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Electrostatics of random walks: A numerical study

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Electrostatic properties of polymers have been studied by numerical measurement of the capacitance, polarizability of unrestricted, and self-avoiding random walks of length $L=2,4,8,\ldots,128$. Asymptotic values of the depolarization coefficients have been found. The electrostatic shapes of random walks have been shown to be significantly more aspherical than could be predicted from the components of the squared radius of gyration. Proportionality coefficients of various scaling properties have been established, and a very strong correlation between the shape tensor and the polarizability tensor has been found.

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I. INTRODUCTION

Properties of random walks (RW's) have been extensively investigated due to their relation to the statistical mechanics of polymers [1]. The two most investigated types of such objects are the unrestricted random walks (URW's), which are extremely simple and most susceptible to analytical treatment, and the self-avoiding random walks (SAW's), which correctly reproduce the statistical mechanics of long polymers. The simplest geometrical characteristic of RW's is their radius of gyration (rms size) R_g, which is known to scale with their length (or number of monomers) L as follows: $\langle R_g^2\rangle \sim L^{2\nu}$, where $\nu=\frac{1}{2}$ and 0.558 (Ref. [2]) for URW's and SAW's, respectively. ($\langle\bullet\rangle$ denotes ensemble averaging of the quantity $\bullet$; for the sake of simplicity, in the following text, I will frequently omit the averaging signs where the presence of the averaging is self-evident.) The degree of sphericity, or rather the lack of it, is also an important characteristic of RW's. This absence of spherical symmetry in the individual configurations of polymer molecules was pointed out a long time ago by Kuhn [3]. Typically, the longest linear dimension of a configuration is over three times longer than the shortest one. Such a strong asphericity should not be surprising in an object in which the size fluctuations are of the same order as its linear dimensions. The need to properly account for that asymmetry in the treatment of polymer viscosity, birefringence, diffusion, and dielectric relaxation has resulted in numerous numerical [4–7] and analytical [8,9] studies of the SAW's and the URW's. Most of the analytical studies considered the URW's [8], and only recently have the shapes of SAW's been analyzed [9] to the first order in an $\epsilon=4-d$ expansion (d is the space dimension). While all the studies stressed the importance of the asymmetry for the *physics* of polymers, they concentrated on the investigation of the *geometrical* properties of the RW's, such as various moments of the mass distribution tensor.

The behavior of certain physical quantities can be guessed from general scaling considerations. For example, the hydrodynamic radius of a polymer and the electric capacitance of a conducting polymer should be proportional to its R_g, and therefore their mean values should scale as L^{ν}. Such arguments, however, cannot predict the proportionality coefficients in those relations. The situation is even worse with respect to the more subtle properties related to the *shape* of the polymers. While it seems reasonable to assume that the asphericity of the geometry implies asphericity of the physical properties, there is no simple way to relate the physical and the geometrical shapes, since hydrodynamic or electric properties involve long-range interactions between the monomers. In this work I consider the simplest physical property characterizing the polymers: the behavior of random conducting walks in an external electric field. One may visualize the problem as a solution of electrostatic equations for a long folded conducting wire embedded in a three-dimensional space. The scalar nature of the underlying problem (potential fields or charge distributions) simplifies the numerical treatment, while the fact that one treats a model as opposed to a real polymer does not limit the applicability of the results which are primarily determined by the large-scale structure of the walks.

Some of the results presented in this work have already been reported [10]. In this paper, the model, the methods, and the results are described in detail. In the first two sections I describe the electrostatic model and the numerical method for generation of RW's. Section IV describes the results of geometric shape measurements, and introduces the concept of the "geometrically equivalent ellipsoid," which is used to roughly predict the electrostatic properties of the walks. Section V presents the results of direct electrostatic measurements of the physical properties of the walks, verifies the scaling of their capacitance, and establishes the proper prefactors in the scaling relations, as well as demonstrates that the electrostatic properties of the walks are even less spherical than can be judged from the equivalent geometric ellipsoid. Section VI demonstrates that, despite significant quantitative differences, the geometrical and electrical properties of RW's are strongly correlated. In particular, it shows a strong correlation in the depolarization coefficients, and almost complete coincidence of the major axis of the shape tensor and the polarizability tensor.

Finally, Sec. VII discusses the applicability and possible extensions of this work.

II. THE MODEL

The model system used in this work is supposed to represent (approximately) an L-step chain consisting of $L+1$ small conducting spheres ($L=2,4,8,\ldots,128$) of radius b, connected by conducting wires of negligibly small diameter. It is constructed as an URW or a SAW on a simple-cubic lattice, with the steps of the walk taken along the bonds of the lattice. The spheres of the modeled chain are presumed to be located on the sites of the lattice, and the lattice constant is taken to be the unit of length.

