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Unfold dynamics of generalized Gaussian structures

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We consider the unfold dynamics of generalized Gaussian structures (GGSs) exposed to different kinds of external forces. A GGS consists of N monomers connected by harmonic springs into a network; when its spectral dimension d_s exceeds the critical value of 2 the GGS is in a collapsed state. Sommer and Blumen [J. Phys. A **28**, 6669 (1995)] showed that collapsed structures can be unfolded under external forces; they demonstrate this for the case where each monomer is exposed to a force with a random direction: Then networks with a spectral dimension up to 4 become unfolded. In the present paper we focus on the dynamics of such unfold processes. We investigate GGSs exposed to different kinds of external forces (pulling one monomer, uncorrelated forces, long-range correlated forces, and diblocklike forces). We show that external perturbations that act only on a few monomers are not able to unfold a collapsed structure; on the other hand, more general kinds of forces lead to a stretching of GGSs even for $d_s > 2$ as long as $d_s < d_c$, where d_c depends on the kind of the force field. In general, during the unfold process the size R of the GGS grows via a power law $R \propto t^\alpha$ $(0 \leqslant \alpha \leqslant 1)$, where α depends on d_s as well as on the kind of force field that is applied.
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I. INTRODUCTION

The theoretical investigation of the conformational and dynamical properties of flexible polymers often proceeds from a very simplified model, the Rouse model [1,2]. In this model the polymer is considered as being a sequence of beads connected via harmonic (entropic) springs (Gaussian chain); the chain incessantly changes its shape due to thermal agitation. Though this model disregards many features of a physical chain (e.g., the excluded volume effect, hydrodynamic interactions, and topological effects) it leads in a series of cases (e.g., semidilute solution and melts below the entanglement limit) to a reasonable description of the physical situation [2]. Moreover, due to its simplicity, the model serves in many cases as a first step towards the theoretical formulation and the understanding of polymers in a great variety of environments. Thus, recently a series of works was devoted to the investigation of single polymer chains under different kinds of external forces, namely, polymers in solvent flows [3,4] and charged chains (polyampholytes) in external electrical fields [5,6]. For these cases many conformational and dynamical features were calculated analytically in the framework of the Rouse model.

It is now tempting to augment these investigations to objects that show a more general connectivity, namely, to the so-called generalized Gaussian structures (GGSs), which are generalizations of the Gaussian chain. GGSs may serve as simplified models for membranes, gels, and polymer networks. Note that GGSs do not account for intermolecular interactions, i.e., whether excluded volume or entanglement effects are taken into account. However, in dry polymer networks the excluded volume may be screened (similarly to polymer melts [2,7]); furthermore, entanglement effects should be quite small for sufficiently high cross-link densities and thus short enough network chains. In the present paper we assume the GGS to be an isotropic and locally homogeneous fractal network. Huge fractal macromolecules are expected to be formed during gelation processes (cf., for instance, the percolation model discussed in Ref. [7]). Cates [8] showed that the radius of gyration of such networks obeys

$$R_g^2 \approx b^2 N^{(2-d_s)/d_s} \quad \text{for } d_s < 2 \tag{1}$$

(see also Ref. [9]). Here N denotes the number of beads and b is the mean distance between adjacent beads. d_s is the spectral dimension of the network (see, for instance, Refs. [10,11]); in the case of a regular object, d_s equals the Euclidean dimension. Equation (1) is valid for $d_s < d_c = 2$; on the other hand, for $d_s > d_c$ the radius of gyration is of the order of b, i.e., the overall size of the network is governed by its local properties (collapsed state) [9].

This collapse transition sheds also a light on some recent works on polymer localization [12–14]. Thus Solf and Vilgis [13] and Kantor and Kardar [14] considered the behavior of a one-dimensional Gaussian chain comprising N monomers in which in addition M randomly selected pairs of monomers are restricted to be in contact. They showed that the radius of gyration scales as $R_g^2 \approx b^2 N/M$. Thus the structure is in a collapsed state (with $R_g \approx b$) when M is of the order of N, i.e., when the number of bonds of the resulting structure is of the order $N + M \approx 2N$. Note that for a square lattice (‘‘membrane’’) that obeys $d_s = d_c = 2$ the number of bonds is also approximately $2N$.

The collapsed state of GGSs with $d_s > 2$ is physically not meaningful and the behavior of real networks and membranes will then usually be governed by other effects such as the excluded volume. However, it was shown by Sommer and Blumen [9] that the application of external forces may unfold collapsed GGSs; thus a random force field leads to an unfolding of GGSs with spectral dimensions up to 4. This example shows that the interplay between the chain connectivity (represented by one parameter, the spectral dimension) and the external perturbation can lead to an unfolded structure, even beyond $d_s=2$. In such cases GGSs may serve as useful network models even beyond this critical dimension. It is the purpose of the current paper to investigate the rich dynamical and conformational behavior of GGSs under different kinds of external forces and to calculate the decisive role of the force field on the dimension d_c up to which the collapsed state can be unfolded. We start in the next section with the case when one applies a force on one given monomer of the GGS; by means of this simple example we introduce the model and the appropriate calculation methods. Then, in Secs. III and IV we consider different kinds of random force fields as well as blocklike forces.

II. PULLING ONE MONOMER

In this section we calculate dynamical and conformational properties of networks for the case that an external force acts on one given monomer. Recent optical developments allow one to realize such micromanipulations of macromolecules. Thus Perkins *et al.* [15] and Wirtz [16] have dragged individual DNA molecules by optical or magnetic tweezers; Amblard *et al.* [17] have performed similar experiments with magnetic beads in actin networks.

