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SPECIAL INVITED PAPER

POLYMERS AS SELF-AVOIDING WALKS[1, 2]

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A brief overview is presented of the relation of the properties of real polymers to the problem of self-avoiding random walks. The self-consistent field method is discussed wherein the non-Markovian continuous self-avoiding polymer is replaced by a self-consistent Markovian approximation. An outline is presented of the method of solution of the resultant nonlinear integrodifferential equations. A description is also presented of the scaling theories which provide a means for deducing some exponents in the asymptotic dependence of walk properties on the length of the walk in the limit of infinite length walks.

1. Introduction. It is useful to begin with a description of what a polymer is and of what kinds of properties of the polymers are of interest to polymer chemists and physicists. Then the probabilistic nature of the mathematical description of these "beasts" becomes rather clear, and we can turn to a description of some of our recent work concerning self-consistent field theories [15–17, 19, 27] and scaling theories [28].

Polymers are long chain molecules, composed of many repeat units (monomers) ranging from a hundred or so up to 10^5–10^6 units. Here we consider only linear polymers where the monomer units are sequentially bonded to each other so there is a unique linear sequence of successive units numbered 0, 1, $\cdots$, N beginning from either end. A simple example is provided by the polyethylene chain that is depicted in Figure 1. The repeat units are —CH_2— groups with carbon atoms forming the chain backbone and the hydrogens being the side groups. The example is taken as a typical one for purposes of this paper.

Let $\mathbf{r}_i$ be the vector from the origin of the ith vertex on the chain backbone (carbon atom C_i in Figure 1). Define the bond $\mathbf{b}_i$ along the ith chain backbone bond as $\mathbf{b}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$. Let θ_i be the angle between the vectors $-\mathbf{b}_i$ and $\mathbf{b}_{i+1}$, where $0 < \theta_i \leq \pi$. (θ_i is the angle $C_{i-1} - C_i - C_{i+1}$ in Figure 1). As shown in Figure 1, the bond lengths $|\, b_i \,|$ have a fixed value $b > 0$, and the bond angles θ_i all have the constant value θ. (For other cases, where e.g. atoms of two elements alternate along the backbone, see Flory, 1969, page 2.)

Then, the only degree of freedom in forming the polymer chain is associated with the rotational angles ϕ_i, where ϕ_i is the angle between the plane formed by $\mathbf{b}_{i-2}$ and $\mathbf{b}_{i-1}$ and the plane formed by $\mathbf{b}_{i-1}$ and $\mathbf{b}_i$. The ϕ_i have to do with the relative orientations of "pendant" atoms or groups off the chain backbone.

Here a good approximation is obtained by allowing the individual ϕ_i to assume only three discrete values with differing probabilities. There are often restrictions placed on successive bond angles, ϕ_i and ϕ_{i+1}, providing a widely utilized *ideal* model of the polymer chain [14]. This ideal model is clearly just a restricted random process where successive monomer units may be added with certain probabilities assigned to the rotational angles of the added unit. The resulting process is a simple Markov process, so an exact mathe-

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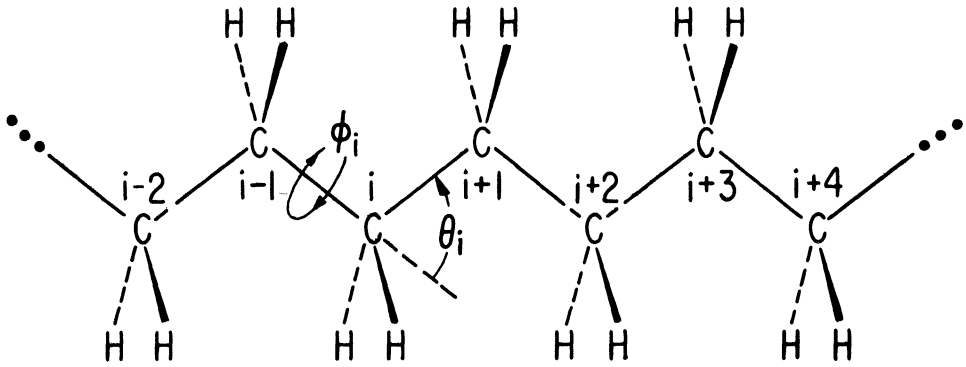

FIG. 1. Part of a polyethylene chain. The carbon atoms (C) are sequentially numbered, $i = 0, \cdots N$. Individual $C_i - C_{i+1}$ bound lengths are fixed as are the angles $\theta_i = \measuredangle (C_{i-1} - C_i - C_{i+1})$. There is some freedom of rotation about the $C_{i-1} - C_i$ bond as represented by the random variable ϕ_i. Various vinyl polymers involve the replacement of one hydrogen (H) on alternate carbons by some other group of atoms.

matical solution is clearly possible. (The phrase "Markov chain" is used sparingly, to avoid confusion with polymer chains.) In practice, the three-dimensional character of the process has led to complexities in the evaluation of desired properties, but hard work has enabled the resolution of the problem [14]. Our interest lies, however, with the nonideal case which is not so simple. This nonideal case is described below after briefly mentioning some of the polymer properties of interest.

Certain physical properties of the polymers derive essentially from their chain-like structure. These long range properties depend on the nature of the chain over distances which are much greater than the length of an individual monomer unit. Hence, the detailed chemical structure of the units is unimportant in the evaluation of the long range properties. These features enable us to introduce mathematical simplifications by collecting together a number of units, on the order of 10–30, into *statistical segments*, as the long range polymer properties do not depend on the intimate details of the statistical segments. Some long range polymer properties include the number of repeat units in the chain (proportional to the molecular weight), the chain size and shape, its flow properties and viscoelasticity, etc..

Polymers are of interest because they are fundamental building blocks in biological systems. Our discussion here is limited to uncharged polymers, so we do not consider the interesting biopolymers. Estimates have been given that about 60% of the chemical industry is associated in some way with polymers, from the production of monomers to that of the polymers themselves. Perhaps, this is one reason why so little polymer research is carried out in major chemistry departments. To probabilists, statisticians, and theoretical chemists and physicists, polymer systems provide a wealth of extremely challenging mathematical and physical problems. In many instances polymers can be synthesized to solve experimentally some mathematically intractable problems, thereby aiding us in filling in the mathematical description.

The above noted simple ideal model of polymer chains leaves out an important feature which is the source of nonideality. As we grow the chain by adding successive monomer units, which satisfy the given bond length, angle, etc., constraints, distant monomer units along the chain (monomers i and j for $|i - j| \gg 1$) may be placed at the identical position in space. The positive size of the monomer units prohibits the multiple occupancy of space by more than one unit. This prohibition defines an excluded volume interaction. Thus, if the chain is sequentially grown, the ith unit must be added by requiring, in addition to the constraints on the ideal model, that it not occupy the regions of space which have already

been allotted to the previous units. This is a self-avoiding random process, a non-Markov process.

For the sake of precision, it should be mentioned that there are experimental conditions, a particular temperature for a given solvent, where the polymers behave according to the ideal model limit. The interested reader is referred to the polymer literature for more details [14, 42].

In the next section we provide a mathematical representation of the polymer excluded volume problem, and in Section 3 a self-consistent field theory is described. Section 4 discusses the scaling theories.

2. Mathematical models for polymers. Because our interest lies in long range polymer properties, we may introduce the concept of a statistical segment, due to Kuhn, containing say, $n \approx 10$–30 actual monomer units. Ignoring the excluded volume interaction temporarily, the statistical segment contains a large number of degrees of freedom, the orientation angles $\{\phi_i\}$ within the statistical segment. The end-to-end vector for the statistical segment is the sum of vectors along each of the bonds of the chain backbone, e.g. the C-C bonds of Figure 1 in the segment. These bond vectors are functions of the orientation, so the end-to-end vector, $\mathbf{R}_{0n}$, for an n-unit statistical segment represents a sum of a large number of random vectors, $\mathbf{R}_{0n} = \sum_{j=1}^{n} \mathbf{b}_j$ with $\mathbf{b}_j = \mathbf{R}_{0j} - \mathbf{R}_{0,j-1}$. The $\mathbf{b}_j$ form a Markov chain to which the central limit theorem applies [12, 29]. For instance, if the rotation angle ϕ_i is uniformly distributed over 0 to 2π, given $\mathbf{b}_{i-1}$, and hence the ϕ_i are independent, then the mean square end-to-end distance, $\langle |\mathbf{R}|^2 \rangle$ for this "freely hinged chain" is given by the well known expression [42, page 37]

$$\langle |\mathbf{R}|^2 \rangle \equiv E[|\mathbf{R}_{0n}|^2] = nb^2\left[\frac{1-\cos\theta}{1+\cos\theta} + \frac{2\cos\theta}{n}\cdot\frac{1-(-\cos\theta)^n}{(1+\cos\theta)^2}\right],$$

which in the limit of large n is asymptotic to $nb^2(1-\cos\theta)/(1+\cos\theta)$. Cases in which the ϕ_i are not uniformly distributed have been considered [14, 42], but for n large they still provide $\langle |\mathbf{R}|^2 \rangle$ proportional to n.