For the purpose of the geometrical measurements, such as the radius of gyration, all sites along the chain are assumed to have the same mass. Thus, in the case of an URW, a particular site may be visited several times, and therefore counted several times. This is a standard practice in such calculations, although other choices, such as counting each site belonging to the URW only once, could slightly modify the values of the geometric quantities without changing their scaling behavior: The most significant part of repeated visits to the same points comes from the short-length-scale behavior; e.g., on a cubic lattice there is a probability of $\frac{1}{6}$ of returning to the same point just after two steps. This probability quickly saturates, and can be "eliminated" by rescaling the step sizes (and, thus modifying the total number of steps of the walk). Due to the local nature of the effect, it does not modify the overall scaling. This, of course, does not mean that one can completely eliminate intersections by a simple rescaling, since a very long, L-step, URW, has essentially constant probability $L/R_g^3 \sim L^{1-3\nu}=L^{-1/2}$ to visit any site within its radius of gyration, thus creating the total of $L^{1/2}$ intersections. This effect could be significant in the thermodynamic treatment of random walks with self-interaction. However, it carries a negligible weight in the treatment of the geometrical properties where the main "weight factor" is proportional to the total mass L.

The electrostatic problem of the random walk is formulated in terms of charges q_i situated on the spheres positioned on discrete lattice sites. The interaction energy between two charges positioned at $\mathbf{r}_i$ and $\mathbf{r}_j$, namely, a distance $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ apart, is q_iq_j/r_{ij}, while the self-interaction energy of a charge q_i is $q_i^2/2b$. Any electrostatic problem in this model can be solved by minimizing the total energy with respect to q_i's under appropriate constraints, such as constraint on the total charge and the behavior of the potential at an infinite distance from the chain. One should bear in mind that the discrete energy function only approximates the true energy of such a chain in a continuous three-dimensional space. In particular, it ignores the dipole and higher multipole interactions between the neighboring spheres. If the charges are approximately homogeneously distributed along the chain, then the total self-interaction energy, as well as the energy of closely located sites, increase as L. At the same time the interaction between remote pairs of charges ($\sim L^2$ such pairs) separated by typical distances of R_g increases as $L^2/R_g \sim L^{2-\nu}$, which for both an URW ($\nu=\frac{1}{2}$) and a SAW ($\nu\approx 0.588$) increases much faster than the local interaction energy. Obviously, the minimum of energy is primarily achieved by minimizing the large distance contributions, and therefore the exact definition of the short-range interaction is irrelevant to the electrostatic behavior of very long chains. (Similar argument excludes the necessity of introduction of multipole interactions at large distances.) Exclusion of multipole interactions between the charges on the spheres, however, sacrifices the detailed knowledge of charge distribution on short-length scales, i.e., if one compares the solution of this discrete model with an actual distribution of charges on the spheres of size b in a continuous three-dimensional space, one may discover significant differences on individual spheres. (Such sensitivity of the *exact* solutions has been reported in the literature [11].) The continuous and discrete problems coincide only in the limit $b\to 0$, which makes the multipole interactions negligible. (Actually, it would suffice to take $b \ll 1$.) However, the object of this work is the *long-length-scale* behavior of the chains, and therefore the definitions may be chosen to ensure the fastest approach to the asymptotic regime, in complete disregard of the accuracy of local charge distribution. In particular, one would like to choose the sphere radius b in such a way that the local interaction energy is negligible compared with the interactions of remote charges, i.e., $L/b \ll L^2/R_g \sim L^{2-\nu}/a$, or $b \gg aL^{\nu-1}$, where the prefactor a depends on the lattice and on the detailed way in which the energy estimate is performed, but is typically somewhat smaller than unity. To have such an inequality even for modest values of L one should choose $b \gg 0.1$. However, b cannot be arbitrarily large: From a purely physical point of view, the diameter of a sphere should not exceed the separation between the neighboring spheres. Thus, only $b<\frac{1}{2}$ represents (at least approximately) a real physical situation. This physical argument indicates the possible presence of a mathematical problem in the discrete energy function. Indeed, the exact (continuum) energy functional is positive definite with respect to charges. No such property is *a priori* present in the definition of discrete energy. Consider, for example, an $L=1$ chain, i.e., two neighboring connected spheres charged by a total charge Q. The charges of the spheres, q_0 and $q_1=Q-q_0$, can be found by minimizing $U=(1/2b)q_0^2+(1/2b)(Q-q_0)^2+q_0(Q-q_0)$. The extremum of U is always $q_0=q_1=Q/2$. However, for $b>1$ it becomes *maximum*, i.e., the system starts gaining energy by transferring charge from one sphere to another, since the energies of the (opposite) charges of the spheres are offset by the decreasing (negative) energy of the intersphere interaction. For a general configuration with spheres positioned at $\mathbf{r}_i$ ($i=0,1,\ldots,L$) the matrix A_{ij} defined by

$$A_{ij}=\begin{cases}1/r_{ij} & \text{for } r_{ij}>0\\ 1/b & \text{for } r_{ij}=0\end{cases} \tag{2.1}$$

should be positive definite. I could not find a general bound on b that would satisfy this condition. A detailed

inspection of all possible configurations with $L=2$ produced more stringent (lower) bounds than the $L=1$ case. In all cases, however, the maximal physically possible value of $b=\frac{1}{2}$ produced a positive-definite form. This conclusion has also been confirmed in a sample of $L=3$ cases. Presumably, one can safely choose any $b<\frac{1}{2}$ for any chain. In the actual calculation, I used $b=\frac{1}{4}$, which reasonably compromises between the opposite requirements on the size of b.