We model the network as a GGS consisting of N beads, connected by harmonic springs. The configuration of the GGS is given by the set of vectors $\{\mathbf{r}_n(t)\}$, where $\mathbf{r}_n(t)=(x_n(t),y_n(t),z_n(t))$ denotes the position of the nth bead at time t; $n=1,\ldots,N$. The potential energy $U(\{\mathbf{r}_n(t)\})$ of the GGS contains only the elastic contributions of neighboring segments and of the external force that acts on one monomer, say the kth one. This leads to

$$\begin{aligned}U(\{\mathbf{r}_n(t)\})&=\frac{K}{2}\sum_{\{i,j\}\in\mathcal{B}}[\mathbf{r}_i(t)-\mathbf{r}_j(t)]^2-\mathbf{f}(t)\mathbf{r}_k(t)\\&=\frac{K}{2}\sum_{i,j=1}^{N}\mathbf{r}_i(t)\mathbf{M}_{ij}\mathbf{r}_j(t)-\mathbf{f}(t)\mathbf{r}_k(t),\end{aligned}\tag{2}$$

where the summation extends over all pairs $\{i,j\}$ of the set of bonds $\mathcal{B}$ between the N monomers. In Eq. (2) $K=3T/b^2$ is the (entropic) spring constant, where T denotes the temperature in units of the Boltzmann constant k_B and b is the mean distance between neighboring beads. Furthermore, we introduce in Eq. (2) $\mathbf{M}_{ij}=(M_{ij},M_{ij},M_{ij})$, where M_{ij} is an element of M, the so-called generalized Gaussian Rouse matrix (GRM) [18–20]. M can be constructed as follows: Start with all matrix elements set to zero. Then account for each bond between the monomers n and m by increasing the diagonal elements M_{nn} and M_{mm} by $+1$ and the nondiagonal elements M_{nm} and M_{mn} by -1. For a linear structure (i.e., a polymer chain) this procedure leads to a tridiagonal matrix, which is the well-known Rouse matrix [1].

The dynamics of the GGS is described by N coupled Langevin equations, the generalized Rouse equations [8,20–22]

$$\zeta\,\frac{\partial\mathbf{r}_n(t)}{\partial t}=-\frac{\partial U(\{\mathbf{r}_n(t)\})}{\partial\mathbf{r}_n(t)}+\varphi(n,t).\tag{3}$$

Here ζ is the friction constant per monomer and $\varphi(n,t)$ is the thermal noise that mimics the collisions of the nth bead with the solvent molecules. The thermal noise is Gaussian (white) with zero mean, so that one has

$$\langle\varphi_i(n,t)\rangle=0,\quad\langle\varphi_i(n,t)\varphi_j(n',t')\rangle=2\zeta T\delta_{ij}\delta_{nn'}\delta(t-t').\tag{4}$$

In Eq. (4) i and j denote the components of the force vector, i.e., $i,j=X,Y,Z$, and the angular brackets stand for thermal averaging, i.e., averaging over the realizations of the Langevin forces $\varphi(n,t)$. From Eqs. (2) and (4) it follows that Eq. (3) decouples in the X, Y, and Z directions. Hence, in the following we can restrict ourselves to one component, say the X component, which obeys

$$\frac{\partial x_n(t)}{\partial t}=-\frac{K}{\zeta}\sum_m M_{nm}x_m(t)+\frac{1}{\zeta}f(t)\delta_{nk}+\frac{1}{\zeta}\varphi_X(n,t),\tag{5}$$

where we set $\mathbf{f}(t)=(f(t),0,0)$.

The solution of Eq. (5) is given by

$$\begin{aligned}x_n(t)=&\frac{1}{\zeta}\int_{-\infty}^{t}d\tau\sum_m\,(e^{-(K/\zeta)M(t-\tau)})_{nm}f(\tau)\delta_{mk}\\&+\frac{1}{\zeta}\int_{-\infty}^{t}d\tau\sum_m\,(e^{-(K/\zeta)M(t-\tau)})_{nm}\varphi_X(m,\tau)\end{aligned}\tag{6}$$

(cf. also Ref. [20]). From Eq. (6) we find that the mean-averaged position of the kth monomer (on which the external force acts) obeys $\langle x_k(t)\rangle=(f/\zeta)\int_0^t d\tau(e^{-(K/\zeta)M\tau})_{kk}$, where we assumed that the force is switched on at $t=0$, i.e., $f(t)=f\theta(t)$. By further performing the average over k (structural average) we obtain

$$\begin{aligned}\langle\langle x(t)\rangle\rangle&=\frac{f}{\zeta N}\sum_0^t\,d\tau\ \mathrm{Tr}(e^{-(K/\zeta)M\tau})\\&=\frac{f}{\zeta N}\int_0^t d\tau\sum_{k=1}^{N}e^{-(K/\zeta)\lambda_k\tau}.\end{aligned}\tag{7}$$

Thus the average displacement of the bead on which the force is applied follows from the trace of the matrix $e^{-(K/\zeta)M\tau}$, which equals the sum over its eigenvalues $e^{-(K/\zeta)\lambda_k\tau}$. Here $\{\lambda_k\}$, with $k=1,\ldots,N$, denotes the set of eigenvalues of the GRM M.

