

Relaxation of disordered polymer networks: Regular lattice made up of small-world Rouse networks

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As models for inhomogeneous polymer networks, we investigate the Rouse dynamics of regular lattices built from subunits with arbitrary internal structure. We analyze as an example a two-dimensional lattice, consisting of small-world networks (SWNs). Using analytical and numerical calculations we study the stretching of such a structure under an external force. We find that the network shows interesting relaxation features and an unusual behavior in the intermediate time (frequency) domain, which lies in the region between the modes of the SWN subunits and those of the lattice. This behavior is related to the SWN-density of states, which leads to the appearance of a “pseudogap” between the highest lattice eigenvalue and the lowest SWN eigenvalue. © 2001 American Institute of Physics. [DOI: 10.1063/1.1395562]

I. INTRODUCTION

Polymer networks are a very important class of materials. Due to numerous technological applications, understanding the structural and dynamical properties of polymer networks is a problem of long standing.¹⁻⁷ A very intriguing challenge is to deduce how the topology of the network affects its dynamical properties.⁸⁻¹⁰ Because cross-linking often occurs randomly, real polymer networks are disordered. This fact makes the theoretical treatment of the dynamics of polymer networks extremely difficult. Up to now the main theoretical approaches have concentrated on model systems, such as percolating lattices,^{11,12} on simple topologies, such as Cayley trees (realizations are dendrimeric molecules)^{10,13,14} and on regular lattices with inclusions (decorations).¹⁵⁻¹⁸

Small-angle neutron scattering experiments have shown that in statistical gels the local density of crosslinks varies widely.^{19,20} Moreover, dynamic and static light scattering experiments on hydrogels²¹⁻²³ have also revealed highly heterogeneous structures. We are thus interested in having network models which are very inhomogeneous, but whose dynamical properties are readily accessible. For this we prefer to work in the framework of generalized Gaussian structures (GGS),^{24,25} which are extensions of the classical Rouse model.^{26,27}

Recently, a new class of GGS, the so-called small-world Rouse networks (SWRN) has emerged.²⁸ SWRN are based on the small-world networks (SWNs) introduced by Watts and Strogatz,²⁹ which mimic the properties of social systems; SWNs are built from an underlying ordered lattice, to which one adds additional bonds between randomly chosen pairs of points.²⁹⁻³⁵ SWRN are the GGS based on SWN, by which the sites of the structure are interpreted as Rouse beads. SWRN are of great theoretical interest since they are an extension of the basic linear Rouse model, in which the ad-

ditional SWN links create *loops*; the ensuing GGS are distinct from the *trees* (GGS examples are the dendrimers), structures which are devoid of loops.

On the other hand we note that the SWRN approach captures only part of the story since the long-range structure of real polymer networks is (distinct from their medium-scale structure) rather homogeneous. This fact is reflected in the appearance of a nonzero value for their equilibrium modulus.³⁶ A simple way to take into account this large-scale relatively homogeneous connectivity is to “decorate” the bonds of a regular lattice (say square or cubic) by replacing the bonds with polymeric segments (subunits); in this way the sites of the lattice become the crosslinks of the network.

In previous work one has taken the subunits to be Rouse chains;¹⁵⁻¹⁸ in this paper we let the subunits be SWRN.²⁸ In this way we are led to networks which have on small scales a highly-connected, disordered structure (SWRN), and which are on large scales quite regular.¹⁵⁻¹⁸ This allows us to study the interplay between ordered and disordered features, as well as to highlight the connection between topology and dynamics.

We note that recently the micromanipulation of polymers has become possible; the procedures consist in using optical tweezers or in applying external fields on specific charged monomers or on magnetic beads.³⁷⁻⁴⁰ In this way one can selectively move parts of the network. Here we study the displacements of a bead on which an external force acts; as we proceed to show, this reveals important aspects of the network's dynamics.

II. POLYMER NETWORKS UNDER EXTERNAL FORCES

We perform our study in the framework of the Rouse model^{26,27} and its GGS-extension.^{24,25} The GGS consist of

beads connected to each other by springs (with elasticity constant K) and subject to the friction constant ζ . In the Langevin framework, the position vector $\mathbf{r}_l(t)$ of the l th bead of the GGS, subject to the external force $\mathbf{F}_l(t)$ obeys

$$\zeta \frac{d\mathbf{r}_l(t)}{dt} + K \sum_{m=1}^{N_{\text{tot}}} A_{lm} \mathbf{r}_m(t) = \mathbf{F}_l(t) + \zeta \mathbf{w}_l(t), \quad (1)$$