A somewhat related problem is what to do with the coinciding sites of an URW; I chose the numerically simpler approach, namely to treat the coinciding sites as a single sphere. Therefore, the number of unknown charges (as well as the number of equations used to find them) in an L-step URW frequently was smaller than $L+1$. Since the short-range interactions do not influence the long-range behavior, this choice does not change the large-L results.

It should be noted that minimization of the total energy U, i.e., equating its derivatives to zero, reduces any electrostatic problem to a set of linear equations. Essentially, $\partial U/\partial q_i$ is simply the potential of the ith sphere, and the solution of the linear equations represents a search for charges q_i, ensuring that the entire walk is equipotential under the defined boundary conditions.

III. THE NUMERICAL PROCEDURE

The numerical procedure begins by generating a complete set of all self-avoiding and unrestricted random walks of lengths $L=2,4,8$ and a random set of $S=1000$ (mutually uncorrelated) random walks for each of the lengths $L=16,32,64,128$. The generation of a random sample of a long URW is very simple: one simply has to make L steps in random directions on a simple-cubic lattice. The problem arises when one tries to generate long SAW's: The total number of SAW's of length L is given by $\mathcal{N}_L=Az^L L^{\gamma-1}$, where A is a lattice-dependent prefactor, z is the lattice-dependent *effective* coordination number (for a simple-cubic lattice $z\approx 4.68$), and $\gamma\approx 1.162$ [2] is a universal constant that, for a given space dimension ($d=3$), does not depend on the lattice. If one attempts to generate a SAW by simply performing a random walk on a lattice [each consequent step being made in one of the randomly chosen five directions (no steps in direction opposite to the preceding steps)], then out of 5^L possible random walks only the fraction $\sim(z/5)^L L^{\gamma-1}$ will survive. The exponentially decaying factor $(z/5)^L\approx e^{-0.064L}$ shows that the attrition (number of walks to be discarded) practically prevents the usage of this method for the generation of very long SAW's. Other algorithms that have been suggested may have a smaller attrition; however, they produce highly correlated sets of SAW's.

There exists an efficient algorithm for creation of such walks [12]: Suppose we have generated a complete set of L-step SAW's that begin at a particular lattice site, say, the origin (two walks of identical shape but different orientation are treated as different walks in this algorithm). We now attempt to generate all $2L$-step walks by taking all possible pairs of L-step walks and attaching the beginning of one of them to the end of the other (no "rotation" of the walks is attempted). If the newly generated walk does not self-intersect, it is added to the list; otherwise it is discarded. Clearly, this method produces *all* SAW's of length $2L$, and every different walk is produced only *once*. The "survival" rate in this process is $\mathcal{N}_{2L}/\mathcal{N}_L^2=(1/A)(2/L)^{\gamma-1}\approx(1/A)(2/L)^{0.16}$, which means that for $L\sim 100$ a significant part (~ 0.5) of the attempts are successful. The main drawback of the procedure is that it requires keeping complete lists of all SAW's of a given length. I created such lists for $L=2,4,8,16$. From the last list, only a subset of $S=1000$ walks has been randomly selected for further investigation of their electrostatic properties. Beyond that point the generation of complete sets of SAW's is practically impossible. Of course, one can resort to a partially random procedure: One may select a reasonably small subset of $L=16$ SAW's and use them to generate all $2L$-step SAW's which can possibly be created from that subset, followed, again, by selection of a random subset of the resulting SAW's for creation of even longer SAW's. Such course of action, however, introduces correlations in the sampling, since the longest generated walks will include very large amounts of repeating (identical) subchains, as compared to a random sample of SAW's selected from a complete set of such walks. To circumvent the problem of the correlations, I adopted the following procedure: A random subset of S_{16} 16-step SAW's has been selected from a complete set of those walks and has been divided into two halves. An attempt to pair the first SAW in the first half with the first SAW in the second half was made, followed by an attempt for the second walks in the halves, etc. All successful pairings were recorded in a new list. The resulting set of S_{32} 32-step walks was as uncorrelated as if it was selected directly from a complete set of 32-step walks. It was again divided into two halves, and the process was repeated. The process was terminated by obtaining $S_{128}\approx 1000$ SAW's of length $L=128$. Notice that S_{2L} is approximately equal to $S_L/2$ multiplied by the known survival rate. Therefore, the size of the starting sample, S_{16}, was calculated in advance in such a way as to ensure the sample of 1000 walks of length $L=128$. Maintaining the lists of chains of intermediate lengths is not a necessity of the algorithm, since the longest chains can be generated one by one, thus keeping only a small amount of information about the subchains.

The number of operations required to create a sample of S SAW's of length L, from twice shorter walks, is proportional to SL^γ (the number of operations required to check self-avoidance is $\sim L$, while the survival rate is $\sim L^{1-\gamma}$). The total time required to generate all SAW's up to length L (even taking into account the need for larger subsets of walks at the lower levels) is also proportional to L^γ. Thus, we have an extremely efficient procedure for generating sets of very long uncorrelated SAW's. The real limitation on the size of walks in this work is imposed by the need to solve the electrostatic problems on these walks, which requires a number of operations increasing as L^3. A typical calculation in this work consumed less than an hour of CPU time on a Sun

4/110 minicomputer. Thus, if necessary, the length of the walks can be doubled or quadrupled and the sample size can be increased by an order of magnitude, within reasonable computation times.

