $[\eta] \sim M^{0.79}$ and $\langle r^2 \rangle^{1/2} \sim M^{0.60}$ in chloroform.

Their final conclusion is that in a good solvent, the root mean square extension of a polymethylmethacrylate molecule is proportional to $M^{0.6}$.

The values of $\langle r^2 \rangle$ calculated from light scattering lie between the values calculated by the KR and DB theories, and are in good agreement with the empirical values, giving additional support to the empirical result Eq. (1.8). $\langle r^2 \rangle^{1/2}$ can be calculated from Eq. (1.8) when M is determined by

VISCOSITY MEASUREMENTS OF THE DIMENSIONS

OF POLYMETHYLMETHACRYLATES

IN ACETONE; BENZENE, CHLOROFORM (42)

TABLE 1

Sample	$M \times 10^{-3}$	$[\eta]$ (100 cm³/gm.)			$\langle r^2 \rangle^{1/2}$ (Å)								
					Acetone			Benzene			Chloroform		
		Acetone	Benzene	Chloroform	KR	DB	EMP	KR	DB	EMP	KR	DB	EMP
A	7440	5.50	8.90	14.0	2880	2300	2690	3520	2820	3160	4310	3460	3670
B	4590	3.88	6.70	9.65	2180	1740	2040	2730	2180	2450	3240	2600	2760
C	3210	3.10	4.70	7.23	1800	1432	1680	2160	1720	1930	2610	2085	2230
D	2020	1.96	3.42	5.20	1320	1054	1240	1660	1324	1490	2000	1608	1710
E	1420	1.49	2.69	3.80	1070	856	1000	1360	1088	1220	1610	1288	1370
F	611	0.830	1.31	1.90	666	532	623	809	646	725	944	772	821
G	306	0.520	0.881	1.28	453	361	423	564	449	504	670	537	571
H	148	0.315	0.478	0.695	301	240	281	360	288	323	429	344	366
I	63.5	0.175	0.240	0.350	186	149	174	216	172	194	248	206	220
K	24.6	0.102	0.126	0.182	113	91	106	127	102	114	151	121	129

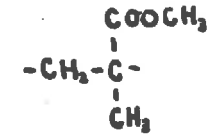
some independent means, such as from sedimentation and diffusion constants (11). This procedure for determining $\langle r^2 \rangle$ is largely empirical, and unlike light scattering, does not give any direct indication of the actual distribution of the segments. It is to be hoped that as additional light scattering data is obtained, and uncertainties due to extrapolations and incomplete knowledge of polymerization distribution are reduced, that the angular distribution of the scattered light can give additional information on the actual distribution of segments in the chain.

3. Statistical Models

The simplest example of an unbranched chain polymer is one having a formula of the type

$$A' - A - A - A - \cdots - A - A'',$$

which can also be written as $A' (- A -)_{x-2} A''$. The principal structural unit is designated by A, and x is the degree of polymerization. For example, in polymethylmethacrylate, the principal structural unit is (11, p. 254)



The end units A' and A'' are monovalent and are usually related to the principal structural unit. In general, in such covalent structures, the bond angles are fixed, but a great variety of configurations are still possible because of rotations about bonds, both those within the structural units, and those joining structural units. Since the bond

lengths are of the same order of magnitude as atomic dimensions, the over-all structure will resemble that of closely packed spheres, arranged in such a way as to form a rather jagged chain. (See, for example, Fig. 1 of Reference 32.) We shall not discuss the detailed structure of real polymers, but shall consider highly idealized models that are useful in predicting and understanding the physical behavior of these molecules.

The simplest such model is the perfectly flexible chain model. We consider a chain of t links, each link having the fixed length l. The chain is said to be perfectly flexible if there is no potential energy depending on the relative orientation of the links. With the neglection of kinetic effects to be mentioned below, every configuration of a perfectly flexible chain will be equally probable. We desire to calculate $\mathcal{P}_t(t, \vec{r})$, where $\mathcal{P}_t(t, \vec{r})d\vec{r}$ is the probability that a chain of t links has end to end separation $\vec{r}$ to within $d\vec{r}$*. (For convenience, we shall henceforth refer to $\mathcal{P}_t(t,\vec{r})$ as "the distribution of extensions.") This problem can also be formulated in terms of a random walk of t steps, each step having fixed length l, but random orientation; the problem is then to determine the probability that after t steps one is at a directed distance $\vec{r}$ (to within $d\vec{r}$) from the origin. For large t and for $r \ll lt$, the distribution of extensions is given by [see, for instance,

*In this work $d\vec{r}$ always refers to a three dimensional volume element, and $\int d\vec{r}\ldots$ refers to an integration over all space.

Chandrasekhar (3).]

$$\bar{\Phi}_0(t,\vec{r}) = \left(\frac{3}{2\pi t l^2}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{l^2 t}\right). \tag{1.9}$$

From Eq. (1.9) it follows that the mean square extension, $\langle r^2 \rangle$, is given by

$$\langle r^2 \rangle = l^2 t. \tag{1.10}$$

Equation (1.10) is an exact result valid for all t. It does not depend on the approximations made in the derivation of Eq. (1.9). This can be seen by calculating $\langle r^2 \rangle$ directly. Since

$$\vec{r} = \sum_{i=1}^{t} \vec{l}_i \tag{1.11}$$

it follows that

$$\langle r^2 \rangle = \sum_{i=1}^{t} \sum_{j=1}^{t} \langle \vec{l}_i \cdot \vec{l}_j \rangle . \tag{1.12}$$

For a perfectly flexible chain

$$\langle \vec{l}_i \cdot \vec{l}_j \rangle = l^2 \delta_{ij} \tag{1.13}$$

and Eq. (1.10) follows immediately.

If one attempts to use Eq. (1.10) to calculate $\langle r^2 \rangle$ for an actual polymer, with t being the degree of polymerization, and l being the C – C distance, 1.54 Å (6), one finds in general values considerably less than those obtained from experimental measurements. This will be illustrated by considering the results of Schultz, Cantow, and Meyerhoff (42) given in Table 1. The structural unit in polymethylmethacrylate has a molecular weight of 100, so that

the degree of polymerization of sample A (see Table 1) is 7.44×10^4. From Eq. (1.10)

$$\langle r^2 \rangle^{1/2} = \sqrt{7.44 \times 10^4} \times 1.54 \text{ Å} = 421 \text{ Å}.$$

Comparison with Table 1 shows that the above value is several times smaller than the experimental values.

To avoid this discrepancy, use is sometimes made of a somewhat more realistic model in which there is a fixed angle θ between consecutive links of the chain (9, 51). If one assumes free rotation about the links, (see Fig. 1), Eq. (1.12) leads to

$$\langle r^2 \rangle = tl^2 \frac{1 - \cos\theta}{1 + \cos\theta}, \qquad (1.14)$$

where terms independent of t are neglected.

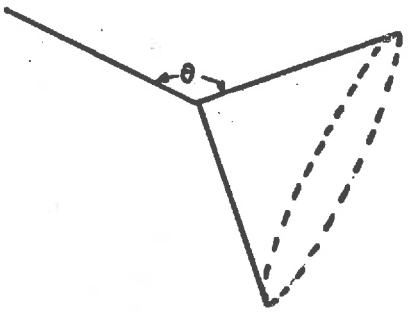


Fig. 1
Illustration of Free Rotation

Another refinement of the model that has been considered is that of hindered rotation about the links (45, 46, 7)—

that is, the rotations, instead of being free, are restricted by a potential. All such models lead to results of the form

$$\langle r^2 \rangle = t l_{eff}^2 \quad , \tag{1.15}$$

where the effective link length, l_{eff} , will depend upon the nature of the hindrances. For t sufficiently large and for r much less than maximum extension, it can be shown (3, 47) that the distribution of extensions is given by Eq. (1.9) with l replaced by l_{eff} . This can be seen roughly by considering the "statistical chain element" of Kuhn (30, 31, 32). In a chain with local correlations (such as a fixed angle between consecutive links) units of τ links can be taken, such that while there is a correlation between orientations of consecutive links, there will be no appreciable correlation between the direction of the vectors joining the ends of these units. Thus Kuhn reduces the chain of t links with local correlations to that of a perfectly flexible chain of t/τ units, for which the distribution is known to be Gaussian with dispersion equal to $\frac{t}{\tau}\langle r^2 \rangle_\tau$. But we can write

$$\langle r^2 \rangle_\tau = \tau \, l_{eff}^2 \quad ,$$

which leads to the desired result

$$\Phi_0(t,\vec{r}) = \left(\frac{3}{2\pi t l_{eff}^2}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{l_{eff}^2 t}\right). \tag{1.16}$$

(The above argument assumes both τ and t/τ relatively large.)

In considering massless chains, all of the above models have neglected kinetic effects. More generally, one can follow a common procedure in statistical mechanics and con-

sider a canonical ensemble of molecules, in which the density of molecules in phase space is proportional to $e^{-\text{Energy}/kT}$. To determine $\Phi_0(t, \vec{r})$ one then integrates the ensemble density function over all of phase space consistent with the condition that the extension of the molecule be $\vec{r}$. (For a discussion of the various degrees of freedom specifying the phase space of a real chain molecule, and the approximations that are commonly made when one is only interested in configurational properties, see for example Kubo (29).) The integration over degrees of freedom other than the configurational co-ordinates affects $\Phi_0(t, \vec{r})$ if the results of these integrations depend upon the configurational co-ordinates. It is known, for example, that integration over the momenta conjugate to the configurational co-ordinates gives $(2\pi kT)^{n/2} \cdot D^{1/2}$, (16), where n is the number of generalized co-ordinates, and D is the determinant of the coefficients of the generalized velocities in the expression for the kinetic energy. Kramers (28) considers the behavior of a system of mutually connected point masses (pearl necklace model) under the action of an inhomogeneous flow of solvent. He explicitly evaluates D for a small number of point masses, and finds that it is larger for more highly coiled configurations than it is for extended configurations. For long chains, however, it is always tacitly assumed that these effects can be neglected, and we shall not consider this point any further. Thus, for example, the perfectly flexible chain model starts with the basic assumption that all

configurations of the chain are equally probable.

It has been pointed out for the case of nearest neighbor correlations (such as fixed bond angles and hindered rotation about bonds) that the mean square chain extension is given by

$$\langle r^2 \rangle = t\, l_{eff}^2 \quad . \tag{1.15}$$

Since the correlations usually increase the effective link length, Eq. (1.15) can be used to explain partially the discrepancy found when calculating $\langle r^2 \rangle$ using the perfectly flexible chain model. It is seen, however, that Eq. (1.15) predicts that $\langle r^2 \rangle$ is proportional to t, and this prediction follows for any short-range correlation (47)—that is, correlations between links separated by less than a fixed number of links. Since the molecular weight M is proportional to t, all the above theories predict $\langle r^2 \rangle$ to be proportional to the first power of molecular weight. We have seen, however, that experimentally determined values of $\langle r^2 \rangle$ increase more rapidly than the first power of molecular weight.

The above discrepancy is generally attributed to the volume exclusion effect--that is, the fact that the location of a segment of the chain in a particular region of space excludes that region from occupancy by <u>any</u> other segment. This is not a short-range correlation; the distribution of each segment is affected by all other segments. A real polymer chain may resemble a heavy rope, the effect of volume exclusion being to disallow those figurations in which the

rope passes through itself. In the theoretical treatment of this effect, however, a variation of the pearl necklace model is most frequently used. In this model, instead of considering the "pearls" to be point masses, they are taken to be spherical beads with radii small compared to the length of the links joining them. Thus instead of considering a continuous distribution of volume, the volume of the chain is considered to be localized at the junctions of consecutive links.

Theories for the distribution of configurations of flexible chain molecules that have treated volume exclusion will be critically discussed and inter-related in Chapter II. We shall particularly consider the range of validity and the physical significance of various approximations in the hope of clarifying several misconceptions that have arisen. The need for additional theoretical work will be made clear, and succeeding chapters of this paper will consider the problem in detail. An outline of these chapters will be given at the end of Chapter II.

CHAPTER II

CRITICAL DISCUSSION OF THE LITERATURE ON VOLUME EXCLUSION

I. Importance of the Dimensionality of the Problem

In a paper appearing in 1934, Kuhn (30) recognized that the volume exclusion effect was not negligible. However, it was not until 1949 that there appeared any theory of chain extensions taking account of volume exclusion (12). From 1949 to the present time, there have been many such theories. Before discussing these, however, we shall mention some theorems, related to the excluded volume problem, which indicate the important dependence of the results upon the dimensionality of the problem.

We have already noted the equivalence of a perfectly flexible chain and a random walk. In turn there is clearly a similarity between a random walk and the Brownian motion of a free particle. (See for example Chandrasekhar (3), Chapter 2.) A path of a particle undergoing Brownian motion is said to have a double point if the path for infinitely large times passes through that point twice. Paths with double points correspond to chain configurations eliminated from consideration by the volume exclusion effect. The following theorems, quoted by Rubin (39), are of interest. In an n-dimensional Brownian motion ($n > 4$), almost all

paths (that is, all except for a set of paths having probability zero) have no double points, whereas in a two-dimensional Brownian motion, almost all paths come back to any neighborhood of any given point infinitely many times for infinitely large time. That is, in two dimensions, almost all paths constitute an everywhere dense set. Thus we may expect volume exclusion to be quite important in two dimensions, and negligible in four dimensions. The physically interesting case of three dimensions has caused considerable disagreement. In the case of a Brownian motion in three-dimensional space, almost all paths have infinitely many double points. However, almost all paths constitute a nowhere dense set; that is, the set of points of any path (except perhaps one having probability zero) is not dense to any interval of space. Thus it appears that three-dimensional problems of this type are significantly different from those in two or in four dimensions, in such a way that one can not foresee with confidence even the qualitative character of the effects of volume exclusion.

There are analogous theorems for recurrences in random walks on regular lattices. Consider in particular a random walk on a generalized square lattice, each lattice point having 2n nearest neighbors, where n is again the dimensionality of the space. Each step proceeds from a lattice site to a nearest neighbor, each of the 2n possible steps having probability 1/2n. With this model, there is probability one that the walk will return to its starting point in two

dimensions, while in three dimensions, this probability is 0.35 (10).

These results, while not indicating anything definite concerning the effect of volume exclusion in three dimensions, at least indicate the marked dimensional dependence of the problem. Quite frequently in statistical mechanical problems considerable insight into a three-dimensional problem can be gained by treating simpler problems in one or two dimensions. Such is not the case for volume exclusion.

2. Volume Exclusion as a Swelling Phenomenon

The first theory considering the effect of volume exclusion upon molecular dimensions was that of Flory (12). Subsequent papers by Flory and others (13, 14, 2, 50) have modified some of the details of the calculation but start with the basic assumption of Flory's original paper and arrive at essentially the same result. The basic assumption of Flory is that volume exclusion does not change the form of the distribution of extensions, but affects only the dispersion of the distribution. Thus he assumes that the distribution, taking account of volume exclusion, is given by

$$\Psi(t,\vec{r}) = \left[\frac{3}{2\pi\langle r^2\rangle}\right]^{3/2} \exp\left\{-\frac{3}{2}\frac{r^2}{\langle r^2\rangle}\right\}. \qquad (2.1)$$

He then writes

$$\langle r^2\rangle = \alpha^2\langle r_0^2\rangle \qquad (2.2)$$

where $\langle r_0^2\rangle$ is the mean square extension in the absence of volume exclusion, and by the theories of Chapter I is proportional to M. Flory proceeds to calculate α by

maximizing, with respect to α , the free energy of mixing of polymer and solvent. He obtains the relation

$$\alpha^5 - \alpha^3 = C' \left(1 - \frac{\Theta}{T}\right) M^{1/2} \qquad (2.3)$$

where Θ is a parameter characterizing the interaction of polymer and solvent having the dimension of temperature. (In a good solvent, $\Theta < 0$.) In the limit of very large M and for $T > \Theta$, $\alpha \sim M^{0.1}$, so that $\langle r^2 \rangle \sim M^{1.2}$. This result is in excellent agreement with the experimental results quoted in Chapter I. Also, the temperature dependence predicted by Eq. (2.3) is in accord with experiment (36, 55).

The basic assumption of Flory's theory is arbitrary, and no theoretical justification is given in any of his papers. To determine the reliability of these results, one would have to know how well the expanded Gaussian approximates the actual distribution. The difficulty inherent in this method, however, is that the basic assumption precludes any possibility of actually determining the distribution.

The theory of Flory is an approximate thermodynamic treatment of the effect of the interaction between polymer and solvent. It is not a statistical theory of chain configurations, the problem with which we are directly concerned.

3. Short-Ranged Correlations

Several of the earlier approaches have taken the orientation of a given link to be affected only by a fixed number

of the immediately preceding and following links, thus enabling the problem to be reduced to that of a Markoff chain (34). Montroll (35) considers a random walk on a two dimensional square lattice, such that each step is one unit at right angles to the previous step. He excludes "first-order overlaps," that is closed squares, but allows closed polygons of twelve or more steps. Thus the probability for making a given step depends on the previous three steps, but is independent of any of the earlier steps. Frisch, Collins, and Friedman (15) carry out similar calculations on a square lattice with no overlap in either four or twelve steps, and a diamond lattice with no overlap in six steps. King (25, 26) considers by punched card methods a polymer on a tetrahedral lattice. He takes sliding segments of twenty links whose configurations he assumes to be independent of any outside segments.

Frisch, Collins and Friedman do not arrive at any definite conclusion. Both Montroll and King are led to the conclusion that the extension $\vec{r}$ is still normally distributed, with $\langle r^2 \rangle$ proportional to the number of links (steps) in the chain (walk). As both Montroll (35) and Tchen (47) have noted, this result is to be expected for chains with any type of short-range correlation. However, the essential feature of the volume exclusion problem is that interactions between all parts of the chain must be considered. Any approach that considers only short-range correlations, and thus makes the problem equivalent to a Markoff process,

misses the essential and difficult feature of the volume exclusion problem.

4. Distribution of Extensions as a Definite Integral

Several authors (17, 38, 41, 48) have essentially considered the phase integral of an ensemble density function for a pearl necklace model with rigid sphere or other short range interactions*, in which the effects of all but the configurational co-ordinates are neglected, and the integration over the configurational co-ordinates is subject to the condition that the chain has fixed extension $\vec{r}$. The resulting integral, a function of $\vec{r}$, is proportional to the relative number of configurations of a chain with extension $\vec{r}$. From this function, which we have called the distribution of extensions, $\langle r^2 \rangle$ can be directly evaluated.

As is pointed out by Zimm, Stockmayer, and Fixman (56), Grimley's (17) model, which equates the chain of beads to an imperfect gas in a central force field, can be immediately dismissed, since correlations in the positions of the beads due to their being connected in a chain are neglected.

We shall consider here the work of Rubin (38),

*We are using "short-range correlation" and "short-range interaction" in decidedly different senses. The correlation refers to the orientation of the links in the chain, and the correlation is short ranged if the orientation of a given link is affected only by a fixed number of the immediately preceding and following links. The interaction refers to the forces between pairs of beads, and is of short range if these forces are appreciable only for small spatial separations of the beads. Thus an account of the volume exclusion effect for a pearl necklace model must consider long-range correlations but short-range interactions.

Teramoto (48) and Bueche (2, Sect. I); the approximations of Saito (41) are best understood in terms of material discussed in the next section of this chapter. For convenience in description, we shall outline the general formalism for the case of a pearl necklace of $t+1$ beads connected by t links, each of length l. We define a factor Δ_{ij} which is zero when beads i and j interfere, and one otherwise. The relative number of configurations having extension $\vec{r}$ is given by

$$\Phi_t(t,\vec{r}) = \int\cdots\int_{|\vec{r}_{i+1}-\vec{r}_i|=l} d\vec{r}_1 \cdots d\vec{r}_t \; \delta(\vec{r}_t-\vec{r}) \prod_{j>i} \Delta_{ij} \tag{2.4}$$

Letting

$$\varepsilon_{ij} = \Delta_{ij} - 1 \tag{2.5}$$

and expanding, we obtain

$$\Phi_t(t,\vec{r}) = \int\cdots\int d\vec{r}_1 \cdots d\vec{r}_t \left[1 + \sum \varepsilon_{ij} + \sum\sum \varepsilon_{ij}\,\varepsilon_{i'j'} + \cdots\right] \delta(\vec{r}_t-\vec{r}), \tag{2.6}$$

where the first sum goes over all pairs of beads, the second sum over all doublet of pairs, and so on. Neglecting all but the first two terms in the bracketed expression in Eq. (2.6), both Teramoto and Bueche obtain essentially the same result:

$$\langle r^2 \rangle = l^2 t \left[1 + k\left(b/l\right)^3 t^{1/2}\right], \tag{2.7}$$

where the constant k depends on the details of the model, and b is the effective diameter of the beads. While it is

true that the additional factors in Eq. (2.6) would give corrections depending on higher powers of b/l, it is not true that these corrections are negligible for very large t. In fact, as Rubin shows, the additional terms depend on higher powers of t, and hence for fixed b/l, become very large in the limit of large t. The range of validity of Eq. (2.7) is indicated by James (24), whose work will be discussed in the following section.

Rubin (38) recognizes that the higher order terms in Eq. (2.6) are important, but he is not able to obtain an explicit general result, taking account of all interactions. He then states that, if one considers only a restricted class of interactions, $\langle r^2 \rangle$ can easily be calculated. This class of interactions has the characteristic that when beads i and j interact, there are no interactions involving intermediate beads. (A similar approximation will be considered in Chapter IV.) It is to be emphasized, however, that while Rubin states that he will consider this approximation, he actually does not.

> One can therefore calculate separately the increase in $(\langle r^2 \rangle)$, caused by the interference of the j^{th} and $j+s^{th}$ (beads) and sum up the increments δ_s to obtain the total increase. δ_s is a useful quantity since it is an upper bound on the increase in size caused by the interaction of the j^{th} and $j+s^{th}$ (beads) when intermediate (beads) interact. The reason for this fact is that the interaction of intermediate (beads) increases the average distance between the j^{th} and $j+s^{th}$ (beads) and therefore decreases the contribution of their interaction to $(\langle r^2 \rangle)$ *.

*Quoted from page 1943 of reference 38. To conform to the terminology and notation we have been using, the word "step" has been replaced by "bead" and $\langle R_n^2 \rangle$ has been replaced by $\langle r^2 \rangle$.

This approximation is by no means equivalent to the one originally described. In fact by comparing Rubin's Eqs. (24) and (36) with his general result Eq. (12), it is seen that his actual approximation, like that of Bueche and Teramoto, is to include only the first sum in our Eq. (2.6); and he is led, like them, to a correction in $\langle r^2 \rangle$ that is proportional to $t^{3/2}$. Rubin, by the argument we have quoted above, says that this gives an upper bound to $\langle r^2 \rangle$.

That Rubin does not do what he originally says he is going to do, does not, of course, have any bearing on the validity of the conclusion he obtains from the calculation he actually makes. However, the last sentence of the material quoted from Rubin is open to question. The fact that the interaction of intermediate beads increases the average distance between the j^{th} and $(j+s)^{th}$ beads, only means that the probability for interference of these beads has been over-estimated. It does not mean that the contribution to $\langle r^2 \rangle$ has been over estimated; that will depend upon whether the over-estimation of the probability for interference of the j^{th} and $(j+s)^{th}$ beads is more important for configurations with large extension or for configurations with small extension. Thus Rubin inappropriately discusses the magnitude of the probability for interference when it is the gradient with respect to $\vec{r}$ of this quantity that is significant.

Even more important, James (24) gives a counter-example showing that Rubin's upper limit is based on an assumption

that is not mathematically rigorous. There is no reason to suppose that the sum of increments of $\langle r^2 \rangle$ due to several effects is an upper limit on the increment due to all effects acting together, or that a similar relation holds for upper limits of increments; for example, the effects may co-operate and reinforce each other. Thus, the conclusion of Rubin, while not necessarily incorrect, does not appear to be justified.

5. Integro-Difference Equations

Following a common procedure in random flight problems, many authors (18, 19, 21, 22, 23, 24, 52, 56) have considered the formulation of the excluded volume problem by means of integro-difference equations. Again, it will be convenient to develop some of the formalism here, before discussing these papers.

We consider a pearl necklace model, such that, in the absence of interactions, the probability that a link has a length between s and s + ds is given by $\left[4\pi s^2 g(s)ds\right]$. By definition g(s) is normalized; that is

$$\int d\vec{s}\, g(s) = 4\pi \int_0^\infty ds\, s^2 g(s) = 1 . \tag{2.8}$$

The mean-square link length is given by

$$\int d\vec{s}\, g(s) s^2 = 4\pi \int_0^\infty ds \cdot s^4 g(s) = l^2 . \tag{2.9}$$

We define $\vec{\Phi}_0(t,\vec{r})d\vec{r}$ to be the total weight of all configurations of a chain of t links with ends separated by $\vec{r}$ (to within $d\vec{r}$), subject to the following basic assumption

concerning weights. The weight W given to a configuration with link lengths s_i, $i = 1, 2, \ldots, t$, is given by

$$W = \begin{cases} 0 & \text{if any two beads interfere,} \\ \prod_{i=1}^{t} g(s_i)\,d\vec{s}_i & \text{if there are no interferences.} \end{cases} \tag{2.10}$$

This assumption reduces to that of giving equal weight to all configurations containing no interferences when the links have fixed length, and is a natural generalization for the more general case where the link lengths are described by a distribution g(s).

By considering the possibility of adding another link to the chain, one can write (21, 22, 23, 24).

$$\bar{\Phi}_0(t+1,\vec{r}) = \int d\vec{s}\, g(s)\, \bar{\Phi}_0(t,\vec{r}-\vec{s})\, \Psi(t,\vec{s},\vec{r}-\vec{s}) \tag{2.11}$$

where $\Psi(t, \vec{s}, \vec{r}-\vec{s})$ is the fraction of cases in which one can add a link of extension $\vec{s}$ to a chain of t links and extension $\vec{r}-\vec{s}$ without overlapping any other bead in the chain. We shall call the product,

$$Q(t, \vec{s}, \vec{r}-\vec{s}) = g(s)\, \Psi(t,\vec{s},\vec{r}-\vec{s}), \tag{2.12}$$

the "transition weight." Taking account of volume exclusion, James (24) obtains the following relation for the transition weight:

$$Q(t,\vec{s},\vec{r}-\vec{s}) = g(s)\left[1 - v\, F(t,\vec{r}-\vec{s};\vec{r})\right], \tag{2.13}$$

where $F(t, \vec{r}-\vec{s};\vec{r})$ is the density of beads at $\vec{r}$ when the t^{th} bead is at $\vec{r}-\vec{s}$, and the "excluded volume" v is equal to eight times the volume of a bead, and is assumed to be small compared to l^3.

A detailed systematic formulation of the problem will be given in the next chapter, where Eq. (2.13) will be derived, and $F(t, \vec{r}-\vec{s}, \vec{r})$ and v will be more precisely defined. The fact that Eqs. (2.11) and (2.13) are consistent with the basic assumption of Eq. (2.10) will also be seen to be an immediate consequence of the derivation given in the next chapter.

a. Normalization of the Transition Weight

Since the transition weight given by Eq. (2.13) is not normalized, the $\Phi_0(t, \vec{r})$ calculated from Eq. (2.11) will not be normalized. From Eq. (2.10) it can be shown that $\int d\vec{r}\, \Phi_0(t, \vec{r})$ gives the probability that there are no interferences in a chain of t links. Hermans (22), and Hermans, Klamkin, and Ullman (23, henceforth referred to as HKU) multiply the transition weight given by Eq. (2.13) by a normalizing factor, so that the $\Phi_0(t, \vec{r})$ calculated from Eq. (2.11) will be normalized. However, the $\Phi_0(t, \vec{r})$ so calculated would not be weighted according to our basic assumption, Eq. (2.10). This has been pointed out by Suzuki (44) in criticism of Montroll (35), and by James (24) in criticism of HKU (23). Since this point is apparently still causing confusion, [e.g. Wall (52)], it may be well to rephrase the argument here. We shall first illustrate the error due to using a normalized transition weight by considering a chain of six links on a two-dimensional square lattice, where successive links are required to be perpendicular. The total number of configurations of this chain is

$4 \times 2^5 = 128$. Of these, a simple enumeration shows that 64 involve double occupancies, so that there are only 64 remaining allowable configurations. Our basic assumption for this lattice, corresponding to Eq. (2.10), is that all allowable configurations have equal probability 1/64. If, on the other hand, we were to compute the probability of these configurations using normalized transition weights, we would consider each configuration as built up by adding successive links, with the probability of a given orientation of the link at each step equal to the reciprocal of the number of possible orientations for that link. With this weighting we would have for the respective probabilities of configurations a, b, c of Fig. 2

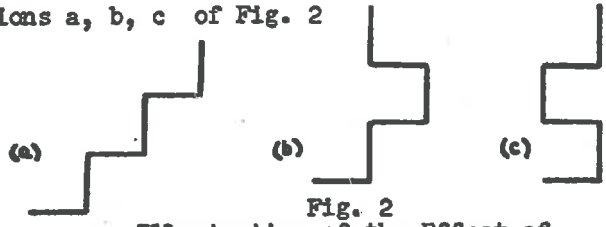


Fig. 2
Illustration of the Effect of
Normalized Transition Weights

$$P_a = (\tfrac{1}{4})(\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2}) = \frac{1}{128},$$

$$P_b = (\tfrac{1}{4})(\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2})(\tfrac{1}{2})(1) = \frac{1}{64},$$

$$P_c = (\tfrac{1}{4})(\tfrac{1}{2})(\tfrac{1}{2})(1)(\tfrac{1}{2})(1) = \frac{1}{32},$$

which does not correspond to the basic assumption of equal weights. It is easily seen that normalization of the transition weights tends to underweight the more extended configurations of the chain, and hence under-estimate the volume exclusion effect.

When the transition weight is normalized, the volume exclusion effect is only manifest in the dissymmetry of the transition weight at a given point; that is, it is more probable for the next link to go away from rather than towards the fixed end of the chain. This, however, is a secondary effect. The dominant effect is due to the fact that the transition weight depends upon the point at which the additional link is to be added, being greater the further this point is from the origin. Normalization of the transition weight loses this effect.

It should be emphasized that it is necessary to make some basic assumption concerning the assignment of weights. If one is to neglect the effect of kinetic factors, Eq. (2.10) is certainly the most reasonable choice. Unfortunately, in many works no such assumption is explicitly stated, and the physical significance of the actual assumption is hidden in the mathematical formalism.

b. Distribution of an Interior Bead

Bueche (2) has criticized the general approach that uses Eq. (2.11), specifically referring only to HKU. His argument is that in considering the building up of the chain link by link, proper cognizance is not taken of the fact that the distribution of a given bead is also affected by the following beads in the chain. It will not be maintained here, and it certainly is not true, that $\Phi_t(t, \vec{r})$ will give the distribution of the t^{th} bead when there are more than t links in the chain--that is, when the t^{th} bead is an

interior bead. The formalism that has been outlined here, and that will be developed in detail in the next chapter, is one for calculating the distribution of one end about the other fixed end of the chain. It will be shown in Appendix D how the theory can be modified to consider the distribution of an interior bead.