For large N it is convenient to transform in Eq. (7) the sum over k into an integral over λ by introducing the spectral density $n(\lambda)$ of M. This leads to

$$\langle\langle x(t)\rangle\rangle\simeq\frac{f}{\zeta}\int_0^t d\tau\int_0^\infty d\lambda\,n(\lambda)e^{-(K/\zeta)\lambda\tau}.\tag{8}$$

The spectral density reflects the connectivity of the GGS; for isotropic and locally homogeneous fractals $n(\lambda)$ obeys a power law [11]

$$n(\lambda)\simeq\lambda^{d_s/2-1},\tag{9}$$

i.e., here the connectivity of the network is characterized by one parameter, the spectral dimension d_s. The use of a continuous spectrum in Eq. (8) is reasonable as long as $\lambda_{\max}^{-1}\ll(K/\zeta)t\ll\lambda_{\min}^{-1}$. Here $\lambda_{\max}$, the largest eigenvalue of M, is determined by the local network properties and is of order unity [20]. Furthermore, the smallest nonvanishing eigenvalue is given by $\lambda_{\min} \simeq N^{-2/d_s}$ (cf., for instance, Ref. [8]). For $d_s < 2$ this can be seen by the following simple argument: The minimal nonvanishing eigenvalue $\lambda_{\min}$ is inversely proportional to the time t it takes a random walker to explore the whole fractal lattice that has N sites [note that Eq. (3) is directly related to the master equation for a random walker on the corresponding lattice; see, for instance, Ref. [23]]. Now the number $S(t)$ of different sites visited by the random walker grows with time as

$$S(t) \simeq (T/\zeta b^2)^{d_s/2} t^{d_s/2} \tag{10}$$

for $d_s < 2$ [10,11]. Setting $S(\tau_G) = N$ one obtains

$$\tau_G \simeq \zeta b^2 N^{2/d_s}/T \tag{11}$$

and thus indeed $\lambda_{\min} = (\zeta b^2/T)\tau_G^{-1} \simeq N^{-2/d_s}$.

In order to calculate $\langle\langle x(t)\rangle\rangle$ for $\zeta/K \ll t \ll \tau_G$ we insert the spectral density (9) into Eq. (8). For $d_s < 2$ this leads to

$$\langle\langle x(t)\rangle\rangle \simeq \frac{f}{\zeta}\left(\frac{\zeta}{K}\right)^{d_s/2} \int_0^t d\tau\, \tau^{-d_s/2} \simeq \frac{f b^{d_s}}{\zeta^{1-d_s/2} T^{d_s/2}}\, t^{1-d_s/2}. \tag{12}$$

Thus, in this time range the displacement of the tagged bead follows a power law with an exponent that decreases with increasing d_s. In the case of a one-dimensional chain, i.e., for $d_s = 1$, $\langle\langle x(t)\rangle\rangle$ shows a $t^{1/2}$-subdrift behavior, a result that was reported in Ref. [5].

For $d_s \geqslant 2$ the integral in Eq. (12) diverges at the lower bound; note, however, that for very short times $t \ll \zeta/K = \zeta b^2/T$ the behavior of the GGS is governed by its local properties. Thus let us introduce ζ/K as a lower cutoff. For $d_s > 2$ this leads to

$$\begin{aligned}\langle\langle x(t)\rangle\rangle &\simeq x_0 + \frac{f}{\zeta}\left(\frac{\zeta}{K}\right)^{d_s/2} \int_{\zeta/K}^t d\tau\, \tau^{-d_s/2} \\ &= x_0 + \frac{f b^2}{T} - \frac{f b^{d_s}}{\zeta^{1-d_s/2} T^{d_s/2}}\, t^{1-d_s/2},\end{aligned} \tag{13}$$

where x_0 denotes the bead's displacement at the time ζ/K, i.e., $x_0 = \langle\langle x(\zeta/K)\rangle\rangle$. For $d_s = 2$ one finds a logarithmic time dependence. We note that in the force-free case the mean-squared displacement of a single bead shows similar behavior patterns [24].

Before we provide a physical interpretation of these results, we calculate the short- and long-time behavior of $\langle\langle x(t)\rangle\rangle$. As mentioned above, the continuous description of the spectrum in Eq. (8) is not valid for $t < \zeta/K$ and $t > \tau_G$ and we have to go back to the exact formula, Eq. (7). We consider here only the case of connected objects so that only one eigenvalue vanishes, say λ_1; thus

$$\langle\langle x(t)\rangle\rangle = \frac{f}{\zeta N}\, t + \frac{f}{NK} \sum_{k=2}^{N} \frac{1 - e^{-(K/\zeta)\lambda_k t}}{\lambda_k}. \tag{14}$$

For $t \ll \zeta/K$ this leads to $\langle\langle x(t)\rangle\rangle \simeq (f/\zeta)t$. On the other hand, for long times $t \gg \tau_G$ Eq. (14) takes the form $\langle\langle x(t)\rangle\rangle \simeq (f/\zeta N)t + L$, where the time-independent term is given by