Let Δs be the maximum possible value of $|\mathbf{R}_{0n}|$. Then for n even,

$$|\mathbf{R}_{0n}| \leq |\mathbf{b}_1 + \mathbf{b}_2| + |\mathbf{b}_3 + \mathbf{b}_4| + \cdots + |\mathbf{b}_{n-1} + \mathbf{b}_n|.$$

This inequality becomes an equality when all ϕ_i are 0. For each j, $|\mathbf{b}_j + \mathbf{b}_{j+1}| = 2b\sin(\theta/2)$. So if $\phi_i \equiv 0$ is possible, $\Delta s = nb\sin(\theta/2)$ for n even, and the two are asymptotic as $n \to \infty$ for n odd. For n large enough the probability distribution for $\mathbf{R}_{0n}$ is approximately Gaussian with density

$$[3/(2\pi l\Delta s)]^{3/2}\exp[-3|\mathbf{r}|^2/(2l\Delta s)], \tag{2.1}$$

where

$$l \equiv \lim_{n\to\infty}(\Delta s)^{-1}E[|\mathbf{R}_{0n}|^2]$$

is called the Kuhn length and is characteristic of the monomer bond lengths and angles. [For constant b and θ as above, and $\phi_i \equiv 0$ permitted, we have $l = 2b\sin(\theta/2)/(1+\cos\theta)$.] The size of the statistical segment is, in fact, chosen such that the limit (2.1) applies. For some types of polymers the accessible chain sizes are insufficient to insure the limiting behavior (2.1), but we consider only those cases where the values of n in (2.1) are large enough to apply the limiting form, but are much smaller than the total number of monomer units in the polymer chain. It should be noted that (2.1) applies to walks in 3-space, but, as discussed later in this section, it is useful to generalize the analysis to d-space.

We now invoke the simplifying model of the polymer wherein the chain is replaced by $N+1$ statistical segments with positions at the points $\{\mathbf{r}_i \mid i = 0, 1, \cdots, N\}$. Still ignoring excluded volume interactions, the probability density function for the segment positions of

this Gaussian chain is

$$G_0(\{\mathbf{r}_i\}) = \prod_{i=1}^{N} \{[3/(2\pi l\Delta s)]^{3/2} \exp[-3|\mathbf{r}_i - \mathbf{r}_{i-1}|^2/(2l\Delta s)]\}, \tag{2.2}$$

corresponding to a random walk of N steps $\mathbf{t}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$ where the $\mathbf{t}_i$ are independent and identically distributed random vectors with a spherically symmetric Gaussian distribution.

In order to introduce a true excluded volume interaction, it would be necessary to introduce a total prohibition for any pair of the $\{\mathbf{r}_i\}$ to be equal, or more generally to have $|\mathbf{r}_i - \mathbf{r}_j| \leq \epsilon$ for some $\epsilon > 0$ and any $i \neq j$. Instead, the mathematically more tractable soft excluded volume interaction is utilized wherein for a given set of segment positions $\{\mathbf{r}_i\}$ the probability density is proportional to (2.2) times a factor $\exp(-n_c v)$. Here n_c is a measure of the number of times $\mathbf{r}_i$ and $\mathbf{r}_j$ are close as we run over all $i \neq j$. The quantity v is the excluded volume. Its variation goes from the ideal Gaussian chain limit of $v \to 0$ to a high prohibition of contacts when $v \to \infty$. A mathematical representation of this soft excluded volume prohibition provides the unnormalized probability density function as

$$G(\{\mathbf{r}_i\}) = G_0(\{\mathbf{r}_i\})\exp[-(v/2)\sum_{i\neq j=0}^{N} J(\mathbf{r}_i - \mathbf{r}_j)], \tag{2.3}$$

where $J(\mathbf{r})$ is a nonnegative, sharply peaked function about $|\mathbf{r}| = 0$ of the form, perhaps, of $J(\mathbf{r}) = (4\pi\epsilon^4)^{-1}\exp(-|\mathbf{r}|\epsilon^{-1})$ for ϵ small, such that $\int d\mathbf{r} J(\mathbf{r}) \equiv 1$.

Taking the initial unit to be at the origin (that is $\mathbf{r}_0 = 0$) the density function for the location of the other end $\mathbf{R}$, the end-to-end vector distribution, is

$$P(\mathbf{r}_N, N) = \left[\prod_{i=1}^{N-1} \int d\mathbf{r}_i\right] G(\{\mathbf{r}_i\}) \Big/ \left[\prod_{j=1}^{N} \int d\mathbf{r}_j\right] G(\{\mathbf{r}_j\}), \tag{2.4}$$

and the mean square end-to-end distance is

$$\langle |\mathbf{R}^2| \rangle = \int d\mathbf{r}\, |\mathbf{r}|^2 P(\mathbf{r}, N). \tag{2.5}$$

Here, as always, $\langle \cdot \rangle$ denotes expectation $E(\cdot)$. Our interest is in the behavior of quantities like $\langle |\mathbf{R}|^2 \rangle$ as $N \to \infty$ where the power law dependence,

$$\langle |\mathbf{R}|^2 \rangle \sim N^{2\nu}, \qquad 1 \leq 2\nu \leq 2 \tag{2.6}$$

for $N \to \infty$ displays the exponent $\nu \in [\frac{1}{2}, 1]$. This exponent ν has been the focus of many theoretical studies. It is useful to mention briefly some approaches that have been applied to the problem.

When v is small enough, it is tempting to expand the exponential in (2.3) in a power series in v, the perturbation expansion. The leading few terms may be evaluated [42], and if the dominant N-dependence is retained, the perturbation series is found to be an expansion in powers of $vl^{-d}N^{1/2}$. This series is very likely asymptotic [8, 11, 33]. Such an expansion is of no help in understanding the behavior as $N \to \infty$.

Another general approach to the problem considers walks on a lattice with a complete prohibition for having more than one walk end (segment) reside on any lattice position [6]. With graphical methods it is possible to enumerate all the walks [6, 7, 20, 21, 30, 38] for $N \leq 20$, and then extrapolations to large N, although somewhat unsatisfying, are invoked. For larger N, Monte Carlo sampling procedures are often employed [37, 39–41]. Here a step is randomly added to a walk. If the last added unit ends at a position, $\mathbf{r}_{\text{last}}$, which coincides with a previous one, i.e., $\mathbf{r}_{\text{last}} = \mathbf{r}_i$, $i <$ last, the walk has zero weight and must be discarded. The sample attrition is $1\text{–}O(\exp(-aN))$ for some $a > 0$, i.e., out of all N-step random walk paths, only $O(e^{-aN})$ are self-avoiding. So, "sample enrichment" methods have been developed to arrange that many fewer attempts are aborted [37, 39, 40].

Our interest has been with analytical approaches which are capable of describing the $N \to \infty$ asymptotic limits. In particular, these methods involve the self-consistent field method, scaling theories, and the renormalization group approach [35]. A discussion of our work on the former two is described in Sections 3 and 4, respectively.

Both the totally non-Markovian nature of the problem and the emergence of fractional exponents in (2.6) are indications of the essential mathematical difficulties posed by the polymer excluded volume problem (2.2)–(2.6). However, let us indulge in some momentary wishful thinking and assume that somehow we are given an explicit probability distribution of the walks. We could then evaluate (2.5) directly, but it would also be possible to calculate the expected density of walks at all points in space. Let $\mathbf{R}_0 = 0, \mathbf{R}_1, \cdots, \mathbf{R}_{N-1}, \mathbf{R}_N \equiv \mathbf{R}$ be random variables with joint density given by the normalization of (2.3). Using the approximate delta function J, the sum of the conditional distributions of $\mathbf{R}_j, j \leq N$ given $\mathbf{R}_N = \mathbf{R}$, can be approximated by the number distribution (of total number $N + 1$) with density given by

$$\rho(\mathbf{r} \mid \mathbf{R}) \equiv E[\textstyle\sum_{j=0}^{N} J(\mathbf{r} - \mathbf{R}_j) \mid \mathbf{R}],$$

that is

$$(2.7) \quad \rho(\mathbf{r} \mid \mathbf{r}_N) = \left[\prod_{i=1}^{N-1} \int d\mathbf{r}_i\right][\textstyle\sum_{j=0}^{N} J(\mathbf{r} - \mathbf{r}_j) G(\{\mathbf{r}_j\})]\Big/\left[\prod_{i=1}^{N-1} \int d\mathbf{r}'_i\right] G(\{\mathbf{r}'_i\}).$$

Given the "density of walks," $\rho(\mathbf{r} \mid \mathbf{R})$ we approximate $\sum_{j;j\neq i} J(\mathbf{r}_i - \mathbf{r}_j)$ for each i in (2.3) by $\rho(\mathbf{r}_i \mid \mathbf{R})$, so (2.3) is replaced by the self-consistent field (SCF) approximation [10, 13, 15–17, 19, 27] defined as follows:

This approximation replaces, for each fixed i, the sum $\sum_{j;j\neq i} J(\mathbf{r}_i - \mathbf{r}_j)$ by its conditional expectation given $\mathbf{r}_N$. Note that $\sum_{i=j=1}^{N} J(\mathbf{r}_i - \mathbf{r}_j) = NJ(0)$, a constant which disappears under normalization of (2.3).

