On the statistics of generalized Gaussian structures: collapse and random external fields

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Abstract. We consider the statistics of generalized Gaussian structures (GGS) exposed to a random external field. A GGS comprises N monomers connected to each other by harmonic potentials. When the spectral dimension d_s of a GGS exceeds the value of two its radius of gyration R becomes independent of its mass N. The cross-over into this collapse can be treated continuously by cross-linking m precursor chains of length n in the stretched state to an object which we call a polymer bundle. We demonstrate that an external field f applied to each monomer can 'unfold' such a collapsed state. In the case where every monomer has an individual, randomly distributed, charge the critical spectral dimension for the collapse is raised to four. R scales like $f N^{\alpha}$ with $\alpha = (4 - d_s)/(2d_s)$ for $d_s < 4$.

1. Introduction

The successful theoretical investigation of many polymer systems such as solutions and melts composed of linear chains is based upon a very simplified model: that of a Gaussian chain. To explain the universal features of polymers on length scales much larger than a few monomers one assumes that the polymer chain is a sequence of N Brownian beads connected by harmonic entropic forces [1]. This reflects, in a reasonable way, the static and dynamical properties due to the chain connectivity, see for instance [2] for a series of cases in which the model describes the physical situation properly. If nothing else is assumed the model is called an ideal chain. One may even implement additional features into the model, such as interactions between the monomers (e.g. the excluded volume effect due to van der Waals forces, electrostatic interactions, etc) by the use of corresponding statistical weights. However, what distinguishes polymers from simple fluids is just the chain connectivity, so that the understanding and mathematical formulation of the physics of Gaussian chains is the first important step in theoretical polymer physics.

It is tempting to extend the Gaussian chain idea to nonlinear polymers such as gels, membranes and polymer networks or, more generally, to any connected structure built from monomers. Provided there are N monomers connected to each other, the connectivity potential reads in d spatial dimensions:

$$H_c = \frac{kT}{2l^2} \sum_{(i,k) \in \mathcal{B}} (r_i - r_k)^2 = \frac{kT}{2l^2} \sum_{i,k=0}^{N-1} r_i M_{ik} r_k \tag{1}$$

where the first sum extends over all pairs $\{i, j\}$ which form the set of bonds $\mathcal{B}$ between the N monomers. In equation (1) r_i denotes the position of the ith monomer and kT is, as usual,

the product of Boltzmann's constant and temperature. In equation (1) l is the mean bond-length in each Euclidean direction, see [2] for details. One notes, moreover, that the potential in (1) is entropic, it is *not* of energetic nature, such as a chemical bond between monomers. Without further terms the different Euclidean coordinates decouple in (1) and H_c is a sum of d independent terms. Hence, we can restrict ourselves to only one spatial dimension. Extending the usage for linear chains we call the matrix M in (1) the generalized Rouse matrix (GRM) [3, 4]. Note that similar matrices which describe connectivity are known from other areas of physics. Examples are the Hückel matrix used for determining energy levels in PPP (MO) semiempirical quantum calculations [5] and the Kirchhoff matrix in the study of resistor networks. In polymer physics the GRM was already discussed by Graessley [6] as well as by Eichinger *et al* [7]. Knowing the connectivity of a given set of monomers the construction of the GRM proceeds as follows. Starting with all matrix elements set to zero a bond between monomers i and k is accounted for by incrementing the diagonal elements M_{ii} and M_{kk} by $+1$ and M_{ik} and M_{ki} by -1. A linear connectivity yields the tridiagonal Rouse matrix which is, by itself, a discretization of the one-dimensional Laplace operator. From the construction of the matrix M it follows directly that the normalized vector $m_0 = \{1/\sqrt{N}, 1/\sqrt{N}, \ldots\}$ is an eigenvector corresponding to the zero eigenvalue $\omega_0 = 0$; this may be easily seen from the fact that the sum over all row elements of M is equal to zero, i.e. $\det(M) = 0$. Moreover, the sum over all vector components of m_0 obeys: $\sum_{k=0,N-1} m_0^k = \sqrt{N}$; this is also the largest value the sum $\sum_{k=0,N-1} m^k$ can take under the constraint that m is normalized. This relation will be useful later.