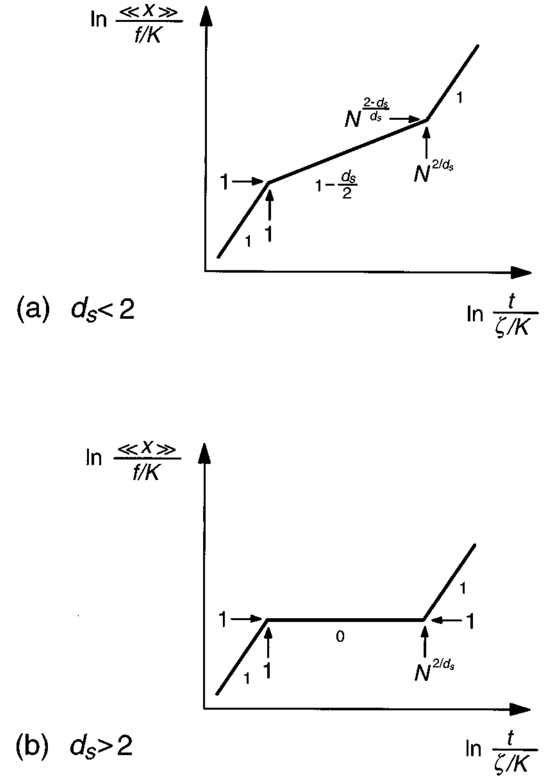

FIG. 1. Response of a GGS with (a) $d_s < 2$ and (b) $d_s > 2$ to an external force that acts on one given monomer. Schematically depicted is the displacement of the tagged monomer as a function of time (see the text for details).

$$\begin{aligned} L &\simeq \frac{f b^2}{T} \int_{\lambda_{\min}}^{\lambda_{\max}} d\lambda\, \lambda^{d_s/2-2} \\ &\simeq \begin{cases} \dfrac{f b^2}{T}\lambda_{\min}^{d_s/2-1} \simeq \dfrac{f b^2}{T} N^{(2-d_s)/d_s} & \text{for } d_s < 2 \\ \dfrac{f b^2}{T}\lambda_{\max}^{d_s/2-1} \simeq \dfrac{f b^2}{T} & \text{for } d_s > 2\,. \end{cases} \end{aligned} \tag{15}$$

Note that depending on the value of d_s, the lower or the upper bound of the integral in Eq. (15) determines the behavior of L.

Let us now survey and discuss the results. In Fig. 1(a) for the case $d_s < 2$ the displacement of the tagged bead is plotted logarithmically against time. For very small times $t \ll \zeta/K$ the bead does not "feel" any constraints that arise from the connection to neighboring beads. It moves ballistically with the constant velocity $v = f/\zeta$; see below Eq. (14). Then, in the intermediate-time regime more and more beads are involved in a collective motion; consequently, the velocity of the tagged monomer decreases with time, following a $t^{-d_s/2}$ behavior; cf. Eq. (12). Note that this time domain is very broad for large N. Finally, at $t = \tau_G$ the motion of the tagged bead crosses over into a small drift motion [see above Eq. (15)]. The velocity obeys $v = f/\zeta N$, which follows from the balance between the external force f and the friction ζN of the whole GGS, i.e., for $t > \tau_G$ the whole network moves ballistically and the tagged bead mirrors the motion of the center of mass. Note further the time-independent term (15). It represents the equilibrium value of the stretching of the

GGS due to the external force and follows from the summation over the $1/\lambda_k$ values. It can also be obtained by setting $t=\tau_G$ in Eq. (12). The stretching leads to an $N^{(2-d_s)/d_s}$ dependence of the size of the GGS, which is significantly larger than the typical size in the force-free case, which is proportional to $N^{(2-d_s)/2d_s}$ [cf. Eq. (1)].

In Fig. 1(b) we depict the case $d_s>2$. The behavior for very short times $t\ll\zeta/K$ and long times $t\gg\tau_G$ is again governed by the ballistic motion of the tagged bead and of the whole network, respectively. On the other hand, in the intermediate-time regime $\zeta/K\ll t\ll\tau_G$ one has a very small displacement of the bead: At $t=\zeta/K$ one finds $\langle\langle x(t)\rangle\rangle \simeq f/K$; see below Eq. (14); then, during the following intermediate regime the tagged monomer moves only a distance f/K [cf. Eq. (13)], which is of the *same* order as the elongation at $t=\zeta/K$. Thus the conformation at $t=\tau_G$ is still governed by the *local* properties of the network. Now, as noted above, GGS with $d_s>2$ are collapsed in the force-free case. Our considerations show that it is not sufficient to pull at one monomer in order to unfold the collapsed structure.

We give now a scaling argument from which Eq. (12) follows directly (cf. also Ref. [26]). As already discussed above, the generalized Rouse equation is formally equivalent to a diffusion equation on the corresponding fractal lattice. For $d_s<2$ the number $S(t)$ of different sites visited by a random walker grows with time following Eq. (10). In the framework of the Rouse dynamics, $S(t)$ can be interpreted as being the number of monomers that move collectively with the tagged bead. The domain that moves collectively has the velocity $v(t)=[\zeta S(t)]^{-1}f$. The average displacement of the single bead can be estimated from the average displacement of the $S(t)$ monomers, i.e., $x(t)\simeq\int_0^t d\tau\, v(\tau)$, which (for $d_s<2$) leads again to Eq. (12). Note that Eq. (10) is valid as long as the network does not move as a whole. At later times $t>\tau_G$, $g(t)=N$ holds and we recover the drift motion of the c.m. with $v=f/\zeta N$. The crossover time τ_G can be interpreted as being the largest internal relaxation time of the GGS. We close this section by noting that the above-given considerations also hold for the case when one applies external forces to a group of g monomers as long as $g\ll N$ (a situation that occurs in a class of rheological experiments [27]).