We have actually considered only a special case of the HKU theory, since that theory was designed to consider the distribution of an interior bead. Their basic integro-difference equation relates the distribution of the t^{th} and $(t+1)^{th}$ beads in a chain of N links, $N > t+1$. Although HKU attempt to improve upon the transition weight used by Hermans (22), it has been pointed out by James, that, in addition to the question of normalization, the transition weight of HKU is arbitrary when concerned with an interior bead. The formulation of Zimm, Stockmayer, and Fixman (56) avoids the errors and arbitrary features of HKU, but they are left with expressions they can evaluate only in an approximation they realize to be inadequate for large t. They reach no specific conclusion, but conjecture, contrary to HKU, that $\langle r^2 \rangle / t$ increases without limit as $t \to \infty$.

c. Work of Hadwiger

A brief discussion of the work of Hadwiger (21) will now be given, not because of any intrinsic interest of this work, but because it has been widely misquoted in the literature (24, 38, 52, 56) as indicating that $\langle r^2 \rangle / t$ approaches a finite limit as $t \to \infty$. Actually Hadwiger's

results are essentially identical with the James' result, which predicts a divergence of $\langle r^2 \rangle / t$. Hadwiger arbitrarily assumes that the density of beads at $\vec{r}$, when the end of the chain is at $\vec{r}-\vec{s}$, is linear in $|\vec{r}-\vec{s}| - r$. As is pointed out by HKU (23), this would be a reasonable approximation for $r \gg s$, provided the proportionality constant is taken to be r dependent, which Hadwiger does not do. The partial differential equation for $\bar{\Phi}_0(t, \vec{r})$ derived by Hadwiger, while not the same as the equation derived by James, has the same solution except for factors affecting the normalization. Hadwiger's basic assumption is certainly unjustified, and the similarity of his result to that of James appears to be a mathematical accident. It should be mentioned that (contrary to an impression given by Eq. (5) of HKU) Hadwiger's transition weight is unnormalized. In fact it can easily be shown that if Hadwiger had normalized his transition weight, his dominant correction term would not occur.

d. The Work of James

In succeeding chapters, James' (24) results will be considered in considerable detail in an attempt to extend that theory. However, for the purpose of summarizing the significance of the approximations of the theories mentioned in this and the previous section, and to indicate the necessity for additional work, it will be useful to summarize James' results here.

By suitable expansions and approximations, the basic integral equation was rewritten in the form

$$\frac{\partial \Phi_s(t,\vec{r})}{\partial t} - \frac{1}{6}\nabla^2 \Phi_s(t,\vec{r}) = -v F(t,\vec{r};\vec{r})\,\Phi_s(t,\vec{r}). \tag{2.14}$$

As a first approximation, F was replaced by F_s, the value in the absence of volume exclusion, and the solution of Eq. (2.14) was then found to be

$$\Phi_s(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-cvt + c'v^{1/2}t\right) \exp\left\{\frac{-3}{2t}\left(r - \frac{3vt}{2\pi}\right)^2\right\}, \tag{2.15}$$

where c and c' are positive constants the values of which will be given later. The distribution given by Eq. (2.15) can be characterized as a displaced Gaussian distribution. For $vt^{1/2} \ll 1$, it follows from Eq. (2.15) that

$$\langle r^2 \rangle = t\left[1 + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} v t^{1/2} + \text{higher powers of } vt^{1/2}\right]. \tag{2.16}$$

It is interesting to note that if the entire right hand side of Eq. (2.14) were approximated, instead of only $F(t,\vec{r};\vec{r})$, that the effect of volume exclusion would be to add a term proportional to v to the distribution function, leading only to the first-order correction term in Eq. (2.16). Saito (41) and Grimley (18, 19) make just such an approximation and are thus led to the conclusion that $\langle r^2 \rangle$ increases as $t^{3/2}$. This approximation is equivalent to keeping only the first correction term in Eq. (2.6). As has been mentioned, Bueche (2) and Teramoto (46), using this approximation, have been led to the same result. [See Eq. (2.7).] However,

it is apparent from Eq. (2.16) that an expansion in powers of v is not a useful approach for calculating $\langle r^2 \rangle$ in the limit of large t. As we have seen, it is also unjustifiable to consider the first-order correction term as giving an upper bound on $\langle r^2 \rangle$.

For $vt^{3/2} \gg 1$, it follows formally from Eq. (2.15) (although James notes that this is outside the actual range of validity of his theory) that

$$\langle r^2 \rangle \cong \frac{9}{4\pi} v^2 t^2. \qquad (2.17)$$

Thus, on the basis of a first-order perturbation calculation, James predicts the divergence of $\langle r^2 \rangle / t$ for large t, although the nature of this divergence is not clear. This is contrary to the results of Hermans (22), HKU (23), and Wall (52) who conclude that $\langle r^2 \rangle / t$ approaches a finite limit as $t \to \infty$. Their conclusion, however, is readily attributed to the faulty weighting that was discussed under sub-heading a.

James' results are based upon a first-order perturbation calculation in which $F(t, \vec{r}; \vec{r})$ is replaced by $F_0(t, \vec{r}; \vec{r})$.* It is clear that when a first-order perturbation calculation gives a large correction, the reliability of these results is uncertain, and a second-order calculation is desirable.

6. Monte Carlo Calculations

Recently, Wall, Hiller, and Wheeler (53) have considered the excluded volume problem by generating random

*The criticism of HKU by Rubin (40) is essentially a criticism of the replacement of F by F_0.

walks on regular lattices, using the electronic digital computer (ILLIAC) at the University of Illinois. Correct weighting was assured by having the walk start over whenever there was a return to a lattice point previously occupied, and by giving equal weight to each successful walk--a successful walk corresponding to a configuration without interferences. The disadvantage of this procedure is that an exceptionally large number of walks must be started to obtain a moderate number of successful walks for more than, say, 100 steps. Because of this, the preliminary results reported were statistically inadequate to describe the behavior of $\langle r^2 \rangle / t$ for large t, although the tentative result $\langle r^2 \rangle \sim t^{1.22}$ was reported. The main conclusion of this preliminary work is the already known result that the number of allowable configurations decreases exponentially with t.

More recently, Rosenbluth and Rosenbluth (37) have made similar calculations on a three-dimensional cubic lattice and a two-dimensional square lattice using the electronic digital computer (MANIAC) at the Los Alamos Scientific Laboratory. Their procedure has the significant advantage that the walk does not start over whenever there is a return to a previously occupied site--the machine just makes another choice.* This procedure alone would give the incorrect weighting corresponding to the normalized transition

*If, however, a lattice site is reached such that all nearest neighbor sites have been previously occupied, the walk is terminated and begun anew.

weights discussed previously. Consider specifically the three-dimensional cubic lattice where each lattice point has six nearest neighbors. Assume that after $\tau-1$ steps we find ourselves at a lattice point such that there are N_τ possible choices for the next step, $0 \leq N_\tau \leq 5$, where N_τ is the number of nearest neighbor sites that have not been previously occupied. Consider two allowable configurations of t steps such that for (a) $N_\tau = 5$ for all τ, and for (b) $N_\tau = 5$ for $\tau = 0, 1, \ldots, t-1$, and $N_t = 1$. Since the last step of configuration (b) is added with probability one, this configuration will be generated (on the average) five times more frequently than configuration (a). Therefore to conform to the basic assumption that each allowable configuration be given equal weight, the configurations generated are not to be given equal weights, but weight W_t determined by the relation

$$W_t = \frac{N_t}{5} W_{t-1}, \quad (W_1 = 1). \tag{2.18}$$

Rosenbluth and Rosenbluth (37) use the above weighting procedure to calculate the mean square extension of chains of up to 64 links. (In three dimensions, 4769 chains of 64 links were generated.) Their results are

$$\langle r^2 \rangle \sim t^{1.22} \quad \text{in three dimensions,} \tag{2.19}$$

$$\langle r^2 \rangle \sim t^{1.45} \quad \text{in two dimensions.} \tag{2.20}$$

There is a remarkable agreement between the result of Eq. (2.19) and the preliminary results reported by Wall, Hiller, and Wheeler (53) whose calculations were for different

lattices. The results are also in excellent agreement with experimental results.

Wall, Hiller, and Wheeler (53) have indicated that their calculations will be extended to more steps and to other lattices. As additional results become available, it would be of interest to obtain not only $\langle r^2 \rangle$, but also to obtain the actual distribution function $\Phi_t(t, \vec{r})$, and the mean square displacement from the center of gravity, so that light scattering data can be more properly interpreted.

While these results are extremely interesting, they are of a semi-empirical nature, and do not obviate the desirability of an analytic treatment of the excluded volume problem, which will be considered in detail in succeeding chapters.

With the use of the pearl necklace model, a systematic mathematical formulation of the problem will be presented in Chapter III. We shall derive a system of integro-difference equations for the relative number of configurations $\Phi_t(t,\vec{r})$ of a chain of t links with extension $\vec{r}$, and the corresponding relative number of configurations $\Phi_i(t, \vec{r}; \vec{R}_1, \cdots \vec{R}_i)$ when the chain is also required to pass through given fixed points $\vec{R}_1, \vec{R}_2, \cdots, \vec{R}_i$. A method of successive approximations for the determination of $\Phi_t(t, \vec{r})$ will be proposed. Both the zeroth-order approximation (no volume exclusion) and the first-order approximation will be obtained, making use of generating functions and Fourier integrals. The physical significance

of the first-order approximation will be discussed in terms of the configurations which are properly weighted by this result. The second-order calculation will be discussed as far as the point to which the writer has successfully carried it. The difficulties in adequately completing this calculation and proceeding to higher order calculations will be mentioned.

In Chapter IV, the integro-difference equation for $\bar{\Phi}_0(t,\vec{r})$ will be converted into a partial differential equation, Eq. (2.14), by means of a limiting procedure, the physical significance of which will be discussed. The first-order result, obtained by James (24), will be shown to be formally valid over a wider range of values of r than he considers. A need for a second-order calculation will be indicated, and a procedure for making this calculation will be developed in detail. Because of mathematical difficulties that will be described, the writer has not carried this procedure to a successful conclusion.

In Chapter V, the direct evaluation of $\langle r^2 \rangle$ from the partial differential equation for $\bar{\Phi}_0(t,\vec{r})$ will be considered, both in the first and second approximations. It will be shown that for large values of t, the results are quite sensitive to the approximations made, and that no definite conclusion concerning the limiting behavior of $\langle r^2 \rangle / t$ for large t can be reached from these results.

In Chapter VI, we shall summarize this thesis, particularly comparing the theory given here and elsewhere,

and the relevant experimental results. The inherent difficulties in applying a perturbation procedure to the volume exclusion problem will also be discussed.

CHAPTER III

FORMULATION OF THE THEORY

1. Description of the Model

We consider a chain of t+1 beads, numbered 0,1,...t, connected by t links, such that the apriori probability density for link extension $\vec{s}$, in the absence of volume exclusion, is given by

$$q(s) = \left(\frac{3}{2\pi}\right)^{3/2} \exp\left(-\frac{3}{2}s^2\right). \tag{3.1}$$

We have consequently chosen the rms link length to be our unit of length.

In the absence of volume exclusion, the probability density for finding the ends of the chain separated by a distance $\vec{r}$ is given exactly by

$$\Phi_0^{(0)}(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{t}\right). \tag{3.2}$$

Associated with each bead, there is a volume v into which the center of no other bead can enter. This is called the excluded volume. For the case of spherical beads, the excluded volume is eight times the volume of a single bead.

We have chosen the same model as James (24) since it will enable us to consider the effect of volume exclusion without the additional complications of fixed link lengths,

fixed bond angle, and hindered rotations. The localization of the excluded volume in small beads, while not very realistic, appears to take account of the salient features of the problem. It is here assumed, as is commonly done, that the qualitative characteristics of the effect are independent of the form and distribution of the excluded volume.

2. Integro-Difference Equations

Our basic assumption will be that the relative weight of a configuration with link extensions $\vec{s}_i$ is given by $\prod_{i=1}^{t} g(s_i)d\vec{s}_i$ if no two interior beads overlap, and weight zero if there is such an overlap. (This corresponds to giving equal weight to all allowable configurations in the case of a chain having fixed link lengths.)

Let $W_t(\vec{r}_1, \ldots, \vec{r}_t)\, d\vec{r}_1 \ldots d\vec{r}_t$ be the relative weight of a configuration of a chain of t links, with the zeroth bead fixed at the origin, and the i^{th} bead, $(i = 1,2, \ldots,t)$, in the volume element $d\vec{r}_i$ surrounding $\vec{r}_i$, taking account of volume exclusion due to all beads except the two end ones. This inclusion of some configurations containing interferences will not have an appreciable effect on the results for large t, but the approximation will appreciably facilitate the calculation.

We define $\varphi_\nu(t, \vec{r}; j_1, \vec{R}_1; \ldots; j_\nu, \vec{R}_\nu)\, d\vec{r}\, d\vec{R}_1 \ldots d\vec{R}_\nu$, $\nu \geq 1$, to be the relative weight of configurations in which the t^{th} bead is in $d\vec{r}$ about $\vec{r}$, and bead j_μ is in $d\vec{R}_\mu$ about $\vec{R}_\mu$, $\mu = 1,2, \ldots,\nu$. Specifically, φ_1, and φ_2 are

calculated from W_t in the following way:

$$\varphi_1(t,\vec{r}:i,\vec{R}) = \int d\vec{r}_1 \cdots \int d\vec{r}_{t-1}\, W_t(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_{t-1},\vec{r})\,\delta(\vec{r}_i-\vec{R}), \tag{3.3}$$

$$\varphi_2(t,\vec{r}:i,\vec{R}_1;j,\vec{R}_2) = \int d\vec{r}_1 \cdots \int d\vec{r}_{t-1}\, W_t(\vec{r}_1,\cdots,\vec{r})\,\delta(\vec{r}_i-\vec{R}_1)\,\delta(\vec{r}_j-\vec{R}_2), \tag{3.4}$$

We define $\bar{\varphi}_\nu(t,\vec{r}:\vec{R}_1,\cdots,\vec{R}_\nu)\,d\vec{R}_1 d\vec{R}_2\cdots d\vec{R}_\nu$ to be the relative weight of configurations in which the t^{th} bead is in $d\vec{r}$ about $\vec{r}$, and some other bead is in $d\vec{R}_\mu$ about $\vec{R}_\mu$, $\mu = 1, 2, \cdots, \nu$. For $\nu = 0$,

$$\bar{\varphi}_0(t,\vec{r})\,d\vec{r} = d\vec{r}\int d\vec{r}_1 \cdots \int d\vec{r}_{t-1}\, W_t(\vec{r}_1,\cdots\vec{r}_{t-1},\vec{r}) \tag{3.5}$$

is the relative weight of configurations in which the t^{th} bead is in $d\vec{r}$ about $\vec{r}$ regardless of the location of the other beads.

Since beads j_μ and j_λ can not both be at $\vec{R}$,

$$\bar{\varphi}_\nu(t,\vec{r}:\vec{R}_1,\cdots,\vec{R}_\nu) = \sum_{\substack{i_1=1 \\ (i_1\neq i_2\neq\cdots\neq i_\nu)}}^{t-1}\sum_{i_2=1}^{t-1}\cdots\sum_{i_\nu=1}^{t-1}\varphi_\nu(t,\vec{r}:i_1,\vec{R}_1;i_2,\vec{R}_2;\cdots;i_\nu,\vec{R}_\nu). \tag{3.6}$$

Therefore,

$$\bar{\varphi}_1(t,\vec{r}:\vec{R}) = \sum_{i=1}^{t-1}\varphi_1(t,\vec{r}:i,\vec{R}) = \int d\vec{r}_1\cdots\int d\vec{r}_{t-1}\, W_t(\vec{r}_1,\cdots,\vec{r}_{t-1},\vec{r})\sum_{i=1}^{t-1}\delta(\vec{r}_i-\vec{R}), \tag{3.7}$$

$$\bar{\varphi}_2(t,\vec{r}:\vec{R}_1,\vec{R}_2) = \sum_{\substack{i=1 \\ (i\neq j)}}^{t-1}\sum_{j=1}^{t-1}\varphi_2(t,\vec{r}:i,\vec{R}_1;j,\vec{R}_2), \tag{3.8}$$

and so on.

The basic integro-difference equations of our theory will be obtained by relating W_{t-1} and W_t. We have

$$W_{t+1}(\vec{r}_1, \cdots, \vec{r}_t, \vec{r}_{t+1}) = W_t(\vec{r}_1, \cdots, \vec{r}_t)\, g(\vec{r}_{t+1} - \vec{r}_t)\, \Psi, \tag{3.9}$$

where, for rigid sphere interactions, Ψ is one if the t^{th} bead does not interfere with any of beads $1,2,\ldots,t$, and zero if it does. We define an interaction function $\epsilon(r_t - r_i)$ that is 1 when there is a steric interference involving beads i and t, and zero otherwise. For a rigid sphere interaction, ϵ will be discontinuous. If we wish to consider a more general short range interaction, an effective volume can still be defined by the relation

$$\int d\vec{r}\, \epsilon(\vec{r}) = v. \tag{3.10}$$

Since $\epsilon(\vec{r}_t - \vec{r}_i)$ is a short-range function, if $f(\vec{r}_t)$ is not too strongly varying in the neighborhood of $\vec{r}_i$, we can write

$$\int d\vec{r}_t\, f(\vec{r}_t)\, \epsilon(\vec{r}_t - \vec{r}_i) \cong v\, f(\vec{r}_i). \tag{3.11}$$

Thus $\epsilon(\vec{r}_t - \vec{r}_i)$ has the same integral behavior as $v\,\delta(\vec{r}_t - \vec{r}_i)$.

If ϵ_i denotes $\epsilon(\vec{r}_t - \vec{r}_i)$, Ψ is clearly given by

$$\Psi = \prod_{i=1}^{t-1} (1 - \epsilon_i) = 1 - \sum_{i=1}^{t-1} \epsilon_i + \sum\sum_{i<j} \epsilon_i \epsilon_j - \cdots \tag{3.12}$$

We consider the 3t-dimensional configuration space. $\epsilon_i \epsilon_j$ will be unequal to zero only in those regions of the space corresponding to configurations in which both the i^{th} and j^{th} beads interfere with the t^{th} bead. While it is possible for such configurations to occur without the i^{th} and j^{th}

beads interfering with each other, such occurrences will not be considered. Thus it is assumed that W_t is zero in those regions of configuration space where $\epsilon_i\epsilon_j$ and higher order terms are unequal to zero. (We shall consider the implications of this approximation in more detail in Appendix B.) It therefore follows that

$$W_{t+1}(\vec{r}_1,\cdots\vec{r}_{t+1}) = W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}_{t+1}-\vec{r}_t)\left[1-\sum_{i=1}^{t}\epsilon(\vec{r}_i-\vec{r}_t)\right]. \quad (3.13)$$

Equation (3.13) is the basic equation of our theory.

From Eqs. (3.5), (3.7), (3.11), and (3.13) it readily follows that

$$\Phi_0(t+1,\vec{r}) = \int d\vec{r}'\,g(\vec{r}-\vec{r}')\,\Phi_0(t,\vec{r}') - v\int d\vec{r}'\,g(\vec{r}-\vec{r}')\,\Phi_1(t,\vec{r}':\vec{r}'). \quad (3.14)$$

The derivation of the corresponding equation for Φ_1, will be given in detail. From Eqs. (3.7) and (3.13) it readily follows that

$$\Phi_1(t+1,\vec{r}:\vec{R}) = \int d\vec{r}_1\cdots\int d\vec{r}_t\,W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\left[1-\sum_{j=1}^{t}\epsilon(\vec{r}_t-\vec{r}_j)\right]\sum_{k=1}^{t}\delta(\vec{r}_k-\vec{R})$$

$$-\int d\vec{r}_1\cdots\int d\vec{r}_t\,W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\sum_{k=1}^{t}\delta(\vec{r}_k-\vec{R}) \quad (a)$$

$$-\int d\vec{r}_1\cdots\int d\vec{r}_t\,W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\sum_{k=1}^{t}\delta(\vec{r}_k-\vec{R})\sum_{j=1}^{t}\epsilon(\vec{r}_t-\vec{r}_j) \quad (b)$$

$$+\int d\vec{r}_1\cdots\int d\vec{r}_t\,W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\,\delta(\vec{r}_t-\vec{R}) \quad (c)$$

$$-\int d\vec{r}_1\cdots\int d\vec{r}_t\,W_t(\vec{r}_1,\cdots,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\,\delta(\vec{r}_t-\vec{R})\sum_{j=1}^{t}\epsilon(\vec{r}_t-\vec{r}_j). \quad (d)$$

From Eq. (3.7), (a) is $\int d\vec{r}_t\,\Phi_1(t,\vec{r}_t:\vec{R})\,g(\vec{r}-\vec{r}_t)$.

From Eq. (3.5), (c) is

$$\int d\vec{r}_t\,\Phi_0(t,\vec{r}_t)\,g(\vec{r}-\vec{r}_t)\,\delta(\vec{r}_t-\vec{R}) = \Phi_0(t,\vec{R})\,g(\vec{r}-\vec{R}).$$

In (d) we replace

$$\sum_{j=1}^{t}\epsilon(\vec{r}_t-\vec{r}_j) \quad \text{by} \quad v\sum_{j=1}^{t}\delta(\vec{r}_t-\vec{r}_j)$$

to obtain

$$-v\int d\vec{r}_k\, \Phi_1(t,\vec{r}_k:\vec{r}_k)\, g(\vec{r}-\vec{r}_k)\,\delta(\vec{r}_k-\vec{R}) = -v\,\Phi_1(t,\vec{R}:\vec{R})\, g(\vec{r}-\vec{R}).$$

In (b) we replace $\epsilon(\vec{r}_k - \vec{r}_j)$ by $v\,\delta(\vec{r}_k - \vec{r}_j)$ for $j \neq k$. Thus, for $j \neq k$, (b) gives

$$-v\int d\vec{r}_k\, \Phi_2(t,\vec{r}_k:\vec{R},\vec{r}_k)\, g(\vec{r}-\vec{r}_k).$$

For $j = k$, we have terms of the form

$$-\int d\vec{r}_1 \cdots \int d\vec{r}_N\, W_N(\vec{r}_1,\cdots,\vec{r}_N)\, g(\vec{r}-\vec{r}_k)\,\delta(\vec{r}_k-\vec{R})\,\epsilon(\vec{r}_k-\vec{r}_{k'})$$

$$= -\int d\vec{r}_k \int d\vec{r}_{k'}\, \varphi_1(t,\vec{r}_k:k,\vec{r}_{k'})\, g(\vec{r}-\vec{r}_k)\,\delta(\vec{r}_{k'}-\vec{R})\,\epsilon(\vec{r}_k-\vec{r}_{k'})$$

$$\cong -v\int d\vec{r}_{k'}\, \varphi_1(t,\vec{r}_{k'}:k,\vec{r}_{k'})\, g(\vec{r}-\vec{r}_{k'})\,\delta(\vec{r}_{k'}-\vec{R})$$

$$= -v\,\varphi_1(t,\vec{R}:k,\vec{R})\, g(\vec{r}-\vec{R}).$$

Summing over k, we get $-v\,\Phi_1(t,\vec{R}:\vec{R})g(\vec{r}-\vec{R})$. Collecting terms, our result is then

$$\Phi_1(t+1,\vec{r}:\vec{R}) = \int d\vec{r}'\, \Phi_1(t,\vec{r}':\vec{R})\, g(\vec{r}-\vec{r}') + \Phi_0(t,\vec{R})\, g(\vec{r}-\vec{R})$$
$$- v\int d\vec{r}'\, \Phi_2(t,\vec{r}':\vec{r}',\vec{R})\, g(\vec{r}-\vec{r}')$$
$$- 2v\,\Phi_1(t,\vec{R}:\vec{R})\, g(\vec{r}-\vec{R}). \qquad (3.15)$$

Following a similar procedure (see Appendix C for the details of the calculation) we obtain

$$\Phi_2(t+1,\vec{r}:\vec{R}_1,\vec{R}_2) = \int d\vec{r}'\, \Phi_2(t,\vec{r}':\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{r}') \qquad (3.16)$$
$$+ \left\{\Phi_1(t,\vec{R}_1:\vec{R}_1)\, g(\vec{r}-\vec{R}_1) + \Phi_1(t,\vec{R}_2:\vec{R}_1)\, g(\vec{r}-\vec{R}_2)\right\}\left[1-\epsilon(\vec{R}_1-\vec{R}_2)\right]$$
$$- 2v\,\Phi_2(t,\vec{R}_1:\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{R}_1) - 2v\,\Phi_2(t,\vec{R}_2:\vec{R}_2,\vec{R}_1)\, g(\vec{r}-\vec{R}_2)$$
$$- v\int d\vec{r}'\, \Phi_3(t,\vec{r}':\vec{r}',\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{r}').$$

Proceeding in the same way, we can derive an equation for $\bar{\Phi}_3$ that will involve $\bar{\Phi}_4$ in the correction term. Thus we can build up a system of $(t-1)$ equations.

To check the consistency of Eqs. (3.14), (3.15), and (3.16), we note that in general

$$\int d\vec{R}_n\, \bar{\Phi}_n(t,\vec{r}:\vec{R}_1,\vec{R}_2,\cdots,\vec{R}_n) = (t-n)\,\bar{\Phi}_{n-1}(t,\vec{r}:\vec{R}_1,\vec{R}_2,\cdots,\vec{R}_{n-1}), \tag{3.17}$$

since

$$(t-n) = \frac{(t-1)_n}{(t-1)_{n-1}} = \frac{(t-1)(t-2)\cdots(t-1-\{n-1\})}{(t-1)(t-2)\cdots(t-1-\{n-2\})}$$

is the ratio of the number of ways n beads can be fixed to the number of ways $(n-1)$ beads can be fixed in a chain of t links. (In a chain of t links, there are t-1 beads that can be assigned to the various $\vec{R}_i$, since the 0^{th} and t^{th} beads are restrained to the origin and $\vec{r}$ respectively.)

Setting $\vec{R}_1 = \vec{R}$ in Eq. (3.16), and integrating over all $\vec{R}_2$, we have by Eq. (3.17)

$$\begin{aligned}(t-1)\,\bar{\Phi}_1(t+1,\vec{r}:\vec{R}) = {} & (t-2)\int d\vec{r}'\,\bar{\Phi}_1(t,\vec{r}':\vec{R})\,g(\vec{r}-\vec{r}') + (t-1)\,\bar{\Phi}_0(t,\vec{R})\,g(\vec{r}-\vec{R}) \\ & + \int d\vec{R}_2\,\bar{\Phi}_1(t,\vec{R}_2:\vec{R})\,g(\vec{r}-\vec{R}_2) - 2v\,\bar{\Phi}_1(t,\vec{R}:\vec{R})\,g(\vec{r}-\vec{R}) \\ & - 2v(t-2)\,\bar{\Phi}_1(t,\vec{R}:\vec{R})\,g(\vec{r}-\vec{R}) - 2v\int d\vec{R}_2\,\bar{\Phi}_2(t,\vec{R}_2:\vec{R},\vec{R}_2)\,g(\vec{r}-\vec{R}_2) \\ & - v(t-3)\int d\vec{r}'\,\bar{\Phi}_2(t,\vec{r}',\vec{r};\vec{R})\,g(\vec{r}-\vec{r}').\end{aligned}$$

Collecting terms and dividing by (t-1), we obtain Eq. (3.15). Likewise, integration of Eq. (3.15) over all $\vec{R}_1$ leads exactly to Eq. (3.14).

3. Generating Functions

In attempting to solve the system of equations of which Eqs. (3.14), (3.15) and (3.16) are the first three members, it is useful to consider the generating functions $\Psi_i(z,\vec{r}:\vec{R}_1,\ldots,\vec{R}_i)$ defined by the relation

$$\Psi_i(z,\vec{r}:\vec{R}_1,\ldots,\vec{R}_i) = \sum_{t=i}^{\infty} z^t \Phi_i(t,\vec{r}:\vec{R}_1,\ldots,\vec{R}_i), \qquad |z|<1. \tag{3.18}$$

Multiplying Eqs. (3.14), (3.15) and (3.16) by z^t and summing over all t, we obtain

$$z^{-1}\Psi_0(z,\vec{r}) - g(r) = \int d\vec{r}'\, g(\vec{r}-\vec{r}')\Psi_0(z,\vec{r}') - v\int d\vec{r}'\, g(\vec{r}-\vec{r}')\Psi_1(z,\vec{r}',\vec{r}'), \tag{3.19}$$

$$z^{-1}\Psi_1(z,\vec{r}:\vec{R}) = \int d\vec{r}'\, g(\vec{r}-\vec{r}')\Psi_1(z,\vec{r}':\vec{R}) + \Psi_0(z,\vec{R})\, g(\vec{r}-\vec{R})$$
$$- v\int d\vec{r}'\, g(\vec{r}-\vec{r}')\Psi_2(z,\vec{r}':\vec{r}',\vec{R}) - 2v\Psi_1(z,\vec{R}:\vec{R})\, g(\vec{r}-\vec{R}), \tag{3.20}$$

$$z^{-1}\Psi_2(z,\vec{r}:\vec{R}_1,\vec{R}_2) = \int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\Psi_2(z,\vec{r}':\vec{R}_1,\vec{R}_2)$$
$$+\left[\Psi_1(z,\vec{R}_1:\vec{R}_2)\, g(\vec{r}-\vec{R}_1) + \Psi_1(z,\vec{R}_2:\vec{R}_1)\, g(\vec{r}-\vec{R}_2)\right]\left[1-\epsilon(\vec{R}_1-\vec{R}_2)\right]$$
$$- 2v\Psi_2(z,\vec{R}_1:\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{R}_1) - 2v\Psi_2(z,\vec{R}_2:\vec{R}_2,\vec{R}_1)\, g(\vec{r}-\vec{R}_2)$$
$$- v\int d\vec{r}'\,\Psi_3(z,\vec{r}':\vec{r}',\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{r}'). \tag{3.21}$$

We have assumed that the order of summation with respect to t, and integration over all $\vec{r}'$ can be interchanged. We have also made use of the initial conditions

$$\Phi_i(t,\vec{r}:\vec{R}_1,\cdots,\vec{R}_i) = \begin{cases} g(r) & \text{for } i=0 \\ 0 & \text{for } i\neq 0 \end{cases} \tag{3.22}$$

The equations that result upon setting $v=0$ in Eqs. (3.19), (3.20) and (3.21) will be designated by $(3.19)_0$, $(3.20)_0$, and $(3.21)_0$ respectively. The following scheme of successive approximations will now be considered.