Given any integrable density function $G \geq 0$, (2.7) defines from it a conditional density $\rho_G(\mathbf{r} \mid \mathbf{r}_N)$. Conversely, given any density function $\rho = \rho(\cdot \mid \mathbf{R})$ on $\mathbb{R}^3$ depending on the vector parameter $\mathbf{R}$, we can define from it a density G_ρ by

$$(2.8) \qquad G_\rho(\{\mathbf{r}_i\}) = G_0(\{\mathbf{r}_i\}) \exp[-(v/2) \textstyle\sum_{i=1}^{N} \rho(\mathbf{r}_i \mid \mathbf{r}_N)].$$

Densities G and ρ such that $G = G_\rho$ and $\rho = \rho_G$ are said to define a self-consistent field [1–5, 11, 12] and are written $G = G_{\mathrm{SCF}}$, $\rho = \rho_{\mathrm{SCF}}$. One method of solution for G_{SCF} and ρ_{SCF} is to begin with some G or ρ, iteratively apply (2.7) alternating with (2.8), and try to obtain convergence to solutions. Note that (2.8) is nonlinear in ρ. [Presently, nothing has been proved about existence or uniqueness of solutions; Section 3 presents a method of attack.]

Note that, given ρ and given $\mathbf{r}_N$, the density G_ρ in (2.8), when normalized, gives the probability density of a *Markov* sequence $\mathbf{r}_0, \mathbf{r}_1, \cdots, \mathbf{r}_{N-1}$. But, the dependence of ρ_{SCF} on G_{SCF} makes the pair of coupled equations highly nonlinear.

The SCF approach invoked here should not be confused with the deceptively similar simple mean field theory which is widely used in statistical mechanics as follows: given a set of random variables defined throughout all space or, more simply, on a lattice, the simple mean field method produces an optimal approximate value for these random variables which is *constant throughout space or on the lattice.* Near certain "critical points" singularities emerge which are incorrectly represented by the simple mean field theory because the fluctuations in the random variables become more important than their mean. The SCF treatment of polymer excluded volume is qualitatively different as follows: here we fix the position of one of the walk ends, so the self-consistent field is *inhomogeneous*; $\rho(\mathbf{r} \mid \mathbf{R})$ varies with $\mathbf{r}$ in an extremely complicated fashion. In fact, the walk density may be viewed as a fluctuation imposed on empty space, so the polymer SCF approach directly attempts to approximate this fluctuating density, providing a method of enormous mathematical complexity and of greater accuracy in contrast to the great simplicity of the simple mean field method.

Flory's approach [13] to this self-consistent field method is as follows:
Define the quantity,

$$(2.9) \qquad Z_N = \left[\prod_{i=1}^{N} \int d\mathbf{r}_i\right] G(\{\mathbf{r}_i\} \mid \mathbf{r}_0 \equiv 0),$$

so that G/Z_N is the normalized probability density for the walks given by the Gaussian distribution (2.2) and the excluded volume constraint (2.3). Approximate the distribution G by

$$\hat{G}_N(\{\mathbf{r}_i\}) = \prod_{i=1}^{N} \{[3\alpha^{-2}/(2\pi l\Delta s)]^{3/2}\exp[-\alpha^{-2}(\mathbf{r}_i - \mathbf{r}_{i-1})^2/(2l\Delta s)]\}, \tag{2.10}$$

with $\alpha = \alpha(N) > 1$ a parameter to be determined.

Using the relationship, $\langle e^X \rangle \geq e^{\langle X \rangle}$ (Jensen's inequality), we have

(2.11)

$$\begin{aligned} Z_N &= \left[\prod_{i=1}^{N} \int d\mathbf{r}_i\right] G(\{\mathbf{r}_i\}) \\ &= \alpha^{-3N}\left[\prod_{i=1}^{N} \int d\mathbf{r}_i\right] \hat{G}_n(\{\mathbf{r}_i\})\exp\left[\frac{\alpha^{-2}-1}{2l\Delta s}\sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{r}_{i-1}|^2 - \frac{v}{2}\sum_{i\neq j} J(\mathbf{r}_i - \mathbf{r}_j)\right] \\ &\geq \alpha^{-3N}\exp\left\{\left[\prod_{i=1}^{N} \int d\mathbf{r}_i\right] \hat{G}_N(\{\mathbf{r}_i\})\left[\frac{\alpha^{-2}-1}{2l\Delta s}\sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{r}_{i-1}|^2 - \frac{v}{2}\sum_{i\neq j} J(\mathbf{r}_i - \mathbf{r}_j)\right]\right\}. \end{aligned}$$

Select α to maximize the right hand side. Then an approximate value of $\langle |\mathbf{R}|^2 \rangle$ is obtained from $\hat{G}_N\{\mathbf{r}_i\}$ as

$$\begin{aligned} \langle |\mathbf{R}|^2 \rangle &= \left[\prod_{i=1}^{N} \int d\mathbf{r}_i\right] |\mathbf{r}_N|^2 \hat{G}_N(\{\mathbf{r}_i\}) \\ &\sim N^{6/(2+d)}, \; N \to \infty, \end{aligned} \tag{2.12}$$

where the result is quoted for a d-dimensional space.

The difficulty with the Flory approach is that the choice of different, apparently reasonable, models for $\hat{G}$ other than (2.10) yields a different power law form in (2.12) [42, pp. 97–102]. The Flory formula, (2.12), is believed to be almost exact (for $d \leq 4$), but this result arises because of a delicate cancellation of errors that does not persist with other models for $\hat{G}$ or other related problems. The prime deficiency of the Flory method lies in its explicit lack of self-consistency. If we were to feed the model $\hat{G}$ into (2.7) and use (2.8) to iterate an improved value of $\hat{G}^i$, it is unclear whether the procedure would ever converge, because $\langle |\mathbf{R}|^2 \rangle$ and G_{SCF}, etc., depend on fractional powers of the variables.

Edwards' method is to attempt to solve (2.8) for G_{SCF} as a functional of the, as yet unknown, $\rho(\mathbf{r}) \equiv \rho_{\text{SCF}}(\mathbf{r}\,|\,\mathbf{R})$ and then to choose an optimal value of this $\rho(\mathbf{r})$ [10]. His solution is again not self-consistent, but the results provide a preview of the correct SCF dependences. Edwards obtains the Flory formula again. Let $p(r) = \int_{|\mathbf{r}|=r} \rho(r)\, d\Omega$ where Ω denotes a solid angle. Edwards finds that $p(r)$ varies as $r^{-4/3}$ for r in the range of the maximum in the distribution $P(\mathbf{r}, N)$—the kind of fractional power dependence mentioned in the previous paragraph. It should be noted that, as $N \to \infty$, $\rho(r)$ for a random walk varies as r^{-1} while for a rigid rod (straight walk) it goes as r^{-2}, so the self-avoiding walk must display some intermediate power [just as in (2.6)].

Since we are interested only in the asymptotic large N, long distance behavior of the self-avoiding walks, it is rather immaterial (see more discussion in Section 4) how the subdivisions N and Δs are chosen so long as N is large and $N\Delta s = L$ is fixed.

In order to discuss self-consistent approaches to the self-consistent field method more fully in Section 3, it is convenient to introduce the continuous chain limit of (2.3) wherein $N \to \infty$, $\Delta s \to 0$, but $N\Delta s = L$ remains fixed.

On the space $C[0, L]$ of all continuous functions from $[0, L]$ into $\mathbb{R}^3$, let G_0^N be the probability distribution of a stochastic process whose value at $i\Delta s$ is $\mathbf{r}_i$, $i = 0, 1 \cdots, N$, which is linear in between, and where the joint probability density of the $\mathbf{r}_i$ is G_0 (2.2). Then as $N \to \infty$ and $\Delta s = L/N \to 0$, G_0^N converges by the invariance principle (Donsker, [9]) to the distribution, call it H, of $(l/3)^{1/2}\mathbf{W}$ where $s \to W(s, \omega)$ is a standard 3-dimensional Wiener process (Brownian motion process). Then introducing $v \to v(\Delta s)^2/l^2$, the limit yields a measure G on $C[0, L]$ with

$$dG(\mathbf{r}(\cdot)) = \exp\left\{-\frac{v}{2l^2}\int_0^L ds \int_0^L ds_0 J[\mathbf{r}(s) - \mathbf{r}(s_0)]\right\} dH(\mathbf{r}(\cdot)) \tag{2.13'}$$

and which can be written heuristically as [18, 23–26]

$$G([\mathbf{r}(s)]) = \mathscr{D}[\mathbf{r}(s)]\exp\left\{-\frac{3}{2l}\int_0^L |d\mathbf{r}(s)/ds|^2\, ds - (v/2l^2)\int_0^L ds \int_0^L ds_0 J[\mathbf{r}(s) - r(s_0)]\right\}. \tag{2.13}$$

For any fixed value of $\mathbf{R}(L) = \mathbf{r}$, there is a good conditional distribution of the process $\mathbf{R}$, as with the Brownian bridge in one dimension.