III. UNCORRELATED FORCE FIELD

In this section we assume that each monomer is exposed to a constant force with a random direction independently from the force directions of the neighboring monomers. Denote by f_k the force on the kth monomer; the force on each monomer is taken to be directed either in the positive or in the negative X direction, i.e., $f_k=\pm f$. Then one has

$$\langle f_n f_m\rangle = f^2\delta_{nm}, \tag{16}$$

where the angular brackets denote the average with respect to different realizations of $\{f_k\}$. Polyampholytic networks in external electrical fields and copolymers or networks of copolymers at interfaces are examples of such kinds of external perturbations [29].

Following the preceding section [cf. Eqs. (2)–(6)], we find for the displacement of the kth bead after switching on the force field at $t=0$

$$\langle x_k(t)\rangle = \frac{1}{\zeta}\int_0^t d\tau \sum_m \left(e^{-(K/\zeta)M\tau}\right)_{km} f_m, \tag{17}$$

where the angular brackets denote the thermal average. Here we are interested in the mean-squared displacement. Taking the square of Eq. (17), then averaging over k, and, finally, averaging over the different realizations of $\{f_n\}$ leads to

$$\begin{aligned}\langle\langle\langle x(t)\rangle^2\rangle\rangle &= \frac{1}{\zeta^2 N}\int_0^t d\tau_1\int_0^t d\tau_2 \\ &\quad\times\sum_{m,n}\left(e^{-(K/\zeta)M(\tau_1+\tau_2)}\right)_{mn}\langle f_n f_m\rangle \\ &= \frac{f^2}{\zeta^2 N}\int_0^t d\tau_1\int_0^t d\tau_2\sum_{k=1}^{N} e^{-(K/\zeta)\lambda_k(\tau_1+\tau_2)}.\end{aligned} \tag{18}$$

Similarly to Sec. II, we calculate now the intermediate-time behavior $\zeta/K\ll t\ll\tau_G$ by going to a continuous distribution of the eigenvalues. For $d_s<2$ this leads to

$$\begin{aligned}\langle\langle\langle x(t)\rangle^2\rangle\rangle &\simeq \frac{f^2}{\zeta^2}\left(\frac{\zeta}{K}\right)^{d_s/2}\int_0^t d\tau_1\int_0^t d\tau_2(\tau_1+\tau_2)^{-d_s/2} \\ &= \frac{f^2 b^{d_s}}{\zeta^{2-d_s/2}T^{d_s/2}}\, t^{2-ds/2}.\end{aligned} \tag{19}$$

For $d_s=1$ one recovers the $t^{3/2}$ dependence that was found in Ref. [5].

Now Eq. (19) is also valid for $2\leqslant d_s<4$. This can be seen by introducing a small positive cutoff ε at the lower bound of the integral over τ_2; one finds then the displacement to be proportional to $(2t)^{2-d_s/2}-\varepsilon^{2-d_s/2}$ so that for $d_s<4$ the behavior for very short times can be neglected. For $d_s\geqslant 4$, however, the displacement shows a strong dependence on ε; here we introduce, similarly to Eq. (13), ζ/K as a lower cutoff for both integrations in Eq. (19). This leads to

$$\langle\langle\langle x(t)\rangle^2\rangle\rangle \simeq \frac{f^2}{K^2}\left[1-\left(\frac{K}{\zeta}t\right)^{2-d_s/2}\right]. \tag{20}$$

The behavior for $t\ll\zeta/K$ and $t\gg\tau_G$ can be calculated similarly to Sec. II by treating in Eq. (18) the contribution of the vanishing eigenvalue separately. For $t\ll\zeta/K$ one finds a mean-squared displacement that goes as $(f^2/\zeta^2)t^2$; this corresponds to the single-bead drift that we already discussed below Eq. (14). Furthermore, the long-time behavior $t\gg\tau_R$ obeys $\langle\langle\langle x(t)\rangle^2\rangle\rangle\simeq(f^2/\zeta^2 N)t^2+L^2$. We find, similarly to Sec. II, that the long-time behavior has two contributions: a drift motion (here, however, by a factor $N^{1/2}$ larger, which follows from the fact that the typical total force is of the order $N^{1/2}$) and a time-independent stretching term, which represents the typical equilibrium size L of the stretched network:

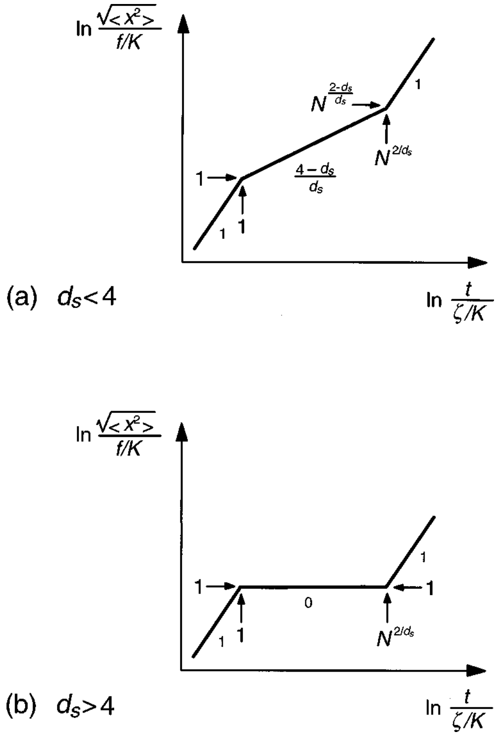

FIG. 2. Response of a GGS with (a) $d_s<4$ and (b) $d_s>4$ to an uncorrelated force field. Depicted is the mean-squared displacement of a single monomer averaged over the different realizations of the force field (see the text).