IV. GEOMETRY OF RANDOM WALKS

The simplest measure of the geometrical size of a random walk is provided by its radius of gyration. More detailed information can be provided by various moments of the mass distribution. The first-order moment provides only the coordinates of the center of mass, which is of no interest to us. The simplest description of the shape of the walk can be provided by the second-order central moment tensor, denoted the shape tensor,

$$T_{\alpha\beta}\equiv\frac{1}{L+1}\sum_i r_{i,\alpha}r_{i,\beta}-\frac{1}{(L+1)^2}\sum_i r_{i,\alpha}\sum_i r_{i,\beta}\ ,$$

where the summation if performed over all sites i of the walk, while the Greek subscripts represent the Cartesian components. The trace of T is R_g^2 of the walk, and it is closely related to the inertia tensor $\mathsf{M}=\mathsf{1}\,\mathrm{Tr}\mathsf{T}-\mathsf{T}$, where $\mathsf{1}$ is the identity tensor. The shape tensor is frequently used to describe the shapes of polymers [5] and polymeric surfaces [13]. Its eigenvalues $R_1^2\geq R_2^2\geq R_3^2$, called ordered components of R_g^2, provide a convenient criterion of the ansitropy of the random walk. Since each R_α^2 scales as L^ν, the ensemble-averaged quantities $(\langle R_1^2\rangle/R_g^2, \langle R_2^2\rangle/R_g^2 \langle R_3^2\rangle/R_g^2)$ approach constant values $(0.76, 0.176, 0.065)$ for an URW, and $(0.79, 0.161, 0.054)$ for a SAW, as $L\to\infty$. The quoted numerical results were obtained by Kranbuehl and Verdier [7] a long time ago for somewhat shorter chains, and they coincide within the statistical errors with the results of the present work. It is interesting to note that these ratios practically reach their asymptotic values already at $L=8$, and the accuracy of the result depends primarily on the size of the sample. To apply the knowledge of the components of R_g^2 to some physical properties, it is convenient to represent the random walk by a homogeneous solid body of a simple shape with an identical T. While, in the absence of higher-order information on the mass distribution, the choice of a specific shape is quite arbitrary (it could be a right prism or an nth-order oval shape [6]), I choose to represent it as an ellipsoid, which is the most standard representation for such properties as inertia tensor, or the tensor of dielectric constants. A compelling argument for this choice is simplicity: an ellipsoid is one of very few shapes with analytically solvable electrostatics. The major semiaxes of this geometrically equivalent ellipsoid are defined as $a'_\alpha=\sqrt{5}R_\alpha$. The prefactor $\sqrt{5}$ is selected in such a way that the shape tensor of a homogeneous ellipsoid of this size would coincide with the T of a given chain. Since such definition of the "real" linear size is somewhat arbitrary, in most of the following definitions I will omit the prefactor $\sqrt{5}$ and simply use an ellipsoid defined by the semiaxes $a_\alpha=R_\alpha$. The spatial orientation of the equivalent ellipsoid will be determined by a triplet of mutually perpendicular unit vectors $\{\mathbf{d}_{(\alpha)}^{(g)}\}$ $(\alpha=1,2,3)$, which are the eigendirections of the symmetric tensor T, corresponding to eigenvalues $\{R_\alpha^2\}$. Actually, the $\mathbf{d}^{(g)}$'s are *directors* rather than vectors, since they are defined up to a sign. Figure 1 depicts a SAW projected onto the $\mathbf{d}_{(1)}^{(g)}-\mathbf{d}_{(2)}^{(g)}$ plane. The smaller ellipse is the projection of the ellipsoid with semiaxes a'_1 and a'_2. One can, therefore, talk about the "geometrical volume" of the walk defined, e.g., by $V_g\equiv(4\pi/3)a_1a_2a_3$. A conducting ellipsoid with semiaxes a_1,a_2,a_3 would have [14] capacitance

$$C_g=2\Big/\int_0^\infty ds/[(s+a_1^2)(s+a_2^2)(s+a_3^2)]^{1/2}\ . \tag{4.1}$$

The behavior of such an ellipsoid in an external electric field E is determined by the depolarization tensor $\mathsf{N}^{(g)}$, which relates that field to the induced dipole moment P via the relation $(4\pi/V_g)N_{\alpha\beta}^{(g)}P_\beta=E_\alpha$. The principal eigendirectors of the tensor coincide with the directions of the ellipsoid axes, and the sum of its eigenvalues (depolarization coefficients) $n_1^{(g)}\leq n_2^{(g)}\leq n_3^{(g)}$ is unity. (Notice that the smallest depolarization coefficient corresponds to the largest component of the R_g^2.) For an ellipsoid [14,15]

$$n_\alpha^{(g)}=\tfrac{1}{2}a_1a_2a_3\times\int_0^\infty\frac{ds}{(s+a_\alpha^2)[(s+a_1^2)(s+a_2^2)(s+a_3^2)]^{1/2}}\ . \tag{4.2}$$