(a) Solve Eq.$(3.19)_0$ for $\Psi_0^{(0)}(z,\vec{r})$.

(i) Simultaneously solve Eqs. $(3.20)_0$ and (3.19) for $\Psi_0^{(1)}(z,\vec{r})$ and $\Psi_1^{(0)}(z,\vec{r}:\vec{R})$.

(ii) Simultaneously solve Eqs. $(3.21)_0$, (3.20) and (3.19) for $\Psi_0^{(2)}(z,\vec{r})$, $\Psi_1^{(1)}(z,\vec{r}:\vec{R})$, $\Psi_2^{(0)}(z,\vec{r}:\vec{R}_1,\vec{R}_2)$.

Inversion of the transformation Eq. (3.18) would then enable us to obtain the successive approximations to $\Phi_0(t,\vec{r})$; that is, $\Phi_0^{(0)}(t,\vec{r})$, $\Phi_0^{(1)}(t,\vec{r})$, $\Phi_0^{(2)}(t,\vec{r})$, and so on.

4. Solution of the Integral Equation

In this calculation, one must solve integral equations of the form

$$\psi(\vec{r}) = f(\vec{r}) + \mu\int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\psi(\vec{r}'). \tag{3.23}$$

This is most simply accomplished by the use of Fourier integrals, (49). We define

$$\Psi(\vec{u}) = \left(\frac{1}{2\pi}\right)^{3/2}\int d\vec{r}\,\psi(\vec{r})\,e^{i\vec{r}\cdot\vec{u}}, \tag{3.24}$$

and define $G(\vec{u})$ and $F(\vec{u})$ similarly to be the transforms of $g(\vec{r})$ and $f(\vec{r})$. The Fourier transform of Eq. (3.23) can

then be simply written as

$$\Psi(\vec{u}) = F(\vec{u}) + (2\pi)^{3/2}\mu\, G(\vec{u})\,\Psi(\vec{u}), \tag{3.25}$$

so that,

$$\psi(\vec{r}) = \left(\frac{1}{2\pi}\right)^{3/2}\int d\vec{u}\ \frac{F(\vec{u})}{1-(2\pi)^{3/2}\mu\, G(\vec{u})}\ e^{-i\vec{r}\cdot\vec{u}}\ . \tag{3.26}$$

The above procedure is of course purely formal, but the conditions of validity are so broad (49) that we need expect no difficulty with the functions of this theory.

In this chapter we are specifically considering

$$g(\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2}\exp\left(-\tfrac{3}{2}r^2\right). \tag{3.27}$$

A straight forward integration shows that the Fourier transform of $g(\vec{r})$ is given by

$$G(\vec{u}) = \left(\frac{1}{3\pi}\right)^{3/2} e^{-u^2/6}, \tag{3.28}$$

so that Eq. (3.26) becomes

$$\psi(\vec{r}) = \left(\frac{1}{2\pi}\right)^{3/2}\int d\vec{u}\ \frac{F(\vec{u})}{1-\mu\, e^{-u^2/6}}\ e^{-i\vec{r}\cdot\vec{u}}\ . \tag{3.29}$$

5. Solution for $v = 0$

The first step in the method of successive approximations previously outlined is the solution of Eq. $(3.19)_0$:

$$\psi_0^{(n)}(z,\vec{r}) = z\,q(r) + z\int d\vec{r}'\, q(\vec{r}-\vec{r}')\,\psi_0^{(n)}(z,\vec{r}'). \tag{3.19}$$

By the use of Eqs. (3.28) and (3.29), one can immediately write the solution of this equation as

$$\Psi_0^{(\infty)}(z,\vec{r}) = \left(\frac{1}{2\pi}\right)^3 z \int d\vec{u}\, \frac{e^{-u^2/6}}{1 - z\, e^{-u^2/6}}\, e^{-i\vec{r}\cdot\vec{u}} \tag{3.30}$$

$$= \left(\frac{1}{2\pi}\right)^3 \sum_{t=1}^{\infty} z^t \int d\vec{u}\, e^{-u^2 t/6} e^{-i\vec{r}\cdot\vec{u}}$$

$$= \sum_{t=1}^{\infty} z^t \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{t}\right). \tag{3.31}$$

Comparison with Eq. (3.18) shows that

$$\Phi_0^{(\infty)}(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{t}\right). \tag{3.32}$$

This is the well known distribution function in the absence of volume exclusion.

6. First Approximation

We now consider Eq. $(3.20)_0$

$$\Psi_1^{(\infty)}(z,\vec{r};\vec{R}) = z\,\Psi_0^{(\infty)}(z,\vec{R})\, g(\vec{r}-\vec{R}) + z\int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\Psi_1^{(\infty)}(z,\vec{r}';\vec{R}), \tag{3.20}_0$$

the Fourier transform of which is

$$\Psi_1^{(\infty)}(z,\vec{u};\vec{R}) = z\,\Psi_0^{(\infty)}(z,\vec{R})\, G(\vec{u})\, e^{i\vec{R}\cdot\vec{u}} + (2\pi)^{3/2} z\, G(\vec{u})\,\Psi_1^{(\infty)}(z,\vec{u};\vec{R}). \tag{3.33}$$

Therefore, by Eqs. (3.28) and (3.29)

$$\Psi_1^{(\infty)}(z,\vec{r};\vec{R}) = \left(\frac{1}{2\pi}\right)^3 \Psi_0^{(\infty)}(z,\vec{R})\, z \int d\vec{u}\, \frac{e^{-u^2/6}\, e^{-i(\vec{r}-\vec{R})\cdot\vec{u}}}{1 - z\, e^{-u^2/6}}. \tag{3.34}$$

Comparison of Eqs. (3.34) and (3.30) shows that one can write

$$\Psi_1^{(\omega)}(z,\vec{r}:\vec{R}) = \Psi_0^{(\omega)}(z,\vec{R})\,\Psi_0^{(\omega)}(z,\vec{r}-\vec{R}). \tag{3.35}$$

Since the product of Ψ's corresponds to the convolution of the corresponding $\bar{\Phi}$'s, we have thus

$$\bar{\Phi}_1^{(\omega)}(t,\vec{r}:\vec{R}) = \sum_{j=1}^{t-1} \bar{\Phi}_0^{(\omega)}(j,\vec{r}-\vec{R})\,\bar{\Phi}_0^{(\omega)}(t-j,\vec{R}), \tag{3.36}$$

and in particular

$$\bar{\Phi}_1^{(\omega)}(t,\vec{r}:\vec{r}) = \sum_{j=1}^{t-1} \bar{\Phi}_0^{(\omega)}(j,0)\,\bar{\Phi}_0^{(\omega)}(t-j,\vec{r}). \tag{3.37}$$

Equation (3.37) has a simple interpretation. The exact value of $v\,\bar{\Phi}_1(t,\vec{r}:\vec{r})\,d\vec{r}$ gives the relative weight of configurations in which the t^{th} bead is in $d\vec{r}$ about $\vec{r}$, and there is an interference between the t^{th} bead and an interior bead; but no interferences involving any pair of interior beads. (See Fig. 3.) It follows

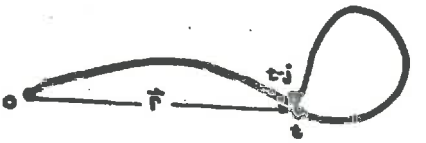


Fig. 3
A Configuration Contributing to $v\bar{\Phi}_1(t,\vec{r}:\vec{r})$

from Eq. (3.7) that

$$\bar{\Phi}_1(t,\vec{r}:\vec{r}) = \sum_{j=1}^{t-1} \Phi_1(t,\vec{r}:t-j,\vec{r}), \tag{3.38}$$

where

$$\Phi_1(t,\vec{r}:t-j,\vec{r}) = \bar{\Phi}_0(t-j,\vec{r})\,\bar{\Phi}_0(j,0)\,p(j,0:t-j,\vec{r}), \tag{3.39}$$

and $p(j,o:t-j,\vec{r})$ is the probability that there are no interferences between a chain of $(t-j)$ links having extension $\vec{r}$, and a closed loop of j links, the closure being at $\vec{r}$. (See Fig. 3). Comparison of Eq. (3.37) with Eqs. (3.38) and (3.39) shows that the approximation given by Eq. (3.37) does not take account of interactions within the closed loop, and what is even more important, does not take account of interactions between the closed loop and the rest of the chain.

To proceed with the solution, we replace Ψ_1 in Eq. (3.19) by $\Psi_0^{(\omega)}$ as given in Eq. (3.35) to obtain

$$\Psi_0^{(1)}(z,\vec{r}) = zq(r) + z\left[1-v\Psi_0^{(\omega)}(z,o)\right]\int d\vec{r}'\, q(\vec{r}-\vec{r}')\Psi_0^{(1)}(z,\vec{r}'), \tag{3.40}$$

where

$$\Psi_0^{(\omega)}(z,o) = \frac{1}{2\pi^2} z\int_0^\infty du\, \frac{u^2 e^{-u^2/6}}{1-z e^{-u^2/6}} = \left(\frac{3}{2\pi}\right)^{3/2}\sum_{t=1}^{\infty}\frac{z^t}{t^{3/2}}. \tag{3.41}$$

As solution of Eq. (3.40) we have, by the method of Section 4

$$\Psi_0^{(\omega)}(z,\vec{r}) = \left(\frac{1}{2\pi}\right)^3 z\int d\vec{u}\, \frac{e^{-u^2/6}}{1-\mu_1(z)e^{-u^2/6}}\, e^{-i\vec{r}\cdot\vec{u}}, \tag{3.42}$$

where

$$\mu_1(z) = z\left[1-v\Psi_0^{(\omega)}(z,o)\right]. \tag{3.43}$$

By again expanding the denominator, we obtain from Eq. (3.42)

$$\Psi_0^{(\omega)}(z,\vec{r}) = z\sum_{\tau=1}^{\infty}\mu_1(z)^{\tau-1}\left(\frac{3}{2\pi\tau}\right)^{3/2}\exp\left(-\frac{3}{2}\frac{r^2}{\tau}\right), \tag{3.44}$$

from which it follows that one can write

$$\bar{\Phi}_o^{(v)}(t,\vec{r}) = \sum_{\tau=2}^{t} c_\tau(t)\, \bar{\Phi}_o^{(\omega)}(\tau,\vec{r}) \qquad (3.45)$$

where $c_\tau(t)$ equals the coefficient of $z^{t-\tau}$ in

$$\left\{1 - \left(\frac{3}{2\pi}\right)^{3/2} v \sum_{j=1}^{\infty} z^j / j^{3/2}\right\}^{\tau-1}.$$

While Eq.(3.45) is not in convenient form for computation, it does permit an interesting interpretation. In explicit form, we can write Eq. (3.45) as

$$\begin{aligned}\bar{\Phi}_o^{(v)}(t,\vec{r}) = {} & \bar{\Phi}_o^{(\omega)}(t,\vec{r}) \\ & -\left(\frac{3}{2\pi}\right)^{3/2} v \left\{(t-2)\bar{\Phi}_o^{(\omega)}(t-1,\vec{r}) + \frac{t-3}{2^{3/2}}\bar{\Phi}_o^{(\omega)}(t-2,\vec{r}) + \cdots\right\} \\ & +\left(\frac{3}{2\pi}\right)^{3} v^2 \left\{\binom{t-3}{2}\bar{\Phi}_o^{(\omega)}(t-2,\vec{r}) + \binom{t-4}{2}\frac{1}{2^{3/2}}\bar{\Phi}_o^{(\omega)}(t-3,\vec{r}) + \cdots\right\} \\ & + \cdots\end{aligned} \qquad (3.46)$$

The v independent term gives the relative number of configurations, omitting volume exclusion. The terms proportional to v subtract with weight N configurations containing N interferences. Thus $(t-2)\left(\frac{3}{2\pi}\right)^{3/2} v\, \bar{\Phi}_o^{(\omega)}(t-1,\vec{r})$ gives the relative number of single link loops. $(t-3)\left(\frac{3}{2\pi}\right)^{3/2}\frac{v}{2^{3/2}}\bar{\Phi}_o^{(\omega)}(t-2,\vec{r})$ gives the relative number of loops of two links, and so on. Clearly by this procedure we subtract out too many configurations, since if there are two interferences in the same configuration, this configuration will be subtracted twice, and so on. The v^2-terms over-compensate for this by adding back configurations with non-overlapping pairs of interferences. Thus $\left(\frac{3}{2\pi}\right)^3 v^2 \binom{t-3}{2}\bar{\Phi}_o^{(\omega)}(t-2,\vec{r})$ gives the relative number of configurations with pairs of single link loops; $\left(\frac{3}{2\pi}\right)^3 v^2 \binom{t-4}{2}\frac{1}{2^{3/2}}\bar{\Phi}_o^{(\omega)}(t-3,\vec{r})$ gives the relative number of non-overlapping pairs of single link and double

link loops, and so on. (See Fig. 4). Equation (3.46)

Fig.4
Pairs of Interferences
(a) non-overlapping
(b) overlapping

weights the excluded configurations in the following way: It gives the configuration weight 1 for each single interference, weight -1 for each pair of separate non-overlapping interferences, weight 1 for each trio of separate non-overlapping interferences, and so on. Ideally of course, one would wish to exclude with weight one any configuration containing an interference.

In order to determine the significance of such a weighting, consider a chain divided into two sections such that there are no interferences across the division point. Let a_j equal the number of sets of j separate non-overlapping closed loops that can be chosen before the division point, and let b_j equal the corresponding number after the division point. The weight for exclusion assigned to the two parts of the chain will be

$$N_A = 1 + \sum_{j=0}^{\infty} (-1)^{j+1} a_j \quad , \qquad a_0 = 1 \; ; \tag{3.47}$$

$$N_B = 1 + \sum_{j=0}^{\infty} (-1)^{j+1} b_j , \qquad b_0 = 1 . \tag{3.47}$$

The weight for the entire chain is

$$N_{AB} = 1 + \sum_{j=0}^{\infty} (-1)^{j+1} \sum_{\tau=0}^{\infty} a_{j-\tau} b_\tau , \tag{3.48}$$

where $a_{-m} = 0$. It immediately follows from Eqs. (3.47) and (3.48) that

$$N_{AB} - 1 = -(N_A - 1)(N_B - 1). \tag{3.49}$$

Thus Eq. (3.46) assigns the correct weight for exclusion, $N_{AB} = 1$, to any configuration for which a point of division exists, such that $N_A = 1$ or $N_B = 1$. By induction, it follows easily that the correct weight $N_{AB} = 1$ is assigned to every configuration in which there is an interference between two beads, say i and j, but no interference between beads on opposite sides of either the i^{th} or j^{th} beads, or between beads both of which are between the i^{th} and j^{th} beads.

It appears likely that most configurations containing interferences will contain an interference satisfying the above condition, and will consequently be weighted correctly. While the number of configurations which are incorrectly weighted will be small, it must be remembered that the relative number of configurations without any interferences at all (these being the configurations in which we are

interested) is itself very small. Consequently a small relative error in the number of excluded configurations may mean a large relative error in the number of allowed configurations. There will be some compensation due to positive and negative weights, but all these factors make it difficult to say how accurate the first-order calculation really is. Clearly, a second-order calculation is desirable.

7. Second Approximation

We now consider Eq. (3.21).

$$\Psi_2^{(\omega)}(z,\vec{r}:\vec{R}_1,\vec{R}_2) = z\left[\Psi_1^{(\omega)}(z,\vec{R}_1:\vec{R}_2)\,q(\vec{r}-\vec{R}_1) + \Psi_1^{(\omega)}(z,\vec{R}_2:\vec{R}_1)\,q(\vec{r}-\vec{R}_2)\right] + z\int d\vec{r}'\,q(\vec{r}-\vec{r}')\,\Psi_2^{(\omega)}(z,\vec{r}':\vec{R}_1,\vec{R}_2). \tag{3.21}$$

It follows immediately, upon use of the same procedure as in Section 6, that

$$\Psi_2^{(\omega)}(z,\vec{r}:\vec{R}_1,\vec{R}_2) = \Psi_1^{(\omega)}(z,\vec{R}_1:\vec{R}_2)\,\Psi_0^{(\omega)}(z,\vec{r}-\vec{R}_1) + \Psi_1^{(\omega)}(z,\vec{R}_2:\vec{R}_1)\,\Psi_0^{(\omega)}(z,\vec{r}-\vec{R}_2). \tag{3.50}$$

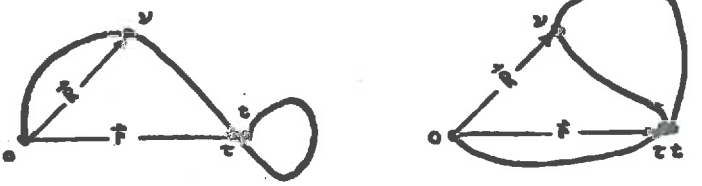
Setting $\vec{R}_1 = \vec{r}$ and $\vec{R}_2 = \vec{R}$, and again using the fact that the product of Ψ's is the convolution of the corresponding $\bar{\Phi}$'s, we obtain

$$\bar{\Phi}_2^{(\omega)}(t,\vec{r}:\vec{r},\vec{R}) = \sum_{j=1}^{t-1} \bar{\Phi}_1^{(\omega)}(t-j,\vec{r}:\vec{R})\,\bar{\Phi}_0^{(\omega)}(j,0) + \sum_{j=1}^{t-1} \bar{\Phi}_1^{(\omega)}(t-j,\vec{R}:\vec{r})\,\bar{\Phi}_0^{(\omega)}(j,\vec{r}-\vec{R}). \tag{3.51}$$

$\bar{\Phi}_2(t,\vec{r}:\vec{r},\vec{R})$ gives the weight density of configurations in which the end beads are at 0, $\vec{r}$, and intermediate beads are at $\vec{r}$ and $\vec{R}$. It follows from Eq. (3.8) that

$$\Phi_2(t,\vec{r};\vec{r},\vec{R}) = \sum_{\tau \neq \nu} \sum \Psi_2(t,\vec{r};\tau,\vec{r};\nu,\vec{R}) \qquad (3.52)$$

Two cases need be distinguished, $\tau > \nu$ and $\tau < \nu$ — configurations corresponding to each are shown in Fig. 5a and 5b respectively. The sum in Eq. (3.52) is essentially the sum over all ν and τ of the weights for these configurations.



(a) (b)

Fig. 5
Configurations which Contribute to $\Phi_2(t,\vec{r};\vec{r},\vec{R})$

The first sum in Eq. (3.51) corresponds to the sum over configurations of the type shown in Fig. 5a, while the second sum corresponds to configurations of the type shown in Fig 5b. The first sum, however, does not take account of interactions within the closed loop (Fig 5a) or between the closed loop and the rest of the chain. The second sum does not take account of interactions within the part of the chain between beads ν and t (Fig 5b), and does not take account of interactions between that part of the chain and the remainder.

Substitution of Eq. (3.50) into Eq. (3.20) gives

$$\psi_1^{(1)}(z,\vec{r}:\vec{R}) = z\left[1-\nu\psi_0^{(\infty)}(z,0)\right]\int d\vec{r}'\,g(\vec{r}-\vec{r}')\,\psi_1^{(1)}(z,\vec{r}':\vec{R})$$

$$+\psi_0^{(\infty)}(z,\vec{R})\,g(\vec{r}-\vec{R})z - \lambda\nu\,\psi_1^{(1)}(z,\vec{R}:\vec{R})\,g(\vec{r}-\vec{R})z$$

$$-\nu\int d\vec{r}'\,g(\vec{r}-\vec{r}')\,\psi_1^{(1)}(z,\vec{R}:\vec{r}')\,\psi_0^{(\infty)}(z,\vec{r}'-\vec{R})z.$$

(3.53)

The last integral in Eq. (3.53) makes impracticable the further use of the Fourier transform. It is clear that as one attempts to improve the calculation, higher-order distribution functions need be considered, which confront one with more complicated integral equations to solve. The writer has not been successful in carrying the outlined procedure beyond Eq. (3.53).

The result of the first approximation, while admitting an interesting interpretation, is of little value as far as numerical computation is concerned. Thus, while we have indicated a systematic means of successive approximations, this procedure has not proved fruitful.

In the next chapter we shall consider the passage from integral to partial differential equations, a procedure that is common in random-flight problems.

CHAPTER IV

THE ANALOGOUS BOUNDARY VALUE PROBLEM

It is common procedure in random-flight problems to pass from integro-difference equations to a boundary value problem in partial differential equations. A good description of the method has been given by Chandrasekhar (3), and the method has been applied to the excluded volume problem by several authors, (21, 22, 23, 24, 56).

1. The Continuous Model

The pearl necklace model was considered in Chapter III. Specifically we considered a chain of t links with beads at each juncture, such that the presence of the center of an interior bead at a given point in space excludes a surrounding volume v from occupancy by the center of any other interior bead. (Volume exclusion due to the end beads is not considered.) The integro-difference equation obtained for $\Phi_t(t,\vec{r})$ [Eq. (3.14)] can be written

$$\Phi_t(t+1,\vec{r}) = \int d\vec{s}\, g(s)\, \Phi_t(t,\vec{r}-\vec{s}) - v \int d\vec{s}\, g(s)\, \Phi_t(t,\vec{r}-\vec{s};\vec{r}-\vec{s}). \qquad (4.1)$$

We now consider another model, to be called the continuous model, which we define as the limiting form of the pearl necklace model reached by letting the number of links per unit rms extension become infinite, while holding constant the excluded volume per unit rms extension. More

specifically, let us now divide each link of the pearl necklace model into $1/\Delta t$ sub-links, such that the a-priori probability that a sub-link has the extension $\vec{s}$ to within $d\vec{s}$ is given by

$$q^{*}(s)\,d\vec{s} = \left(\frac{3}{2\pi\Delta t}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{s^2}{\Delta t}\right) d\vec{s}. \tag{4.2}$$

Thus the mean square extension of a sub-link is Δt; the mean square extension of the composite link, if interactions within the link are neglected, is $(\Delta t)(1/\Delta t) = 1$, as before. The excluded volume associated with each sub-link will be

$$\Delta v = v\,\Delta t, \tag{4.3}$$

so that the total excluded volume is the same as before. The continuous model will then be obtained by letting Δt pass to the limit zero.

Let $1/\Delta t$ be finite. If instead of numbering the beads by integers, we number them $0, \Delta t, 2\Delta t, \ldots, t-\Delta t, t$, it follows immediately from Eq. (4.1) that

$$\bar{\Phi}_n(t+\Delta t,\vec{r}) = \int d\vec{s}\; q^{*}(s)\,\bar{\Phi}_n(t,\vec{r}-\vec{s}) - \Delta v \int d\vec{s}\; q^{*}(s)\,\bar{\Phi}_{n1}(t,\vec{r}-\vec{s}:\vec{r}-\vec{s}) \tag{4.4}$$

We shall make use of the following expansions:

$$\bar{\Phi}_n(t+\Delta t,\vec{r}) = \bar{\Phi}_n(t,\vec{r}) + \Delta t\,\frac{\partial \bar{\Phi}_n(t,\vec{r})}{\partial t} + \frac{(\Delta t)^2}{2!}\frac{\partial^2 \bar{\Phi}_n(t,\vec{r})}{\partial t^2} + \cdots, \tag{4.5}$$

$$\bar{\Phi}_n(t,\vec{r}-\vec{s}) = \bar{\Phi}_n(t,\vec{r}) - \vec{s}\cdot\vec{\nabla}\,\bar{\Phi}_n(t,\vec{r}) + \frac{1}{2!}(\vec{s}\cdot\vec{\nabla})^2\bar{\Phi}_n(t,\vec{r}) + \cdots, \tag{4.6}$$

and an identical expansion for $\bar{\Phi}_1(t,\vec{r}-\vec{s}:\vec{r}-\vec{s})$. It can easily be shown that for $n > -2$

$$\int d\vec{s}\; s^{n} q^{*}(s) = \frac{1}{\sqrt{\pi}}\left(\frac{2\Delta t}{3}\right)^{n/2}\Gamma\left(\frac{n+3}{2}\right). \tag{4.7}$$

It follows from the spherical symmetry of $g^*(s)$ and Eqs. (4.3) through (4.7) that in the limit $\Delta t \to 0$, in which we go over to the continuous model, we obtain

$$\frac{\partial \Phi_0(t,\vec{r})}{\partial t} - \frac{1}{6}\nabla^2 \Phi_0(t,\vec{r}) = -v\,\Phi_1(t,\vec{r};\vec{r}). \tag{4.8}$$

The continuous parameter t, referring to position along the chain, can be defined as

$$t = M/M_0, \tag{4.9}$$

where M is the molecular weight of that portion of chain extending from the origin to the point in question, and M_0 is the molecular weight corresponding to a link in the original pearl necklace model. (We consider a link to be equivalent to the "statistical element" of Kuhn (30).) The apriori probability that an added molecular weight ΔM has extension $\vec{s}$ to within $d\vec{s}$ is given by $g^*(s)d\vec{s}$, where $\Delta t = \Delta M/M_0$. The extension $\vec{s}$ has again been taken to be dimensionless; it (as well as all other lengths and volumes) is measured in multiples of the rms extension of the statistical element.

The excluded volume v can be interpreted in terms of known physical properties of long chain molecules. It follows from Eqs. (4.3) and (4.9) that

$$v = \frac{\Delta v}{\Delta t} = \frac{\Delta v}{\Delta M} M_0 . \tag{4.10}$$

If ΔV is the volume in cm^3 corresponding to Δv, and l is the rms extension in cm of a statistical element, it follows that

$$v = \frac{\Delta V}{\Delta m} \cdot \frac{M_0}{l^3 N} \quad , \tag{4.11}$$

where N is Avogadro's number, and Δm is the added mass in grams. The excluded volume ΔV may not be the actual volume of the added mass, but in terms of orders of magnitude,

$$\frac{\Delta V}{\Delta m} \cong \frac{1}{\rho} \tag{4.12}$$

so that

$$v \cong \frac{1}{\rho l^3} \frac{M_0}{N} \quad , \tag{4.13}$$

where ρ is the density of the polymer in gm/cm^3. Isoprene will be considered as an example. The statistical element corresponds to 2.8 monomers and has an rms extension of 13 Å, (32). The use of Eq. (4.13) with $M_0 = 68 \times 2.8 = 190$ gm. and $\rho \cong 1 gm./cm^3$ gives $v \cong 0.1$. For $M = 100{,}000$, it follows that $t = 525$ and $vt^{1/2} \cong 2$.

A model in which the mass is uniformly distributed along a chain would certainly be more realistic than a pearl necklace model. However, the limiting procedure described above does not give a uniform distribution of mass, but rather a continuous model having rather peculiar properties. Consider, for example, the geometric length of the chain, which we define (in the case of the pearl necklace model) to be the sum of the rms link lengths. Thus for the original pearl necklace of t links, each link having unit rms extension, the geometric length of the chain equals t. After subdivision of each link into $1/\Delta t$ sub-links, each sub-link has rms extension $(\Delta t)^{1/2}$, so that the total geometric length of the

subdivided chain, $(\Delta t)^{1/2}\frac{t}{\Delta t} = \frac{t}{(\Delta t)^{1/2}}$, becomes infinite as $\Delta t \to 0$. Therefore, the continuous model does not correspond to a chain of finite length, but rather an infinite thread.

It is difficult to describe physically the excluded volume problem directly in terms of the continuous model. In addition, the model as described, leads to certain mathematical difficulties. Thus, after subdivision, the rms distance between consecutive beads is $(\Delta t)^{1/2}$, while the radii of these beads is of the order $(\Delta t)^{1/3}$. (See Eq. (4.3).). Therefore as $(\Delta t) \to 0$, the separation of consecutive beads goes to zero more rapidly than the radii of these beads. Consequently there will be a value of $\Delta t > 0$ for which virtually no configuration of the chain is allowable, since all configurations will, with a high degree of probability, contain next neighbor interferences. To remove this difficulty, it is necessary to include, in the description of the continuous model, the condition that there are fixed chain segments (for example, the statistical chain element) within which interferences are not considered.

Because of the arbitrary character and additional conditions that are associated with the continuous model, it will not be convenient to describe the work of this chapter in terms of this model. Equation (4.8) was obtained by James (24) essentially by directly expanding Eq. (4.1), and neglecting second-order derivatives of $\bar{\Phi}_0(t,\vec{r})$ with respect to t, fourth-order derivatives of $\bar{\Phi}_0(t,\vec{r})$ with respect to r, and second-order derivatives of $\bar{\Phi}_1(t,\vec{r}:\vec{r})$

with respect to r. These neglections are partially justified by the consideration of the order of magnitude of these quantities in the absence of volume exclusion. It will be convenient for us to continue to use the terminology and physical picture of the original pearl necklace model, even though we consider the result, Eq. (4.8), of the limiting procedure.

2. Introduction of the Density Function $F(t,\vec{r}:\vec{R})$

We define $F(t,\vec{r}:\vec{R})$ by the relation

$$F(t,\vec{r}:\vec{R}) = \frac{\Phi_1(t,\vec{r}:\vec{R})}{\Phi_0(t,\vec{r})} . \tag{4.14}$$

Therefore, $F(t,\vec{r}:\vec{R})d\vec{R}$ is the probability for finding any bead, other than the fixed end beads, in the volume element $d\vec{R}$ about $\vec{R}$ when the end beads are fixed at 0 and $\vec{r}$. Equation (4.8) can then be rewritten

$$\frac{\partial \Phi_0(t,\vec{r})}{\partial t} - \frac{1}{6}\nabla^2 \Phi_0(t,\vec{r}) = -\nu F(t,\vec{r}:\vec{r})\,\Phi_0(t,\vec{r}). \tag{4.15}$$

We desire a solution of Eq. (4.15), subject to the boundary conditions that there is a source at the origin for $t=0$* such that

$$\Phi_0(0,\vec{r}) = 0 \quad \text{for} \quad \vec{r} \neq 0,$$

$$\lim_{t\to 0} \int d\vec{r}\, \Phi_0(t,\vec{r}) = 1,$$

and for any fixed t, $\Phi_0(t,\vec{r}) \to 0$ as $r \to \infty$. (4.16)

*Instead of a source at the origin for $t=0$, it would be more precise to require that $\Phi_0(1,\vec{r}) = g(r)$. However, as is well known in diffusion type problems, the distribution for large values of t is relatively insensitive to the form of the distribution for small values of t.