$$L^2 \cong \frac{f^2}{K^2}\int_{\lambda_{\min}}^{\lambda_{\max}} d\lambda\, \lambda^{d_s/2-3} \simeq \begin{cases} (f^2b^4/T^2)\lambda_{\min}^{(d_s-4)/2} \simeq (f^2b^4/T^2)N^{(4-d_s)/d_s} & \text{for } d_s<4 \\ (f^2b^4/T^2)\lambda_{\max}^{(d_s-4)/2} \simeq f^2b^4/T^2 \quad \text{for } d_s>4, \end{cases} \tag{21}$$

a result that was already found by Sommer and Blumen [9]. For the one-dimensional chain one has $L^2 \propto N^3$ [5,31] (cf. also Ref. [34]). From Eq. (21) it can be seen that the random force field is able to unfold collapsed GGSs as long as $d_s < d_c = 4$. Hereby the unfold dynamics follows the power law (19); setting $t = \zeta b^2/T\lambda_{\min}$, one recovers Eq. (21). On the other hand, in order to unfold a GGS with $d_s > 4$ it is not sufficient to apply an uncorrelated force field [cf. Eqs. (20) and (21)]. In Fig. 2 we display the dynamics of a single bead for both cases $d_s<4$ and $d_s>4$.

It can be seen from Eq. (21) that for $d_s<4$ the external force may lead to a quite strong stretching of the GGS. Due to its linearity, the model of entropic Gaussian forces will fail for large external perturbations, resulting in an unphysical overstretching. Hence we are led to the condition that the size of the stretched network (21) is smaller than the size of the completely unfolded structure $L \approx N^{1/d_s}$. This leads to the requirement $f < (T/b)N^{(2-d_s)/2d_s}$. Thus, for $d_s > 2$ the external force may be quite strong without contradicting the Gaussian assumption. Explicit studies of the role of the finite extensibility for one-dimensional chains can be found in Refs. [35, 36].

Let us try now to derive the power law (19) through a scaling argument similar to that presented at the end of Sec. II. For a given monomer the number $S(t)$ of neighboring beads that move collectively with it is given by Eq. (10) for $d_s \leq 2$. The typical total force that acts on these $S(t)$ beads is of the order $f\sqrt{N}$. The typical velocity $v(t)$ of this collectively moving group is thus of the order $[\zeta\sqrt{S(t)}]^{-1}f$. Inserting now Eq. (10) for $d_s<2$ and integrating the velocity over t leads to Eq. (19), the power law that we have found by the more rigorous calculation. Now we have shown above that Eq. (19) is also valid for $2 \leq d_s < 4$. For $d_s>2$, however, $S(t)$ obeys $S(t) \propto t$ [instead of $S(t) \propto t^{d_s/2}$; the number of different sites visited by a random walker can at least grow linearly with time]. So here the spectral dimension does not enter into the scaling expression, contrary to the explicit d_s dependence of Eq. (19).

IV. CORRELATED FORCE FIELDS AND THE DIBLOCK SITUATION

Keeping this intricacy in mind, we use the above-given scaling argument in order to estimate the behavior of GGSs that are exposed to more general kinds of random force fields, namely, force fields with long-range correlations (cf. also Ref. [26]). Assume that the forces are distributed in such a way that the total force f_{tot} obeys $\langle f_{\text{tot}}^2 \rangle \cong f^2 N^{2\gamma}$, with $0 \leq \gamma \leq 1$. The case $\gamma = \frac{1}{2}$ corresponds to the uncorrelated case discussed above, whereas for $\gamma > \frac{1}{2}$ the forces are positively and for $\gamma < \frac{1}{2}$ negatively correlated. Note that the cases $\gamma = \frac{1}{2}$ and 1 can be simply realized, whereas long-ranged (anti)correlations cannot be simply induced for many nontrivial connectivities. Using Eq. (10), one finds with $v(t) \simeq [S(t)]^{\gamma-1} f/\zeta$ that the displacement for $d_s<2$ is given by

$$x(t) \simeq \frac{f}{\zeta}\left(\frac{\zeta b^2}{T}\right)^{(1-\gamma)d_s/2} t^{1-(1-\gamma)d_s/2}. \tag{22}$$

Equation (22) is also valid for the range $2 \leq d_s < d_c$, where d_c depends on γ (see below). The equilibrium value of the typical size R_g of the GGS in the force field is reached at $t = \tau_G$; using Eq. (11) we find

$$R_g \simeq x(\tau_G) \simeq (fb^2/T)N^{[2-(1-\gamma)d_s]/d_s} \quad \text{for } d_s < d_c. \tag{23}$$

Equation (23) suggests that the correlated force field is able to unfold the structure up to the critical dimension

$$d_c = \frac{2}{1-\gamma}. \tag{24}$$

We show now that this conjecture holds for three different cases. (i) For $\gamma = \frac{1}{2}$ Eq. (24) leads indeed to $d_c = 4$ (see Sec. III). (ii) The case $\gamma = 0$ corresponds to the alternating case, which can be realized for linear chains, square lattices, cubic lattices, etc. In this case the forces of two neighboring monomers cancel each other. However, one additional force acts similarly to the case where one applies a force only to one monomer and thus leads only to a stretching of networks with $d_s < 2$ (i.e., $d_c = 2$; cf. Sec. II) [37]. (iii) $\gamma \to 1$. In this case one has very long-ranged correlations. A typical force distribution consists of a few, say two, parts of groups where all forces act in the same direction. We discuss now this diblock case and show that $d_c \to \infty$, which is consistent with Eq. (24).