In place of the numerator of (2.4) we can define

$$G(\mathbf{r}, L) = E\left[\exp\left\{-v/(2l^2)\int_0^L ds \int_0^L ds_0 J(\mathbf{R}(s) - R(s_0))\right\} | \mathbf{R}(L) = \mathbf{r}\right]. \tag{2.14}$$

Throughout the remainder of the paper this continuous chain representation is utilized.

3. Self-consistent solutions. Before analyzing the solutions of the SCF equations, it proves instructive to introduce the method of random fields [26] which provides a direct mathematical framework in which the self-consistent field method emerges as the natural leading first approximation [10, 15–17, 19, 27].

Let $\phi: \mathbf{r} \to \phi(\mathbf{r})$ be a Gaussian random process, indexed by $\mathbf{r}$ in $\mathbb{R}^3$, having mean 0 and covariance given by

$$\langle \phi(\mathbf{r})\phi(\mathbf{r}')\rangle_\phi \equiv vJ(\mathbf{r} - \mathbf{r}')/l^2. \tag{3.1}$$

Expectations with respect to the distribution of ϕ are denoted $\langle \cdot \rangle_\phi$.

Then for any measurable function $\mathbf{r}(\cdot)$, $\int_0^L ds\, \phi(\mathbf{r}(s))$ is a Gaussian variable with mean 0 and variance $\int_0^L ds \int_0^L ds_0 J[\mathbf{r}(s) - \mathbf{r}(s_0)]$, so it has the characteristic function

$$\left\langle \exp\left\{i\int_0^L ds\, \phi[\mathbf{r}(s)]\right\}\right\rangle_\phi = \exp\left\{-v/(2l^2)\int_0^L ds \int_0^L ds_0 J[\mathbf{r}(s) - \mathbf{r}(s_0)]\right\}. \tag{3.2}$$

Substituting (3.2) into (2.14) gives

$$G(\mathbf{R}, L) = \langle G(\mathbf{R}; L\,|\,[\phi])\rangle_\phi \tag{3.3}$$

where

$$G(\mathbf{R}; L\,|\,[\phi]) \equiv E\left[\exp\left\{i\int_0^L ds\, \phi[\mathbf{r}(s)]\right\} \Big| \mathbf{r}(L) = \mathbf{R}\right]. \tag{3.4}$$

For a fixed function ϕ the function defined by (3.4) is known [18, 23, 24] to satisfy the differential equation

$$\left[\frac{\partial}{\partial L} - \frac{l}{6}\nabla_r^2 + i\phi(\mathbf{r})\right] G(\mathbf{r}; L\,|\,[\phi]) = \delta(L)\delta(\mathbf{r}), \tag{3.5}$$

corresponding to diffusion in a purely imaginary field. The boundary conditions associated with (3.5) are regularity of G as $r \to 0$ and vanishing of G as $|\mathbf{r}| \to \infty$.

Let J^{-1} be the convolution inverse of J, so that [formally]

$$\int d\mathbf{r}''\, J^{-1}(\mathbf{r} - \mathbf{r}'')J(\mathbf{r}'' - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{3.6}$$

If $\hat{J}(\mathbf{k})$ and $\hat{J}^{-1}(\mathbf{k})$ are the Fourier transforms of J and J^{-1}, respectively, then (3.6) implies

$\hat{J}^{-1}(\mathbf{k}) = 1/\hat{J}(\mathbf{k})$. In general J^{-1} may contain differential operators and generalized functions.

Edwards' approach is to approximate $G(\phi)$ by phase integral methods, assuming $\phi = \phi(|\mathbf{r}|)$ and then to evaluate $\langle \cdot \rangle_\phi$ by steepest descents [10]. It is useful to dispense with the initial approximation and to consider the formal content of the steepest descent approach [15, 17, 19, 27]. As is described below, the formal application of this method to (3.3) produces the SCF theory as the leading approximation. While the SCF method can be motivated heuristically as described in Section 2, the formal analysis enables the treatment of corrections due to fluctuations about the SCF [27], and it also provides the means by analogy for introducing other self-consistent schemes which cannot be heuristically generated by arguments like the ones given in Section 2.

We are unaware of a rigorous treatment of the steepest descents in function space, but perhaps one could be constructed by expressing the following heuristic equations on a lattice of points X_j with the variables $\phi(X_j)$ having mean 0 and covariance (3.1) with the restriction of J to the lattice points [15, pages 111–116]. The steepest descents approximation to the multiple ϕ-integrations would then be converted to a continuum limit. In the heuristic continuum limit notation (3.3) is written as [15, pages 111–116]

$$G(\mathbf{r}, L) = \frac{\int \delta\phi G(\mathbf{r}; L\,|\,[\phi]) \exp\left[-\frac{l^2}{2v}\int d\mathbf{r}\int d\mathbf{r}'\phi(\mathbf{r})J^{-1}(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}')\right]}{\int \delta\phi \exp\left[-\frac{l^2}{2v}\int d\mathbf{r}\int d\mathbf{r}'\phi(\mathbf{r})J^{-1}(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}')\right]}. \tag{3.3a}$$

Writing $G([\phi]) = \exp\{\ln G([\phi])\}$ the steepest descent method looks for the solution ϕ_0 making the exponential in the numerator integrand stationary

$$\left[\frac{\delta}{\delta\phi(\mathbf{R}')}\left\{\ln G(\mathbf{R}; L\,|\,[\phi]) - (l^2/2v)\int_0^L d\mathbf{r}\int d\mathbf{r}' J^{-1}(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r})\phi(\mathbf{r}')\right\}\right]_{\phi=\phi_0} = 0. \tag{3.7}$$

Then we expand $\ln G - (l^2/2v)\iint \phi J^{-1}\phi$ in a functional Taylor series about $\phi = \phi_0$ retaining the quadratic terms in the exponential. The functional derivatives of G arising from (3.7) may be evaluated with the aid of (3.5). The simple saddle point approximation then yields

$$\left[\frac{\delta}{\delta s'} - \frac{l}{6}\nabla_{\mathbf{r}}^2 + V_{\mathrm{SCF}}(\mathbf{r}\,|\,\mathbf{R}, L)\right] G_{\mathrm{SCF}}(\mathbf{r}, \mathbf{r}'; s, s'\,|\,\mathbf{R}, L) = \delta(\mathbf{r}-\mathbf{r}')\delta(s-s'), \tag{3.8}$$

$$V_{\mathrm{SCF}}(\mathbf{r}\,|\,\mathbf{R}, L) = \frac{v\int_0^L ds G_{\mathrm{SCF}}(\mathbf{R}, \mathbf{r}; L, s\,|\,\mathbf{R}, L) G_{\mathrm{SCF}}(\mathbf{r}, \mathbf{0}; s, 0\,|\,\mathbf{R}, L)}{G_{\mathrm{SCF}}(\mathbf{R}, 0; L, 0\,|\,\mathbf{R}, L)} \tag{3.9}$$

where $V_{\mathrm{SCF}} \equiv i\,\phi_0$ and where the limit $\epsilon \to 0$ has been invoked as no singularities can now arise by virtue of taking J to be infinitely sharply peaked. Equation (3.9) may be seen to be the continuum analog of the self-consistent field equations (2.7) and (2.8). Thus, the dominant field ϕ_0 is found to be purely imaginary, and the SCF method emerges as the leading approximation in the evaluation of the ϕ-average. Note again that (3.8)–(3.9) present us with a highly nonlinear integrodifferential equation. However, that is an enormous improvement over the original non-Markovian process as progress can be made with the differential equation. The steepest descents method may be applied to the approximation of ϕ – averages other than $\langle G([\phi])\rangle$ [27].

The symmetry properties of (3.9) are highly instructive. It may be seen that $V_{\mathrm{SCF}}(\mathbf{r}\,|\,\mathbf{R}, L)$ has ellipsoidal symmetry about the chain end-points 0 and $\mathbf{R}$. Consequently, the solution of (3.8) is mathematically equivalent to the three-body problem of quantum mechanics because of the inseparability introduced by V_{SCF}. The approach to the problem requires some simplifications.