A basic structural feature of a polymer is its radius of gyration R. Now R^2 is given by the sum of the squared distances of all monomers from the centre of mass. In one dimension:

$$R^2 = \frac{1}{N} \sum_{k=0}^{N-1} \left(r_k - \frac{1}{N} \sum_{i=0}^{N-1} r_i \right)^2 = \frac{1}{N} \sum_{k=0}^{N-1} r_k^2 - \frac{1}{N^2} \sum_{k,i=0}^{N-1} r_k r_i . \tag{2}$$

For Gaussian linear chains one has the well known scaling relation $\langle R^2 \rangle \sim N$ between the average of R^2 over all realizations and the degree of polymerization N ('mass' of the polymer).

Since in the following we perform averages over powers of r_i, it is convenient to introduce here the partition function (i.e. the generating function). For a GGS comprising N monomers subject to external forces $\{F_k\}$ the partition function is

$$Z(f) = \int \{dr_k\} \exp\left\{ -\frac{H_c}{kT} - \frac{U_{ext}}{kT} \right\} = \int \left(\prod_{k=0}^{N-1} dr_k \right) \exp\left\{ -\frac{1}{2l^2} \sum_{i,j} r_i M_{ij} r_j - \frac{1}{l} \sum_i r_i f_i \right\} . \tag{3}$$

In equation (3) the integrations run over the volume V and we set $f_k = l F_k / kT$.

Now we switch from the $\{r_k\}$ to the normal coordinates $\{u_a\}$; they are given by the unitary transformation [2]: $r_k = l \sum_a m_k^a u_a$, where m_k^a is the ath component of the normalized kth eigenvector of M, corresponding to the eigenvalue ω_k. In terms of normal coordinates the radius of gyration is

$$R^2 / l^2 = \frac{1}{N} \sum_{a \neq 0} u_a^2 - \frac{1}{N^2} \sum_{k,l} \sum_{a,b \neq 0} m_k^a m_l^b u_a u_b . \tag{4}$$

Note that to R^2 only those normal coordinates contribute which correspond to the non-zero eigenvalues (see the appendix for details). In terms of normal coordinates the partition

function takes the form

$$Z(f)/l^N = \int \left(\prod_{a=0}^{N-1} \mathrm{d}u_a \right) \exp\left\{ -\frac{1}{2} \sum_{a=1}^{N-1} \omega_a u_a^2 - \sum_{a=1}^{N-1} f^a u_a - f^0 u_0 \right\}$$

$$= \left(\prod_{a=1}^{N-1} \int \mathrm{d}u_a \, \mathrm{e}^{-\frac{1}{2}\omega_a u_a^2 - f^a u_a} \right) \int \mathrm{d}u_0 \, \mathrm{e}^{-f^0 u_0} \tag{5}$$

with $f^a = \sum_k m_k^a f_k$. We assume that the volume V is very large. The integrations over all non-zero modes u_a with $a > 0$ can be extended to infinity. Only the u_0 integration depends on the volume. Note that $u_0/\sqrt{N}$ is the centre-of-mass coordinate of the structure. Because of the structure of $Z(f)$, averages of u_a can be expressed through the derivatives of $Z(f)$. If $g(u_a)$ is some (analytic) function of u_a, its thermodynamic average $\langle g \rangle$ can be evaluated using

$$\langle g \rangle = \frac{g\left(\frac{\partial}{\partial f^a}\right) Z(f)}{Z(f)}. \tag{6}$$

Now R^2 does not depend on u_0, and thus in its evaluation from $Z(f)$ we may disregard the term depending on f^0 (the last integral on the right-hand side of (5)), since according to the above equation this term drops out. (Physically, this means that the translational degree of freedom does not affect the internal properties of the GGS). With equations (5) and (6) the thermodynamic average of R^2 as given by (4) takes for arbitrary external forces the form

$$\langle R^2(f) \rangle / l^2 = \frac{1}{N} \sum_{a=1}^{N-1} \frac{1}{\omega_a} - \frac{1}{N^2} \sum_{a=1}^{N-1} \sum_{k,l=0}^{N-1} m_k^a m_l^a \frac{1}{\omega_a}$$

$$+ \frac{1}{N} \sum_{a=1}^{N-1} (f^a)^2 \frac{1}{\omega_a^2} - \frac{1}{N^2} \sum_{a,b=1}^{N-1} \sum_{k,l=0}^{N-1} f^a f^b m_k^a m_l^b \frac{1}{\omega_a} \frac{1}{\omega_b}. \tag{7}$$