We start with the one-dimensional case where all monomers of one half of the chain are exposed to forces in the positive X direction and of the other half in the negative X direction (‘‘tug of war’’). In a simplified picture the polymer may be interpreted as a dumbbell exposed to a force of order fN; furthermore, since one has N sequential springs, the effective spring constant is $K_{\mathrm{eff}}=K/N$. This results in an elongation $R \simeq fN/K_{\mathrm{eff}}=(f/K)N^2$, which is consistent with the result of the exact calculation, Eq. (21) of Ref. [31]. Now let us turn to a square lattice ($d_s=2$) that is exposed to a diblocklike force field. Here one has $N^{1/2}$ rows, each composed of $N^{1/2}$ sequential springs, which counteract the external tension. Furthermore, one has $N^{1/2}$ columns, each comprising $N^{1/2}$ springs that are perpendicular to the force field so that we can neglect them for the current consideration. The effective spring constant of the structure is now $K_{\mathrm{eff}} = N^{1/2}K/N^{1/2}=K$, whereas the force is again of the order fN. Thus the typical size of the stretched membrane is given by $R \simeq fN/K_{\mathrm{eff}}=(f/K)N$.

This argument can be easily extended to hypercubic lattices of arbitrary integer dimension $d_s \geqslant 1$. One finds then that the effective spring constant is given by $K_{\mathrm{eff}} = N^{(d_s-1)/d_s}K/N^{1/d_s}=KN^{(d_s-2)/d_s}$. Thus the size of stretched structure is given by $R \simeq fN/K_{\mathrm{eff}}$, which leads to

$$R \simeq (f/K)N^{2/d_s}. \tag{25}$$

We conjecture that this relation also holds for fractal networks with noninteger d_s values. As can be seen from Eq. (25), a diblocklike force field can unfold collapsed structures of any given spectral dimension, i.e., here one has indeed $d_c \to \infty$.

Let us now discuss the unfold dynamics in the diblock situation. After switching on the field, a given monomer and, typically, also the monomers in the neighborhood feel a force in the same direction. Thus all monomers move ballistically with a velocity $v=f/\zeta$. The typical displacement of the given monomer is thus given by

$$x(t) \simeq (f/\zeta)t. \tag{26}$$

After the time τ_G the two groups that move collectively in opposite directions will feel the connectivity of the overall structure and the stretching process stops. It follows indeed from Eqs. (25) and (26) that the new (internal) equilibrium is reached at $\tau_G \propto \lambda_{\mathrm{min}}^{-1} \propto N^{2/d_s}$.

We close this section by noting that this simple picture also holds for the general case of correlated force fields. Consider again a regular d_s-dimensional cubic lattice with $K_{\mathrm{eff}}=KN^{(d_s-2)/d_s}$. In the correlated case the typical force that acts on the structure is of the order fN^{γ}. From $R \simeq fN^{\gamma}/K_{\mathrm{eff}}$ we recover Eq. (23).

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[1] P. E. Rouse, J. Chem. Phys. **21**, 1272 (1953).

[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[3] G. Oshanin and A. Blumen, Phys. Rev. E **49**, 4185 (1994).

[4] W. Carl, Macromol. Theory Simul. **5**, 1 (1996).

[5] H. Schiessel, G. Oshanin, and A. Blumen, J. Chem. Phys. **103**, 5070 (1995).

[6] H. Schiessel, G. Oshanin, and A. Blumen, Macromol. Theory Simul. **5**, 45 (1996).

[7] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[8] M. E. Cates, Phys. Rev. Lett. **53**, 926 (1984); M. E. Cates, J. Phys. (Paris) **46**, 1059 (1985).

[9] J.-U. Sommer and A. Blumen, J. Phys. A **28**, 6669 (1995).

[10] D. Dhar, J. Math. Phys. **18**, 577 (1977); S. Alexander and R. Orbach, J. Phys. (France) Lett. **43**, L625 (1983); R. Hilfer and A. Blumen, J. Phys. A **17**, L537 (1984).

[11] S. Havlin and A. Bunde, in *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer, Berlin, 1991), p. 97.

[12] J. D. Bryngelson and D. Thirumalai, Phys. Rev. Lett. **76**, 542 (1996); Y. Kantor and M. Kardar, *ibid.* **77**, 4275 (1996); M. P. Solf and T. A. Vilgis, *ibid.* **77**, 4276 (1996); J. D. Bryngelson and D. Thirumalai, *ibid.* **77**, 4277 (1996).

[13] M. P. Solf and T. A. Vilgis, J. Phys. A **28**, 6655 (1995); M. P. Solf and T. A. Vilgis, J. Phys. I **6**, 1451 (1996).

[14] Y. Kantor and M. Kardar, Phys. Rev. E **54**, 5263 (1996).

[15] T. T. Perkins, D. E. Smith, and S. Chu, Science **264**, 819 (1994); T. T. Perkins, D. E. Smith, R. G. Larson, and S. Chu, *ibid.* **268**, 83 (1995).

[16] D. Wirtz, Phys. Rev. Lett. **75**, 2436 (1995).