Gillis and Freed [19] chose the special case, $\mathbf{R} = \mathbf{0}$, of a closed walk (or a ring polymer), so $V_{\mathrm{SCF}}(\mathbf{r} \mid L)$ is now spherically symmetric. Their treatment involves the derivation of new SCF equations by the steepest descents evaluation of the ϕ-averaging. Introducing the eigenfunction expansion

$$G(\mathbf{R}, 0; L, 0 \mid [V]) = \int_0^\infty dE \exp(-EL)\psi(\mathbf{R}, E \mid [V])\psi^*(\mathbf{0}, E \mid [V]), \tag{3.10}$$

with $V = i\phi$ pure real, the eigenfunctions ψ obey the equation

$$\left[-\frac{l}{6}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) - E\right]\psi(\mathbf{r}, E \mid [V]) = 0. \tag{3.11}$$

Interchanging the order of the $\int dE$ and the ϕ-integration in (3.3) and evaluating the latter by steepest descents yields a set of SCF equations in E-space which is similar to (3.8)–(3.9) except that E appears as a parameter as opposed to the derivatives and integrals associated with its conjugate variables. These equations are simpler to solve than (3.8)–(3.9), but they are just as nonlinear in G, and they do not have the simple physical interpretation of the SCF equations.

We know that V_{SCF} must contain fractional powers of r, so for the closed walk, where $V_{\mathrm{SCF}}(\mathbf{r})$ is spherically symmetric, this implies the form

$$V_{\mathrm{SCF}}(\mathbf{r}) = \gamma r^{-a} + \gamma' r^{a'} + \cdots, -a < a', \cdots, \tag{3.12}$$

with the severe difficulty posed by the fact that the powers a and a' are unknown and must be determined self-consistently. The procedure utilized by Gillis and Freed is to integrate the equations term-by-term for (3.12) [19]. For instance, beginning with the form $V_0(\mathbf{r}) = \gamma r^{-a}$, we calculate $G([V_0])$. This is used to obtain $V_{\mathrm{SCF}}(\mathbf{r})$ whose leading dependence for $r \to 0$ is matched to γr^{-a} to provide solutions for γ and a. The exponent a turns out to be ⅔ as in Edwards' work [12]. The next step would involve using the first two terms of (3.12) with γ and a known, but γ' and a' unknown, to generate solutions for γ' and a', etc., and this remains to be done. We do not pursue the details here as some are outlined for the method of Kosmas and Freed [30]. It is just noted that Gillis' approach yields $\langle |\mathbf{R}|^2 \rangle$ for a portion of the long ring polymer as given by the Flory formula (2.12) for $1 \le d \le 4$ and a power $\nu = \frac{1}{2}$ (random walk) for $d \ge 4$.

The difficulty with the SCF method in L or E space resides in the ellipsoidal symmetry of the problem [15]. However, the full end-vector distribution $G_{\mathrm{SCF}}(\mathbf{r}; L \mid [V_{\mathrm{SCF}}])$ contains much more information than is required. It is sufficient to have some of the scalar low order moments,

$$\langle |\mathbf{R}|^{2n} \rangle = \int d\mathbf{r} |\mathbf{r}|^{2n} G(\mathbf{r}; L) \Big/ \int d\mathbf{r} G(\mathbf{r}; L), \qquad n = 1, 2, \cdots. \tag{3.13}$$

The numerator in (3.13) can be written as the ϕ-average

$$I_n = \left\langle \int d\mathbf{r} |\mathbf{r}|^{2n} G(\mathbf{r}; L \mid [\phi]) \right\rangle_{\phi}. \tag{3.14}$$

The steepest descents evaluation of the ϕ-average in (3.14) yields a set of self-consistent equations for the saddle point $V_{2n} = i\phi_{2n}$. The equations depend on n, but the important feature is the fact that the V_{2n} are spherically symmetric. Hence the eigenfunctions of (3.11) for $V \to V_{2n}$ are separable as

$$\psi(\mathbf{r}; E \mid [V_{2n}]) = r^{-1} u_\lambda(r; E \mid [V_{2n}]) Y_{\lambda\mu}(\theta, \phi) \tag{3.15}$$

with $Y_{\lambda\mu}$ a spherical harmonic and u_λ satisfying ($d = 3$)

$$-\frac{l}{6}\frac{d^2 u_\lambda}{dr^2} + \left[\frac{l}{6}\frac{\lambda(\lambda+1)}{r^2} + V_{2n}(r) - E\right] u_\lambda(r) = 0. \tag{3.16}$$

It is assumed that $\lim_{r\to 0} r^2 V_{2n}(r) \to 0$, which is not valid for $d \ge 4$. For $d < 4$ it is possible

to proceed to solve (3.16) by using the uniform asymptotic approximation ($\lambda = 0$) [1, 34]

$$u(r; E|[V_{2n}]) = (6)^{1/2}/4\pi)[\beta(r; E|[V_{2n}])]^{1/4}[\kappa(r; E|[V_{2n}])]^{-1/2} \times Ai[-\beta(r; E|[V_{2n}])], \tag{3.17}$$

$$\frac{2}{3}\beta^{3/2}(r; E|[V_{2n}]) = \int_r^{r_t} dr'\kappa(r'; E|[V_{2n}]) \equiv \int_r^{r_t} dr'\{(6/l)[E - (l/24(r')^2) - V_{2n}(r')]\}^{1/2} \tag{3.18}$$

with Ai the Airy function and r_t the zero of the integrand in (3.18).

Only the $\lambda = 0$ term appears in the SCF equations. Introducing the two solutions to (3.16) for $\lambda = 0$, $u_>$ and $u_<$ which, respectively, satisfy the proper boundary conditions for $r \to \infty$ and $r \to 0$ (exponentially decaying contribution to G and finiteness, respectively) and the Wronskian, W, for these two solutions, the self-consistent equation for V_{2n} is found to be [27]

$$\begin{aligned} V_{2n}(r) = {} & \frac{6v}{4\pi r^2 l^3 W}\int_0^\infty dE \exp(-EL)u(0; E|[V_{2n}])\{u_>(r; E|[V_{2n}]) \\ & \times u(r; E|[V]) \int_0^r dr'(r')^{2n+1}u_<(r') + u_<(r)u(r)\int_r^\infty dr'(r')^{2n+1}u_>(r') \\ & + u_>(r)u(r)\int_0^\infty dr'(r')^{2n+1}u(r')\}\left\{\int_0^\infty dE \exp(-EL) \right. \\ & \left. \times u(0)\int_0^\infty dr'(r')^{2n+1}u(r')\right\}^{-1}, \end{aligned} \tag{3.19}$$

where the arguments E and $[V_{2n}]$ are omitted from the u's for convenience. Kosmas and Freed utilize the first term, $V_{2n}{}^0(r) = \gamma_{2n} r^{-\alpha_{2n}}$ in (3.19) and determine γ_{2n} and a_{2n} self-consistently [27]. They obtain $\gamma_{2n} = \gamma$ and $a_{2n} = a$, the same results as for the ring polymer in the asymptotic limit $L \to \infty$. The contribution from the fluctuations, $\delta\phi$ about ϕ_{2n} are shown to alter only the total number of the distribution of walks but not the moments $\langle|\mathbf{R}|^{2n}\rangle$, $n \geq 1$, for $L \to \infty$ [27].

4. Scaling theories. Scaling theories have been developed to obtain information concerning certain power law dependences [2–4]. These theories cannot generate the structure of the distribution functions $G(\mathbf{r}; L)$ that is available from the SCF method, but their simplicity is very useful. In this section we describe the scaling theories as presented by Kosmas and Freed.

It is instructive to include a general interaction term as in (3.1) and to express explicitly the normalization factor implicit in the Wiener measure by writing ($V \equiv (v/2)J$)

$$\begin{aligned} G(\mathbf{r}; L) &= G(\mathbf{r}|L, l, l^{-2}V) \\ &= E[\exp\left\{-l^2\int_0^L ds \int_0^L ds_0 V[\mathbf{R}(s) - \mathbf{R}(s_0)]\right\}|\mathbf{R}(L) = \mathbf{r}]. \end{aligned} \tag{4.1}$$

Consider now the simple change in variables

$$\mathbf{r}'(s') \equiv b^{1/2}l^{-1}\mathbf{r}(s), \qquad s' \equiv bl^{-1}s. \tag{4.2}$$

Letting $N \equiv L/l$ and substituting (4.3) into (4.1) and (4.2) shows that G is converted to

$$G(\mathbf{r}|L, l, l^{-2}\hat{V}(\mathbf{k})) \equiv (bl^{-2})^{d/2}G(b^{1/2}\mathbf{r}l^{-1}|bN, 1, b^{(d-4)/2}l^{-d}\hat{V}(\mathbf{k}'b^{1/2}l^{-1})), \tag{4.3}$$

where the heuristic representation (2.13) is a useful simple way to obtain (4.3) [28]. The right-hand side of (4.3) corresponds to a walk with a scaled interaction $\hat{V}$ and different values, $L' = bN$, etc, of the relevant parameters. If the original problem, $G(\mathbf{r} \mid L, l, l^{-2}\hat{V}(\mathbf{k}))$ *appears* too intractable, perhaps the transformed problem, the right side of (4.3), is simpler.