where $\mathbf{A} = \{A_{lm}\}$ is the connectivity matrix of the GGS (see Refs. 10 and 24 for details), $\zeta \mathbf{w}_l(t)$ is the thermal noise (here assumed to be Gaussian, with zero mean-value), and N_{tot} is the total number of elements (beads) in the system considered. The linear system of difference-differential equations Eq. (1) can be completely solved through the diagonalization of the matrix \mathbf{A} (see, e.g., Ref. 10), a procedure which involves in general determining both the eigenvalues and the eigenfunctions of \mathbf{A} . For simplicity we focus here only on the stretching (extension) of the GGS under a constant external force $\mathbf{F}(t) = F\theta(t)$, switched on at $t=0$ and acting only on a single bead, say the l th, in the y -direction. As shown in Refs. 10 and 28, the displacement of the bead along the y -direction, $Y(t)$, reads after averaging both over the fluctuating forces $\mathbf{w}_l(t)$ and over all the beads of the GGS,

$$Y(t) = \frac{F}{\zeta N_{\text{tot}}} t + \frac{F\tau_0}{\zeta} \frac{1}{N_{\text{tot}}} \sum_{i=2}^{N_{\text{tot}}} \frac{1 - \exp(-\lambda_i(t/\tau_0))}{\lambda_i}. \quad (2)$$

This expression is very simple, it involves *only* the eigenvalues λ_i (but not the eigenvectors) of the connectivity matrix \mathbf{A} . We thus prefer to present our results concerning regular lattices decorated with SWRN in terms of the (quite visual) $Y(t)$ -functions, rather than plotting the (rather abstract) densities $\rho(\lambda)$ of eigenvalues. Now the first term in Eq. (2) corresponds to the displacement $Y_{\text{CM}}(t)$ of the center of mass (CM) of the network as a whole. The sum in the second term is to be taken over all eigenvalues of the system with the exception of the zero-eigenvalue, $\lambda_1 = 0$, and it corresponds to the stretching of the GGS. As we show below, the problem of determining the eigenvalues λ_i of a regular lattice decorated with identical subunits can be reduced to calculating the eigenvalues of a related problem, involving only the subunit and phase shifts due to the lattice.

III. REGULAR LATTICE CONSISTING OF SUBUNITS

In this section we develop a general approach to treat the dynamics of a GGS, consisting of a regular lattice whose vertices are connected by identical subunits of (at first) arbitrary topology. This regularity allows us (based on previous works¹⁵⁻¹⁸) to simplify the problem using Floquet's theorem (whose special case in solid state physics is Bloch's theorem⁴¹⁻⁴³). In Refs. 15-18 the relaxation behavior of networks built out of Rouse chain subunits was determined analytically. As it was shown,¹⁵⁻¹⁸ for Rouse-chain subunits the relaxation spectrum displays two different, characteristic regions, corresponding to small-scale (intrachain) and to large-scale (interchain) motion. The intrachain part of the spectrum reproduces that of single Rouse chains closely; furthermore, on scales larger than the subunit size, the network shows almost pure lattice modes.¹⁵⁻¹⁸

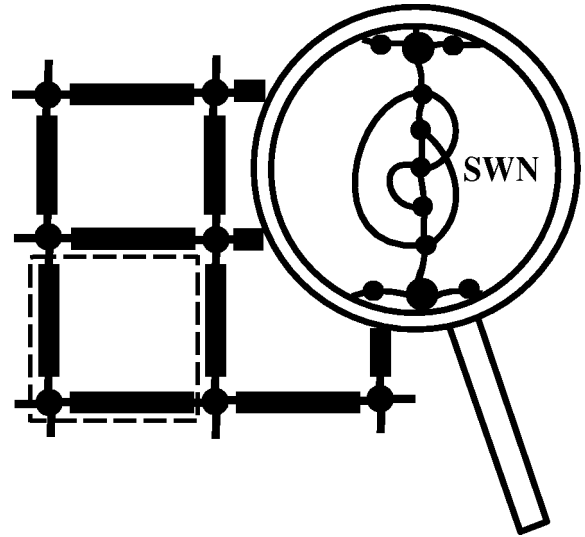


FIG. 1. Two-dimensional regular lattice consisting of subunits between lattice junctions. The subunits here are small-world Rouse networks (see magnifying glass) and a Bravais unit cell is indicated by dashed lines.

Returning to our general case here, we focus on a (topologically) two-dimensional square lattice of vertices connected by subunits containing n beads each (see Fig. 1). We denote the elementary cell of our lattice by a two-component index $\Omega = (\alpha, \beta)$; α and β range from 1 to N . Here such a cell contains a vertex and 2 subunits, i.e., it consists of $s = 2n + 1$ beads, which we number through j , $1 \leq j \leq s$. Our network then consists of sN^2 beads, numbered as $(j, \Omega) \equiv (j, \alpha, \beta)$. In this way we have in Eq. (1),

$$\begin{aligned} \sum_{m=1}^{N_{\text{tot}}} A_{lm} \mathbf{r}_m(t) &= \sum_{i=1}^s \sum_{\Omega''} A_{j\Omega_i \Omega''} \mathbf{r}_{i\Omega''}(t) \\ &= \sum_{i=1}^s A_{j\Omega_i \Omega} \mathbf{r}_{i\Omega}(t) \\ &\quad + \sum_{i=1}^s \sum_{\substack{\Omega'' \\ \Omega'' \neq \Omega}} A_{j\Omega_i \Omega''} \mathbf{r}_{i\Omega''}(t), \end{aligned} \quad (3)$$