[17] F. Amblard, A. C. Maggs, B. Yurke, A. N. Pergellis, and S. Leibler, Phys. Rev. Lett. **77**, 4470 (1996).

[18] B. E. Eichinger and J. E. Martin, J. Chem. Phys. **69**, 4595 (1978).

[19] W. W. Graessley, Macromolecules **13**, 372 (1980).

[20] J.-U. Sommer, M. Schulz, and H. Trautenberg, J. Chem. Phys. **98**, 7515 (1993).

[21] M. Muthukumar, J. Chem. Phys. **83**, 3161 (1985).

[22] M. P. Solf and T. A. Vilgis, Phys. Rev. E **55**, 3037 (1997).

[23] H. Schiessel and A. Blumen, Macromolecules **28**, 4013 (1995).

[24] In the force-free case one finds from Eqs. (4) and (6), with $f \equiv 0$, $\langle [x_n(t)-x_n(0)]^2 \rangle = (2T/\zeta)\int_0^t d\tau (e^{-(2K/\zeta)M\tau})_{nn}$. By performing an average over n and introducing the spectral density $n(\lambda)$, we find for the mean-squared displacement of a single bead $\langle\langle [x(t)-x(0)]^2 \rangle\rangle \simeq (T/\zeta)\int_0^t d\tau \int d\lambda\, n(\lambda) e^{-(2K/\zeta)\lambda\tau}$, an expression that is very similar to Eq. (8). Accordingly, the

mean-squared displacement obeys $(T/\zeta)^{1-d_s/2}b^{d_s}t^{1-d_s/2}$ for $d_s<2$ and const$-(T/\zeta)^{1-d_s/2}b^{d_s}t^{1-d_s/2}$ for $d_s>2$; for $d_s=2$ one has a logarithmic time dependence. These results are in accordance with recent molecular-dynamics simulations of regular lattices with $d_s=1$, 2, and 3 [25]. During the time τ_G each monomer explores the whole volume of the GGS; for $d_s<2$ one finds indeed $\langle\langle[x(\tau_G)-x(0)]^2\rangle\rangle\simeq b^2N^{(2-d_s)/d_s}\simeq R_g^2$ [cf. Eq. (1)].

[25] P. Licinio and A. V. Teixeira, Phys. Rev. E **56**, 631 (1997).

[26] H. Schiessel, C. Friedrich, and A. Blumen, in *Applications of Fractional Calculus in Physics*, edited by R. Hilfer (World Scientific, Singapore, in press).

[27] Consider a shear experiment that probes the mechanical properties of a viscoelastic sample, say cross-linking polymers at the sol-gel transition. The plate (on which the force is applied) may act only on a small part of the overall network. In this case Eq. (12) suggests a shear compliance $J(t)$ that goes as $t^{1-d_s/2}$ [and, consequently, a relaxation modulus of the form $G(t)\propto t^{d_s/2-1}$; we assume here $d_s<2$]. Now, during the gelation process, which is, of course, directly related to the establishment of a more and more connected topological structure, one should expect an increasing d_s and thus a decreasing exponent of $J(t)$ [23], a fact that is indeed observed experimentally [26,28].

[28] F. Chambon and H. H. Winter, J. Rheol. **31**, 683 (1987).

[29] Consider a polyampholytic network where each monomer carries a charge $\pm q$; when one applies an external electrical field (pointing in the X direction) each monomer is exposed to a force $f=\pm qE$. Note that our theory does not include electrostatic interactions between the monomers. Experimentally, this may be realized through not-too-large networks with a sufficiently low density ρ of charges; then the thermal fluctuations dominate and the electrostatic interactions between the monomers can be neglected. A rough estimation can be given in the framework of the Debye-Hückel approximation, which has been successfully applied to linear polyampholytes [30,31] and networks [32]. Consider a network with zero net charge that is prepared with no counterions. Comparing the Debye-Hückel screening length $\kappa^{-1}\approx\sqrt{R_g^3/\rho N l_B}$ of the charged monomers and the size of the unperturbed network, Eq. (1), one finds that the electrostatic interactions can be neglected as long as $b>\rho N^{(3d_s-2)/2d_s}l_B$ $(d_s<2)$. $l_B=q^2/\varepsilon T$ denotes the Bjerrum length, with ε being the dielectric constant; in water ($\varepsilon\simeq 80$) at room temperature $l_B\approx 7$ Å. A similar situation occurs when one has a random A-B copolymer (or network) at the interface between two immiscible homopolymers A and B. The concentration profile at the A-B interface may show an extended gradient region [33] where the monomers of the copolymer will feel forces in different directions.

[30] P. G. Higgs and J. F. Joanny, J. Chem. Phys. **94**, 1543 (1991).

[31] H. Schiessel and A. Blumen, Macromol. Theory Simul. **6**, 103 (1997).

[32] J. P. Baker, H. W. Blanch, and J. M. Prausnitz, Polymer **36**, 1061 (1995).

[33] K. Binder, J. Chem. Phys. **79**, 6387 (1983).

[34] A. V. Dobrynin, M. Rubinstein, and J.-F. Joanny, Macromolecules **30**, 4332 (1997).

[35] H. Schiessel and A. Blumen, J. Chem. Phys. **104**, 6036 (1996).

[36] R. G. Winkler and P. Reineker, J. Chem. Phys. **106**, 2841 (1997).

[37] This remarkable dependence of the overall size of the structure on one single monomer was discussed for one-dimensional chains (alternating polyampholytes) in Ref. [35]; see also [36].