As an example choose

$$bN = 1, \tag{4.4}$$

then the argument of $\hat{V}$ is $\mathbf{k}'N^{-1/2}l^{-1}$, and $L' = bN = 1$ is a walk of unit contour length. As $N \to \infty$ the argument $\mathbf{k}'N^{-1/2}l^{-1} \to 0$ for $\mathbf{k}'$ finite, so assuming $\hat{V}(\mathbf{k})$ has a Taylor series expansion in $\mathbf{k}^2$ implies that

$$\hat{V}(\mathbf{k}'N^{-1/2}l^{-1}) = \hat{V}(0) + \tfrac{1}{2}\,\hat{V}''(0)\,|\,\mathbf{k}'\,|^2 N^{-1}l^{-2} + \cdots, \tag{4.5}$$

and the scaled interaction in (4.3) gives

$$N^{(4-d)/2}l^{-d}\hat{V}(0) + \tfrac{1}{2}\,N^{(2-d)/2}\hat{V}''(0)\,|\,\mathbf{k}'\,|^2 + O(N^{-d/2}). \tag{4.6}$$

The leading term in (4.6) behaves as $N^{(4-d)/2}l^{-d}\hat{V}(0) \to \infty$ for $N \to \infty$ and $d < 4$, so if $\hat{V}''(0)$ is finite, the $\hat{V}(0)$ term strongly dominates for $4 > d > 2$. Hence, for $N \to \infty$ and $d > 2$ only the leading term of (4.6) need be retained. Since $\hat{V}(0)$ has the inverse Fourier transform $\delta(\mathbf{r})$, Equation (4.6) demonstrates why the nature of the function $V(\mathbf{r})$ in (4.1) is quite irrelevant for $G(\mathbf{r}, L)$ in the limit $N \to \infty$ provided V is "polite" enough that (4.5) can be used. This heuristically explains the universal character of the asymptotic properties of whole classes of different self-avoiding walk problems, i.e., (3.1) with different choices for V, and it justifies the use of the sharply peaked function J. For $d > 4$ and $N \to \infty$, $N^{(4-d)/2}l^{-d}\hat{V} \to 0$ for $\hat{V}(k)$ bounded, so the segment-segment interaction V is irrelevant for $d > 4$. In this case the right-hand side of (4.3) is just the $(d > 4)$-dimensional Gaussian, $(N^{-1}l^{-2})^{d/2}G(N^{-1/2}l^{-1}\mathbf{r} \mid 1, 1, 0)$. Brownian motion for $d > 4$ self-intersects only on a set of measure zero.

When the definition (3.13) for $n = 1$ is inserted into the identity (4.3) and the leading $v \equiv \hat{V}(0)$ term is retained, transformation to dimensionless spatial variables yields,

$$\langle\,|\,\mathbf{R}\,|^2\rangle_d = Nl^2 f_d(N^{\frac{4-d}{2}}vl^{-d}) \tag{4.7}$$

with f_d an unknown scaling function. For $N^{\frac{4-d}{2}}vl^{-d} \to 0$ it is clear that $f_d \to 1$, the random walk limit. This obviously ensues for $N \to \infty$ and $d > 4$ since v is bounded. Furthermore, f_d has an asymptotic power series expansion in powers of $N^{\frac{4-d}{2}}vl^{-d}$. For $N^{\frac{4-d}{2}}vl^{-d} \to \infty$ on the other hand, (2.6) tells us that f_d has a power law form

$$f_d(x) \to x^{2(2\nu_d-1)/(4-d)},\ x \to \infty, \tag{4.8}$$

so the proportionality constant in (2.6) varies as $v^{2(2\nu_d-1)/(4-d)}$ [28]. This information plus an additional scaling argument suffices to enable the evaluation of the exponent ν_d of (2.6) and (4.8) [28].

Consider our polymer (or walk) in a d-dimensional space which is confined between a pair of parallel hyperplanes with spacing D. The spatial integrals in the heuristic representation of (4.1) in the form of (2.13) only run over the semiinfinite region confined between the hyperplanes, so G must develop an explicit dependence on D. The transformed function corresponding to the one on the right in (4.4) then depends on $D/lN^{1/2}$ for the choice (4.4) so the confined analog of (4.7) is

$$\langle\,|\,\mathbf{R}\,|^2\rangle_{d,D} = Nl^2 f_{d,D}(N^{\frac{4-d}{2}}vl^{-d}, D/lN^{1/2}). \tag{4.9}$$

Clearly, as $D/lN^{1/2} \to \infty$, the walk is effectively unconfined and $f_{d,D} \to f_d$. Since we may

always rearrange the arguments of functions, (4.9) may be rewritten in the more suggestive form

$$\langle |\mathbf{R}|^2\rangle_{d,D} = \langle \mathbf{R}^2\rangle_d g_{d,D}(N^{\frac{4-d}{2}} v l^{-d}, D/[\langle |\mathbf{R}|^2\rangle_d]^{1/2}), \tag{4.10}$$

where the relevant variable $D/[\langle |\mathbf{R}|^2\rangle_d]^{1/2}$ relates the confinement dimensions to the dimension of an unrestricted polymer. The overall factor of $\langle |\mathbf{R}|^2\rangle_d$ gives the correct limit when $D/[\langle |\mathbf{R}|^2\rangle_d]^{1/2} \to \infty$ as then $g_{d,D}$ must approach unity. It is assumed that the dependence on $N^{(4-d)/2} v l^{-d}$ is already totally encompassed by the $\langle |\mathbf{R}|^2\rangle_d$ parts, so (4.10) is taken to reduce to

$$\langle |\mathbf{R}|^2\rangle_{d,D} = \langle |\mathbf{R}|^2\rangle_d \hat{g}(D/[\langle |\mathbf{R}|^2\rangle_d]^{1/2}). \tag{4.11}$$

Just like all asymptotic properties of long polymers, $g_{d,D}(x)$ is assumed to have a power law form x^{2y}, for $x \ll 1$. However, when the spacing between the hyperplanes gets that small, the polymer is a $(d-1)$-dimensional one, so (4.11) and the power law assumption imply

$$\langle |\mathbf{R}|^2\rangle_{d-1} \propto \langle |\mathbf{R}|^2\rangle_{d,D} \to \langle |\mathbf{R}|^2\rangle_d [D^2/\langle |\mathbf{R}|^2\rangle_d]^y \quad \text{for} \quad \frac{D^2}{\langle |\mathbf{R}|^2\rangle_d} \ll 1. \tag{4.12}$$

Comparing powers of N *and* v on both sides of (4.12) and eliminating y between the two equations leads to the recursion relation [22, 28]

$$(2 - \nu_d^{-1}) = [(4-d)/(5-d)](2 - \nu_{d-1}^{-1}) \tag{4.13}$$

between ν_d and ν_{d-1}. A one-dimensional self-avoiding walk is just a rod. Consequently, a boundary condition, $\nu_1 = 1$ in (4.13) yields

$$\nu_d = \begin{cases} \dfrac{3}{2+d} & 1 \le d \le 4 \\ \dfrac{1}{2} & d \ge 4 \end{cases} \tag{4.14}$$

which agrees with Flory for $d \le 4$. The results (4.14) are also in good agreement with Monte Carlo calculations of Domb and others [6, 37, 39–41].

The scaling transformation can likewise be applied to the description of the asymptotic $N \to \infty$ properties associated with n-interacting chains in a volume in the thermodynamic limit $n \to \infty$, $v \to \infty$, n/V finite—a set of mutually (and self) avoiding walks [2–4, 28]. The analysis proceeds in a rather similar vein, and it has applications to a number of different problems. However, there has been a slight subterfuge, and the scaling relationships are not mathematically correct [28]. In the discrete representation (2.3) the large self-interaction term for $i = j$ is explicitly omitted, whereas in the continuous limit of (2.13) and (2.14) it has sneaked in, and it becomes infinite as $\epsilon \to 0$ (this ϵ was introduced first after (2, 3)). The infinity must, of course, be removed by interpreting the double integrals in (2.13) and (2.14) to omit a region of size α ($\alpha \sim O(l)$) about $s = s_0$. Then all scaling relations also contain a dependence on $\alpha N^{-1/2} l^{-1}$ (choosing $bN = 1$) which might appear to be irrelevant as $N \to \infty$. Unfortunately, the original problem contains integrals, the $s = s_0$ contributions, which diverge as $\alpha, \epsilon \to 0$, so the dependence on $\alpha N^{-1/2} l^{-1}$ must persist. For the polymer excluded volume problem the most accurate treatment, including the cut-off α, comes from the renormalization group method and gives the result [31] $\nu_3 = .59$ which is very close to .6 of (4.14). For other problems the errors incurred by this neglect of the cut-off are larger, providing 5–10% accuracy for certain exponents and taking other small ones to be zero. Nevertheless, the scaling approach is quick and simple for deducing the information it provides.