We are interested in the scaling behaviour of $\langle R^2 \rangle$ as a function of N and f. Here we restrict ourselves to the discussion of the first and third term on the right-hand side of (7), by noticing that these terms are larger than the absolute values of the second and fourth term, respectively, as can be shown by using the inequality $|\sum_k m^k| \leqslant \sqrt{N}$, which holds for normalized vectors. Hence we expect under usual conditions the corrections due to the latter terms to be (at most) of the order of the terms which we now analyse. For instance, in the extreme case of a linear chain the correction terms change the prefactors by $\frac{1}{3}$ for the first term and by $\frac{1}{2}$ for the third term. Notice that the first and the third term of the right-hand side of (7) are determined solely by the eigenvalue spectrum.

2. The force-free case: collapse transition

Firstly, we consider the case $f_k = 0$. According to (7) we have

$$\langle R^2 \rangle \sim \frac{1}{N} \sum_{a=1}^{N-1} \frac{1}{\omega} \sim \int_{\omega_{min}}^{\omega_{max}} \mathrm{d}\omega \, n(\omega) \frac{1}{\omega} \tag{8}$$

where the last equation makes explicit use of the spectral density $n(\omega)$. In equation (8) ω_{min} is the smallest non-vanishing eigenvalue. Physically it is connected with the extension and topology of the object and is given by its universal (scaling) properties (see equation (10) below). On the other hand ω_{max} is the largest value ω can take and is due to local (non-universal) properties of the object. As was shown in [3], ω_{max} is determined by the entropic spring constant and by the maximal number of nearest neighbours of a site (monomer).

General networks are characterized by their connectivity, i.e. by a topological feature. For them the GRM is related (being a generalized Laplace operator) to the spectral dimension d_s of the GGS, see for instance [8]. As is well known, d_s is directly reflected in the spectral density $n(\omega)$. For isotropic and locally homogeneous fractal objects (these include regular lattices as special cases) one has [8]

$$n(\omega) \sim \omega^{d_s/2-1} = \omega^{(d_s-2)/2}. \tag{9}$$

For $d_s < 2$ the minimal eigenvalue ω_{min} is inversely proportional to the time t it takes a random walker to explore the whole fractal of size ('mass') N. With $N \sim t^{d_s/2}$ it follows:

$$\omega_{min} \sim t^{-1} \sim N^{-2/d_s}. \tag{10}$$

Inserting equation (10) into (8) we obtain for $d_s < 2$: $\langle R^2 \rangle \sim \omega_{min}^{(d_s-2)/2}$, since the lower bound dominates the situation. Hence, for $d_s < 2$, using (10) it follows:

$$\langle R^2 \rangle \sim N^{\frac{2-d_s}{d_s}}. \tag{11}$$

On the other hand for $d_s > 2$, $\langle R^2 \rangle$ does not depend on ω_{min}. Thus it is no longer controlled by the mass N of the object. This, of course, holds under the Gaussian assumption of lack of any self-volume. Further, below we will show that random external fields can change the collapse situation.

Firstly, however, to further highlight the role of the dimension we focus on m parallel polymer chains of length n, a polymer *bundle* containing $N = mn$ monomers. Polymers may arrange themselves in this way under large shear strain. We now let the nearest-neighbour monomers of different chains be connected to each other; the resulting cross-linking topology is then orthogonal to the already-existing chain connectivity: the system may be visualized as being a tennis net. For instance, for $m = 2$ the construction leads to a 'rope ladder', where the rungs are represented by cross-links (DNA-molecules have a similar, very regular structure). We consider first a two-dimensional system, i.e. the bundle is taken from m 2D-parallel chains. The connectivity term in (1) takes the form:

$$\frac{2l^2}{kT} H_c = \sum_{i,k=0}^{N-1} r_i M_{ik} r_k = \sum_{K,I=0}^{n-1} \sum_{\alpha=0}^{m} r_K^\alpha \mathcal{M}_{KI} r_I^\alpha + \sum_{I=0}^{n-1} \sum_{\alpha,\beta=0}^{m} r_I^\alpha \mathcal{M}^{\alpha\beta} r_I^\beta. \tag{12}$$