It will be necessary to make some approximations in solving Eq. (4.15), since the function $F(t,\vec{r}:\vec{r})$ is not known. It would be a poor approximation to replace the entire right hand side of Eq. (4.15) by its value in the absence of volume exclusion, because the relative number of configurations having both an end at $\vec{r}$ and another bead in the volume v about $\vec{r}$ is greatly affected by volume exclusion. However, the fraction of the configurations with end at $\vec{r}$ in which there is another bead in v about $\vec{r}$ will be less drastically affected, and consequently the approximation of the fraction F is a far better procedure.

For $v = 0$, the fundamental solution of the boundary value problem given by Eqs. (4.15) and (4.16) is the well known result

$$\Phi_0^{(0)}(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{t}\right). \qquad (4.17)$$

We shall call this the zeroth-order approximation. For $v \neq 0$, we shall attempt the solution of the problem by successive approximations of $F(t,\vec{r}:\vec{r})$. The calculation of this quantity will be discussed in the next section. In the following sections we shall calculate $F_0(t,\vec{r}:\vec{r})$, the value of $F(t,\vec{r}:\vec{r})$ in the absence of volume exclusion, and use the result to obtain a first-order approximation of $\Phi_0(t,\vec{r})$. A procedure for obtaining a second-order approximation will then be discussed, although the writer has not been successful in carrying this procedure to a fruitful conclusion.

3. Discussion of $F(t,\vec{r}:\vec{r})$

Let $f_\tau(t,\vec{r}:\vec{r})$ be the probability density for finding the center of the τ^{th} bead at $\vec{r}$ when the end of the chain (center of the t^{th} bead) is at $\vec{r}$. Since these probabilities are mutually exclusive

$$F(t,\vec{r}:\vec{r}) = \sum_{\tau=1}^{t-1} f_\tau(t,\vec{r}:\vec{r}). \tag{4.18}$$

Although we are still using the terminology of the pearl necklace model, it is consistent with the replacement of Eq. (4.1) by Eq. (4.8) to replace the sum in Eq. (4.18) by the integral

$$F(t,\vec{r}:\vec{r}) = \int_{1/2}^{t-1/2} d\tau\, f_\tau(t,\vec{r}:\vec{r}). \tag{4.19}$$

The particular choice of $\frac{1}{2}$, $t-\frac{1}{2}$ as the limits of integration is arbitrary, but as will be seen later, the qualitative features of the results are independent of this choice.

One can express $f_\tau(t,\vec{r}:\vec{r})$ by the relation

$$f_\tau(t,\vec{r}:\vec{r}) = \frac{\bar{\Phi}_0(\tau,\vec{r})\bar{\Phi}_0(t-\tau,0)}{\bar{\Phi}_0(t,\vec{r})}\, p(\tau,\vec{r}:t-\tau,0), \tag{4.20}$$

where $p(\tau,\vec{r}:\, t-\tau,\vec{s})$ is the probability that there are no interferences between a chain of τ links with extension $\vec{r}$ and a chain of $t-\tau$ links of extension $\vec{s}$ beginning at the end of the first chain, calculated taking account of volume exclusion within the two chains.

Let $p(t,\vec{r})$ be the probability that there are no interferences in a chain of t links and extension $\vec{r}$. Then

$$\bar{\Phi}_0(t,\vec{r}) = p(t,\vec{r})\,\bar{\Phi}_0^{(\infty)}(t,\vec{r}). \tag{4.21}$$

It follows from Eqs. (4.19), (4.20), and (4.21) that

$$F(t,\vec{r}:\vec{r}) = \int_{t/2}^{t-t_0} d\tau \; \frac{\bar{\Phi}_0^{(2)}(\tau,\vec{r})\,\bar{\Phi}_0^{(2)}(t-\tau,o)}{\bar{\Phi}_0^{(2)}(t,\vec{r})} \; \frac{\rho(\tau,\vec{r})\,\rho(t-\tau,o)}{\rho(t,\vec{r})} \; \rho(\tau,\vec{r}:t-\tau,o). \tag{4.22}$$

By the use of Eq. (4.17) and the change of variables

$$x = \frac{t-\tau}{t} \tag{4.23}$$

it follows that

$$F(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} t^{-3/2} \pi \int_{1/2t}^{1-\frac{t_0}{t}} dx \cdot x^{-3/2}(1-x)^{-3/2} \exp\left(-\xi^2 \frac{x}{1-x}\right) \frac{\rho(\tau,\vec{r})\,\rho(t-\tau,o)}{\rho(t,\vec{r})}\, \rho(\tau,\vec{r}:t-\tau,o) \tag{4.24}$$

where

$$\xi = \sqrt{\frac{3}{2}}\,\frac{r}{t^{1/2}} \; . \tag{4.25}$$

We shall use Eq. (4.24) to obtain successive approximations to $F(t,\vec{r}:\vec{r})$ from which successive approximations to $\bar{\Phi}_0(t,\vec{r})$ can be obtained by the solution of Eq. (4.15).

4. Calculation of $F_0(t,\vec{r}:\vec{r})$

As a first approximation, we shall consider $F_0(t,\vec{r}:\vec{r})$, the value of $F(t,\vec{r}:\vec{r})$ computed in the absence of volume exclusion. It follows from Eq. (4.24) that

$$F_0(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{1}{t^{3/2}} \int_{1/2t}^{1-\frac{t_0}{2t}} dx \cdot x^{-3/2}(1-x)^{-3/2} \exp\left(-\xi^2 \frac{x}{1-x}\right). \tag{4.26}$$

Let

$$y^2 = \frac{x}{1-x}\,, \qquad \delta = \sqrt{\frac{1}{2t-1}} \cong \frac{1}{\sqrt{2t}}\,; \tag{4.27}$$

then,

$$F_0(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{2}{t^{3/2}} \int_\delta^{\gamma_\delta} dy \; \frac{1+y^2}{y^4} \; e^{-\xi^2 y^2}. \tag{4.28}$$

Integration by parts gives

$$F_0(t,\vec{r}\,;\vec{r}\,) = \left(\frac{2}{2\pi}\right)^{3/2} 2\pi \exp\left(-r^2/2t\right) - \left(\frac{2}{2\pi}\right)^{3/2} \frac{\sqrt{\pi}}{t} \exp\left(-2\xi^2 t\right)$$
$$+ \left(\frac{2}{2\pi}\right)\sqrt{\frac{2}{2t}}\left(\frac{1}{r} - 2\xi\right)\left[\operatorname{erfc}\left(\frac{r}{\sqrt{2t}}\right) - \operatorname{erfc}\left(\xi\sqrt{2t}\right)\right], \tag{4.29}$$

where the complementary error function is defined as

$$\operatorname{erfc} u = \frac{2}{\sqrt{\pi}} \int_u^\infty dz\, e^{-z^2}, \tag{4.30}$$

and is given by the power series

$$\operatorname{erfc} u = 1 - \frac{2}{\sqrt{\pi}}\left(u - \frac{u^3}{3\cdot 1!} + \frac{u^5}{5\cdot 2!} - \frac{u^7}{7\cdot 3!} + \cdots\right). \tag{4.31}$$

For large u, the asymptotic expansion

$$\operatorname{erfc} u \doteq \frac{e^{-u^2}}{u\sqrt{\pi}}\left(1 - \frac{1}{2u^2} + \frac{1\cdot 3}{(2u^2)^2} - \frac{1\cdot 3\cdot 5}{(2u^2)^3} + \cdots\right) \tag{4.32}$$

is convenient.

From Eqs. (4.25) and (4.29) it follows that

$$F_0(t,\vec{r}\,;\vec{r}\,) = c \exp\left(-\frac{3r^2}{4t^2}\right) - \frac{c}{2t} \exp\left(-3r^2\right)$$
$$+ \left(\frac{3}{2\pi r} - \frac{9r}{2\pi t}\right)\left[\operatorname{erfc}\left(\frac{\sqrt{3}}{2}\frac{r}{t}\right) - \operatorname{erfc}\left(\sqrt{3}\,r\right)\right], \tag{4.33}$$

where

$$c = \left(\frac{2}{2\pi}\right)^{3/2} 2\sqrt{2} = \left(\frac{2}{\pi}\right)^{3/2}. \tag{4.34}$$

For $2 < r \ll O(t^{1/2})$, neglection of terms that are $O(t^{-1})$ and $O(e^{-3r^2})$ leads to the result

$$F_0(t,\vec{r}\,;\vec{r}\,) \cong c + \frac{3}{2\pi r} - \frac{9r}{2\pi t}. \tag{4.35}$$

Equation (4.35) is the result obtained by James (24), except

for a slight difference in the numerical factor c.* Equation (4.33) is valid, however, over a much wider range than is Eq. (4.35). In particular, Eq. (4.33) indicates that for fixed t and very large r, $F_0(t,\vec{r}\cdot\vec{r})$ decreases as $\exp\left(-\frac{3}{4}\frac{r^2}{t^2}\right)$. That this should be so can be seen from the following argument. For very large r, the chain will essentially be straight. The integral in Eq. (4.19) considers interactions to within half a link of the end. For such straight configurations, only that small segment of chain half a link removed from the end will have any appreciable opportunity to interfere with the end. The probability distribution of this segment will be centered around a point at a distance $\frac{r}{2t}$ from the end, and the probability that the segment is located at this distance from the center of its distribution will be proportional to $\exp\left(-\frac{3}{4}\frac{r^2}{t^2}\right)$.

5. First Approximation: Calculation of $\Phi_0^{(1)}(t,\vec{r})$

Upon substitution of Eq. (4.35) into Eq. (4.15) there results a partial differential equation for the first-order

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*Instead of $c=(3/2\pi)^{3/2}2\sqrt{\pi}=2.83(3/\pi)^{3/2}$, the corresponding term in the James result is $(3/\pi)^{3/2}\zeta(3/2)=2.61(3/\pi)^{3/2}$. The reason for this difference is that we have here effectively replaced $\sum_{\tau=1}^{\infty}\frac{1}{\tau^{3/2}}=\zeta\left(\frac{3}{2}\right)$ by $\int_{1/2}^{\infty}\frac{d\tau}{\tau^{3/2}}=2\sqrt{2}$. It should be emphasized that if the limiting procedure in passing from an integro-difference equation to a partial differential equation is valid, then the replacement of the sum by an integral is also valid. The limits of integration can be chosen to give numerical agreement between the two calculations, although there is no reason why we should require this.

approximation to $\bar{\Phi}_2(t,\vec{r})$:

$$\frac{\partial \bar{\Phi}_0^{(1)}(t,\vec{r})}{\partial t} - \frac{1}{6}\nabla^2 \bar{\Phi}_0^{(1)}(t,\vec{r}) = -v\left\{c + \frac{3}{2\pi r} - \frac{9r}{2\pi t}\right\}\bar{\Phi}_0^{(1)}(t,\vec{r}). \tag{4.36}$$

(The first approximation defined here is not the same as the first approximation defined in the previous chapter. The connection between the two approximations will be discussed later.) Equation (4.36) is exactly the equation considered by James, the solution of which is found by inspection to be

$$\bar{\Phi}_0^{(1)}(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(\frac{-3r^2}{2t}\right) \exp\left\{-cvt + \frac{27}{8\pi^2}v^2 t + \frac{9}{2\pi}vr\right\}. \tag{4.37}$$

$\bar{\Phi}_0^{(1)}(t,\vec{r})$ satisfies the boundary conditions [see Eq. (4.16)] and also reduces for $v = 0$ to the known solution in the absence of volume exclusion.

It will be convenient to consider the distribution function expressed as a function of the variables

$$\vec{\xi} = \sqrt{\frac{3}{2}}\,\frac{\vec{r}}{t^{1/2}}, \tag{4.25}$$

and

$$\lambda = \sqrt{\frac{27}{8\pi^2}}\, v t^{1/2}. \tag{4.38}$$

The distribution function $D_0(\lambda,\vec{\xi})$ is defined by the relation

$$D_0(\lambda,\vec{\xi})\, d\vec{\xi} = \bar{\Phi}_0(t,\vec{r})\, d\vec{r}. \tag{4.39}$$

It follows from Eqs. (4.17), (4.37) and (4.39) that

$$D_0^{(1)}(\lambda,\vec{\xi}) = \frac{1}{\pi^{3/2}}\, e^{-\xi^2}, \tag{4.40}$$

and

$$D_0^{(\infty)}(\lambda,\vec{\xi}) = \frac{1}{\pi^{3/2}} \exp\left\{-(\xi-\lambda)^2\right\} \exp\left\{-c\nu t + 2\lambda^2\right\}. \tag{4.41}$$

The most probable extension ξ_0 is defined as the value of ξ for which $\xi^2 D_0(\lambda,\xi)$ is maximum. Therefore, it follows from Eqs. (4.40) and (4.41) that

$$\xi_0^{(\infty)} = 1, \tag{4.42}$$

and

$$\xi_0^{(\infty)} = \frac{\lambda}{2} + \sqrt{1+(\lambda/2)^2}\,. \tag{4.43}$$

By the use of Eq. (4.35) for $F_0(t,\vec{r}:\vec{r})$ we have essentially restricted our attention to $\xi \leq O(1)$. Therefore, by Eq. (4.43) and similar reasoning of James (24), it follows that the above theory leading to Eq. (4.37) is valid over the interesting range of ξ only for $\lambda \leq O(1)$. This restriction, however, can be removed rather simply by the use of Eq. (4.33), which is also valid for $\xi > O(1)$.

In particular let us consider $\lambda = O(t^{1/4})$. Then, by Eq. (4.43) we need to consider values of $\xi = O(t^{1/4})$ and hence values of $r = O(t^{3/4})$. By expanding $\exp\left(\frac{-3r^2}{4t^2}\right)$ and $\operatorname{erfc}\left(\frac{\sqrt{3}}{2}\frac{r}{t}\right)$ in Eq. (4.33), and neglecting terms that are $O(1/t)$ and $O(e^{-3r^2})$, we obtain

$$F_0(t,\vec{r}:\vec{r}) = c + \frac{3}{2\pi r} - \frac{9r}{2\pi t} + \frac{k r^2}{t^2} \tag{4.44}$$

where

$$k = \frac{3\sqrt{2}}{2}\left(\frac{3}{2\pi}\right)^{3/2}. \tag{4.45}$$

The effect of considering values of r as large as $t^{3/4}$ is to make terms proportional to r^2/t^2 no longer negligible. Corresponding to Eq. (4.36) we now have

$$\frac{\partial \bar{\Phi}_o^{(\infty)}(t,\vec{r})}{\partial t} - \frac{1}{6}\nabla^2 \bar{\Phi}_o^{(\infty)}(t,\vec{r}) = -v\left[c + \frac{3}{2\pi r} - \frac{9r}{2\pi t} + \frac{3r^2}{t^2}\right]\bar{\Phi}_o^{(\infty)}(t,\vec{r}). \tag{4.46}$$

If $\bar{\Phi}_o^{(\infty)}(t,\vec{r})$ is multiplied by $\exp\left(-\frac{3vr^2}{t}\right)$, the function that is obtained is not an exact solution of Eq. (4.46). However, the additional terms that would have to be added to Eq. (4.46) to make this function a solution are terms proportional to v^2, and are of the order of magnitude of terms that have been neglected. The additional factor, $\exp\left(-\frac{3vr^2}{t}\right)$, is, however, negligible in comparison to the dominant r-dependent correction term, $\exp\left(\frac{9}{2\pi}vr\right)$. Thus, even for $vt^{1/2} = O(t^{1/4})$, the James' result, Eq. (4.37) is still formally valid. It follows from this result that

$$\frac{\langle r^2\rangle}{t} = \frac{\left(1+4\lambda^2+\frac{4}{3}\lambda^4\right)\frac{\sqrt{\pi}}{2}\left(2+\operatorname{erfc}\lambda\right) + \left(\frac{5}{3}\lambda+\frac{2}{3}\lambda^3\right)e^{-\lambda^2}}{\left(1+2\lambda^2\right)\frac{\sqrt{\pi}}{2}\left(2+\operatorname{erfc}\lambda\right) + \lambda e^{-\lambda^2}}, \tag{4.47}$$

from which for small λ

$$\frac{\langle r^2\rangle}{t} = 1 + \frac{4}{3\sqrt{\pi}}\lambda + \text{higher powers of } \lambda, \tag{4.48}$$

and for $\lambda \gg 1$

$$\frac{\langle r^2\rangle}{t} \cong \frac{2}{3}\lambda^2. \tag{4.49}$$

[See James (24), Eq. (54) through Eq. (59).] Thus for small values of λ, $\frac{\langle r^2\rangle}{t}$ begins to increase as $t^{1/2}$, but for $\lambda \gg 1$, $\frac{\langle r^2\rangle}{t}$ increases as t. It can be seen from Eq. (4.43) that the most probable extension exhibits the same behavior.

The prediction that $\langle r^2\rangle/t$ increases as the first power of t for large values of t indicates, on the basis

of the experimental results quoted in Chapter I, that the first-order calculation gives an over-correction of the volume exclusion effect for large t. The reason for this is clear. We replaced $F(t,\vec{r}:\vec{r})$ by $F_o(t,\vec{r}:\vec{r})$; that is, we calculated the probability for finding another bead at the location of the t^{th} bead, neglecting volume exclusion. The probability that we calculate neglecting volume exclusion is larger than the actual probability. This error will be largest for configurations with small extension, since volume exclusion is most important for these configurations. Thus, $F_o(t,\vec{r}:\vec{r})$ is too large for small r, and consequently $\Phi_o^{(n)}(t,\vec{r})$ will be too small for small r. For large values of t, this error is by no means small, and consequently a more accurate evaluation of $F(t,\vec{r}:\vec{r})$ is required. It will therefore be necessary to evaluate approximately the probabilities for no interference, $\rho(t,\vec{r})$ and $\rho(\tau,\vec{r}:\ t-\tau,0)$, that appear in the general expression for $F(t,\vec{r}:\vec{r})$, Eq. (4.24).

6. Procedure for the Determination of $\rho(t,\vec{r})$

In Section 6 of James' paper, $\rho(t,\vec{r})$ is calculated approximately by a method that will presently be described. The calculations will be repeated here in a somewhat more general way, so that the results will be valid not only for the large t and $r = O(t^{1/4})$ that James considers, but also for small values of t and for values of r as large as $O(t^{3/4})$. We shall also formulate a general method by which $\rho(t,\vec{r})$ can be calculated, and shall show in what way the James result is a first approximation.

We consider all configurations of a perfectly flexible chain of t links in which the end beads--that is, the 0^{th} and t^{th} beads--are fixed at the origin and at $\vec{r}$ respectively. There are $\binom{t-1}{2}$ pairs of interior beads that can interfere. (We shall not consider here the effects of ternary or higher-order interferences. See Appendix B for a discussion of this question.) These pairs are numbered by the single index $\nu = 1, 2, \ldots, \binom{t-1}{2}$. Let $N_\nu(t,\vec{r})$ be the relative number of configurations in which the ν^{th} pair interfere, regardless of any other interference that may be present. Likewise let $N_{\nu,\mu}(t,\vec{r})$ be the relative number of configurations in which both the ν^{th} and μ^{th} pairs interfere, again regardless of any other interference that may be present, and so on. If $\Phi_0(t,\vec{r})$ is the relative number of configurations containing no interferences, and $\Phi_0^{(\omega)}(t,\vec{r})$ the relative number regardless of interferences, then

$$\Phi_0(t,\vec{r}) = \Phi_0^{(\omega)}(t,\vec{r}) - \sum_{\nu=1}^{\binom{t-1}{2}} N_\nu(t,\vec{r}) + \sum\sum_{\nu>\mu} N_{\nu,\mu}(t,\vec{r}) - \cdots \tag{4.50}$$

It is easy to see that Eq. (4.50) gives weight zero to any configuration containing an interference. Consider, for example, a configuration containing n interferences. It is given weight +1 by the first term on the right hand side, weight $-\binom{n}{1}$ by the next, weight $\binom{n}{2}$ by the next, and so on. Since

$$\sum_{i=0}^{n} (-1)^i \binom{n}{i} = (1-1)^n = 0 , \tag{4.51}$$

the total weight given to this configuration is zero.

The probability that there are no interferences is given by

$$\rho(t,\vec{r}) = \frac{\Phi_0(t,\vec{r})}{\Phi_0^{(\omega)}(t,\vec{r})} \,. \tag{4.21}$$

Likewise, the probability that the ν^{th} pair interfere regardless of any other interference, $P_\nu(t,\vec{r})$, is given by

$$P_\nu(t,\vec{r}) = \frac{N_\nu(t,\vec{r})}{\Phi_0^{(\omega)}(t,\vec{r})} \,. \tag{4.52}$$

Divide Eq. (4.50) by $\Phi_0^{(\omega)}(t,\vec{r})$; it can then be written as

$$\rho(t,\vec{r}) = 1 - \sum_{\nu=1}^{\binom{k}{2}} P_\nu + \sum_{\nu>} \sum_{\mu} P_{\nu\mu} - \sum_{\nu>} \sum_{\mu>} \sum_{\lambda} P_{\nu\mu\lambda} + \cdots \tag{4.53}$$

where the P_ν, $P_{\nu\mu}$, $P_{\nu\mu\lambda}$, ...are the normalized values of N_ν, $N_{\nu\mu}$, $N_{\nu\mu\lambda}$, ... respectively.

We define the conditional probabilities

$$P_{(\nu):\mu} = P_{\nu\mu} / P_\nu \tag{4.54}$$

$$P_{(\nu\mu):\lambda} = P_{\nu\mu\lambda} / P_{\nu\mu} \,, \tag{4.55}$$

and so on. Therefore $P_{(\nu):\mu}$ is the fraction of the configurations having the ν^{th} pair interfere in which the μ^{th} pair interferes; that is, it is the conditional probability for interference μ subject to the occurrence of interference ν. The other conditional probabilities are defined analogously. It then follows that

$$p(t,\vec{r}) = 1 - \sum_{\nu} P_{\nu} + \sum_{\nu>\mu}\sum P_{\nu} P_{(\nu):\mu} - \sum_{\nu>\mu>\lambda}\sum\sum P_{\nu} P_{(\nu):\mu} P_{(\nu\mu):\lambda} + \cdots \tag{4.56}$$

We now define

$$P^{(0)} = 1 , \tag{4.57}$$

$$P^{(1)} = \sum_{\nu} P_{\nu} , \tag{4.58}$$

$$P^{(2)} = \overline{\sum_{\mu(\neq\nu)} P_{(\nu):\mu}}^{\nu} = \sum_{\mu\neq\nu}\sum P_{\nu} P_{(\nu):\mu} \Big/ \sum_{\nu} P_{\nu}$$

$$= 2\sum_{\nu>\mu}\sum P_{\nu\mu} \Big/ \sum_{\nu} P_{\nu} , \tag{4.59}$$

$$P^{(3)} = \overline{\sum_{\lambda(\neq\nu,\mu)} P_{(\nu\mu):\lambda}}^{\nu\mu} = \sum_{\nu>\mu}\sum_{\lambda(\neq\nu,\mu)}\sum P_{\nu\mu} P_{(\nu\mu):\lambda} \Big/ \sum_{\nu>\mu}\sum P_{\nu\mu}$$

$$= 3\sum_{\nu>\mu>\lambda}\sum\sum P_{\nu\mu\lambda} \Big/ \sum_{\nu>\mu}\sum P_{\nu\mu} , \tag{4.60}$$

and so on. Thus $P^{(1)}$ is the sum over all pairs of the probability for the interference of a pair. $P^{(2)}$ is the sum over all pairs $(\neq\nu)$ of the probability for interference of a pair subject to the interference of the ν^{th} pair, averaged over all ν; and so on.

With the definitions of Eqs. (4.57), (4.58), (4.59) and (4.60), Eq. (4.53) can be rewritten in the following simple form:

$$p(t,\vec{r}) = \sum_{k=0}^{\binom{n}{2}} \frac{(-1)^k}{k!} \prod_{j=0}^{k} P^{(j)} . \tag{4.61}$$

The second method of James calculates $p(t,\vec{r})$ using the approximation that the probabilities for non-interference

are independent. Thus

$$\rho_0(t,\vec{r}) = \prod_\nu (1 - P_\nu) \tag{4.62}$$

$$= 1 - \sum_\nu P_\nu + \sum_{\nu>\mu}\sum P_\nu P_\mu - \sum_{\nu>\mu>\lambda}\sum\sum P_\nu P_\mu P_\lambda + \cdots$$

$$\cong 1 - P^{(1)} + P^{(2)}/2! - P^{(3)}/3! + \cdots$$

$$\cong \sum_{k=0}^{(k-1)} \frac{(-1)^k}{k!} P^{(1)k} . \tag{4.63}$$

Comparison of Eqs. (4.61) and (4.63) shows that the approximation made in replacing $\rho(t,\vec{r})$ by $\rho_0(t,\vec{r})$ is essentially equivalent to assuming

$$P^{(1)} = P^{(2)} = P^{(3)} = \cdots \tag{4.64}$$

This relation is of course satisfied if the conditional probabilities defined by Eqs. (4.54) and (4.55) are the same as the unconditional probability P_μ. This is not necessary, however, to satisfy Eq. (4.64). All that assumption (4.64) requires is that the sum over all pairs of a conditional probability averaged over the "conditions" is the same as the sum over all pairs of the unconditional probability.

It is a reasonable first approximation to assume that the probabilities for non-interference are independent, since the knowledge that beads m and n do not interfere does not appreciably restrict their distributions. On the other hand, the assumption that the probabilities for interference are independent would be a very poor approximation, because the knowledge of the interference of m and n considerably

enhances the likelihood, for example, that beads (m+1) and (n-1) interfere. This approximation is equivalent to considering only the first summation term in Eq. (4.56), and is essentially the approximation used by Bueche (2), Teramoto (48), and Rubin(38), whose works were criticized in Chapter II. We shall use the much more reasonable approximation given by Eq. (4.62).

7. Calculation of $p_\nu(t,\vec{r})$

Let the index ν refer to the pair of beads m,n. The probability that m and n interfere regardless of any other interferences is given by

$$P_\nu(t,\vec{r}) = \frac{\upsilon \int d\vec{s}\; \Phi_0^{(\omega)}(n,\vec{s})\,\Phi_0^{(\omega)}(m-n,o)\,\Phi_0^{(\omega)}(t-m+n,\vec{r}-\vec{s})}{\int d\vec{s}\int d\vec{s}'\,\Phi_0^{(\omega)}(n,\vec{s})\,\Phi_0^{(\omega)}(m-n,\vec{s}')\,\Phi_0^{(\omega)}(t-m+n,\vec{r}-\vec{s}-\vec{s}')} \tag{4.65}$$

which reduces to

$$P_\nu(t,\vec{r}) = \upsilon \frac{\Phi_0(m-n,o)\,\Phi_0^{(\omega)}(t-m+n,\vec{r})}{\Phi_0^{(\omega)}(t,\vec{r})}. \tag{4.66}$$

It follows from Eqs. (4.58) and (4.66) that

$$p^{(1)}(t,\vec{r}) = \upsilon \sum_{\substack{m=2 \\ m>n}}^{t-1} \sum_{n=1}^{t-2} \frac{\Phi_0^{(\omega)}(m-n,o)\,\Phi_0^{(\omega)}(t-m+n,\vec{r})}{\Phi_0^{(\omega)}(t,\vec{r})}. \tag{4.67}$$

For a given $j=m-n$, there are $t-1-j$ equal terms in the above sum. Therefore,

$$p^{(1)}(t,\vec{r}) = \upsilon \sum_{j=1}^{t-2} (t-1-j)\left(\frac{3}{2\pi}\right)^{3/2}\left[\frac{t}{j(t-j)}\right]^{3/2} \exp\left(-\frac{3}{2}\frac{r^2 j}{t(t-j)}\right). \tag{4.68}$$

With negligible error, we can replace $(t-1-j)$ by $(t-j)$ and change the upper limit of summation to t-1 to obtain

$$P^{(1)}(t,\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} vt \sum_{j=1}^{t-1} \left(\frac{t}{t-j}\right)^{1/2} \frac{1}{j^{3/2}} \exp\left(-\frac{3}{2} r^2 \frac{j}{t(t-j)}\right). \tag{4.69}$$

We again replace the sum by an integral from $\frac{1}{2}$ to $t-\frac{1}{2}$ and use the substitution

$$y^2 = j/t-j \tag{4.70}$$

to obtain

$$P^{(1)}(t,\vec{r}) = 2\left(\frac{3}{2\pi}\right)^{3/2} vt^{1/2} \int_{\beta}^{\infty} \frac{dy}{y^2} e^{-\beta^2 y^2}. \tag{4.71}$$

This integral has been evaluated previously; see Eqs. (4.25), (4.27), (4.28), (4.29), (4.33) and (4.34). The result is

$$P^{(1)}(t,\vec{r}) = cvt \exp\left(-\frac{3r^2}{4t^2}\right) - \frac{cv}{2} \exp(-3r^2) - \frac{3\sqrt{3}vr}{2\pi}\left[\operatorname{erfc}\left(\frac{\sqrt{3}}{2}\frac{r}{t}\right) - \operatorname{erfc}\left(\sqrt{3}\,r\right)\right]. \tag{4.72}$$

For $2 < r \ll O(t^{3/4})$

$$P^{(1)}(t,\vec{r}) = vt\left[c - \frac{3r}{2\pi t} + \frac{kr^2}{t^2} + \begin{matrix}\text{terms } O(t^{-3}) \\ \text{and } O(\exp -3r^2)\end{matrix}\right], \tag{4.73}$$

where $c = (3/\pi)^{3/2}$ and $k = \frac{3}{4}\left(\frac{3}{\pi}\right)^{3/2}$. [See Eqs. (4.34) and (4.45)]

For $r = 0$, it follows from Eq. (4.72) that

$$P^{(1)}(t,0) = cvt - \frac{cv}{2} \cong cvt. \tag{4.74}$$

Since the maximum term in the sum

$$P_0(t,\vec{r}) = \sum_{n=0}^{(t-1)} \frac{(-1)^n}{n!} P^{(1)n} \tag{4.63}$$

occurs for $n = P^{(1)} = O(vt)$, there will be negligible error in

replacing the upper limit of the sum by infinity. Therefore,

$$P_0(t,\vec{r}) \cong \exp\left(-\bar{P}^{(1)}(t,\vec{r})\right), \tag{4.75}$$

which is exactly the approximation used by James. It then follows from Eqs. (4.73) and (4.75) that

$$P_0(t,\vec{r}) = \exp\left\{-cvt + \frac{qvr}{2\pi} - \frac{kvr^2}{t}\right\}. \tag{4.76}$$

Equation (4.76) is consistent with the results of Section 5. In particular, we note that except for the unimportant normalization factor $\exp\left(\frac{27}{8\pi^2}v^2t\right)$, we can write

$$P_0(t,\vec{r}) = \bar{\Phi}_0^{(1)}(t,\vec{r}) \Big/ \bar{\Phi}_0^{(\infty)}(t,\vec{r}). \tag{4.77}$$

8. Importance of Cross-Interferences in the Calculation of $F(t,\vec{r}:\vec{r})$

An exact relation for $F(t,\vec{r}:\vec{r})$ is

$$F(t,\vec{r}:\vec{r}) = \int_{t/2}^{t-t/2} d\tau \; \frac{\bar{\Phi}_0^{(\infty)}(\tau,\vec{r})\,\bar{\Phi}_0^{(\infty)}(t-\tau,0)}{\bar{\Phi}_0^{(\infty)}(t,\vec{r})} \times \frac{p(\tau,\vec{r})\,p(t-\tau,0)}{p(t,\vec{r})} \times p(\tau,\vec{r}:t-\tau,0). \tag{4.22}$$

We define a "cross-interference" as an interference between a chain of τ links having extension $\vec{r}$, and a closed loop of $(t-\tau)$ links beginning at the end of the first chain. (See Fig. 6) The term "cross-interference" is used, because

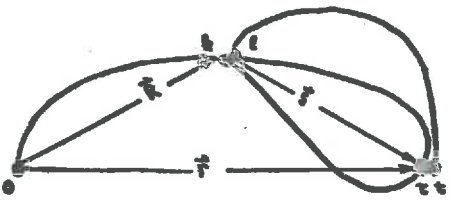


Fig. 6
Illustration of a Cross-Interference

the interference (of beads k and l in Fig. 6) is "across" the fixed τ^{th} bead. Then $\rho(\tau,\vec{r}:t-\tau,o)$ is the probability that there are no cross-interferences, computed taking account of volume exclusion within the two chains. In the first approximation considered in Section 4, the ρ's were replaced by one; that is, $F(t,\vec{r}:\vec{r})$ was calculated in the absence of volume exclusion. In the next approximation, we shall calculate the ρ's assuming that the probabilities for non-interference are independent. Therefore, as the next approximation of $F(t,\vec{r}:\vec{r})$, we define

$$F(t,\vec{r}:\vec{r}) = \int_{\frac{t}{N}}^{t-\frac{t}{N}} d\tau \; \frac{\bar{\rho}_o^{(\omega)}(\tau,\vec{r})\,\bar{\rho}_o^{(\omega)}(t-\tau,o)}{\bar{\rho}_o^{(\omega)}(t,\vec{r})} \times \frac{\rho_o(\tau,\vec{r})\,\rho_o(t-\tau,o)}{\rho_o(t,\vec{r})} \times \rho_o(\tau,\vec{r}:t-\tau,o), \tag{4.78}$$

where $\rho_o(\tau,\vec{r}:t-\tau,o)$ is the probability that there are no cross-interferences, calculated assuming the probabilities for non-interference are independent. We have defined $\rho_o(t,\vec{r})$ in Eq. (4.62), and its value is given in Eq. (4.67), from which it follows that

$$\frac{\rho_o(\tau,\vec{r})\,\rho_o(t-\tau,o)}{\rho_o(t,\vec{r})} = \exp\left\{ \tfrac{3}{2} u r^2 \, \frac{t-\tau}{t\tau} \right\}. \tag{4.79}$$

It follows from Eqs. (4.24), (4.78), and (4.79) that $F_1(t,\vec{r}:\vec{r})$ can be expressed as

$$F_1(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{1}{t^{3/2}} \int_{1/N}^{1-\frac{1}{N}} dx \cdot x^{-3/2}(1-x)^{-3/2} \exp\left\{ -\tfrac{3}{2}\left(1+\tfrac{2}{3}kv\right)\frac{x}{1-x} \right\} \rho_o(\tau,\vec{r}:t-\tau,o). \tag{4.80}$$

If the effects of cross-interferences are neglected--that is, if one sets $\rho_o(\tau,r:t-\tau,o) = 1$--then $F_1(t,\vec{r}:\vec{r})$ as calculated from Eq. (4.80) differs negligibly from $F_o(t,\vec{r}:\vec{r})$.