Cursory reference has been made to the renormalization group method. As books have recently been written on the subject [32], it would take up too much space to describe fully the many variants of this approach. We can, however, provide a brief heuristic introduction

to the general ideas behind the method. Suppose that in the evaluation of (2.9) with G of (2.3) we begin by integrating over only the odd indexed $\mathbf{r}_i$,

$$G^{(1)}(\{\mathbf{r}_j^{(1)}\}) = \left[\prod_{n=1}^{N/2}\int d\mathbf{r}_{2n-1}\right] G(\{\mathbf{r}_i\}) \equiv \exp[-F^{(1)}(\{\mathbf{r}_j^{(1)}\})], \tag{4.15}$$

where we set $\mathbf{r}_j^{(1)} \equiv \mathbf{r}_{2j}$. $G^{(1)}$ now has half as many variables as in G, but the former still suffices to determine Z of (2.9). We could continue this "decimation" transformation to obtain $G^{(2)}(\{\mathbf{r}_j^{(2)}\})$, $G^{(3)}$, etc., in terms of the corresponding $F^{(2)}$, $F^{(3)}$, etc. In the $N \to \infty$ asymptotic limit the renormalization group method considers the fixed point solutions, $\lim_{m\to\infty} F^{(m)} = F^*$, as well as solutions in the neighborhood of this fixed point. The fixed point solutions determine the properties of certain types of systems, such as the polymer excluded volume problem and those where the presence of critical points produces long range correlations in the system. The existence of fixed points has to our knowledge not been proven. For the polymer problem the application of renormalization group methods generally utilizes a formulation in terms of random fields [19]. The approach outlined in (4.15) has not been given for the polymer problem, but a related one has recently been developed [35]. However, (4.15) provides a simple introduction to the essential concepts of the method.

A number of pertinent works have appeared after the completion of this manuscript. Firstly, Westwater [43] has proven the existence of the probability measure (2.3) for sufficiently small v. He has also proven [44] that the $r \to 0^+$ limit of the self-consistent field equations yields the limiting $r^{-4/3}$ discussed in Section 3 above. This work does *not* derive the SCF theory which represents an interesting but nonrigorous approximation. Secondly, we have utilized an alternative formulation of the renormalization group to calculate [45] the unnormalized end-to-end vector distribution (2.14), the corresponding distribution function for separations between pairs of internal segments on the chain [46], and the coherent scattering [47] function,

$$E\left[\int_0^L ds \int_0^L ds_0 \exp\left\{i\mathbf{k}\cdot[\mathbf{r}(s) - \mathbf{r}(s_0)]\right\} \exp\left\{-(v/2l^2)\int_0^L ds \int_0^L ds_0 J[\mathbf{r}(s) - \mathbf{r}(s_0)]\right\}\right],$$

to lowest order in an expansion in $\epsilon = 4 - d$ with d the spatial dimensionality. The rationale for the ϵ-expansion follows from the simple fact that an expansion of the exponent in, say, (2.14) in powers of v generates a series in powers of the dimensionless quantity $vl^{-d}(L/l)^{\epsilon/2}$. The expansion parameter is troublesome [11, 33, 34] for $L \to \infty$ unless ϵ is taken to be sufficiently small; hence, a double expansion in vl^{-d} and ϵ. The renormalization group theory then provides information concerning the general analytic structure of the solution, enabling the analytic continuation from small ϵ to ϵ on order of unity.

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DISCUSSION

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Professor Freed's paper studies polymers by means of probabilistic models and techniques of differing complexity and sophistication. The analysis of these models involves a number of fascinating problems, some of which may be totally new to probabilists. Although in several places the arguments are heuristic, the results are interesting and the methods yield accurate numerical values. More work in making these arguments rigorous seems worthwhile. Polymer systems bear numerous similarities to systems encountered in statistical mechanics and a number of techniques used in the paper are closely related to techniques used in the latter field. For example, in statistical mechanics, analogues of the scaling theories discussed in Section 4 have had remarkable success in the study of critical phenomena (phase transitions).

For probabilists, a polymer can be considered to be a sequence of random vectors $\{\mathbf{R}_1, \cdots, \mathbf{R}_N\}$ subject to an interaction known as the "excluded volume interaction." The vector $\mathbf{R}_j$ denotes the end vector of the jth subsystem (or statistical segment) of a polymer composed of N segments. It is useful to allow the $\{\mathbf{R}_j\}$ to take values in $\mathbb{R}^d$, $d \in \{1, 2, \cdots\}$, with $d = 3$ being the most important. Polymers are related to self-avoiding random walks, which are well known in the probabilistic and physical literature. Professor Freed's main interest is to describe the $N \to \infty$ asymptotic limit of polymer systems; e.g., the asymptotics of $E(|\mathbf{R}_N|^2)$, the mean square end-to-end length of the polymer.

A number of separate problems are considered in the paper. The first is to determine a reasonable choice for the joint distribution of the $\{\mathbf{R}_j\}$ (Section 2). The second is to find accurate, tractable approximations to this distribution, according to the type of asymptotic

information desired. For example, in order to study $E(|\mathbf{R}_N|^2)$, a so-called continuous chain limit is introduced at the end of Section 2. The distribution of the $\{\mathbf{R}_j\}$, a measure on $\mathbb{R}^{Nd}$, is replaced by a measure on function space (absolutely continuous with respect to Wiener measure).

In Section 4, using the latter measure together with some clever scaling techniques, Professor Freed gives a nice plausibility argument for the asymptotic relation

$$(1) \qquad E(|\mathbf{R}_N|^2) \sim AN^{2\nu_d}, \qquad \text{where} \quad \nu_d = \begin{cases} 3/(2+d) & \text{if } 1 \le d \le 3, \\ 1/2 & \text{if } d \ge 4, \end{cases}$$

and A is a positive constant. I consider (1) to be the main result of the paper. An important feature of (1) is that the exponent ν_d is (believed to be) independent of the detailed form of the excluded volume interaction; the particular form of the interaction affects only the constant A. Interestingly, exactly the same asymptotic relation has been found numerically for the mean square end-to-end length of self-avoiding random walks on regular lattices in $\mathbb{R}^d$ [Domb (1963)]. Again, the exponent ν_d is independent of the form of the lattice (e.g., square vs. triangular); the latter affects A only. What we are seeing is the universal character of the asymptotic properties of whole classes of different excluded volume problems. See [Fisher-Sykes (1959)] for a discussion of the relationship between self-avoiding random walks and the Ising model of ferromagnetism.

The fact that in (1) $\nu_d = \frac{1}{2}$ arises for $d \ge 4$ is related to the fact that in $\mathbb{R}^d$, $d \ge 4$, Brownian paths have self-intersections only on a set of measure zero. The (almost sure) absence of self-intersections is tantamount to the absence of any excluded volume interaction, in which case one expects $E(|\mathbf{R}_N|^2) \sim$ (const) N. Understanding the role of Brownian self-intersections for $d < 4$ is a deep question which also arises in quantum field theory [Symanzik (1969)]. For this reason a rigorous proof of (1) would be very worthwhile. (As Professor Freed points out in the next-to-last paragraph of the paper, the values of ν_d for $d < 4$ may not be exact because of difficulties caused by self-intersecting paths.)

In the middle of Section 2 and in Section 3, Professor Freed proposes a so-called "self-consistent field" (SCF) approximation to the polymer distribution function and to its continuous chain limit. This approximation has been used to study the asymptotics of quantities as in (1), and it gives accurate numerical values. However, more work must be done on the SCF approximation in order to justify the steps used in its construction.

In order to make this interesting paper more accessible to probabilists, I shall highlight its main features.

A polymer is a long chain molecule composed of a large number of repeat units, called monomers, which are sequentially bonded to each other in a linear sequence. The finite size of the monomers prohibits the multiple occupancy of space by more than one monomer unit. This prohibition defines an excluded volume interaction.

As a first step, one neglects the interaction and models the monomer by a Markov chain. In order to simplify the form of this chain, the monomers are grouped into N statistical segments, each consisting of a large number n of monomer units. The first unit in the first segment is placed at the origin. The end-to-end vector for each segment can be written as the sum of n differences of the successive monomer position vectors within the segment. Since n is large, it is not unreasonable to suppose that this vector has a Gaussian distribution. This leads to (2.2). In the absence of interactions, the polymer is modeled by a sequence of N random vectors $\{\mathbf{R}_j\}$ which represent the end vectors of the N statistical segments. The joint distribution of the $\{\mathbf{R}_j\}$ is the distribution function $G_0(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ with density

$$(2) \qquad g_0(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \left(\frac{3}{2\pi l \Delta s}\right)^{3N/2} \exp[-3 \textstyle\sum_{j=1}^{N} |\mathbf{r}_j - \mathbf{r}_{j-1}|^2/(2l\Delta s)].$$

Here $\mathbf{r}_0 = 0$ and l and Δs are physical constants (Δs is proportional to n).