The depolarization coefficients are independent of the overall size of the ellipsoid, and therefore the $n^{(g)}$'s are insensitive to the arbitrary scale factor that we used in the definition of a_α's. Since the capacitance of an object of a given shape is proportional to its linear dimensions, one expects the ensemble-averaged value $\langle C_g\rangle$ to scale as L^ν, while the depolarization coefficients are expected to approach constant values as $L\to\infty$. The open signs in Figs. 2(a) and 2(b) depict the $1/L$ dependence of the ensemble averages of the geometrically calculated depolarization coefficients of URW's and SAW's, respectively. As in the case of R_α^2's, the convergence to the asymptotic $(L=\infty)$ values is extremely fast. The extrapolated values of those coefficients are $(0.133, 0.323, 0.543)$ for URW's, and $(0.118, 0.317, 0.566)$ for SAW's, with an estimated (statistical) error ±0.002 in each of these coefficients. Note that for a spherical object one expects to have $n_1^{(g)}=n_2^{(g)}=n_3^{(g)}=\frac{1}{3}$. The results in Fig. 2 display the

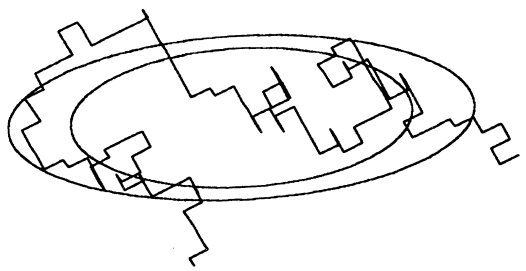


FIG. 1. Self-avoiding walk projected onto the plane of the eigendirections of the shape tensor corresponding to the two largest eigenvalues. The ellipses represent the equivalent geometric (inner) and electric (outer) ellipsoids (see text).

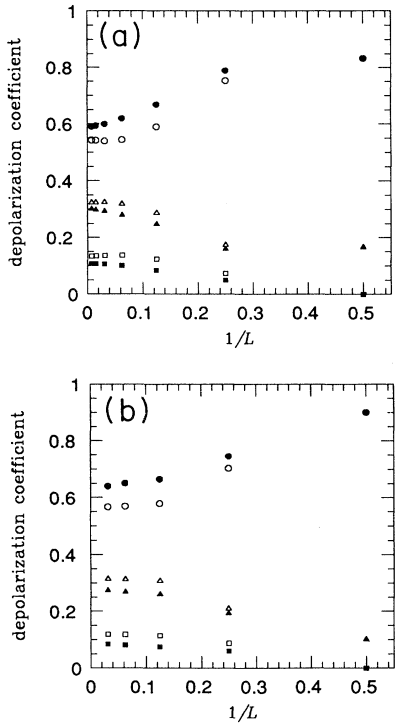


FIG. 2. Geometrical depolarization coefficients $n^{(g)}$ (open symbols) and directly measured depolarization coefficients $n^{(e)}$ (solid symbols) corresponding to the largest (squares), intermediate (triangles), and shortest (circles) axes of equivalent ellipsoids vs the inverse length of the walk, for (a) URW's and (b) SAW's.

lack of *geometrical* sphericity from an "electrostatic point of view." The information contained in these estimates does not differ significantly from the information contained in the ensemble-averaged moments of R_g^2, since in each configuration they are related by definition. The relation, however, is nonlinear, and thus the results in Fig. 2 represent a somewhat different ensemble averaging. The geometrical depolarization coefficients are strongly fluctuating quantities: the fluctuations reach 50% for $n_1^{(g)}$ and are somewhat smaller for other coefficients. Thus the knowledge of the averages provides little practically useful information.

V. CAPACITANCE AND POLARIZABILITY OF RANDOM WALKS

The simplest measure of the "electrostatic size" of the walk can be obtained from a direct measurement of its capacitance C_e. Since, as argued in Sec. II, the energy of a RW depends on the interactions of remote charges, it is expected that $m_0\langle C_e\rangle = R_g$. For practical reasons it would be useful to establish the proportionality coefficient m_0 in this relation. The capacitance of the chain is determined via $C_e \equiv Q/\phi$, where Q is its total charge, while ϕ is its potential (relative to infinitely remote points). For a given (particular) configuration of a RW, I assume that the entire chain has a constant potential $\phi = 1$, and find the charge distribution from a set of linear equations [16]:

$$\sum_j A_{ij} q_j = 1 \quad \text{for each } i \ , \tag{5.1}$$

where A_{ij} is defined in (2.1). In the case of an URW, coinciding sites are treated as a single site, and, therefore, the number of equations and unknowns may be smaller than $L+1$. The capacitance is $C_e = \sum_i q_i$.

Not surprisingly, I find that the ensemble-averaged capacitances indeed scale as the radius of gyration. However, their numerical values are extremely small: For large L the coefficient $m_0 \equiv (\langle R_g^2\rangle)^{1/2}/\langle C_e\rangle$ approaches the values 1.30 for an URW and 1.45 for a SAW (estimated error ± 0.02). This is an unexpectedly large number, i.e., the capacitance is unexpectedly small: In the preceding section, I argued that the radius of gyration (and its ordered components) underestimated the "actual" size of the equivalent ellipsoid, and suggested using a scaling factor of $\sqrt{5}$ to correct that underestimate. Taking that argument seriously, one would expect $m_0 \approx \sqrt{3/5}$. It might appear that the result is about 2 times larger than expected. However, we must keep in mind that the investigated object is not spherical, and even for a homogeneous conducting ellipsoid $C_e < \sqrt{5/3} R_g$. Indeed, a more careful consideration reduces the apparent size of the discrepancy. Due to the asphericity of the object, one should instead use the value C_g, which has been calculated by assuming that the object is an ellipsoid, as the "geometrical measure" of the linear dimension of the RW. Since both $\langle C_e\rangle$ and $\langle C_g\rangle$ are expected to scale as R_g, the ratio $m_1 \equiv \langle C_g\rangle/\langle C_e\rangle$ can be used as an indicator of the ratio of the "geometric" and "electrostatic" linear dimensions of the walks. The upper solid and dotted-dashed lines of Fig. 3 depict the $1/L$ dependence of m_1 for the URW and SAW, respectively. Notice that this time the asymptotic values are significantly smaller than the corresponding m_0's. Later in this section, I shall