Thus the essential factor in the improved calculation is the probability that there are no cross-interferences, $P_0(\tau,\vec{r}:t-\tau,o)$.

In Chapter III the first-order approximation was defined differently; it led to the result [see Eq. (3.37)]

$$\bar{\Phi}_1(t,\vec{r}:\vec{r}) = \sum_{j=1}^{t-1} \bar{\Phi}_0^{(o)}(j,o)\,\bar{\Phi}_0(t-j,\vec{r}). \tag{4.81}$$

Thus the first approximation in Chapter III neglects cross-interferences and also neglects interferences within the closed loop. The result and interpretation given in Chapter III, Section 5 would not be significantly altered if interferences within the closed loop were considered, by setting

$$\bar{\Phi}_1(t,\vec{r}:\vec{r}) = \sum_{j=1}^{t-1} \bar{\Phi}_0(j,o)\,\bar{\Phi}_0(t-j,\vec{r}). \tag{4.82}$$

It might appear that the approximation implicit in Eq. (4.82) would give better results than the first approximation defined in this chapter, since only interactions of a limited class are neglected in Eq. (4.82). We have seen, however, that it is just these cross-interferences that cause $F_1(t,\vec{r}:\vec{r})$ to differ appreciably from $F_0(t,\vec{r}:\vec{r})$. The systematic neglection of the interactions between the closed loop and the remainder of the chain would lead to the same result as the first-order calculation of this chapter. To improve this result, it is necessary to consider the effect of the cross-interferences.

We consider now the class of cross-interferences--that is, those interferences involving both a bead in the closed

loop of $(t-\tau)$ links and a bead in the remainder of the chain. (See Fig. 6). There are $(t-1-\tau)$ $(\tau-1)$ such pairs. We shall denote these pairs by the single index α, and $\sum_{\alpha}$ will designate a sum over all such pairs. P_α is defined to be the probability that there is an interference of pair α regardless of any other interferences that may be present. In the first approximation, with the same degree of validity as Eq. (4.75), the probability that there are no cross-interferences is given by

$$P_0(\tau,\vec{r}: t-\tau, 0) = \exp\left(-\sum_{\alpha} P_\alpha\right). \tag{4.83}$$

If α corresponds to the interference of beads k, l (see Fig. 6) then P_α is given by

$$P_\alpha = \upsilon \int d\vec{s}\; \frac{\Phi_0^{(\omega)}(k,\vec{r}-\vec{s})\,\Phi_0^{(\omega)}(\tau-k,\vec{s})}{\Phi_0^{(\omega)}(\tau,\vec{r})} \times \frac{\Phi_0^{(\omega)}(l-\tau,-\vec{s})\,\Phi_0^{(\omega)}(t-l,\vec{s})}{\Phi_0(t-\tau,0)}. \tag{4.84}$$

From the definition of F_0, it follows that

$$\sum_{\alpha} P_\alpha = \upsilon \int d\vec{s}\; F_0(\tau,\vec{r}:\vec{r}-\vec{s})\,F_0(t-\tau,0:\vec{s}). \tag{4.85}$$

It is shown in Appendix E that for $R \gg 1$, $s \gg 1$, with the neglection of terms of the orders of magnitude of τ^{-1}, e^{-3R^2} and e^{-3s^2},

$$F_0(\tau,\vec{R}+\vec{s}:\vec{R}) \cong \left(\frac{3}{2\pi R}+\frac{3}{2\pi s}\right)\exp\left[\frac{3}{\tau}\left(\vec{R}\cdot\vec{s}-Rs\right)\right]. \tag{4.86}$$

[A more complete expression, valid for small R and s is given by Eq. (E.16).]

It follows from Eq. (4.86) that

$$F_0(j,o;\vec{s}) \cong \frac{2}{\pi s} \exp\left(-\frac{6s^2}{j}\right). \tag{4.87}$$

This approximation can be checked by considering the exact relation

$$\int d\vec{s}\, F_0(j,o;\vec{s}) = \int_{k_0}^{j-k_0} dk \int d\vec{s}\, \frac{\Phi_0^{(o)}(k,\vec{s})\,\Phi_0^{(o)}(j-k,\vec{s})}{\Phi_0^{(o)}(j,o)} = j-1. \tag{4.88}$$

Integration of the approximation given by Eq. (4.87) gives

$$\int d\vec{s}\, \frac{3}{\pi s} \exp\left(-\frac{6s^2}{j}\right) = 12\int_0^\infty ds\, \exp\left(-\frac{6s^2}{j}\right) = j, \tag{4.89}$$

in excellent agreement with Eq. (4.88).

From Eqs. (4.85), (4.86), and (4.87) it follows that

$$\sum_{\alpha} P_{\alpha} \cong \nu \int d\vec{s}\, \frac{3}{\pi s} \exp\left(-\frac{6s^2}{j}\right)\left[\frac{3}{2\pi R}+\frac{3}{2\pi s}\right]\exp\left[\frac{3}{\tau}\left(\hat{R}\cdot\vec{s}-Rs\right)\right] \tag{4.90}$$

where $j=t-\tau$. It should of course be remembered that $\vec{R}=\vec{r}-\vec{s}$, and that the integration in Eq. (4.90) is over all $\vec{s}$ for fixed $\vec{r}$. The use of Eq. (4.90) without further approximation is impracticable; therefore an appropriate approximation will be sought for $p_0(\tau,\vec{r};t-\tau,o)$ for use in Eq. (4.80). Such an approximation will be discussed in the next section. Additional justification for this approximation will be given in Appendix F, where the integral in Eq. (4.90) will be discussed further.

9. Probability for No Cross-Interferences when Chain Extension is Not Fixed

Consider a chain of t links with unspecified extension, but such that the last $(t-\tau)$ links form a closed loop. Let $p(\tau;t-\tau,o)$ be the probability that there are no

interferences between the first τ links and the closed loop (cross-interferences) in those configurations in which there are no interferences within the two parts of the chain. Let $p_0(\tau : t-\tau, o)$ be the corresponding probability calculated assuming that the probabilities for non-interference are independent.

Analogous to Eqs. (4.83) and (4.85) we now have

$$p_0(\tau : t-\tau, o) = \exp\Big(-\sum_\alpha P_\alpha'\Big), \tag{4.91}$$

where

$$\sum_\alpha P_\alpha' = v \int d\vec{s}\; F_0(\tau : \vec{s})\, F_0(t-\tau, o : \vec{s}). \tag{4.92}$$

The probability density, $F_0(\tau : \vec{s})$, in the absence of volume exclusion, in a chain of τ links, that a bead be at $\vec{s}$ when one end of the chain is held fixed at the origin, is given by:

$$F_0(\tau : \vec{s}) = \int_{1/2}^{\tau-1/2} dk\; \Phi_0^{(o)}(k, \vec{s}). \tag{4.93}$$

Equation (4.93) can be rewritten

$$F_0(\tau : \vec{s}) = \int d\vec{r}\; F_0(\tau, \vec{r} : \vec{s})\, \Phi_0^{(o)}(\tau, \vec{r}), \tag{4.94}$$

so that

$$\sum_\alpha P_\alpha' = v \int d\vec{r}\; \Phi_0^{(o)}(\tau, \vec{r}) \int d\vec{s}\; F_0(\tau, \vec{r} : \vec{s}) F_0(t-\tau, o : \vec{s})$$

$$= \overline{\sum_\alpha P_\alpha}^{\,\tau}\,; \tag{4.95}$$

that is, the sum over all cross-interferences when the extension is not constrained is the r-average (with weight equal to the weight of the configuration, $\bar{\Phi}_0^{(\infty)}(\tau,\vec{r})$) of the corresponding sum for fixed extension. Thus $p_0(\tau:t-\tau,0)$ is analogous to our previously defined $p_0(\tau,\vec{r}:t-\tau,0)$; the natural logarithm of the former probability is the average over all r (with weight $\bar{\Phi}_0^{(\infty)}(\tau,\vec{r})$) of the natural logarithm of the latter.

In the remainder of this work, $p_0(\tau,\vec{r}:t-\tau,0)$ will be approximated by $p_0(\tau:t-\tau,0)$. Since it is more likely that there are no interferences between the two parts of the chain (the closed loop and the remainder) for configurations having large extension, we shall be using a value of p_0 that is too large for small extensions, and too small for large extensions. Thus the effect of this approximation is to overweight small extensions in the calculations of $F_1(t,\vec{r}:\vec{r})$ and hence to under-weight small extensions in the calculation of $\bar{\Phi}_0(t,\vec{r})$. Since the effect of the first-order calculation is to increase the weight given to large extensions, the effect of the approximation discussed here is to under-correct the first order result. We shall discuss this point further after first calculating $p_0(\tau:t-\tau,0)$.

It follows from Eqs. (4.17), (4.87) and a simple integration that

$$\int d\vec{s}\; F_0(j,0:\vec{s})\,\bar{\Phi}_0^{(\infty)}(k,\vec{s}) = 4j\left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{k^{3/2}}\,\frac{1}{j+4k}\,. \tag{4.96}$$

It then follows from Eqs. (4.92), (4.93), and (4.96) that

$$\sum_{\alpha} P'_{\alpha} \cong 4j \left(\frac{3}{2\pi}\right)^{3/2} \int_{1/2}^{\tau-1/2} dk \; \frac{1}{k^{1/2}} \cdot \frac{1}{j+4k}$$

$$= 4j^{1/2} \left(\frac{3}{2\pi}\right)^{3/2} \left[\arctan\left(2\sqrt{\frac{\tau-1/2}{j}}\right) - \arctan\left(2\sqrt{\frac{1}{2j}}\right)\right]. \tag{4.97}$$

Since we are interested primarily in the case of large t, both $j \gg 1$ and $\tau \gg 1$ are true over most of the range of integration in the expression for $F_1(t, \vec{r}:\vec{r})$. [See Eq. (4.80).] Therefore, neglecting terms of order j^{-1} we have

$$\sum_{\alpha} P'_{\alpha} \cong 4j^{1/2} \left(\frac{3}{2\pi}\right)^{3/2} \arctan\left[2\left(\frac{t-j}{j}\right)^{1/2}\right]. \tag{4.98}$$

As before, let

$$x = \frac{j}{t} = \frac{t-\tau}{t}, \tag{4.23}$$

and

$$\lambda = \left(\frac{27}{8\pi^2}\right)^{1/2} v t^{1/2}. \tag{4.38}$$

It then follows from Eq. (4.91) that

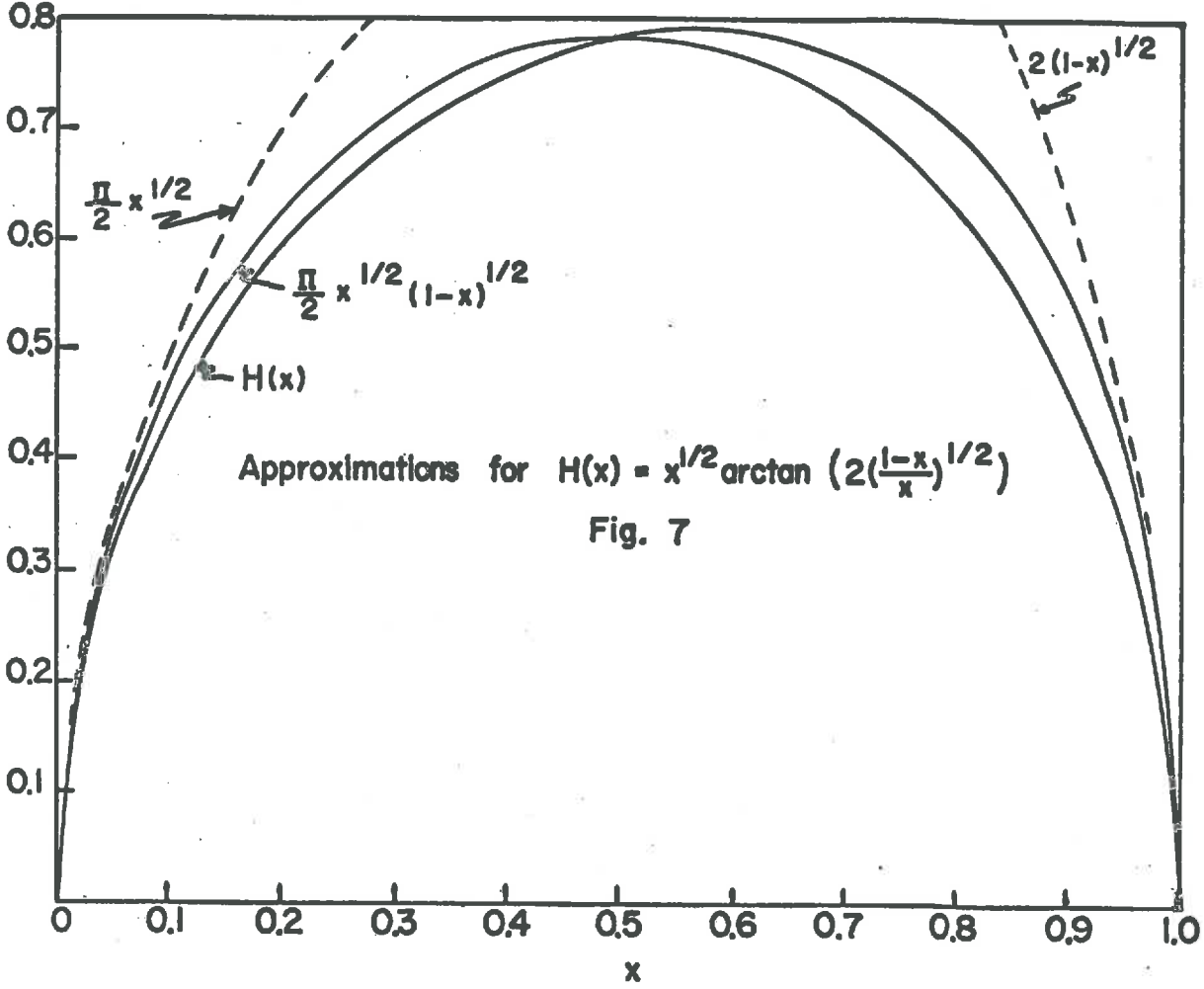
$$P_0(t-j : j, 0) = \exp\left\{\frac{-4}{\sqrt{\pi}} \lambda x^{1/2} \arctan\left[2\left(\frac{1-x}{x}\right)^{1/2}\right]\right\}. \tag{4.99}$$

Consider the function

$$H(x) = x^{1/2} \arctan\left[2\left(\frac{1-x}{x}\right)^{1/2}\right] \tag{4.100}$$

which is plotted in Fig. 7. For small x, H(x) increases like $\frac{\pi}{2} x^{1/2}$. For small (1-x), $H(x) \cong 2(1-x)^{1/2}$. We shall consider the approximation

$$H_0(x) = \frac{\pi}{2} x^{1/2} (1-x)^{1/2} \tag{4.101}$$



Approximations for $H(x) = x^{1/2}\arctan\left(2\left(\frac{1-x}{x}\right)^{1/2}\right)$

Fig. 7

which is also plotted in Fig. 7, and is seen to have the essential features of $H(x)$. $H_0(x)$ has been chosen so that the approximation is best for small x, because the integrand in Eq. (4.80) is largest for small x--that is, for a relatively small number of links in the closed loop. With the use of this approximation,

$$P_0(t-j:j,0) \cong \exp\left\{-2\sqrt{\pi}\,\lambda\, x^{1/2}(1-x)^{1/2}\right\}. \tag{4.102}$$

It therefore follows from Eq. (4.80), with the replacement of $P_0(t-j,\vec{r}:j,0)$ by $P_0(t-j:j,0)$ and the neglection of $\frac{2}{3}\lambda x$ with respect to 1, that

$$F_1(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{t^{1/2}}\int_{1/2t}^{1-1/2t} dx\, x^{-3/2}(1-x)^{-3/2}\exp\left(-\xi^2\frac{x}{1-x}\right)\exp\left\{-2\sqrt{\pi}\,\lambda\, x^{1/2}(1-x)^{1/2}\right\}. \tag{4.103}$$

Again let

$$y^2 = \frac{x}{1-x}\,, \qquad \delta = \frac{1}{\sqrt{2t-1}} \cong \frac{1}{\sqrt{2t}}\,. \tag{4.27}$$

Equation (4.103) can then be rewritten

$$F_1(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{t^{1/2}}\int_{\delta}^{1/\delta} dy\,\frac{1+y^2}{y^2}\exp\left(-\xi^2y^2\right)\exp\left\{-2\sqrt{\pi}\lambda\,\frac{y}{1+y^2}\right\}. \tag{4.104}$$

10. $F_1(t,\vec{r}:\vec{r})$: Expansion in Powers of λ

Equation (4.104) can be written

$$F_1(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{t^{1/2}}\int_{\delta}^{1/\delta} dy\,\frac{1+y^2}{y^2}\exp\left(-\xi^2y^2\right)\sum_{n=0}^{\infty}\frac{(-1)^n\left(2\sqrt{\pi}\lambda\right)^n}{n!}\,\frac{y^n}{(1+y^2)^n}\,. \tag{4.105}$$

Let

$$B_n(\xi^2) = \int_{\delta}^{1/\delta} dy\,\frac{y^{n-2}}{(1+y^2)^{n-1}}\,e^{-\xi^2y^2}\,; \tag{4.106}$$

then

$$F_n(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{\sqrt{t}}\sum_{n=0}^{\infty}\frac{(-1)^n(2\sqrt{\pi}\lambda)^n}{n!}B_n(\xi^2). \tag{4.107}$$

It follows from Eq. (4.28) that

$$F_0(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{\sqrt{t}}B_0(\xi^2). \tag{4.108}$$

From Eq. (4.106), it follows that

$$B_1(\xi^2) = \int_0^{1/\delta}\frac{dy}{y}e^{-\xi^2y^2} = \frac{1}{2}\int_{\xi^2\delta^2}^{\xi^2/\delta^2}\frac{dz}{z}e^{-z}. \tag{4.109}$$

For $r>1$ $\left(\xi^2/\delta^2 = 3r^2\right)$, the upper limit of integration can be replaced by infinity to obtain

$$B_1(\xi^2) \cong -\frac{1}{2}Ei(-\xi^2\delta^2). \tag{4.110}$$

[The exponential integral $-Ei(-u)$ is defined as

$$-Ei(-u) = \int_u^{\infty}dz\,\frac{e^{-z}}{z}. \tag{4.111}$$

For $u>0$, $-Ei(-u)$ is given by the convergent series

$$-Ei(-u) = -0.5772 - \ln u + u - \frac{u^2}{2\cdot 2!} + \frac{u^3}{3\cdot 3!} + \cdots \tag{4.112}$$

However, for large values of u, the asymptotic expansion

$$-Ei(-u) \doteq \frac{e^{-u}}{u}\left[1 - \frac{1!}{u} + \frac{2!}{u^2} - \frac{3!}{u^3} + \cdots\right] \tag{4.113}$$

is useful.]

For $n \geq 2$, the limits of integration in Eq. (4.106) can be replaced by 0 and ∞ to obtain

$$B_n(\xi^2) \cong e^{\xi^2} \int_0^\infty dy \, \frac{y^{n-2}}{(1+y^2)^{n-1}} \, e^{-\xi^2(y^2+1)} \,, \tag{4.114}$$

from which it follows that

$$\frac{d^{(n-1)}}{d(\xi^2)^{(n-1)}} \left[e^{-\xi^2} B_n(\xi^2) \right] = \frac{(-1)^{n-1} e^{-\xi^2}}{\xi^{n-1}} \frac{1}{2} \Gamma\left(\frac{n-1}{2}\right), \tag{4.115}$$

for $n \geq 2$. Specifically, it follows from Eq. (4.115) that

$$B_2(\xi^2) = \frac{\pi}{2} e^{\xi^2} \operatorname{erfc} \xi \,, \tag{4.116}$$

and

$$B_3(\xi^2) = \frac{1}{2} \left[1 + \xi^2 e^{\xi^2} \operatorname{Ei}(-\xi^2) \right] . \tag{4.117}$$

Combining the above results, we have

$$F_1(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{2}{\sqrt{t}} \left\{ \left[(2\xi)^{1/2} + \frac{\sqrt{\pi}}{2\xi} - \sqrt{\pi}\,\xi \right] + \sqrt{\pi}\,\lambda \operatorname{Ei}(-\xi^2\delta^2) \right.$$
$$+ \tfrac{1}{4}\pi^2\lambda^2 e^{\xi^2} \operatorname{erfc} \xi$$
$$\left. - \tfrac{8}{3}\pi^{3/2}\lambda^3 \left[1 + \xi^2 e^{\xi^2} \operatorname{Ei}(-\xi^2) \right] + \cdots \right\} \tag{4.118}$$

where the λ independent terms are $F_0(t,\vec{r}:\vec{r})$. [See Eq. (4.35).] In order to compare the various terms in the above expansion, consider Table 2, in which the ξ dependent terms in Eq. (4.118) are computed for $\sqrt{\pi}\,\lambda = 1$. The first-order term in λ makes F_1 relatively larger for large ξ and therefore decreases the weight given to configurations with large r in the

	$\xi = 0.5$	$\xi = 1.0$	$\xi = 1.5$	$\xi = 2.0$
$\sqrt{\pi}\left(\frac{1}{2\xi} - \xi\right)$	0.886	-0.886	-2.07	-3.10
$Ei(-\xi^2\delta^2)$ for $\delta^2 = 10^{-3}$	-7.72	-6.33	-5.52	-4.94
$\pi e^{\xi^2} \operatorname{erfc} \xi$	1.93	1.34	1.01	0.803
$-\frac{1}{2}\left\{1 + \xi^2 e^{\xi^2} Ei(-\xi^2)\right\}$	-0.443	-0.269	-0.173	-0.116

Table 2
Comparison of Terms in the Expansion of $F_1(t,\vec{r}:\vec{r})$

calculation of $\bar{\Phi}_0(t,\vec{r})$. For λ sufficiently small so that higher-order terms can be neglected, the correction due to the first-order term will not be important, since in the range of interest $Ei(-\xi^2\delta^2)$ varies more slowly with ξ than do the ξ-dependent terms in $F_0(t,\vec{r}:\vec{r})$. The λ^2-term varies more rapidly with ξ than does the λ-term, becoming proportional to $1/\xi$ for large ξ. It is seen from Table 2 and Eq. (4.118) that this term makes F_1 relatively smaller for large ξ and therefore increases the weight given to configurations with large r in the calculation of $\bar{\Phi}_0(t,\vec{r})$. The third-order term exhibits the same behavior as the first-order term, although it shows a stronger ξ dependence. For $\lambda \gg O(1)$, many terms in the expansion Eq. (4.118) are important and consequently the expansion is not a useful approach. We shall therefore return to the consideration of the integral given in Eq. (4.104).

11. $F_1(t,\vec{r}:\vec{r})$ for Large λ

$F_1(t,\vec{r}:\vec{r})$ is given by the integral

$$F_1(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{t^{3/2}}\int_0^{\infty} dy\ \frac{1+y^2}{y^2}\exp\left(-\xi^2 y^2\right)\exp\left\{-2\sqrt{\pi}\,\lambda\,\frac{y}{1+y^2}\right\}. \tag{4.104}$$

It is clear that the λ dependent factor in the integrand becomes important for large λ. This factor is plotted in Fig. 8 for $2\sqrt{\pi}\lambda = 0.1,\ 1,\ 10$, and, in the same figure, $e^{-\xi^2 y^2}$ is plotted for $\xi = 0.5,\ 1,\ 1.5$. It is clear from Fig. 8 that for $\xi > 1$ and $\lambda \gg 1$, all but a negligible contribution to the integral comes from very small y. The physical significance of this result is clear. Since $y = \frac{j}{t-j}$, where j is the number of links in the closed loop, the above result means that the probability for non-interference between the closed loop and the remainder of the chain is negligibly small except for small loops. The consequences of this assumption will now be indicated. Since the results are of very limited interest, we shall only outline the calculation, omitting all details.