To introduce a true excluded volume interaction, one multiplies the density g_0 in (2) by the characteristic function of the set $\{(\mathbf{r}_1, \cdots, \mathbf{r}_N) \in \mathbb{R}^{Nd} : |\mathbf{r}_i - \mathbf{r}_j| > \epsilon$ for all $0 \le i \ne j \le$

$N\}$, where $\mathbf{r}_0 = 0$ and ϵ is some positive number; one then normalizes the resulting density. Rather than work with the new distribution (which is possible but cumbersome), the more tractable "soft excluded volume interaction" is brought in. Let $n_c(\{\mathbf{r}_j\})$ be some measure of the number of times $\mathbf{r}_i$ and $\mathbf{r}_j$ are close for all $0 \le i \ne j \le N$. One assigns the unnormalized weight $\exp[-vn_c(\{\mathbf{r}_j\})]g_0(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ to the configuration $\{\mathbf{r}_j\}$ of segment positions; v is the excluded volume, a physical constant. The typical choice of n_c is

$$n_c(\{\mathbf{r}_j\}) = \frac{1}{2}\sum_{0\le i\ne j\le N} J(\mathbf{r}_i - \mathbf{r}_j), \tag{3}$$

where J is a nonnegative, spherically symmetric, sharply peaked function about $\mathbf{r} = 0$; i.e., an approximate delta function. The factor ½ is present in (3) because each pair $\mathbf{r}_i, \mathbf{r}_j$ for $i \ne j$ should be counted only once. One now works with the new, non-Markovian distribution function $G_1(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ with density

$$g_1(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{\exp\left[\dfrac{-v}{2}\sum_{0\le i\ne j\le N} J(\mathbf{r}_i - \mathbf{r}_j)\right] g_0(\mathbf{r}_1, \cdots, \mathbf{r}_N)}{\text{normalization}}. \tag{4}$$

Again, (4) is cumbersome to work with, so it is replaced by its continuous chain limit. Let L be a fixed positive number and $P_{\mathbf{r},L}(\mathbf{R})$ d-dimensional conditional Wiener measure, with variance $l/3$, on paths $\{(\mathbf{R}(s); 0 \le s \le L\}$ which satisfy $\mathbf{R}(0) = 0$, $\mathbf{R}(L) = \mathbf{r}$. Now set $L = N\Delta s$. The measure G_0 with density (2) is the projection of $P_{\mathbf{r},L}$ onto the cylinder sets $\{\mathbf{R}(s), 0 \le s \le L : \mathbf{R}\left(\dfrac{jL}{N}\right) \in I_j, j = 1, \cdots, N-1\}$, where $\{I_j\}$ are Borel subsets of $\mathbb{R}^d$. In the limit $N \to \infty$, $\Delta s \to 0$, $N\Delta s = L$ fixed, G_0 tends weakly to $P_{\mathbf{r},L}$. We now state the continuous chain limit. In (4), we replace v by $v(\Delta s)^2/l^2$, obtaining a new measure $\tilde{G}_1$. In the limit $N \to \infty$, $\Delta s \to 0$, $N\Delta s = L$ fixed, $\tilde{G}_1$ tends weakly to

$$d\Gamma_{\mathbf{r},L}(\mathbf{R}) = \frac{\exp\left[-\dfrac{v}{2l^2}\displaystyle\int_0^L\int_0^L J(\mathbf{R}(s) - \mathbf{R}(s_0))\, ds\, ds_0\right] dP_{\mathbf{r},L}(\mathbf{R})}{G(\mathbf{r}, L)}, \tag{5}$$

where $G(\mathbf{r}, L)$ is a normalization (the $P_{\mathbf{r},L}$ expectation of the exponential factor in (5)). This measure is the continuous chain limit of the measure G_1 with density (4). $G(\mathbf{r}, L)$ is the unnormalized density of the endpoint $\mathbf{R}(L)$ of the continuous chain.

Section 4 applies scaling arguments to determine the asymptotics of $E(|\mathbf{R}_N|^2)$ (see (1)). It is argued that this quantity should be well approximated by $\int |\mathbf{r}|^2 G(\mathbf{r}, L)\, d\mathbf{r}$/normalization. The key scaling relation is (4.3). This leads to (4.7) and a second scaling argument yields (4.14), which is (1) above. The discussion after (4.6) motivates the conjecture that the exponent ν_d in (1) is independent of the particular form of the function J in (3)–(5). But notice the difficulty which arises if J is replaced by the quantity it is supposed to approximate; namely, a delta function at 0. Then the double integral in (5) becomes the local time at 0 of $\{\mathbf{R}(s) - \mathbf{R}(s_0), 0 \le s, s_0 \le L\}$. The latter is $+\infty$ for $d < 4$. One can handle this singularity by a cut-off (as discussed in the next-to-last paragraph of the paper) or by renormalization [Symanzik (1969); Section 2.6–2.7, Section 4], [Varadhan (1969)].

The middle of Section 2 treats the self-consistent field (SCF) approximation to the distribution G_1 with density (4). The function n_c in (2) measures for each configuration $\{\mathbf{r}_j\}$ the number of times $\mathbf{r}_i$ is close to $\mathbf{r}_j$ for all $i \ne j$. The SCF approximation replaces n_c by a conditional average over all configurations (conditioned upon $\mathbf{R}_N$, the position of the last segment). In explaining this, I deviate somewhat from the paper. Let $\mathcal{H}$ denote the class of all distribution functions on $\mathbb{R}^{Nd}$. For $H \in \mathcal{H}$, $E_H\{- \mid \mathbf{R}_N = \mathbf{r}\}$ denotes conditional expectation with respect to H, conditioned upon $\mathbf{R}_N = \mathbf{r}$. Define

$$\rho_H^{(i)}(\mathbf{r}_i \mid \mathbf{r}) = E_H\{\textstyle\sum_{\{j:0\le j\ne i\le N\}} J(\mathbf{r}_i - \mathbf{R}_j) \mid \mathbf{R}_N = \mathbf{r}\} \tag{6}$$

and $G^H \in \mathcal{H}$ as the distribution function with density

$$g^H(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{\exp\left[-\frac{v}{2}\sum_{i=0}^{N} \rho_H^{(i)}(\mathbf{r}_i \mid \mathbf{r}_N)\right] g_0(\mathbf{r}_1, \cdots, \mathbf{r}_N)}{\text{normalization}}. \tag{7}$$

The definitions (6)–(7) define a map τ from $\mathscr{H}$ to $\mathscr{H}$: $\tau(H) = G^H$. An SCF distribution H^* is defined to be any fixed point of τ; the associated conditional averages $\{\rho_{H^*}^{(i)}\}$ in (6) are called self-consistent fields. They are related by equations (6)–(7) with H^* written for H. The SCF procedure can be regarded as an attempt to Markovianize the distribution G_1. If the $\{\rho_{H^*}^{(i)}\}$ were explicitly known (which in general they are not), then for fixed $\mathbf{R}_N = \mathbf{r}_N$ g^{H^*} would be the density of a Markov chain.

The SCF procedure is interesting but problematic since it is not clear that SCF distributions even exist for given J and v. On the other hand, for suitable J, it should not be hard to prove that SCF distributions exist for sufficiently small $v > 0$. (For $v = 0$, $\tau(H) = G_0$ for all $H \in \mathscr{H}$ so that G_0 is an SCF distribution.)

Equation (2.7) in the paper defines the analogue of my $\{\rho_H^{(i)}\}$ as a conditional average of a sum involving all $0 \leq j \leq N$ and with a general $\mathbf{r}$ in place of $\mathbf{r}_i$. This quantity is proportional to a conditional density of walks. However, when inserted into (2.8), which corresponds to (7) above, $\mathbf{r}$ is set equal to $\mathbf{r}_i$. In other words, (2.8) includes the large self-intersection term which corresponds to $j = i$ in the sum in (6) and which I have omitted in order to stay consistent with (4). Also, (2.8) excludes the $i = 0$ term from the sum appearing in (7). These changes seem to be significant and to need justification.

The author does not apply the SCF approximation just described. Instead, he shows in Section 3 how self-consistent fields arise in a useful approach to the evaluation of quantities involving the continuous chain limit (5). One first rewrites the latter as an expectation with respect to an auxiliary Gaussian random process ϕ, indexed by $\mathbf{r}$ in $\mathbb{R}^3$, where ϕ has mean zero and covariance $vJ(\mathbf{r} - \mathbf{r}')/l^2$. The method of steepest descent is now used to evaluate the resulting expectation. As a result, the evaluation of quantities involving the continuous chain limit yields a set of self-consistent equations for the corresponding saddle points. These saddle points play the role of self-consistent fields. This method is formal because it is assumed that in each case saddle points are unique. On the other hand, the author outlines several calculations which show that the method yields accurate numerical values.

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