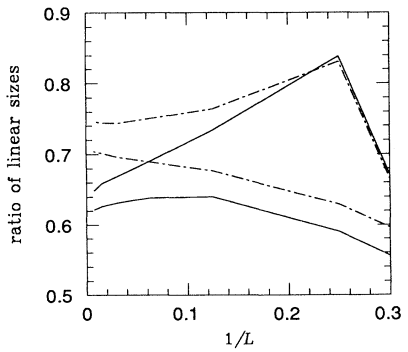


FIG. 3. Ratios of the geometric and electrostatic linear sizes m_1 (top curves) and m_2 (bottom curves) (see text) vs the inverse of the chain length L for URW's (solid lines) and SAW's (dotted-dashed lines).

return to the subject of the linear dimensions of the RW's.

The crudest indicator of the "electrostatic shape" of a random walk is the polarizability tensor Γ, which relates the external field to the dipolar moment of the chain: $P_\alpha=\Gamma_{\alpha\beta}E_\beta$. Its components can be found by calculating the charge distribution on an uncharged random walk embedded in an external electric field of unit strength. If the external field points along a Cartesian direction α, then the potential along the chain *generated by the charges of the chain* should increase linearly along the α direction to compensate the change caused by the external electric field. In addition, the total charge of the chain should vanish. Finding, the corresponding charge distribution $\{q_i^{(\alpha)}\}$, amounts to solving a set of $L+2$ linear equations

$$\sum_j A_{ij}q_j^{(\alpha)}=r_{i,\alpha}+c \quad \text{for each } i \tag{5.2a}$$

$$\sum_i q_i^{(\alpha)}=0\ , \tag{5.2b}$$

where A_{ij} is defined in (2.1), $r_{i,\alpha}$ is the α coordinate of the position of the ith site, and the unknowns are $q_i^{(\alpha)}$'s and the constant c. The set of Eqs. (5.2) should be solved three times: a separate solution should be found for each value of $\alpha=1,2,3$ and the elements of the polarizability tensor Γ can be found from $\Gamma_{\alpha\beta}=\sum_i q_i^{(\alpha)}r_{i,\beta}$. It can be directly verified that this polarizability tensor is symmetric. One may use the eigenvalues of Γ denoted $\gamma_1\geq\gamma_2\geq\gamma_3$ to define an equivalent conducting ellipsoid with identical polarizability. Thus, for each RW generated, I calculated the polarizability tensor, its eigenvalues, and the eigendirections $\{\mathbf{d}_{(\alpha)}^{(e)}\}$ corresponding to those eigenvalues. The depolarization coefficients $n_\alpha^{(e)}$ and the volume V_e of the equivalent electrostatic ellipsoid are defined via three relations $\gamma_\alpha=V_e/(4\pi n_\alpha^{(e)})$ $(\alpha=1,2,3)$, supplemented by the relation $\sum_\alpha n_\alpha^{(e)}=1$. Introduction of these depolarization coefficients provides a convenient tool for the comparison of the geometric and electrostatic shapes and sizes.

The larger ellipse in Fig. 1 represents such an electrically equivalent ellipsoid. Knowledge of the ensemble-averaged V_e provides an additional estimate of the ratio between the linear dimensions of the "geometric" and "electric" ellipsoids: $m_2=(\langle V_g\rangle/\langle V_e\rangle)^{1/3}$. The lower solid and dotted-dashed lines in Fig. 3 depict the $1/L$ dependence of the m_2 for the URW and SAW, respectively. While the definitions of m_1 and m_2 are quite different, their asymptotic values are reasonably close, thus providing a quantitative meaning to the concept of "electrostatic linear size" of a RW. It is interesting to note that the electrostatic ellipsoid in Fig. 1 appears to be bigger than its geometric counterpart; however, its volume is actually smaller since its third axis (perpendicular to the plane of the drawing) is significantly shorter than the geometric a_3'.

The solid symbols in Figs. 2(a) and 2(b) depict the $1/L$ dependence of the ensemble averages of the true depolarization coefficients $n_\alpha^{(e)}$ of URW's and SAW's, respectively. Their extrapolated values are (0.11, 0.30, 0.59) for URW's, and (0.08, 0.28, 0.63) for SAW's with an estimated (statistical) error less than the last significant digit in each of these coefficients. As in the case of $n^{(g)}$, the SAW's are more aspherical than the URW. Also, one can see that for both kinds of RW the true (electrostatic) asphericity is significantly stronger than predicted from the properties of the equivalent ellipsoid. Such differences can be understood: The polarizability of a walk depends primarily on the shape and size of its boundaries. Thus, a single "arm" sticking out of an otherwise spherical dense collection of sites may have little influence on Υ, but may significantly modify Γ. This apparently leads to greater sensitivity of Γ to shape fluctuations, and, therefore, to larger mean asphericity. This intuitive explanation should not be taken too literally: the difference between the geometrical and electric asphericity *does* depend on the particular choice of the equivalent body shape (ellipsoid) and could be different if bodies of different shapes were to be used.