For $\lambda \gg 1$ and $\xi > 1$, Eq. (4.104) can be further approximated by

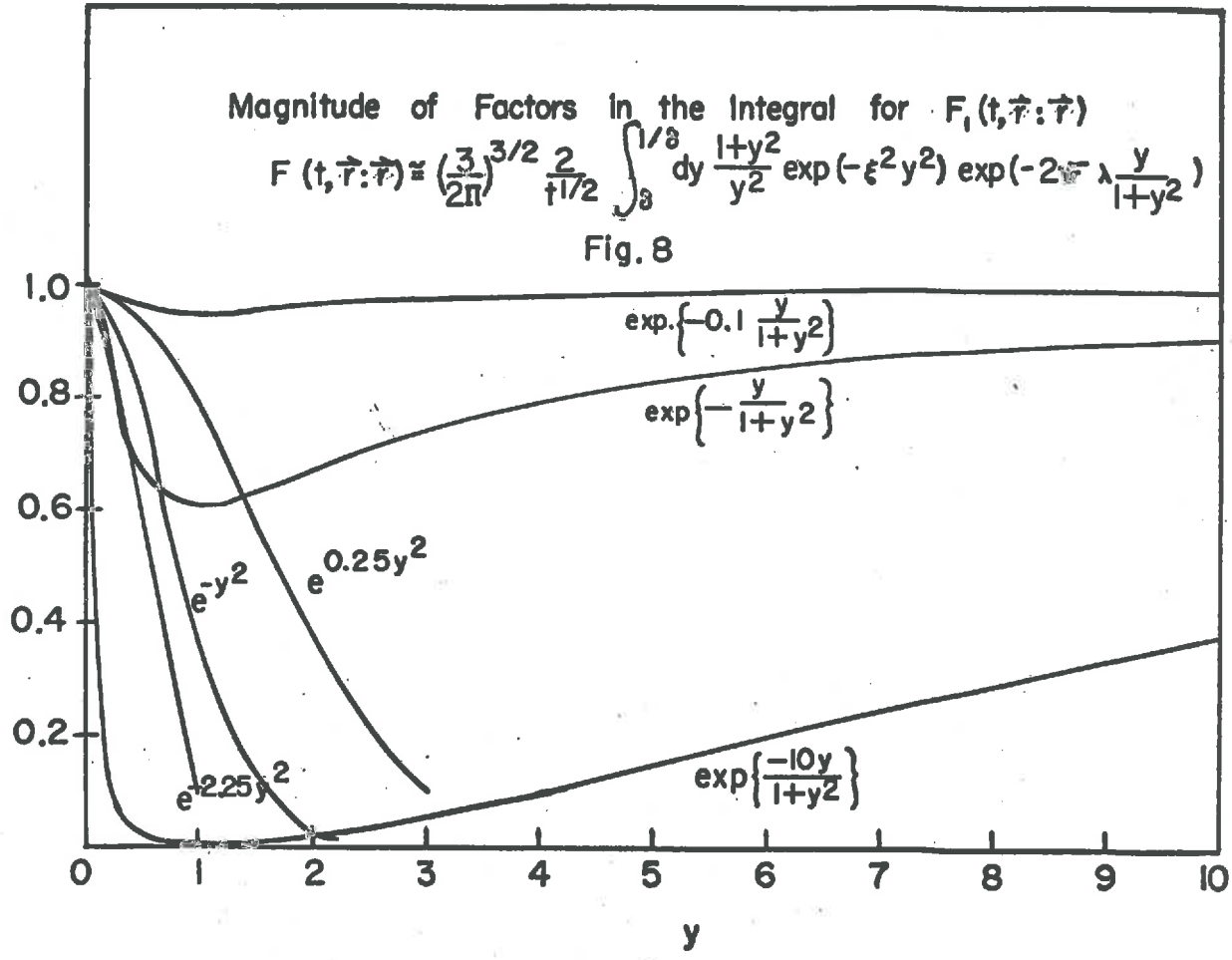
$$F_1(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{\sqrt{t}}\int_0^{\infty} dy\ \frac{1+y^2}{y^2}\exp\left(-\xi^2 y^2\right)\exp\left(-2\sqrt{\pi}\,\lambda\, y\right). \tag{4.119}$$

It follows exactly from Eq. (4.119) that

$$F_1(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{\sqrt{t}}\left\{\frac{1}{\delta}\,e^{-\xi^2\delta^2 - 2\sqrt{\pi}\lambda\delta}\right.$$

$$\left. + \frac{\sqrt{\pi}}{2}\left(\frac{1}{\xi}-2\xi\right)\exp\left(\frac{\pi\lambda^2}{\xi^2}\right)\operatorname{erfc}\left(\xi\delta + \frac{\sqrt{\pi}\lambda}{\xi}\right)\right. \tag{4.120}$$

(over)


Magnitude of Factors in the Integral for $F_1(t,\vec{r}:\vec{r})$
$F(t,\vec{r}:\vec{r}) \cong \left(\frac{3}{2\pi}\right)^{3/2} \frac{2}{t^{1/2}} \int_{\delta}^{1/\delta} dy \frac{1+y^2}{y^2} \exp(-\xi^2 y^2) \exp\left(-2\tau\lambda \frac{y}{1+y^2}\right)$
Fig. 8
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
y
$\exp\left\{-0.1 \frac{y}{1+y^2}\right\}$
$\exp\left\{-\frac{y}{1+y^2}\right\}$
e^{-y^2}
$e^{0.25y^2}$
$e^{-2.25y^2}$
$\exp\left\{\frac{-10y}{1+y^2}\right\}$

$$- \frac{\pi\lambda}{\xi} \int_{2\sqrt{\pi}\lambda}^{\infty} du \cdot e^{\frac{u^2}{4\xi^2}} \operatorname{erfc}\left(\xi\delta + \frac{u}{2\xi}\right) \Bigg\}. \tag{4.120}$$

Using the approximation

$$\operatorname{erfc}\ w \cong \frac{e^{-w^2}}{1+\sqrt{\pi}w} \tag{4.121}$$

and suitable neglections, we obtain the result

$$F_1(t,\vec{r}:\vec{r}) \cong C + \frac{\frac{3}{2\pi r} - \frac{9r}{2\pi t}}{1 + \frac{3vt}{2r}} + \frac{27v}{2\pi^2} \ln\left(3v\sqrt{\frac{3}{2\pi}} + 2\sqrt{\frac{3}{2\pi}}\frac{r}{t}\right). \tag{4.122}$$

An approximate solution of the partial differential equation [Eq. (4.15)] is found by writing

$$\bar{\Phi}_0(t,\vec{r}) = \exp\left\{ T_0(v,t)w^2 + T_1(v,t)w + T_2(v,t) + T_3(v,t)\ln w + T_4(v,t)\frac{1}{w} + \cdots \right\} \tag{4.123}$$

where

$$w = r + \frac{3vt}{2}. \tag{4.124}$$

The detailed result of this calculation indicates that $\bar{\Phi}_0(t,\vec{r})$ is essentially the same as $\bar{\Phi}_0^{(\infty)}(t,\vec{r})$ except that the dispersion of the distribution is increased slightly by a factor independent of t.

The reason why we do not give the details of the calculation here is that the result can be predicted without any calculation. It has already been noted that the approximation implicit in Eq. (4.119) is to consider only the effects of small loops. In doing so, we are effectively

treating volume exclusion as a short range correlation, and, as was pointed out in Chapter II, such treatments will always lead to a Gaussian distribution of extensions with dispersion proportional to t. It is true that small loops are much more probable than large loops; however, the number of configurations without any interferences decreases exponentially with t, and a small error in the number of excluded configurations will mean a large relative error in the number of allowed configurations. For this reason it is necessary to obtain a more accurate evaluation of $F(t,\vec{r}:\vec{r})$ if one is to obtain any conclusion concerning $\Phi_0(t,\vec{r})$ for $vt^{1/4} \gg O(1)$.

The approximation to $F_1(t,\vec{r}:\vec{r})$ that is given in Eq. (4.122) was obtained under the assumption that $\zeta > 1$ and $\lambda \gg 1$. However, the solution of the partial differential equation effectively involves an integration over ζ and λ from zero to the values of interest. Crude approximations that are in serious error for small λ and ζ can not be expected to yield values of $\Phi_0(t,\vec{r})$ that are valid for large values of λ and ζ. The writer has not been successful in obtaining a more accurate evaluation of $F_1(t,\vec{r}:\vec{r})$ as given by the integral in Eq. (4.106). It appears quite difficult to obtain a single approximation valid over the entire range of interest. The only practical procedure apparent to the writer is a numerical evaluation of $F_1(t,\vec{r}:\vec{r})$ followed by a numerical solution of the partial differential equation. The value of such a calculation is questionable, as will

be pointed out in the next section, and the calculation will not be included in this work.

12. Summary of the Approximations

The basic integro-difference equation of the theory was replaced by a boundary value problem by means of a suitable limiting process. The physical significance of this procedure was discussed, and the parameter ν was interpreted in terms of the physical properties of actual chain molecules.

The James solution of Eq. (4.15) for $F=F_0$ was shown to be formally valid even for $vt^{1/2} > O(1)$, but it is to be expected that the replacement of F by F_0 leads to an over-correction for large t.

A general integral expression [Eq. (4.24)] was set up for calculating F. The integrand contained the probabilities for non-interference $\rho(\tau,\vec{r})$, $\rho(\tau,\vec{r}:t-\tau,0)$; and the next approximation F_1 was obtained by considering suitable approximations of the ρ's. A general procedure was formulated for calculating $\rho(t,\vec{r})$, and it was shown that $\rho_0(t,\vec{r})$ corresponds to the assumption that the probabilities for non-interference are independent. [The writer has not been successful in obtaining an approximation better than $\rho_0(t,\vec{r})$ from the general formula given by Eq. (4.61).]

It was shown that the major factor causing $F(t,\vec{r}:\vec{r})$ to differ from $F_0(t,\vec{r}:\vec{r})$ is $\rho(\tau,\vec{r}:t-\tau,0)$, the probability that there are no cross-interferences. Two major

assumptions were made in calculating this probability:

(i) interactions within the two parts of the chain are not considered, and

(ii) the r-dependence is effectively averaged out.

We have already discussed the effect of the second assumption and have concluded that it will tend to under-correct the result of the first order calculation, giving too much weight to configurations with large r. The results of the previous section seem to indicate that the second-order calculation gives an over-correction of the first-order result, essentially removing the first-order perturbation. This over-correction is partially due to the approximations made in going from Eq. (4.104) to Eq. (4.122) and partially due to the assumption (i) above. [By calculating $\rho(\tau,\vec{r}:t-\tau,o)$ without taking account of volume exclusion within the two parts of the chain, too small a value is obtained for highly coiled configurations. Therefore $\Sigma_n(t,\vec{r})$ will be too large for small r.]

In the case of $\lambda \gg O(1)$ there is no reason to assume that a second-order calculation using the assumption (i) gives better results than the first-order calculation. If the result of this second-order calculation appreciably differs from that of the first order, then it would be necessary to calculate $\rho(\tau,\vec{r}: t-\tau,o)$ taking account of interactions within the two parts of the chain. This necessitates knowledge of the distribution of an interior

bead taking account of volume exclusion, a problem we have heretofore not considered and one that raises many new difficulties. [See Appendix D for a discussion of how the theory can be modified to determine the distribution of an interior bead.]

In the conclusion and summary at the close of this thesis, we shall discuss further the feasibility of extending the perturbation calculation. We shall consider first, however, another aspect of the problem. If one is interested primarily in the moments of the distribution, these can be calculated directly from the partial differential equation [Eq. (4.15)], the mathematics involved being somewhat simpler than the problem of evaluating $F(t,\vec{r}:\vec{r})$ and solving the boundary value problem. The direct evaluation of $\langle r^2 \rangle$ will be considered in the next chapter.

CHAPTER V

DIRECT EVALUATION OF $\langle r^2 \rangle$

1. General Theory

Most authors when considering the volume exclusion effect endeavor to calculate $\langle r^2 \rangle$ directly from their formalism without explicitly determining the distribution of extensions $\bar{\Phi}_0(t,\vec{r})$. We shall now show how this procedure can be applied to the boundary value problem discussed in the previous chapter:

$$\frac{\partial \bar{\Phi}_0(t,\vec{r})}{\partial t} - \frac{1}{\zeta} \nabla^2 \bar{\Phi}_0(t,\vec{r}) = -v\, \bar{\Phi}_1(t,\vec{r}:\vec{r}). \tag{5.1}$$

Each term in Eq. (5.1) will be integrated over all space. The integral of $\bar{\Phi}_0(t,\vec{r})$ over all space, $\int d\vec{r}\, \bar{\Phi}_0(t,\vec{r})$, is the fraction of configurations of a chain of t links in which there are no interferences involving pairs of interior beads, since interferences of the fixed end beads are not considered. Configurations that satisfy this condition will be called "allowable." The integral of $v\,\bar{\Phi}_1(t,\vec{r}:\vec{r})$ over all space, $v \int d\vec{r}\; \bar{\Phi}_1(t,\vec{r}:\vec{r})$, is the fraction of configurations that are both allowable and contain an interference at the end t.

Both $\bar{\Phi}_0(t,\vec{r})$ and $\bar{\Phi}_1(t,\vec{r}:\vec{r})$ are spherically symmetric. For very large r (of the order of t), the effect of volume

exclusion is negligible, and consequently $\bar{\Phi}_1(t,\vec{r})$ must eventually decrease like

$$\bar{\Phi}_0^{(\infty)}(t,\vec{r}) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{1}{2}\frac{r^2}{t}\right). \tag{5.2}$$

It therefore follows that

$$r^m \frac{\partial^n \bar{\Phi}_0(t,r)}{\partial r^n} \longrightarrow 0 \quad \text{as} \quad r \to \infty \tag{5.3}$$

for all non-negative integers m,n. It follows from Eq. (5.3) and the spherical symmetry of $\bar{\Phi}_0(t,\vec{r})$ that

$$\int d\vec{r}\, \nabla^2 \bar{\Phi}_0(t,\vec{r}) = 4\pi \int_0^\infty dr\, \frac{\partial}{\partial r}\left(r^2 \frac{\partial \bar{\Phi}_0}{\partial r}\right) = 0. \tag{5.4}$$

If the order of integration over $\vec{r}$ and differentiation with respect to t can be interchanged, it follows that

$$\frac{d}{dt}\left[\int d\vec{r}\, \bar{\Phi}_0(t,\vec{r})\right] = -v \int d\vec{r}\, \bar{\Phi}_1(t,\vec{r};\vec{r}), \tag{5.5}$$

that is, the rate of change with respect to t of the fraction of allowable configurations is given by the fraction of configurations that are both allowable and contain an interference involving the t^{th} bead.

Multiply Eq. (5.1) by r^2 and then integrate over all space. Successive integrations by parts and the use of Eq. (5.3) gives

$$\int d\vec{r}\, r^2 \nabla^2 \bar{\Phi}_0(t,\vec{r}) = 6 \int d\vec{r}\, \bar{\Phi}_0(t,\vec{r}). \tag{5.6}$$

Upon interchange of the order of integration and

differentiation, it follows from Eqs. (5.1) and (5.6) that

$$\frac{d}{dt}\left[\int d\vec{r}\, r^2\, \Phi_0(t,\vec{r})\right] - \int d\vec{r}\, \Phi_0(t,\vec{r}) = -v\int d\vec{r}\, r^2\, \Phi_1(t,\vec{r}:\vec{r}). \tag{5.7}$$

The mean square extension $\langle r^2\rangle_t$ is defined as

$$\langle r^2\rangle_t = \frac{\int d\vec{r}\, r^2\, \Phi_0(t,\vec{r})}{\int d\vec{r}\, \Phi_0(t,\vec{r})}. \tag{5.8}$$

It follows from Eqs. (5.7) and (5.8) that

$$\frac{d}{dt}\langle r^2\rangle_t + \langle r^2\rangle_t \frac{d}{dt}\ln\int d\vec{r}\, \Phi_0(t,\vec{r}) - 1 = -v\,\frac{\int d\vec{r}\, r^2\, \Phi_1(t,\vec{r}:\vec{r})}{\int d\vec{r}\, \Phi_0(t,\vec{r})}. \tag{5.9}$$

Define

$$\{r^2\}_t = \frac{v\int d\vec{r}\, r^2\, \Phi_1(t,\vec{r}:\vec{r})}{v\int d\vec{r}\, \Phi_1(t,\vec{r}:\vec{r})}. \tag{5.10}$$

Thus $\{r^2\}_t$ is the mean square extension of those allowable configurations in which there is an interference involving the t^{th} bead. It follows from Eqs. (5.10) and (5.5) that

$$\frac{-v\int d\vec{r}\, r^2\, \Phi_1(t,\vec{r}:\vec{r})}{\int d\vec{r}\, \Phi_0(t,\vec{r})} = \{r^2\}_t \frac{d}{dt}\ln\int d\vec{r}\, \Phi_0(t,\vec{r}). \tag{5.11}$$

Let

$$K(t) \equiv \frac{d}{dt}\ln\int d\vec{r}\, \Phi_0(t,\vec{r}). \tag{5.12}$$

It then follows from Eqs. (5.9), (5.11) and (5.12) that

$$\frac{d}{dt}\langle r^2\rangle_t = 1 - K(t)\left[\langle r^2\rangle_t - \{r^2\}_t\right]. \tag{5.13}$$

In the absence of volume exclusion

$$\int d\vec{r}\, \Phi_0^{(0)}(t,\vec{r}) = 1 \tag{5.14}$$

and therefore $K(t) \equiv 0$. Equation (5.13) then leads to the well known result that in the absence of volume exclusion $\langle r^2 \rangle_t = t$. When volume exclusion is considered, the fraction of allowable configurations decreases with t; therefore $K(t) < 0$ for all t. If $\{r^2\}_t$ were equal to $\langle r^2 \rangle_t$ then volume exclusion would have no effect upon the second moment, since the configurations excluded would have the same moment as those containing no interferences. However, it is clear that such is not the case. The mean square extension of those allowable configurations in which there is an interference involving the t^{th} bead will be less than the mean square extension of all allowable configurations; that is, $\{r^2\}_t < \langle r^2 \rangle_t$ for all t. Therefore $\frac{d}{dt} \langle r^2 \rangle_t > 1$ and $\langle r^2 \rangle_t$ is larger than the value computed in the absence of volume exclusion.

Equation (5.13) and the discussion given in the preceding paragraph are completely general. In order to discuss the behavior of $\langle r^2 \rangle_t$ in a more quantitative way, it is necessary to calculate $K(t)$ and $\{r^2\}_t$, which in turn necessitates making certain assumptions. We shall consider the calculation making assumptions corresponding to the first- and second-order calculations considered in the preceding chapter, and shall compare our results with those of other authors.

2. Approximate Calculation of $K(t) = \frac{2}{3} b \int d\vec{r}\, \Phi_t(\vec{r})$

In the absence of volume exclusion

$$\bar{\Phi}_1^{(\omega)}(t,\vec{r}:\vec{r}) = \int_{1/2}^{t-1/2} dj\ \bar{\Phi}_0^{(\omega)}(j,o)\,\bar{\Phi}_0^{(\omega)}(t-j,\vec{r}), \tag{5.15}$$

so that

$$\int d\vec{r}\ \bar{\Phi}_1^{(\omega)}(t,\vec{r}:\vec{r}) = \left(\frac{3}{2\pi}\right)^{3/2} \int_{1/2}^{t-1/2} \frac{dj}{j^{3/2}} = c + O\left(t^{-1/2}\right), \tag{5.16}$$

where

$$c = \left(\frac{3}{\pi}\right)^{3/2}. \tag{5.17}$$

Since $\bar{\Phi}_0^{(\omega)}(t,\vec{r})$ is normalized, Eq. (5.16) can be rewritten as

$$\frac{v\int d\vec{r}\ \bar{\Phi}_1^{(\omega)}(t,\vec{r}:\vec{r})}{\int d\vec{r}\ \bar{\Phi}_0^{(\omega)}(t,\vec{r})} = cv + O(vt^{-1/2}). \tag{5.18}$$

Equation (5.18) shows that in the absence of volume exclusion, the fraction of configurations in which the t^{th} bead is involved in an interference becomes constant for large t. (This is analogous to the recurrence theorem in random flights, quoted in Section 1 of Chapter II. See reference (10).) On the basis of the statistical results of Wall, Hiller and Wheeler (53), and the first-order calculation of James (24), it is reasonable to assume even in the case of volume exclusion that the fraction of allowable configurations in which the t^{th} bead is involved in an interference becomes constant in the limit of large t. It then follows from Eqs. (5.5) and (5.12) that

$$\int d\vec{r}\ \bar{\Phi}_0(t,\vec{r}) \cong \exp(-cvt) \tag{5.19}$$

and

$$K(t) \cong -cv. \tag{5.20}$$

Equation (5.13) then becomes

$$\frac{d}{dt}\langle r^2\rangle_t \cong 1 + cv\left[\langle r^2\rangle_t - \{r^2\}_t\right]. \tag{5.21}$$

The approximation embodied in Eq. (5.20), the neglect of terms that are $O(vt^{-1/2})$, will be discussed later. We shall first consider the solution of Eq. (5.21) by successive approximations of $\{r^2\}_t$.

3. General Expression for $\{r^2\}_t$

It follows from Section 3 of Chapter IV that

$$\Phi_1(t,\vec{r}:\vec{r}) = \int_{1/2}^{t-1/2} dj\ \Phi_0(j,0)\,\Phi_0(t-j,\vec{r})\,p(j,0:t-j,\vec{r}). \tag{5.22}$$

[See Eq. (4.22).] The probability that there are no interferences between the closed loop of j links and the remainder of the chain, $p(j,0:t-j,\vec{r})$, will again be approximated by $p(j,0:t-j)$. This approximation has been discussed in the preceding chapter.

Using Eqs. (5.8), (5.10), and (5.22) we then write

$$\{r^2\}_t = \frac{\int_{1/2}^{t-1/2} dj\ \Phi_0(j,0)\,p(j,0:t-j)\,\langle r^2\rangle_{t-j}\int d\vec{r}\ \Phi_0(t-j,\vec{r})}{\int_{1/2}^{t-1/2} dj\ \Phi_0(j,0)\,p(j,0:t-j)\int d\vec{r}\ \Phi_0(t-j,\vec{r})} \tag{5.23}$$

$$= \int_{1/2}^{t-1/2} d\tau\ Q_\tau(t)\,\langle r^2\rangle_\tau \Big/ \int_{1/2}^{t-1/2} d\tau\ Q_\tau(t), \tag{5.24}$$

where

$$Q_\tau(t) = \bar{\Phi}_0(t-\tau,0)\, p(t-\tau,0:\tau) \int d\vec{r}\; \bar{\Sigma}_0(\tau,\vec{r}). \tag{5.25}$$

The significance of $Q_\tau(t)$ follows simply from Eq. (5.25); it is the total weight of allowable configurations of t links in which there is an interference between the τ^{th} and t^{th} beads. Thus Eq. (5.24) expresses $\{r^2\}_t$ as the weighted sum over τ of $\langle r^2\rangle_\tau$, weighted according to the relative weights of configurations containing a closed loop of $(t-\tau)$ links.

We shall assume that

$$\bar{\Phi}_0(j,0) = \left(\frac{3}{2\pi}\right)^{3/2} \frac{e^{-cvj}}{j^{3/2}}, \tag{5.26}$$

which is consistent with the results of the first-order calculation of the preceding chapter [see Eq. (4.37)], and is consistent with Eq. (5.19). It follows from Eqs. (5.19), (5.24), (5.25) and (5.26) that

$$\{r^2\}_t \cong \frac{\int_{1/2}^{t-1/2} \alpha_j \frac{1}{j^{3/2}} \langle r^2\rangle_{t-j}\, p(j,0:t-j)}{\int_{1/2}^{t-1/2} \alpha_j \frac{1}{j^{3/2}}\, p(j,0:t-j)}. \tag{5.27}$$

The above approximate expression for $\{r^2\}_t$ should be adequate for the first-order calculation in which $p(j,0:t-j)$ is replaced by one, and for the second-order calculation in which $p(j,0:t-j)$ is replaced by $p_0(j,0:t-j)$. (See Chapter IV Section 9).

4. First-Order Calculation

In the first-order calculation, $p(j,0:t-j)$ is set

equal to one in Eq. (5.27), to obtain

$$\left\{r^2\right\}_t \cong \frac{1}{2\sqrt{2} - 2t^{-1/2}} \int_{1/2}^{t-1/2} dj \; \frac{1}{j^{3/2}} \langle r^2 \rangle_{t-j} \; * \tag{5.28}$$

It follows from Eq. (5.21) that

$$\frac{d}{dt}\langle r^2\rangle_t \cong 1 + cv\left[\langle r^2\rangle_t - \frac{1}{2\sqrt{2} - \frac{2}{t^{1/2}}} \int_{1/2}^{t-1/2} dj \; \frac{1}{j^{3/2}} \langle r^2\rangle_{t-j}\right]. \tag{5.29}$$

Let

$$A(t) = \frac{d}{dt}\langle r^2\rangle_t . \tag{5.30}$$

It follows from an integration by parts that

$$\int_{1/2}^{t-1/2} \frac{dj}{j^{3/2}} \langle r^2\rangle_{t-j} = 2\sqrt{2}\,\langle r^2\rangle_t - 2\int_0^t \frac{dj}{j^{1/2}} A(t-j) + O(1). \tag{5.31}$$

From Eq. (5.29) and (5.31) it follows that

$$\begin{aligned} A(t) &\cong 1 + cv\left[\langle r^2\rangle_t - \langle r^2\rangle_t \left\{1 + \frac{1}{\sqrt{2t}} - \cdots\right\}\right. \\ &\qquad \left. + \frac{1}{\sqrt{2}}\left\{1 + \frac{1}{\sqrt{2t}} - \cdots\right\} \int_0^t \frac{d\tau}{(t-\tau)^{1/2}} A(\tau)\right] \\ &\cong 1 + \kappa \int_0^t \frac{d\tau}{(t-\tau)^{1/2}} A(\tau) - \frac{\kappa \langle r^2\rangle_t}{t^{1/2}} + O(v), \end{aligned} \tag{5.32}$$

where

$$\kappa = \frac{cv}{\sqrt{2}} = 2\left(\frac{3}{2\pi}\right)^{3/2} v . \tag{5.33}$$

---

*t-½ will be replaced by t in those places in the calculation where the replacement gives rise to negligible error, as in the second term in the denominator of the right hand side of Eq. (5.28).

Since

$$\langle r^2 \rangle_t = \int_0^t d\tau \; A(\tau) \,, \tag{5.34}$$

it follows from Eq. (5.32) that

$$A(t) = 1 + \kappa \int_0^t d\tau \left[\frac{1}{(t-\tau)^{1/2}} - \frac{1}{t^{1/2}} \right] A(\tau) \tag{5.35}$$

which is a Volterra integral equation of the second kind. The solution of this equation can be written as

$$A(t) = \sum_{n=0}^{\infty} \kappa^n \, A_n(t) \,, \tag{5.36}$$

convergent for all κ, (33),

where

$$A_n(t) = \int_0^t d\tau \left[\frac{1}{(t-\tau)^{1/2}} - \frac{1}{t^{1/2}} \right] A_{n-1}(\tau) \quad \text{for } n \geq 1, \tag{5.37}$$

and

$$A_0(t) = 1 \,. \tag{5.38}$$

It follows immediately from Eqs. (5.37) and (5.38) that

$$A_1(t) = t^{1/2} \,. \tag{5.39}$$

$A_n(t)$ will be obtained by induction. Assume

$$A_{n-1}(t) = a_{n-1} \, t^{\frac{n-1}{2}} \tag{5.40}$$

It follows from Eq. (5.37) by comparatively straightforward integration that

$$A_n(t) = a_n \, t^{n/2} \tag{5.41}$$

where

$$a_n = a_{n-1} \left[\frac{\pi}{2^n} \frac{\Gamma(n+1)}{\left\{ \Gamma\left(\frac{n}{2}+1\right) \right\}^2} - \frac{2}{n+1} \right] . \tag{5.42}$$

Since Eqs. (5.40) and (5.41) are satisfied for n = 1, they follow by induction for all n ≥ 1.

It follows from Eqs. (5.30), (5.36) and (5.41) that

$$\langle r^2 \rangle_t = \sum_{n=0}^{\infty} \frac{\kappa^n a_n t^{\frac{n}{2}+1}}{\frac{n}{2}+1} . \tag{5.43}$$

Since

$$\kappa t^{1/2} = 2\left(\frac{3}{2\pi}\right)^{3/2} v t^{1/2} = \frac{2}{\sqrt{\pi}}\lambda, \tag{5.44}$$

Eq. (5.43) can be rewritten

$$\frac{\langle r^2 \rangle_t}{t} = \sum_{n=0}^{\infty} \frac{a_n}{\frac{n}{2}+1} \left(\frac{2}{\sqrt{\pi}}\lambda\right)^n . \tag{5.45}$$

For $\lambda \ll 1$, it follows from Eq. (5.45) that

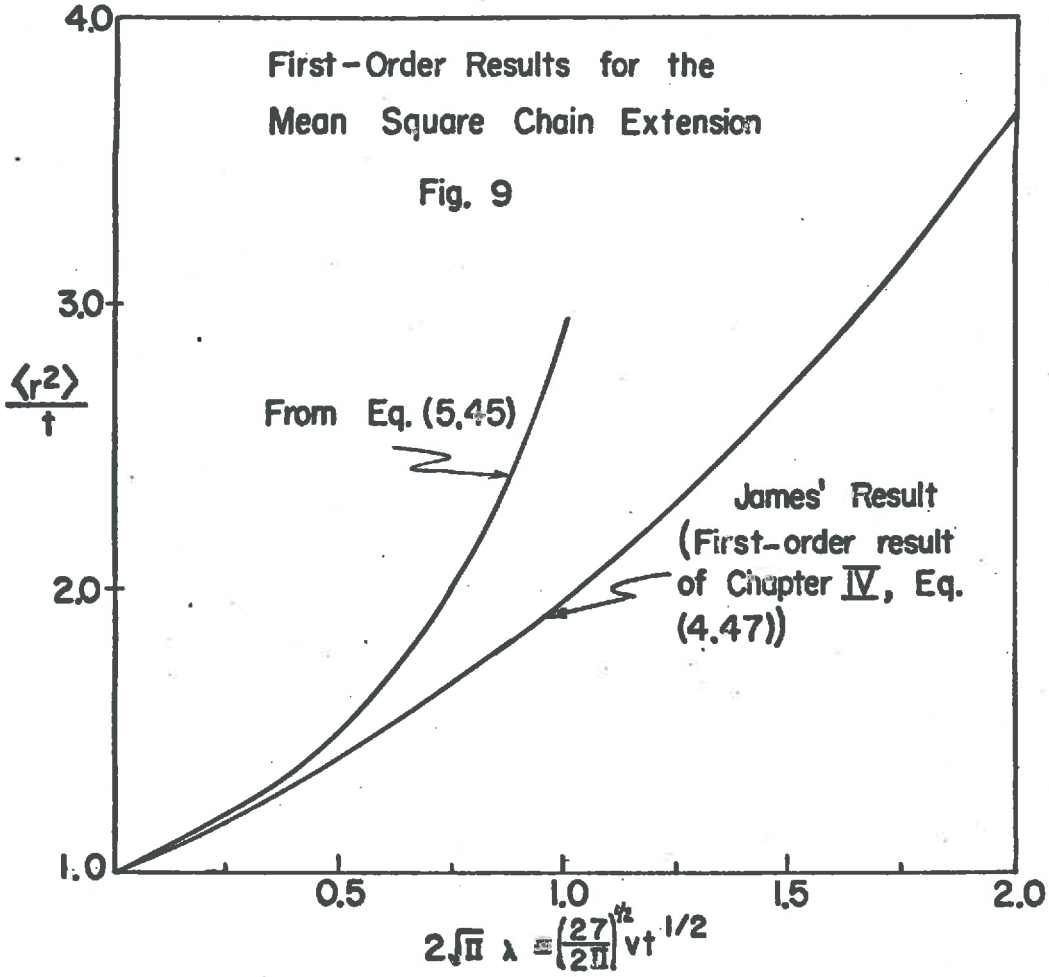
$$\langle r^2 \rangle_t / t \cong 1 + \frac{4\lambda}{3\sqrt{\pi}} = 1 + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} v t^{1/2}. \tag{5.46}$$

This is exactly the James' result for small λ, [see Eq. (4.48)] and is essentially the result obtained by Bueche (2), Grimley (18, 19), Rubin (38), Saito(41), and Teramoto (48), whose works were discussed in Chapter II. As is pointed out by James, and as is evident from the discussion in Chapters II, IV, and the present chapter, Eq. (5.46) is valid only for small λ. It certainly can not be used to conclude that $\langle r^2 \rangle$ increases as $t^{3/2}$ for large λ.

Equation (5.45) essentially gives the result of the first-order calculation as a series, successive partial sums of which can be interpreted as successive approximations to the first-order result. Thus the term for n = 0 corresponds

to the result in the absence of volume exclusion. The terms for $n = 0$ and $n = 1$ correspond to the result one would obtain by replacing $\langle r^2 \rangle$ on the right hand side of Eq.(5.29) by its value in the absence of volume exclusion. (This is essentially what was done in references 2, 18, 19, 38, 41, and 48 mentioned above.) Successive approximations give the higher-order terms. By considering a sufficient number of terms, we can use Eq. (5.45) to calculate $\langle r^2 \rangle / t$ for $\lambda = O(1)$. This has been done, and $\langle r^2 \rangle / t$ is given as a function of λ in Fig. 9. The same figure gives also $\langle r^2 \rangle / t$ as a function of λ, as determined from the James' result. [See the first-order calculation in Chapter IV, Eq. (4.47).] We have seen that this latter result predicts too great an increase in $\langle r^2 \rangle$ with t. Since the result calculated from Eq. (5.45) increases even more rapidly, this result misbehaves rather seriously for $\lambda \gg O(1)$.