Here the Greek indices in the products run over the m precursor chains while the capital latin indices run over the n monomers within each chain. The matrix $\mathcal{M}^{\alpha\beta}$ differs from $\mathcal{M}_{KI}$ only in dimension. Introducing the superindex $i(K, \alpha) = (\alpha-1)n+K$ (which corresponds to the general index we used so far) we can write the eigenvalues as $\omega_i(K, \alpha) = \omega_{K\alpha} = \omega_K + \omega_\alpha$; the last result is obtained by two successive diagonalization procedures of M. The eigenvalues ω_K and ω_α correspond to the matrices $\mathcal{M}_{IK}$ and $\mathcal{M}^{\alpha\beta}$, respectively. In the force free case the mean square radius of gyration now obeys

$$\langle R^2 \rangle \sim \frac{1}{nm} \sum_{k+\alpha \neq 0} \frac{1}{\omega_k + \omega_\alpha}. \tag{13}$$

In the special case of a 'rope ladder', $m = 2$ we get $\omega_{\alpha=0} = 0$ and $\omega_{\alpha=1} = 2$. Hence

$$\langle R^2 \rangle \sim \frac{1}{2n} \left(\sum_{K=1}^{n-1} \frac{1}{\omega_K} + \sum_{K=0}^{n-1} \frac{1}{\omega_K + 2} \right). \tag{14}$$

Since the eigenvalues are always positive the effect of the second term in the brackets on $\langle R^2 \rangle$ is equal to or less than the value $\frac{1}{4}$ and may be suppressed. The first term is exactly the expression for the single chain of length n, except for an additional prefactor of $\frac{1}{2}$, which emerges from the fact that the number of modes has doubled. Hence, coupling two ideal

Gaussian chains through rungs reduces their mean squared radius of gyration by a factor of two. Another point of view is to consider the two-stranded object as a renormalized simple chain having an effective, double-entropic spring constant. For m strands ($m \ll n$) one finds in the same fashion, approximately,

$$\langle R^2 \rangle / l^2 \sim \frac{1}{nm} \omega_{1,0}^{-1} \sim \frac{\langle R_n^2 \rangle}{l^2 m} \sim n/m . \tag{15}$$

When m approaches n, in $d = 2$ a more accurate analysis shows that the smallest eigenvalue of $\mathcal{M}^{\alpha\beta}$ becomes of order n^{-2} and that the corresponding terms in (13) can no longer be neglected. For $m = n$ the two-dimensional object can be viewed as being isotropic so that (11) holds. For $d_s \to 2$ equation (11) leads to a logarithmic N-dependence of $\langle R^2 \rangle$.

Let us now consider m parallel chains in 3D, connected via rungs to each other. The approach is the same as above, except that now each of the *two* cross-linking matrices has the dimension $\sqrt{m}$. For the case $m = n$ the main difference to the 2D bundle is that the eigenvalues of the cross-link matrices are still much larger than the smallest eigenvalue of the strand matrix (actually the smallest value is now of order m). Hence, the argument which has led us to (15) remains valid; the object collapses for $m = n$. Note, that since the thickness of the bundle is of order $m^{1/2}$ the object is still highly anisotropic when it starts its collapse.

3. The role of random external forces

We now turn to the question to determine what happens if external forces are present. We confine ourselves to the case when each monomer k carries a random charge and hence, in an external field, is subject to a force $F_k = kT f_k / l$. We assume that we have both positive and negative 'charges' on the GGS and we take them to be independently distributed random variables, so that $\langle f_k \rangle = 0$ and $\langle f_k f_i \rangle = f^2 \delta_{ki}$ hold. The ensemble average over the quenched (frozen) disorder is denoted by additional brackets $\langle \cdots \rangle$. We do not consider, however, possible intra-molecular interactions between our charges.