The above results represent the relations between the ensemble-averaged properties. One should however, keep in mind that both R_g and C_e are very strongly fluctuating quantities. Similarly, the shapes of walks exhibit strong fluctuations: Figures 4(a) and 4(b) depict the probability densities of $n^{(e)}$'s for URW's and SAW's, respectively. These results have been calculated from 1000 RW samples, with $L=32$ (dotted-dashed lines) and $L=128$ (solid

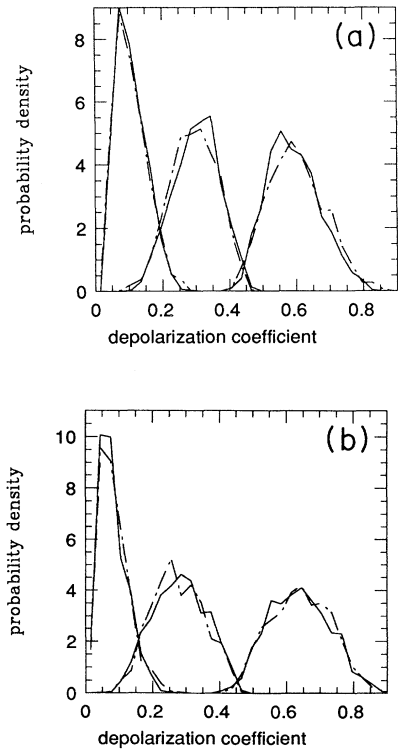


FIG. 4. Probability densities of three depolarization coefficients $n^{(e)}$ for (a) URW's and (b) SAW's of length 128 (solid lines) and 32 (dotted-dashed lines).

lines). From comparison of the $L=32$ and 128 curves, I conclude that the distributions are close to their asymptotic shapes.

VI. CORRELATIONS BETWEEN GEOMETRY AND ELECTROSTATICS

The presence of strong fluctuations in each of the measured quantities may raise the question of whether the rough knowledge of the geometrical shape, as provided by the components of R_g^2, can be of any help in determining the electrostatic behavior of a particular (not ensemble-averaged) RW. The answer to that question is obtained by checking the correlations between the properties in the individual RW's. Figure 5 depicts the probability density of the ratio V_e/V_g for 128- and 32-step URW's (solid and dashed lines, respectively). This distribution is strongly centered, with typical fluctuations several times smaller than the relative fluctuations of V_e and V_g individually.

Not just the electrostatic and geometrical volumes are strongly correlated—the shapes and orientations are correlated as well: A quantitative measure of orientation correlation can be obtained by ensemble averaging squares of the pairwise scalar products of the directors indicating the orientation of the geometric and electrostatic equivalent ellipsoids, and defining $p_{(\alpha)}\equiv\frac{1}{2}[3\langle(\mathbf{d}_{(\alpha)}^{(g)}\cdot\mathbf{d}_{(\alpha)}^{(e)})^2\rangle-1]$, for $\alpha=1,2,3$ [$p_{(\alpha)}=1$ for perfect correlation, and 0 for completely uncorrelated directions]. Figure 6 depicts the $1/L$ dependence of these correlation coefficients for URW's (open symbols) and SAW's (solid symbols). Unsurprisingly, the strongest correlation is exhibited by the longest axes (triangle). The extremely high values of all $p_{(\alpha)}$'s indicate almost a perfect correlation.

Strong correlations between the geometry and electrostatics are also observed in the shapes of the RW's. Figures 7(a) and 7(b) depict $n^{(e)}$ versus $n^{(g)}$ for a sample of 100 URW's and a sample of 100 SAW's, respectively, of length $L=128$. While for a given value of $n^{(g)}$ we still observe $\sim 10\%$ scatter in the corresponding $n^{(e)}$, it is significantly smaller than the overall fluctuations of those coefficients (compare with Fig. 4). Thus, the ordered components of R_g^2 have a large predictive power regarding the polarizability of a polymer.

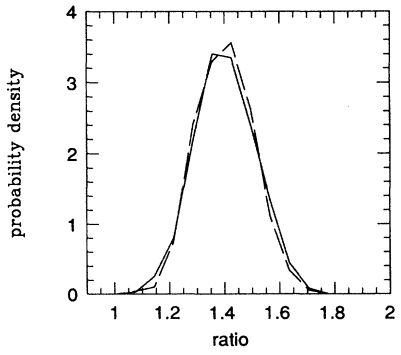


FIG. 5. Probability density for the distribution of the ratio V_e/V_g for URW of length 128 (solid line) and 32 (dotted-dashed line).