It is not easy to evaluate the effects of the approximations made in obtaining Eq. (5.45). Small errors made in approximating $\{r^2\}_t$ can cause a significant error in the small difference $\langle r^2 \rangle_t - \{r^2\}_t$ appearing in Eq. (5.13). For example, if $\frac{2}{t^{3/2}}$ were neglected in comparison to $2\sqrt{2}$ in Eq. (5.29), then even a_1 would not agree with the corresponding coefficient in the James' result. The validity of Eq. (5.45) is restricted by approximations, which, although appearing reasonable, have disastrous effects upon the a_n.


First-Order Results for the
Mean Square Chain Extension
Fig. 9
4.0
3.0
2.0
1.0
$\frac{\langle r^2 \rangle}{t}$
From Eq. (5.45)
James' Result
(First-order result
of Chapter IV, Eq.
(4.47))
0.5
1.0
1.5
2.0
$2\sqrt{\pi}\,\lambda = \left(\frac{27}{2\pi}\right)^{1/2} v t^{1/2}$

The writer does not feel that the direct evaluation of $\langle r^2 \rangle_t$ from the partial differential equation is a useful procedure unless the effects of the various approximations can be more accurately evaluated. Rather than dismiss this method at this point, however, we shall briefly discuss the formalism of a second order calculation.

5. Second-Order Calculation

We define the second-order result as the solution of Eq. (5.21) when $\{r^2\}_t$ is determined by Eq. (5.27) with $p(j,o:t-j)$ replaced by

$$p_o(j,o:t-j) = \exp\left\{-\left(\frac{27}{2\pi}\right)^{1/2} v \left(\frac{t-j}{t}\right)^{1/2} j^{1/2}\right\}. \tag{5.47}$$

[See Eq. (4.102).] Again one can proceed by a method of successive approximations, but we shall here consider only a first approximation, corresponding to the first correction term in Eq. (5.45). The calculation will be outlined with most details omitted.

The first approximation consists of replacing $\langle r^2 \rangle_t$ on the right hand side of Eq. (5.21) by its value in the absence of volume exclusion. With this approximation and the use of Eqs. (5.27) and (5.47), it can be shown that

$$\langle r^2 \rangle_t - \{r^2\}_t \cong \frac{2t^{1/2}\int_0^1 dx \exp\left\{-2\sqrt{\pi}\lambda x(1-x^2)^{1/2}\right\}}{2\sqrt{2}}, \tag{5.48}$$

with the neglection of terms of order v and $t^{-1/2}$. Let

$$I(b) = \int_0^1 dx \exp\left\{-b x (1-x^2)^{1/2}\right\}. \tag{5.49}$$

I(b) has been evaluated numerically using Simpson's rule, and is given in Table 3.

b	I(b)
0	1.00
0.1	0.97
0.5	0.85
1.0	0.73
2.5	0.47
5.0	0.26
10.0	0.13
20.0	0.07

Table 3
Results of the Numerical Integration $I(b)=\int_0^1 dx\, e^{-bx(1-x^2)^{1/2}}$

It follows from Eq. (5.21) that the first approximation in second-order calculation is given by

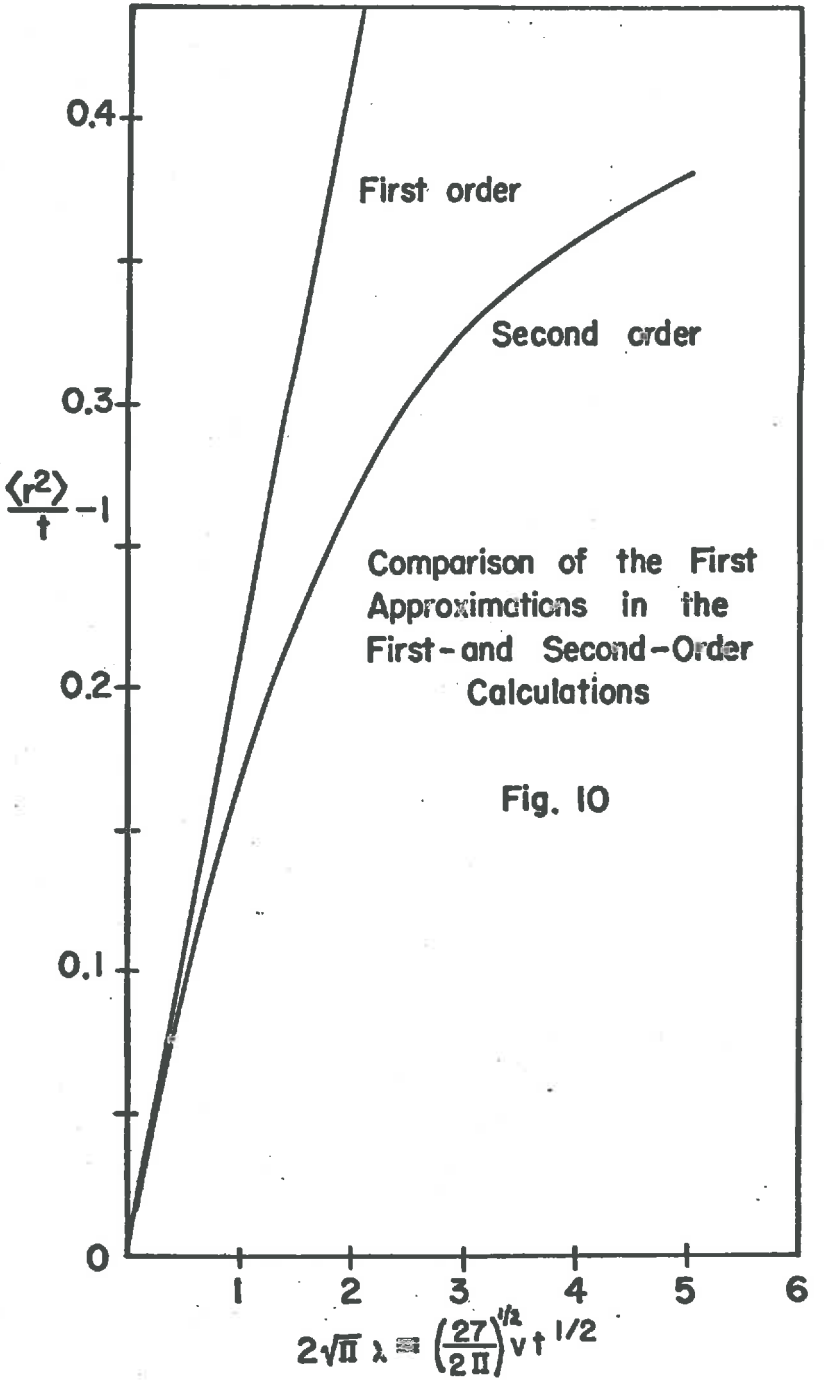
$$\frac{d}{dt}\langle r^2\rangle_t \cong 1 + \frac{cvt^{1/2}}{\sqrt{2}} I(2\sqrt{\pi}\lambda) = 1 + \frac{2\lambda}{\sqrt{\pi}} I(2\sqrt{\pi}\lambda), \tag{5.50}$$

from which it follows that

$$\frac{\langle r^2\rangle_t}{t} \cong 1 + \frac{1}{2\pi^2\lambda^2}\int_0^{2\sqrt{\pi}\lambda} db \cdot b^2 I(b). \tag{5.51}$$

(The first-order calculation corresponds to $I(b) = 1$, in which case Eq. (5.46) is an immediate consequence of Eq. (5.51).)

It follows from Eq. (5.49) that I(b) behaves like $1/b$ for large b. Therefore it follows from Eq. (5.51) that $\langle r^2\rangle/t$ approaches a constant value for large λ. Values of $\langle r^2\rangle_t/t$ evaluated numerically using Eq. (5.51) are given in Fig. 10, where, for comparison, the result of the first approximation in the first-order calculation [Eq. (5.46)] is also given as a function of λ.



Comparison of the First Approximations in the First- and Second-Order Calculations

Fig. 10

It is seen that the first correction in the second-order calculation increases much less rapidly than the corresponding term in the first-order calculation. However, with only these single correction terms, no meaningful prediction can be made concerning the behavior of $\langle r^2 \rangle / t$ for large λ.

The writer does not consider it worth while to continue the second-order calculation to obtain corrections corresponding to the higher-order terms in Eq. (5.45). In the present calculation, we found it necessary to know $\bar{\Phi}_0(t,0)$ and $\int d\vec{r}\ \bar{\Phi}_0(t,\vec{r})$, for which we used results obtained in Chapter IV. Unless these quantities can be obtained more accurately than $\bar{\Phi}_0(t,\vec{r})$ has been thus far, or without the necessity of first explicitly obtaining $\bar{\Phi}_0(t,\vec{r})$, the method of the direct evaluation of $\langle r^2 \rangle$ offers no advantages.

This chapter has been included for completeness; to again point out the inadequacies of the widely obtained result that $\langle r^2 \rangle$ increases as $t^{3/2}$; and to show how the results are critically dependent upon the approximations made.

SUMMARY AND CONCLUSIONS

This thesis has considered the volume exclusion effect in flexible long chain molecules in terms of a pearl necklace model with rigid sphere interactions. The basic equation of the theory was obtained in Chapter III by essentially considering how the chain can be extended, and a system of integro-difference equations for $\bar{\Phi}_1(t,\vec{r})$, $\bar{\Phi}_1(t,\vec{r};\vec{R})$, $\bar{\Phi}_2(t,\vec{r};\vec{R}_1,\vec{R}_2)$, and so on, were derived. The first of these equations, Eq. (3.14), corresponds to an equation considered by many authors, but avoids a serious normalization error frequently made, which was discussed in detail in Chapter II. Equations (3.14), (3.15), (3.16), and higher-order equations that can easily be calculated from the formalism presented, provide in principle a systematic procedure for the determination of $\bar{\Phi}_1(t,\vec{r})$. A method of successive approximations has been proposed in Chapter III. The first-order calculation is shown to correctly exclude all configurations in which there is at least one interference (say between beads i and j) such that there are no interferences between beads on opposite sides of either i or j, or between beads both of which are within the closed loop formed by i and j. It was emphasized that although the relative number of configurations that are incorrectly weighted is small, this must be compared with the relative number of allowable configurations, which decreases exponentially with t. The result of the first-order calculation is not in convenient form for calculating

$\langle r^2 \rangle$ for large t, and this calculation is consequently not considered in Chapter III. A second-order calculation was considered, but was not successfully carried out.

In Chapter IV* a limiting procedure is considered, in which the integro-difference equation for $\bar{\Phi}_s(t,\vec{r})$ is replaced by a boundary value problem, in which the unknown function $F(t,\vec{r}:\vec{r})$ also appears. Successive order approximations to $\bar{\Phi}_s(t,\vec{r})$ are defined by specifying successive approximations of $F(t,\vec{r}:\vec{r})$. The first-order calculation of James, leading to a displacement of the Gaussian distribution, has been considered in detail. As we shall presently show, the agreement with experiment is good for those values of t for which the first-order theory is valid**and that are within the range of experimental results. The experimental results quoted in Chapter I, and the results of the Monte Carlo calculations quoted in Chapter II, indicate that $\langle r^2 \rangle \sim t^{1.2}$. In the solid curve in Fig. 11, $\langle r^2 \rangle$, as calculated from the result of the first-order theory [Eq. (4.47)], is given as a function of t on a log-log plot. Values are calculated assuming $v = 0.1$, which is consistent with the estimation made in Chapter IV, Section 1. As

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*An extensive summary and discussion of the approximations made in Chapter IV is given in the last section of that chapter.

**The limit of validity of the first-order theory is determined by the value of t for which the second-order correction becomes important. The first-order result was shown here to be formally valid even for values of $r \sim O(t^{3/4})$, and is not formally restricted to values of $r \ll O(t^{1/2})$, which James considers.

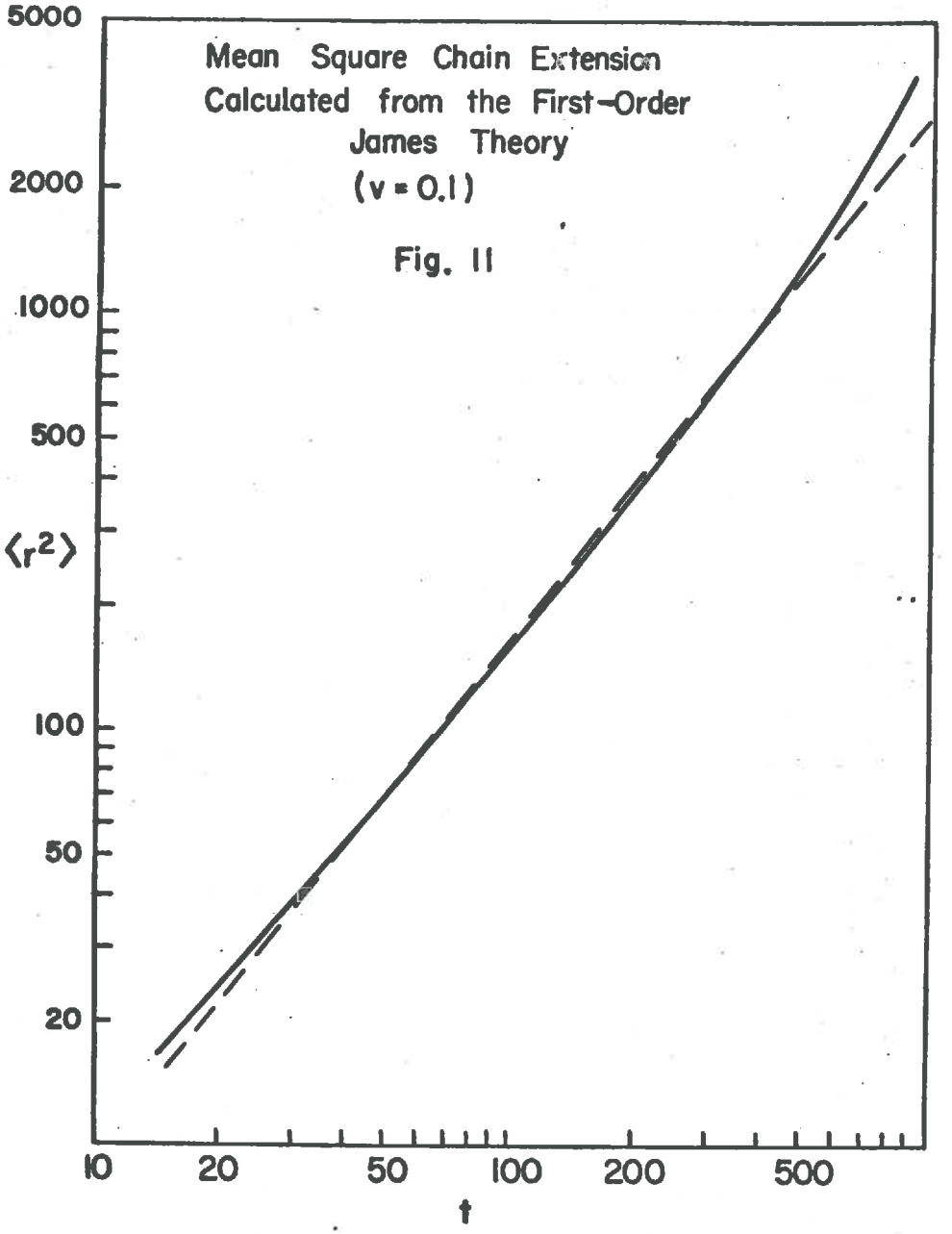
Mean Square Chain Extension
Calculated from the First-Order
James Theory
(v = 0.1)
5000
2000
1000
500
⟨r²⟩
100
50
20
10
20
50
100
200
500
t

Fig. 11

shown by Fig. 11, over the range $t \cong 40$ to 400 ($\lambda \cong 0.4$ to 1.2) the calculated value of $\langle r^2 \rangle$ is closely approximated by the dashed straight line, the slope of which is 1.25. The deviation from the straight line for small values of t is understandable, since for small t, one expects $\langle r^2 \rangle \sim t$. The experimental results quoted in Chapter I do not extend to such small values of t; the data given in Table 1 corresponds to values of t extending from approximately 50 to 10,000.

There is, however, a definite discrepancy between theory and experiment for large values of t: the first-order calculated value of $\langle r^2 \rangle$ increases too rapidly with t--that is, the first-order perturbation calculation gives too large a correction for large t.

A second-order calculation was also considered in Chapters IV and V. It was shown that the second-order correction is in the opposite direction to the first-order correction, and is quite significant for $\lambda > 1$. Mathematical difficulties prevented the writer from completing a successful second-order calculation. The results are extremely sensitive to the approximations made. Depending on the nature of these approximations, the second-order calculation can give values of $\Phi_0(t,\vec{r})$ essentially identical to either the result in the absence of volume exclusion or the first-order result. The procedure has been developed in such detail in Chapters IV and V that a formally valid second-order calculation for $\lambda = O(1)$

appears feasible by numerical methods. This computation was not carried out here.

The perturbation calculation that has been described is of limited applicability in treating the volume exclusion problem because the perturbation is so large. We are effectively calculating the number of allowable configurations of given extension by subtracting from the total number those configurations containing interferences. Since the number of allowed configurations decreases exponentially with t, any small error in the number of excluded configurations will cause a large error in the calculated value of the number of allowed configurations. While higher-order perturbation calculations can extend the range of validity of the results to slightly larger values of λ, such calculations become successively more difficult and hypersensitive to the approximations made.

In conclusion, an exact formulation of the excluded volume problem has been given, but the methods of solution apparent to the writer give interesting results for only a limited range of t values. Agreement with experiment is good within this range. The mathematically interesting question-- what is the limiting form of $\langle r^2 \rangle / t$ as $t \to \infty$ -- can not be answered on the basis of the formalism presented here, and remains, so far as the writer knows, an unsolved problem.

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APPENDICES

APPENDICES

A. The Molecular Dimension Determined by Light Scattering

The use of Eqs. (1.3) and (1.5) to determine $\langle r^2 \rangle$ from light scattering measurements actually assumes that the distribution of segment m about segment n is Gaussian with dispersion proportional to m-n. We shall show here that the experimental procedure actually gives the mean square distance from the elementary scatterersto the center of mass, regardless of the distribution.

One can write Eq. (1.1) as

$$P(\theta) = \sum_{m>n} \sum_{n} \int d\vec{r}_{mn}\, f(m,n;\vec{r}_{mn}) \, \frac{\sin \frac{2\pi}{\lambda} \sigma r_{mn}}{\frac{2\pi}{\lambda} \sigma r_{mn}} , \tag{A.1}$$

where $\sigma = 2 \sin \frac{\theta}{2}$, θ being the scattering angle, and $f(m,n;\vec{r}_{mn})$ gives the probability density that the vector joining segments m and n is $\vec{r}_{mn}$. The wave length of the light (in the solvent), λ, is several times greater than the mean dimensions of the longest molecules considered. In addition, one is interested in the slope of a plot in the neighborhood of $\sigma = 0$. For these reasons one can expand the sin x/x term in Eq. (A.1) to obtain

$$P(\theta) = \sum_{m>n} \sum_{n} \left[1 - \frac{1}{3!} \left(\frac{2\pi}{\lambda} \sigma \right)^2 \langle r_{mn}^2 \rangle + \cdots \right] \tag{A.2}$$

If the vector drawn from segment m to the center of mass is denoted by $\vec{s}_m$, then

$$\sum_{m=1}^{x} \vec{s}_m = 0 , \tag{A.3}$$

and we have

$$\sum_{m=2}^{t}\sum_{n=1}^{t-1} r_{mn}^2 = \sum_{m>n}\sum_{n} \left(\vec{s}_m - \vec{s}_n\right)^2$$

$$= \frac{1}{2}\sum_{m}\sum_{n} \left(s_m^2 + s_n^2 - 2\vec{s}_m\cdot\vec{s}_n\right)$$

$$= t\sum_{m=1}^{t} s_m^2 = t^2 s^2, \qquad (A.4)$$

where s^2 is the mean square distance from the segments to the center of mass, for a given configuration. Averaging over all configurations, we obtain

$$\sum_{m>n}\sum_{n} \langle r_{mn}^2 \rangle = t^2 \langle s^2 \rangle . \qquad (A.5)$$

If we let $P(0) = 1$, then from Eqs. (A.2) and (A.5) it follows that

$$P(\theta) = 1 - \frac{4}{3}\frac{\pi^2\sigma^2}{\lambda^2}\langle s^2 \rangle + \left(\text{higher powers of } s/\lambda\right). \qquad (A.6)$$

Equation (1.3) is consistent with Eq. (A.6) only if

$$\langle r^2 \rangle = 6 \langle s^2 \rangle. \qquad (A.7)$$

Equation (A.7) is not general, however, but is a specific result of the Gaussian distribution. (See, for example, Flory (11), pp. 428-430.) Consequently, experimentally it is $\langle s^2 \rangle$ that is determined, and the form of the distribution of segments must be known or assumed before $\langle r^2 \rangle$ can be calculated.

B. Note on Ternary and Higher-Order Interferences

The formalism developed in Chapter III, Section 2 excludes a configuration upon the addition of the $(t+1)^{st}$ bead if there is an interference involving the t^{th} bead, and there are no interferences between any pair of beads.

i, j in which $i < t$, $j < t$. However, the approximation made in going from Eqs. (3.9) and (3.12) to Eq. (3.13) causes to be excluded twice configurations in which both the i^{th} and j^{th} beads interfere with the t^{th} bead, without interfering with each other. In this appendix we shall show how the theory can be modified to take account of such ternary and higher-order interferences.

It follows exactly from Eqs. (3.9) and (3.12) that

$$W_{t+1}(\vec{r}_1,\cdots,\vec{r}_t,\vec{r}_{t+1}) = W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}_{t+1}-\vec{r}_t)\left[1-\sum_{i=1}^{t-1}\epsilon_i + \sum_{i<j}\sum \epsilon_i\epsilon_j - \cdots\right] \tag{B.1}$$

Using the same procedure as in the derivations of Eqs. (3.14), (3.15), and (3.16), we obtain

$$\begin{aligned}\Phi_1(t+1,\vec{r}) = {} & \int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\Phi_1(t,\vec{r}') \\ & - v\int d\vec{r}'\, g(\vec{r}-\vec{r}')\left[\sum_{i=1}^{t-1}\varphi_1(t,\vec{r}';i,\vec{r}')\right. \\ & \quad - \sum_{i<j}\sum\int d\vec{r}_j\,\varphi_2(t,\vec{r}';i,\vec{r}';j,\vec{r}_j)\,\epsilon(\vec{r}'-\vec{r}_j) \\ & \quad \left. + \cdots\right].\end{aligned} \tag{B.2}$$

Since $\varphi_2(t,\vec{r}';i,\vec{r}';j,\vec{r}_j)$ varies strongly in the neighborhood of $\vec{r}_j = \vec{r}'$, $\epsilon(\vec{r}'-\vec{r}_j)$ can not be replaced by $v\delta(\vec{r}'-\vec{r}_j)$ in the term involving the double sum in Eq.(B.2).

Define

$$v\,\chi_1(t,\vec{r};\vec{r}) = v\,\Phi_1(t,\vec{r};\vec{r}) - v\sum_{j=1}^{t-1}\int d\vec{r}_j\,\Phi_2(t,\vec{r};\vec{r};j,\vec{r}_j)\,\epsilon(\vec{r}-\vec{r}_j) + \cdots, \tag{B.3}$$

where

$$\Phi_2(t,\vec{r}:\vec{r}\,;\,j,\vec{r}_j) = \sum_{\substack{i=1 \\ i\neq j}}^{t-1} \varphi_2(t,\vec{r}:i,\vec{r}\,;\,j,\vec{r}_j) \tag{B.4}$$

is the weight density that the t^{th} bead is at $\vec{r}$, the j^{th} bead is at $\vec{r}_j$, and some other bead is at $\vec{r}$. With the definitions of Eqs. (B.3) and (B.4), it follows from Eq. (B.2) that

$$\Phi_0(t+1,\vec{r}) = \int d\vec{r}'\, q(\vec{r}-\vec{r}')\,\Phi_0(t,\vec{r}') - v\int d\vec{r}'\, q(\vec{r}-\vec{r}')\,\chi_1(t,\vec{r}':\vec{r}'), \tag{B.5}$$

where $v\,\chi_1(t,\vec{r}:\vec{r})d\vec{r}$ gives the weight of configurations in which there is an interference involving the t^{th} bead when it is in $d\vec{r}$ about $\vec{r}$, but no interference of any pair of interior beads. Equation (B.5) is the generalization of Eq. (3.14), taking proper account of ternary and higher order interferences. Similar generalizations of Eqs. (3.15) and (3.16) will not be considered here.

In Chapter IV we considered approximations of $F(t,\vec{r}:\vec{r})$. On the basis of the above discussion, we should consider instead

$$\mathcal{F}(t,\vec{r}:\vec{r}) = \chi_1(t,\vec{r}:\vec{r}) \Big/ \Phi_0(t,\vec{r}) \tag{B.5}$$

$$= F(t,\vec{r}:\vec{r}) - \sum_{j=1}^{t-1}\int d\vec{r}_j\, \frac{\Phi_2(t,\vec{r}:\vec{r}\,;\,j,\vec{r}_j)\,\epsilon(\vec{r}-\vec{r}_j)}{\Phi_0(t,\vec{r})} + \cdots \tag{B.6}$$

In the absence of volume exclusion, $\epsilon = 0$, so that

$$\mathcal{F}_0(t,\vec{r}:\vec{r}) = F_0(t,\vec{r}:\vec{r})\,. \tag{B.7}$$

It is clear that even when volume exclusion is considered, $\bar{F}$ differs from F by terms that are at most of the order νF, and the neglection of such terms is consistent with the approximations of this thesis.

C. Derivation of the Distribution Equation for $\bar{\Phi}_2(t,\vec{r};\vec{R}_1,\vec{R}_2)$

From equations (3.4), (3.8) and (3.13) it follows that

$$\bar{\Phi}_2(t+1,\vec{r};\vec{R}_1,\vec{R}_2) = \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\left[1-\sum_{j=1}^{t-1}\epsilon(\vec{r}_t-\vec{r}_j)\right] \times \sum_{k=1}^{t}\delta(\vec{r}_k-\vec{R}_1)\sum_{\substack{i=1\\(k\neq i)}}^{t}\delta(\vec{r}_i-\vec{R}_2)$$

$$= \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\sum_{k=1}^{t-1}\delta(\vec{r}_k-\vec{R}_1)\sum_{i=1}^{t-1}\delta(\vec{r}_i-\vec{R}_2) \qquad (a)$$

$$- \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\sum_{j=1}^{t-1}\epsilon(\vec{r}_t-\vec{r}_j)\sum_{\substack{k=1\\(k\neq i)}}^{t-1}\delta(\vec{r}_k-\vec{R}_1)\sum_{i=1}^{t-1}\delta(\vec{r}_i-\vec{R}_2) \qquad (b)$$

$$+ \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1\cdots\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\,\delta(\vec{r}_t-\vec{R}_1)\sum_{i=1}^{t-1}\delta(\vec{r}_i-\vec{R}_2) \qquad (c)$$

$$+ \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\sum_{k=1}^{t-1}\delta(\vec{r}_k-\vec{R}_1)\,\delta(\vec{r}_t-\vec{R}_2) \qquad (d)$$

$$- \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\sum_{j=1}^{t-1}\epsilon(\vec{r}_t-\vec{r}_j)\,\delta(\vec{r}_t-\vec{R}_1)\sum_{i=1}^{t-1}\delta(\vec{r}_i-\vec{R}_2) \qquad (e)$$

$$- \int d\vec{r}_1 \cdots \int d\vec{r}_t\; W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\sum_{j=1}^{t-1}\epsilon(\vec{r}_t-\vec{r}_j)\sum_{k=1}^{t-1}\delta(\vec{r}_k-\vec{R}_1)\,\delta(\vec{r}_t-\vec{R}_2) \qquad (f)$$

Line (a) $= \int d\vec{r}_t\; \bar{\Phi}_2(t,\vec{r}_t:\vec{R}_1,\vec{R}_2)\, g(\vec{r}-\vec{r}_t)$.

Line (c): $\int d\vec{r}_t\; \bar{\Phi}_1(t,\vec{r}_t:\vec{R}_2)\, g(\vec{r}-\vec{r}_t)\,\delta(\vec{r}_t-\vec{R}_1) = \bar{\Phi}_1(t,\vec{R}_1:\vec{R}_2)\, g(\vec{r}-\vec{R}_1)$.

Line (d): $\int d\vec{r}\ \Phi_1(t,\vec{r}_1:\vec{R}_1)q(\vec{r}-\vec{r}_1)\delta(\vec{r}_1-\vec{R}_2) = \Phi_1(t,\vec{R}_1:\vec{R}_1)q(\vec{r}-\vec{R}_2)$.

Line (e): for $j\neq 1$, we replace $\sum_{j=1}^{k-1}\epsilon(\vec{r}_1-\vec{r}_j)$ by $v\sum_{j=1}^{k-1}\delta(\vec{r}_1-\vec{r}_j)$

to obtain

$$-v\int d\vec{r}_1\ \Phi_2(t,\vec{r}_1:\vec{r}_1,\vec{R}_2)q(\vec{r}-\vec{r}_1)\delta(\vec{r}_1-\vec{R}_1) = -v\,\Phi_2(t,\vec{R}_1:\vec{R}_1,\vec{R}_2)q(\vec{r}-\vec{R}_1).$$

For $j=1$ we will have terms of the form

$$\begin{aligned}
&-\int d\vec{r}_1\cdots\int d\vec{r}_k\ W_k(\vec{r}_1\cdots\vec{r}_k)q(\vec{r}-\vec{r}_k)\epsilon(\vec{r}_k-\vec{r}_j)\,\delta(\vec{r}_k-\vec{R}_1)\,\delta(\vec{r}_j-\vec{R}_2)\\
&= -\int d\vec{r}_j\int d\vec{r}_k\ \varphi_1(t,\vec{r}_k:j,\vec{r}_j)q(\vec{r}-\vec{r}_k)\epsilon(\vec{r}_k-\vec{r}_j)\,\delta(\vec{r}_j-\vec{R}_2)\,\delta(\vec{r}_k-\vec{R}_1)\\
&= -\int d\vec{r}_j\ \varphi_1(t,\vec{R}_1:j,\vec{r}_j)\epsilon(\vec{R}_1-\vec{r}_j)\,\delta(\vec{r}_j-\vec{R}_2)\,q(\vec{r}-\vec{R}_1)\\
&= -\varphi_1(t,\vec{R}_1:j,\vec{R}_2)\epsilon(\vec{R}_1-\vec{R}_2)q(\vec{r}-\vec{R}_1).
\end{aligned}$$

Summing over j gives $-\Phi_1(t,\vec{R}_1:\vec{R}_2)\epsilon(\vec{R}_1-\vec{R}_2)q(\vec{r}-\vec{R}_1)$.