Note that due to the unitarity of the transformation $\{m_k^a\}$ one also has for the f^a [10]: $\langle f^a f^b \rangle = f^2 \delta^{ab}$. Applying the structural average to $\langle R^2 \rangle$ in (7) we get up to constants:

$$\langle\langle R^2 \rangle\rangle \sim \frac{1}{N} \left(\sum_{\omega \neq 0} \frac{1}{\omega} + f^2 \sum_{\omega \neq 0} \frac{1}{\omega^2} \right) . \tag{16}$$

Making again use of the spectral density it follows:

$$\langle\langle R^2 \rangle\rangle \sim N^{\frac{2-d_s}{d_s}} + f^2 N^{\frac{4-d_s}{d_s}} . \tag{17}$$

Notice that the second term on the right-hand side of (17) depends on N up to $d_s = 4$. Physically this means that due to the presence of positively and negatively charged monomers the external field unfolds the collapsed structure.

When the displacements become large the model of Gaussian entropic forces between the monomers will fail and so will our approach. The structure then becomes overstretched. However, we can estimate the range of validity of the model. Overstretching happens when $\langle R \rangle \sim N^{1/d_s}$ (the structure is no longer folded). Hence we are led to the condition

$$f^2 N^{\frac{4-d_s}{d_s}} \ll N^{\frac{2}{d_s}} \quad \to \quad f^2 \ll N^{\frac{d_s-2}{d_s}} . \tag{18}$$

For $d_s > 2$ the force may be quite strong without contradicting the Gaussian assumption.

In summary, we found that generalized Gaussian structures (GGS) are internally stable as long as their spectral dimension lies below $d_s = 2$. By considering anisotropic bundles

of m cross-linked precursor chains each of length n we can follow the cross-over transition. The bundle collapses when m approaches n. In the case of $d_s = 3$ we find that already a highly anisotropic bundle collapses. Random forces which act on each monomer separately may unfold the GGS as long as $d_s < 4$. If the spectral dimension is larger than two, the applied forces may be quite large without being in conflict with the Gaussian assumption.

Acknowledgments

Appendix. Radius of gyration in normal coordinates

The set of eigenvectors $\{m_k^a\}$ of the GRM simultaneously defines the unitary transformation which diagonalizes the GRM. The normal coordinates are defined by applying this unitary transformation to the vector $\{r_k\}$ ($k = 0, 1, \ldots, N - 1$).

We consider only the case of connected objects so that only one eigenvalue ω_0 vanishes. According to the special property of the GRM, namely that $\sum_{k=0}^{N-1} M_{kl} = 0$ it follows that $m_k^0 = \{N^{-1/2}, N^{-1/2}, \ldots, N^{-1/2}\}$ is a normalized eigenvector to ω_0. This is all that is required to establish (4). Starting from (2) one gets

$$R^2 = \frac{1}{N} \sum_{a=0}^{N-1} u_a^2 - \frac{1}{N^2} \sum_{k,l=0}^{N-1} \sum_{a,b=0}^{N-1} m_k^a m_l^b u_a u_b . \tag{1}$$

As a second step we separate all components with $a = 0$ or $b = 0$ form the sum. Note that $u_0 = (1/\sqrt{N}) \sum_{k=0}^{N-1} r_k$ holds, so that

$$R^2 = \frac{1}{N} \sum_{a=1}^{N-1} u_a^2 - \sum_{k,l=0}^{N-1} \sum_{a,b=1}^{N-1} m_k^a m_l^b u_a u_b - 2u_0 \frac{\sqrt{N}}{N^2} \sum_{l=0}^{N-1} \sum_{a=1}^{N-1} m_l^a u_a . \tag{2}$$

However, the last term vanishes again because of the zero eigenvector property:

$$\sum_{l=0}^{N-1} \sum_{a=1}^{N-1} m_l^a u_a = \sum_{l=0}^{N-1} \sum_{a=0}^{N-1} m_l^a u_a - \sum_{l=0}^{N-1} m_l^0 u_0 = \sum_{l=0}^{N-1} r_l - \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} \sqrt{N} \, r_k = 0 . \tag{3}$$

Hence the squared radius of gyration R^2 is independent of u_0, as it should be, and is given by (4).

References

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     see also Bunde A and Havlin S (eds) 1991 *Fractals and Disordered Systems* (Berlin: Springer)
[9] Note the difference between the spectral and the fractal (Hausdorff) dimensions of an object. Even if the
     spectral dimension is an integer, as for a linear chain $d_s = 1$, the fractal dimension may differ (random
     walk: $d_f = 2$, excluded volume chain in $d = 3$: $d_f \simeq \frac{5}{3}$), a fact used in applications, see Sokolov I M,
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