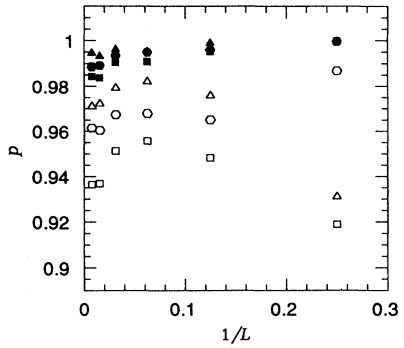
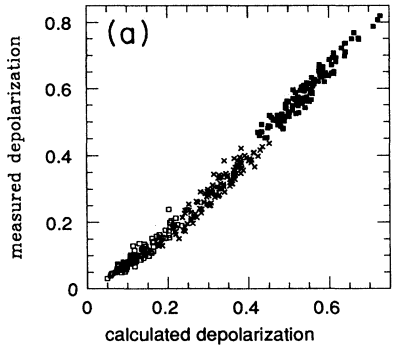


FIG. 6. Correlation coefficients $p_{(\alpha)}$ (see text) of the directors of longest (triangles), intermediate (circles), and smallest (squares) axes for URW's (open symbols) and SAW's (solid symbols).



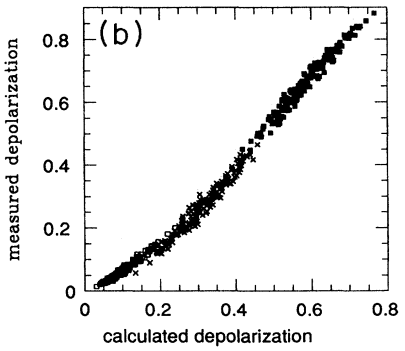


FIG. 7. Geometrical depolarization coefficients $n^{(g)}$ vs directly measured depolarization coefficients $n^{(e)}$ in a sample of (a) 100 URW's, and (b) 100 SAW's of length $L=128$. Solid squares, ×'s, and open squares represent the coefficients corresponding to the shortest, the intermediate, and the longest axes of the equivalent ellipsoids, respectively.

VII. DISCUSSION

In this work a first detailed study of a simple physical property—electrostatic behavior of polymers—has been performed. The work both confirmed the expected scaling relations and established various, previously unknown, prefactors. The polarizability has been found to be significantly more anisotropic than can be expected from the shape tensor. Nevertheless, the shape tensor can be used to predict the electric behavior with reasonable accuracy to specific (*not* ensemble-averaged) configurations. Since all the results are either scaled with respect to R_g or are independent of the overall size of the polymer, they can be directly applied to real polymers. The results also provide a useful guide to the dielectric behavior of nonconducting polymers.

It is conceivable that some electric properties of URW can be calculated analytically. However, the analogous quantities for SAW's will, probably, rely on numerical simulations for quite some time. Most of the results in this study were reasonably well converged and accurate already for $L=128$ and sample sizes of 1000 chains, although an order-of-magnitude increase in both L and the sample size (corresponding to a 10^4 increase in computation time) may still be desirable, e.g., to obtain the values of m_0, m_1, and m_2 to 1% accuracy.

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[1] See, e.g., P. G. de Gennes, *Scaling Concepts in Polymer Plysics* (Cornell University Press, Ithaca, NY, 1979).

[2] J.-L. Le Guillou and J. Zinn-Justin, Phys. Rev. Lett. **39**, 95 (1977).

[3] W. Kuhn, Kolloid-Z. **68**, 2 (1934).

[4] R. Koyama, J. Phys. Soc. Jpn. **22**, 973 (1967); **24**, 580 (1968); R. J. Rubin and J. Mazur, Macromolecules **6**, 872 (1973); J. Chem. Phys. **63**, 5362 (1975); M. Bishop and J. P. J. Michels, *ibid.* **84**, 444 (1986); G. Wei and B. E. Eichinger, Comput. Polym. Sci. **1**, 41 (1991).

[5] K. Šolc and W. Stockmayer, J. Chem. Phys. **54**, 2756 (1971).

[6] R. J. Rubin and J. Mazur, Macromolecules **10**, 139 (1977).

[7] D. E. Kranbuehl and P. H. Verdier, J. Chem. Phys. **67**, 36 (1977).

[8] S. R. Coriel and J. L. Jackson, J. Math. Phys. **8**, 1276 (1967); K. Šolc, J. Chem. Phys. **55**, 335 (1971); J. Rudnick and G. Gaspari, J. Phys. A **19**, L191 (1986).

[9] J. A. Aronovitz and D. R. Nelson, J. Phys. (Paris) **47**, 1445 (1986).

[10] Y. Kantor, Europhys. Lett. **14**, 767 (1991).

[11] J. M. Aguirregabiria, A. Hernández, M. Rivas, and M. A. Valle, Comput. Phys. **4**(1), 60 (1990).

[12] Z. Alexandrowicz, J. Chem. Phys. **51**, 261 (1969).

[13] Y. Kantor and D. R. Nelson, Phys. Rev. A **36**, 4020 (1987).

[14] See, e.g., L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media,* 2nd ed. (Pergamon, Oxford, 1984).

[15] Simple and efficient methods for evaluating C_g and $n_\alpha^{(g)}$ can be found in W. H. Press and S. A. Teukolsky, Comput. Phys. **4**(1), 92 (1990).

[16] See, e.g., W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, New York, 1986).