Likewise, line (f) gives

for $j\neq 1$ $\quad -v\,\Phi_2(t,\vec{R}_2:\vec{R}_2,\vec{R}_1)q(\vec{r}-\vec{R}_2)$;

for $j=1$ $\quad -\Phi_1(t,\vec{R}_2:\vec{R}_1)\epsilon(\vec{R}_2-\vec{R}_1)q(\vec{r}-\vec{R}_2)$.

Line (b): For $j\neq k$, $j\neq 1$, we have $-v\int d\vec{r}_1\ \Phi_3(t,\vec{r}_1:\vec{r}_1,\vec{R}_1,\vec{R}_2)q(\vec{r}-\vec{r}_1)$

For $j=k$ $(\neq 1)$, we have terms of the form

$$\begin{aligned}
&-\int d\vec{r}_1\cdots\int d\vec{r}_k\ W_k(\vec{r}_1\cdots\vec{r}_k)q(\vec{r}-\vec{r}_k)\epsilon(\vec{r}_k-\vec{r}_j)\,\delta(\vec{r}_j-\vec{R}_1)\sum_{l=1\ (l\neq j)}^{k-1}\delta(\vec{r}_l-\vec{R}_2)\\
&= -\int d\vec{r}_k\,d\vec{r}_j\ \Phi_2(t,\vec{r}_k:\vec{R}_2\,;\,j,\vec{r}_j)q(\vec{r}-\vec{r}_k)\epsilon(\vec{r}_k-\vec{r}_j)\,\delta(\vec{r}_j-\vec{R}_1)\\
&= -v\,\Phi_2(t,\vec{R}_1:\vec{R}_2\,;\,j,\vec{R}_1)q(\vec{r}-\vec{R}_1).
\end{aligned}$$

Summing over j, we get $-v\,\Phi_2(t,\vec{R}_1:\vec{R}_2,\vec{R}_1)q(\vec{r}-\vec{R}_1)$.

Likewise for $j=1$ $(\neq k)$, we will get

$$-v\,\Phi_2(t,\vec{R}_2:\vec{R}_1,\vec{R}_2)q(\vec{r}-\vec{R}_2).$$

Collecting terms, we have

$$\Phi_2(t+1,\vec{r}:\vec{R}_1,\vec{R}_2) = \int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\Phi_2(t,\vec{r}':\vec{R}_1,\vec{R}_2)$$
$$+ \Phi_1(t,\vec{R}_1:\vec{R}_2)\,g(\vec{r}-\vec{R}_1)\left[1-\epsilon(\vec{R}_1-\vec{R}_2)\right]$$
$$+ \Phi_1(t,\vec{R}_2:\vec{R}_1)\,g(\vec{r}-\vec{R}_2)\left[1-\epsilon(\vec{R}_2-\vec{R}_1)\right]$$
$$- 2v\,\Phi_2(t,\vec{R}_1:\vec{R}_1,\vec{R}_2)\,g(\vec{r}-\vec{R}_1)$$
$$- 2v\,\Phi_2(t,\vec{R}_2:\vec{R}_2,\vec{R}_1)\,g(\vec{r}-\vec{R}_2)$$
$$- v\int d\vec{r}'\, g(\vec{r}-\vec{r}')\,\Phi_3(t,\vec{r}',\vec{r}';\vec{R}_1,\vec{R}_2) \qquad (3.16)$$

D. Distribution of an Interior Bead

The main body of this thesis has been devoted to the consideration of the distribution of an end (t^{th}) bead about the other end of the chain. However, it would be of interest for many applications to know the distribution about the origin of an interior bead. We shall now show how such a quantity can be calculated using the formalism of ChapterIII.

As in Chapter III, $\Phi_1(t,\vec{r}:j,\vec{R})d\vec{r}d\vec{R}$ is defined to be the relative weight of a chain of t links in which the t^{th} bead is in df about $\vec{r}$ and the j^{th} bead is in $d\vec{R}$ about $\vec{R}$. It follows from Eqs. (3.3) and (3.13) that

$$\Phi_1(t+1,\vec{r}:j,\vec{R}) = \int d\vec{r}_1 \cdots \int d\vec{r}_t\, W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)$$
$$\times \left[1-\sum_{i=1}^{t+1}\epsilon(\vec{r}_i-\vec{r}_i)\right]\delta(\vec{r}_j-\vec{R}), \qquad (D.1)$$

which for $0<j<t$ can be written

$$\Phi_1(t+1,\vec{r}:j,\vec{R}) = \int d\vec{r}_1 \cdots \int d\vec{r}_t\, W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\, \delta(\vec{r}_j-\vec{R})$$
$$-\sum_{i=1}^{t-1}\int_{(i\neq j)} d\vec{r}_1 \cdots \int d\vec{r}_t\, W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\, \epsilon(\vec{r}_t-\vec{r}_i)\, \delta(\vec{r}_j-\vec{R})$$
$$-\int d\vec{r}_1 \cdots \int d\vec{r}_t\, W_t(\vec{r}_1,\cdots,\vec{r}_t)\, g(\vec{r}-\vec{r}_t)\, \epsilon(\vec{r}_t-\vec{r}_j)\, \delta(\vec{r}_j-\vec{R}). \qquad (D.2)$$

It follows from Eqs. (3.3), (3.4) and the δ-function behavior of ϵ that

$$\Phi_1(t+1,\vec{r}:j,\vec{R}) = \int d\vec{r}'\, g(\vec{r}-\vec{r}')\, \Phi_1(t,\vec{r}':j,\vec{R})$$
$$-v\int d\vec{r}'\, g(\vec{r}-\vec{r}')\, \Phi_2(t,\vec{r}':j,\vec{R};\vec{r}') \;*$$
$$-v\,\Phi_1(t,\vec{R}:j,\vec{R})\, g(\vec{r}-\vec{R}), \qquad (D.3)$$

for $0<j<t$. Equation (D.3) can be checked for consistency with the results of Chapter III. In particular, upon integration over all $\vec{R}$

$$\int d\vec{R}\, \Phi_1(t+1,\vec{r}:j,\vec{R}) = \Phi_0(t+1,\vec{r}), \qquad (D.4)$$

and

$$\int d\vec{R}\, \Phi_2(t,\vec{r}':j,\vec{R};\vec{r}') = \Phi_1(t,\vec{r}':\vec{r}') - \Phi_1(t,\vec{r}':j,\vec{r}'). \qquad (D.5)$$

Therefore the result of integrating Eq. (D.3) over all $\vec{R}$ is exactly Eq. (3.14).

Equation (D.3) is valid only for $t>j$. It follows directly from Eq. (D.1) that

---

* $\Phi_2(t,\vec{r}':j,\vec{R}:\vec{r}')$ is the weight density of configurations in which the t^{th} bead is at $\vec{r}'$, the j^{th} bead is at $\vec{R}$ and some other bead is at $\vec{r}'$. See the Glossary for further explanation of this notation.

$$\varphi_1(j+1,\vec{r}:j,\vec{R}) = \int d\vec{r}_1 \cdots \int d\vec{r}_j\, W_j(\vec{r}_1,\cdots,\vec{r}_j)\, g(\vec{r}-\vec{r}_j)\, \delta(\vec{r}_j-\vec{R})$$
$$- \sum_{i=1}^{j-1} \int d\vec{r}_1 \cdots \int d\vec{r}_j\, W_j(\vec{r}_1,\cdots,\vec{r}_j)\, g(\vec{r}-\vec{r}_j)\, e(\vec{r}_j-\vec{r}_i)\, \delta(\vec{r}_j-\vec{R}), \tag{D.6}$$

$$= \int d\vec{r}'\, \Phi_0(j,\vec{r}')\, g(\vec{r}-\vec{r}')\, \delta(\vec{r}'-\vec{R})$$
$$- v \int d\vec{r}'\, \Phi_1(j,\vec{r}':\vec{r}')\, g(\vec{r}-\vec{r}')\, \delta(\vec{r}'-\vec{R})$$
$$= \left[\Phi_0(j,\vec{R}) - v\,\Phi_1(j,\vec{R}:\vec{R})\right] g(\vec{r}-\vec{R}). \tag{D.7}$$

(It can also be noted that the summation over $j = 1$ to $t-1$ of Eq. (D.3) with the use of Eqs. (3.7) and (D.7) leads exactly to Eq. (3.15).)

The formalism in Chapter III gives a method (in principle) for the calculation of $\Phi_0(j,\vec{R})$ and $\Phi_1(j,\vec{R}:\vec{R})$. Then Eq. (D.7) can be used to calculate $\varphi_1(j+1,\vec{r}:j,\vec{R})$. We then can use the iterative procedure described by Eq. (D.3) and analogous higher-order equations to calculate $\varphi_1(t+1,\vec{r}:j,\vec{R})$ for $t > j$. The distribution of the j^{th} bead regardless of the location of the t^{th} bead can then be determined by integrating over all $\vec{r}$:

$$\varphi_1(t:j,\vec{R}) = \int d\vec{r}\; \varphi_1(t,\vec{r}:j,\vec{R}). \tag{D.8}$$

In light of the difficulties encountered in Chapter III, the writer does not consider it practicable to use the above formalism for the calculation of $\varphi_1(t:j,\vec{R})$. Instead, the application of James' second method will be considered.

In the absence of volume exclusion, the distribution about the origin of the j^{th} bead when the t^{th} bead is

unconstrained, is the same as the distribution of the j^{th} bead in a chain of j links--that is

$$\varphi_1^{(\infty)}(t:j,\vec{R}) \equiv \Phi_0^{(\infty)}(j,\vec{R}). \tag{D.9}$$

When volume exclusion is considered,

$$\varphi_1(t:j,\vec{R}) = \Phi_0^{(\infty)}(j,\vec{R})\, p(j,\vec{R})\, p(j,\vec{R}:t-j), \tag{D.10}$$

where $p(j,\vec{R}:t-j)$ is the probability that there are no interferences between a chain of j links and extension $\vec{R}$, and an unconstrained chain of t-j links beginning at $\vec{R}$. We shall again define the first-order approximation as

$$\varphi_1^{(1)}(t:j,\vec{R}) = \Phi_0^{(\infty)}(j,\vec{R})\, p_0(j,\vec{R})\, p_0(j,\vec{R}:t-j). \tag{D.11}$$

It has previously been shown that (See Eq. (4.76))

$$p_0(j,\vec{R}) \cong \exp\left\{-cvj + \frac{9}{2\pi} v R\right\}. \tag{D.12}$$

Analogous to Eq. (4.83), we can write

$$p_0(j,\vec{R}:t-j) = \exp\left\{-\sum_\alpha P_\alpha''\right\} \tag{D.13}$$

where

$$\sum_\alpha P_\alpha'' = v\int d\vec{s}\, F_0(j,\vec{R}:\vec{R}-\vec{s}) \sum_{k=1}^{t-j} \Phi_0^{(\infty)}(k,\vec{s}). \tag{D.14}$$

The details of this calculation will not be considered any further here. It will just be remarked that $p_0(j,\vec{R}:t-j)$ is relatively smaller for small $\vec{R}$ than it is for large $\vec{R}$, so that $\varphi_1^{(1)}(t:j,\vec{R})$ will be relatively more extended than $\Phi_0^{(\infty)}(j,\vec{R})$.

E. Evaluation of $F_0(t,\vec{r}:\vec{R})$

By definition

$$F_0(t,\vec{r}:\vec{R}) = \sum_{j=1}^{t-1} \frac{\Phi_0^{(\infty)}(j,\vec{R})\, \Phi_0^{(\infty)}(t-j,\vec{r})}{\Phi_0^{(\infty)}(t,\vec{R}+\vec{s})}, \tag{E.1}$$

where

$$\vec{s} = \vec{r} - \vec{R}. \tag{E.2}$$

In Chapter IV, such sums were replaced by integrals.

$$F_0(t,\vec{r}:\vec{R}) = \int_{1/2}^{t-1/2} dj \; \frac{\Phi_0^{(\omega)}(j,\vec{R})\,\Phi_0^{(\omega)}(t-j,\vec{s})}{\Phi_0^{(\omega)}(t,\vec{R}+\vec{s})} \; . \tag{E.3}$$

Since

$$\Phi_0^{(\omega)}(j,\vec{R}) = \left(\frac{3}{2\pi j}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{R^2}{j}\right), \tag{E.4}$$

It follows that

$$F_0(t,\vec{r}:\vec{R}) = \left(\frac{3}{2\pi}\right)^{3/2} \exp\left(\frac{3\vec{R}\cdot\vec{s}}{t}\right) \int_{1/2}^{t-1/2} dj \left[\frac{t}{j(t-j)}\right]^{3/2} \exp\left(-\frac{3}{2}R^2\frac{t-j}{jt}\right) \times \exp\left(-\frac{3}{2}s^2\frac{j}{t(t-j)}\right). \tag{E.5}$$

Let

$$y^2 = j/(t-j). \tag{E.6}$$

Then

$$F_0(t,\vec{r}:\vec{R}) = \frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2} \exp\left(\frac{3\vec{R}\cdot\vec{s}}{t}\right) \int_{\delta}^{1/\delta} dy \, \frac{1+y^2}{y^2} \exp\left(-\xi^2/y^2\right) \exp\left(-\eta^2 y^2\right), \tag{E.7}$$

where

$$\delta = \sqrt{\frac{1/2}{t-1/2}} \cong \sqrt{1/2t}, \tag{E.8}$$

$$\xi^2 = \frac{3}{2}\frac{R^2}{t}, \tag{E.9}$$

$$\eta^2 = \frac{3}{2}\frac{s^2}{t}. \tag{E.10}$$

Equation (E.7) can now be written

$$F_0(t,\vec{r}:\vec{R}) = \exp\left(\frac{3\vec{R}\cdot\vec{s}}{t}\right)\left[K(\xi,\eta) + K(\eta,\xi)\right], \tag{E.11}$$

where

$$K(\xi,\eta) = \frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2}\int_{\xi}^{1/\delta} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right) \qquad \text{(E.12)}$$

$$= \frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2}\int_{0}^{\infty} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right) \qquad \text{(a)}$$

$$- \frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2}\int_{1/\delta}^{\infty} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right) \qquad \text{(b)}$$

$$- \frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2}\int_{0}^{\delta} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right). \qquad \text{(c)}$$

From Bierens de Haan (1), Table 26, No.10, it follows that the expression on line (a) is equal to

$$\frac{2}{t^{1/2}}\left(\frac{3}{2\pi}\right)^{3/2}\frac{\sqrt{\pi}}{2\eta}\exp\left(-2\xi\eta\right) = \frac{3}{2\pi s}\exp\left(-\frac{3Rs}{t}\right). \qquad \text{(a)}$$

We consider both $R \ll t$, $s \ll t$; therefore $\xi^2\delta^2 \ll 1$, and $\eta^2\delta^2 \ll 1$. We consequently can expand the first exponential on line (b), and the second exponential on line (c).

$$\int_{1/\delta}^{\infty} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right) = \int_{1/\delta}^{\infty} dy\left[1 - \frac{\xi^2}{y^2} + \ldots\right]\exp\left(-\eta^2 y^2\right)$$

$$= \frac{\sqrt{\pi}}{2\eta}\operatorname{erfc}\frac{\eta}{\delta} - \xi^2\delta\exp\left(\frac{-\eta^2}{\delta^2}\right) + \sqrt{\pi}\,\eta^2\xi^2\operatorname{erfc}\frac{\eta}{\delta} + \ldots \qquad \text{(E.13)}$$

$$\int_{0}^{\delta} dy\, \exp\left(\frac{-\xi^2}{y^2}\right)\exp\left(-\eta^2 y^2\right) = \int_{1/\delta}^{\infty}\frac{dy}{y^2}\exp\left(-\xi^2 y^2\right)\exp\left(\frac{-\eta^2}{y^2}\right)$$

$$= \int_{1/\delta}^{\infty}\frac{dy}{y^2}\exp\left(-\xi^2 y^2\right)\left[1 - \frac{\eta^2}{y^2} + \ldots\right]$$

$$= \delta\exp\left(-\xi^2/\delta^2\right) - \sqrt{\pi}\,\xi^2\operatorname{erfc}\xi/\delta + \ldots \qquad \text{(E.14)}$$

Collecting terms, we obtain with the neglection of terms of $O(t^{-1})$,

$$K(\xi,\tau) = \frac{3}{2\pi s}\exp\left(-\frac{3Rs}{t}\right) - \frac{3}{2\pi s}\operatorname{erfc}\sqrt{3}\,s\,, \tag{E.15}$$

from which it follows that

$$F_0(t,\vec{r}:\vec{R}) = \exp\left(\frac{3\vec{R}\cdot\vec{s}}{t}\right)\left[\left(\frac{3}{2\pi R}+\frac{3}{2\pi s}\right)\exp\left(-\frac{3Rs}{t}\right) - \frac{3}{2\pi R}\operatorname{erfc}\sqrt{3}\,R - \frac{3}{2\pi s}\operatorname{erfc}\sqrt{3}\,s\right] + O(t^{-1}). \tag{E.16}$$

For $\vec{s} = 0$, Eq. (E.16) reduces to

$$F_0(t,\vec{r}:\vec{r}) = \left(\frac{3}{\pi}\right)^{3/2} + \frac{3}{2\pi r} - \frac{9r}{2\pi t} - \frac{3}{2\pi r}\operatorname{erfc}\sqrt{3}\,r \tag{E.17}$$

in substantial agreement with the more accurate direct calculation given in Chapter IV. [See Eqs. (4.33), (4.34), and (4.35).]

For $R > 1$, $s > 1$ the terms in Eq. (E.16) involving the complementary error functions can be neglected, so that

$$F_0(t,\vec{r}:\vec{R}) \cong \exp\left(\frac{3\vec{R}\cdot\vec{s}}{t} - \frac{3Rs}{t}\right)\left(\frac{3}{2\pi R}+\frac{3}{2\pi s}\right). \tag{E.18}$$

F. Evaluation of $\int d\vec{s}\, F_0(i,o:\vec{s})\, F_0(\tau,\vec{r}:\vec{r}-\vec{s})$

The sum over all cross-interferences of the probability for a cross-interference is given by Eq. (4.85):

$$\sum_{\alpha} P_{\alpha} = \nu \int d\vec{s}\, F_0(\tau,\vec{r}:\vec{r}-\vec{s})\, F_0(t-\tau,o,\vec{s}). \tag{F.1}$$

It was shown that $\sum_{\alpha} P_{\alpha}$ is given approximately by [Eq. (4.90)]

$$\sum_{\alpha} P_{\alpha}^{2} = v \int d\vec{s}\, \frac{3}{4\pi s} \exp\left(\frac{-6s^2}{j}\right)\left(\frac{3}{2\pi R} + \frac{3}{2\pi s}\right) \exp\left[\frac{3}{\tau}\left(\vec{R}\cdot\vec{s} - Rs\right)\right], \tag{F.2}$$

where $R = |\vec{r}-\vec{s}|$, and the integration is over all $\vec{s}$ for fixed $\vec{r}$. We shall consider the integration using prolate spheroidal co-ordinates (33). Let

$$\nu = \frac{s+R}{r}, \qquad \mu = \frac{s-R}{r}; \tag{F.3}$$

the volume element $d\vec{s}$ is then given by

$$d\vec{s} = \left(\frac{r}{2}\right)^3 (\nu^2-\mu^2)\, d\nu\, d\mu\, d\varphi = 2\pi \left(\frac{r}{2}\right)^3 (\nu^2-\mu^2)\, d\nu\, d\mu . \tag{F.4}$$

With the above change of variables, Eq. (F.2) can be rewritten as

$$\sum_{\alpha} P_{\alpha}^{2} = \frac{9v}{4\pi}\, r\, e^{\gamma} \int_{1}^{\infty} d\nu \int_{-1}^{1} d\mu\, \frac{\nu}{\nu+\mu} \exp\left[-\gamma\nu^2 - \beta(\nu+\mu)^2\right], \tag{F.5}$$

where

$$\gamma = \frac{3}{2}\frac{r^2}{\tau}, \qquad \beta = \frac{3}{2}\frac{r^2}{j}. \tag{F.6}$$

With appropiate integrations and changes of variables, it can be shown that

$$\sum_{\alpha} P_{\alpha}^{2} = \frac{9v}{2\pi}\frac{r}{\gamma}\left\{2\int_{0}^{\infty}\frac{dz}{z}\, e^{-(\gamma+\beta)z^2} \sinh 2\gamma z + \int_{0}^{2}\frac{dz}{z}\, e^{-\beta z^2}\left[1 - e^{-\gamma z^2 + 2\gamma z}\right]\right\}. \tag{F.7}$$

The integration could not be carried any further exactly. We shall consider here several limiting cases, omitting all details of the calculation, giving only the final results.

i) For γ and β small, with the neglection of second-order terms in γ and β,

$$\sum_{\alpha} P_{\alpha} \cong \nu \left(\frac{54}{\pi}\right)^{1/2} \left(\frac{t-j}{t}\right)^{1/2} j^{1/2} . \tag{F.8}$$

This is exactly the result one would get for $r = 0$. The above result will be a good approximation for those configurations with small extension, $r = 0(1)$.

ii) For γ and $1/\beta$ small, with the neglection of second-order terms in γ and $1/\beta$,

$$\sum_{\alpha} P_{\alpha} \cong \nu \left(\frac{27}{2\pi}\right)^{1/2} j^{1/2} + \frac{3\nu j}{2\pi r} . \tag{F.9}$$

For β large, $r \gg j^{1/2}$; but since γ is small, $r \ll \tau^{1/2}$. This approximation applies, then, primarily to small j (small loops) and $r > 0(1)$. The second term in Eq. (F.9) is smaller than the first, and we note for future reference that over the range of interest of this approximation, the first term can be multiplied by $\left(\frac{t-j}{t}\right)^{1/2}$ with negligible error.

iii) For large γ, $\frac{\gamma}{\sqrt{\gamma+\beta}}$ small, (then β very large),

$$\sum_{\alpha} P_{\alpha} \cong \nu \left(\frac{27}{2\pi}\right)^{1/2} \left(\frac{t-j}{t}\right)^{1/2} j^{1/2} - \frac{9\nu}{2\pi} r \frac{j}{t} . \tag{F.10}$$

The parameter $\frac{\gamma}{\sqrt{\gamma+\beta}}$ is given by

$$\frac{\gamma}{\sqrt{\gamma+\beta}} = \sqrt{\frac{1}{2}}\,\frac{r}{t^{3/2}}\left(\frac{j}{t-j}\right)^{1/2}. \tag{F.11}$$

The above conditions imply that either r or j is large, but not both. In either case the second term on the right hand side of Eq. (F.10) is small compared to the first.

iv) γ large, $\frac{\gamma}{\sqrt{\gamma+\beta}}$ large, β large;

v) γ large, $\frac{\gamma}{\sqrt{\gamma+\beta}}$ large, β small;

both these cases give approximately

$$\sum_{\alpha} P_{\alpha} \cong \frac{3\nu}{\pi r}(t-j). \tag{F.12}$$

However, the conditions γ large, $\frac{\gamma}{\sqrt{\gamma+\beta}}$ large, virtually require both j and r relatively large. These cases will be applicable only for those configurations with $j \sim O(\frac{t}{2})$ and $r \sim O(t^{1/2})$. While such cases can not be neglected, they are certainly not as important as those with small j, and those with large j and small r.

On the basis of the above qualitative discussion, it would seem reasonable to take

$$\sum_{\alpha} P_{\alpha} \cong \left(\frac{27}{2\pi}\right)^{1/2} \nu \left(\frac{t-j}{t}\right)^{1/2} j^{1/2} \tag{F.13}$$

as being adequate over the entire range of interest. A more detailed analysis, however, in which the range of integration in Eq. (4.80) is split into several sub-intervals and the approximation appropiate to each sub-interval is considered, leads one to doubt the validity of using the

single result given by Eq. (F.13).

We have seen in Section 9 of Chapter IV that an independent approximation leads to exactly the same result as Eq. (F.13). While no detailed justification of the approximation is given there, the nature of the error due to the approximation is discussed in some detail. On the basis of these results, the writer chose to consider the approximation given by Eq. (F.13) since it is adequate for the most important limiting cases, and it can be given an independent interpretation from which the nature of the error can be discussed.

GLOSSARY

GLOSSARY OF NOTATION*

c	$c = (3/\pi)^{3/2}$, except in Chapter I where c = concentration by weight.
$F(t,\vec{r}:\vec{R})$	Probability density that in a chain of t links and extension $\vec{r}$, there is another bead at $\vec{R}$. Given by $\Phi_0(t,\vec{r}:\vec{R})/\Phi_0(t,\vec{r})$. When appearing with subscript zero, refers to value calculated in the absence of volume exclusion. $F(t:\vec{R})$ refers to the same probability density in a chain of unconstrained extension.
$g(s)$	$(3/2\pi)^{3/2}\exp(-3s^2/2)$, a priori probability density for link extension $\vec{s}$. (All lengths are measured in multiples of the root mean square link length.)
$P_\nu(t,\vec{r})$	Probability in a chain of t links and extension $\vec{r}$ that there is an interference involving the ν^{th} pair of beads regardless of any other interference that may be present. P_α refers specifically to configurations in which there is a closed loop at $\vec{r}$ (see Fig. 3) and gives the probability that there is a particular cross-interference α (interference between a bead on the loop and one on remainder of chain) regardless of any other interferences that may be present.
$p(t,\vec{r})$	Probability that there are no interferences in a chain of t links and extension $\vec{r}$; $\Phi_0(t,\vec{r})/\Phi_0^{(0)}(t,\vec{r})$. When appearing with a subscript zero, refers to value calculated assuming probalities for non-interference are independent.

*Only those terms are given that recur in several places in the text, far removed from where they are originally defined.

$p(t-j,\vec{r}:j,0)$ Probability that there are no interferences between a chain of t-j links and extension $\vec{r}$, and a closed loop of j links (closure at $\vec{r}$), taking account of volume exclusion within the two chains. (Probability that there are no cross-interferences.) The corresponding quantity without the argument $\vec{r}$, $p(t-j:j,0) \equiv p(j,0:t-j)$, is the probability that there are no cross-interferences when the extension of the chain of t-j links is unconstrained. When appearing with subscript zero, refers to value calculated neglecting volume exclusion within the two parts of the chain, and assuming probabilities for non-cross-interference are independent.

$\langle r^2 \rangle$ Mean square chain extension. When appearing without subscript, refers to chain of t links.
$\langle r^2 \rangle \equiv \langle r^2 \rangle_t \equiv \int d\vec{r}\ r^2\, \Phi_t(t,\vec{r}) / \int d\vec{r}\ \Phi_t(t,\vec{r})$.

$\{r^2\}$ Mean square chain extension for configurations in which both the end (t^{th}) bead and some other bead is at $\vec{r}$.
$\{r^2\} \equiv \{r^2\}_t \equiv \int d\vec{r}\ r^2 \Phi_t(t,\vec{r}:\vec{r}) / \int d\vec{r}\ \Phi_t(t,\vec{r}:\vec{r})$

t Unless specified otherwise, refers to number of links in the chain. Links are numbered 1,2,. . .,t-1,t. Beads are numbered 0,1,. . .,t-1,t.

v The volume associated with each bead, such that the center of no other bead can enter into this volume without giving an interference Called the excluded volume.

δ $\delta \equiv 1/\sqrt{2\pi \cdot t} \cong (2t)^{-1/2}$
(In Chapter III, $\delta(\vec{r})$ is the 3-dimensional Dirac δ-function.)

λ $\lambda \equiv (\pi/2\pi^2)^{1/2}\, v\, t^{1/2}$
(Except in Chapter I where λ is wave length.)

ζ $\zeta \equiv \sqrt{\frac{3}{2}}\, \frac{r}{t^{1/2}}$

$\Phi_\nu(t,\vec{r}:j_1,\vec{R}_1,\cdots j_\nu,\vec{R}_\nu)\, d\vec{r}\, d\vec{R}_1 \cdots d\vec{R}_\nu$

The relative weight of configurations of a chain of t links and extension $\vec{r}$ to within $d\vec{r}$, in which the center of bead j_μ is at $\vec{R}_\mu$ to within $d\vec{R}_\mu$, $\mu=1,2\ldots\nu$; $\nu \geq 1$.
If the argument $\vec{r}$ is suppressed, reference is to a chain with unconstrained extension. Thus $\Phi_t(t:j,\vec{R})d\vec{R}$ is the relative weight of configurations of a chain of t links, bead zero held fixed at the origin, bead t unconstrained, and the center of bead j at $\vec{R}$ to within $d\vec{R}$.

$\bar{\Phi}_\nu(t,\vec{r}:\vec{R}_1,\cdots\vec{R}_\nu)\, d\vec{r}\, d\vec{R}_1 \cdots d\vec{R}_\nu$

The relative weight of configurations of a chain of t links and extension $\vec{r}$ to within $d\vec{r}$ in which there is an unspecified interior bead at $\vec{R}_\mu$ to within $d\vec{R}_\mu$, $\mu=1,2,\ldots,\nu$; $\nu \geq 0$.
Mixed cases in which some fixed points are occupied by specified beads and other fixed points are occupied by unspecified beads have also been denoted by the capital $\bar{\Phi}$.
Thus $\bar{\Phi}_1(t,\vec{r}:\vec{R};j,\vec{\eta})d\vec{r}d\vec{R}d\vec{\eta}$ is the relative weight of congigurations of a chain of t links and extension $\vec{r}$ to within $d\vec{r}$, when bead j is at $\vec{\eta}$ to within $d\vec{\eta}$, and some other bead is at $\vec{R}$ to within $d\vec{R}$.
The superscript zero refers to values calculated in the absence of volume exclusion. The superscripts 1,2,...refer to successive approximations.

VITA

Ira Jacobs was born on January 3, 1931 in Brooklyn, New York. He attended elementary and secondary schools in Brooklyn, graduating from the Brooklyn Technical High School in June 1947. He attended the City College of New York from September 1947 to August 1950, and received the Bachelor of Science degree in August 1950. He was a Graduate Assistant in the Physics Department of Purdue University from September 1950 to June 1952, and received the Master of Science degree in June 1952. In the summer of 1952, he was employed by the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. He returned to Purdue University in September 1952, and was again a Graduate Assistant in the Physics Department from September 1952 to August 1953. In August 1953, he was awarded a fellowship by the Purdue Research Foundation for research in the statistical mechanics of long chain molecules.