where $l \rightarrow (j, \Omega)$ and $m \rightarrow (i, \Omega'')$. Due to obvious symmetries, by setting $B_{ji}^{(\text{int})} \equiv A_{j\Omega_i \Omega}$ and, with $\Omega' = \Omega - \Omega''$, $B_{ji}^{(\text{ext})}(\Omega') \equiv B_{ji}^{(\text{ext})}(\Omega - \Omega'') \equiv A_{j\Omega_i \Omega''}$ in Eq. (3) leads to

$$\begin{aligned} \sum_{m=1}^{N_{\text{tot}}} A_{lm} \mathbf{r}_m(t) &= \sum_{i=1}^s B_{ji}^{(\text{int})} \mathbf{r}_{i\Omega}(t) \\ &\quad + \sum_{i=1}^s \sum_{\Omega'} B_{ji}^{(\text{ext})}(\Omega') \mathbf{r}_{i\Omega-\Omega'}(t). \end{aligned} \quad (4)$$

In Eq. (4) the matrix $\mathbf{B}^{(\text{int})} = \{B_{ji}^{(\text{int})}\}$ is the connectivity matrix inside the cell of s beads, whereas the matrix $\mathbf{B}^{(\text{ext})}(\Omega') = \{B_{ji}^{(\text{ext})}(\Omega')\}$ gives the intercell connections. The nonzero elements of the matrices $B_{ji}^{(\text{ext})}(\Omega')$ are equal to $(-l)$, where l is the total number of connections between the bead j of a cell Ω and the bead i of a cell $\Omega' \neq \Omega$. In our special situation the sum over Ω' in Eq. (4) runs only over the nearest-neighboring cells. In the 2D square network con-

sidered here a given cell $\Omega = (\alpha, \beta)$ is connected to the four neighboring cells: $(\alpha-1, \beta)$, $(\alpha+1, \beta)$, $(\alpha, \beta-1)$, and $(\alpha, \beta+1)$, so that $\Omega' \in \{(1,0), (-1,0), (0,1), (0,-1)\}$.

As before, we are looking for the eigenvalues of the \mathbf{A} -matrix. Now, due to the symmetry inherent in Eq. (4), the diagonalization of Eq. (1) simplifies. In fact one may proceed very formally; here, however, since we want to show qualitative features only, we simply use periodic boundary conditions for our GGS (the Born–von Kármán situation of solid state physics) and seek the solutions of Eq. (1) combined with Eq. (4) in the form,

$$\mathbf{r}_{j\Omega}(t) \equiv \mathbf{r}_{j\alpha\beta}(t) = \sum_{k_1, k_2} \mathbf{C}_j \exp[i(k_1\alpha + k_2\beta)] \times \exp(-\lambda(\mathbf{k})t/\tau_0) \quad (5)$$

(here i denotes the imaginary unit), with

$$k_1 = \frac{2\pi m_1}{N} \quad \text{and} \quad k_2 = \frac{2\pi m_2}{N}, \quad (6)$$

where the integers m_1 and m_2 range from 0 to $(N-1)$, $\tau_0 = \zeta/K$ is a characteristic relaxation time, and the \mathbf{C}_j are constants.

The symmetry of Eqs. (4)–(6) is very reminiscent of solid state physics, but should not be taken literally, since only topological (connectivity) features enter here. Equation (4) under periodic boundary conditions is invariant under shifts in the indices Ω . In the polymeric framework this is not necessarily related to a translational invariance in real space, given that our network can take a very tortuous geometrical shape. In the same spirit, in solid state physics $\mathbf{k} = (k_1, k_2)$ is (apart from a constant with dimension of an inverse length) the two-component wave vector; for us here \mathbf{k} simply counts the eigenvalues (modes).

The exponential term in Eq. (5) gives the phase shift between lattice cells; $\lambda(\mathbf{k})$ are the different eigenvalues, to be determined as functions of \mathbf{k} . Inserting Eqs. (4) and (5) into Eq. (1) and using the symmetries mentioned above leads to

$$\lambda(\mathbf{k})\mathbf{C}_j = \sum_{i=1}^s B_{ji}(\mathbf{k})\mathbf{C}_i. \quad (7)$$

Here $\mathbf{B} = \{B_{ji}(\mathbf{k})\}$ can be viewed as a new connectivity matrix of an elementary cell,

$$B_{ji}(\mathbf{k}) = B_{ji}^{(\text{int})} + \sum_{\Omega'} B_{ji}^{(\text{ext})}(\Omega') \exp[-i\mathbf{k}\Omega']. \quad (8)$$

In Eq. (8), $B_{ji}(\mathbf{k})$ now includes all information concerning the topology inside each cell and the way in which the cells of the lattice are connected to each other. Thus, based on Eq. (7), the problem of obtaining the eigenvalues of the \mathbf{A} -matrix, which is a $(sN^2 \times sN^2)$ -matrix, is reduced to the problem of determining only the eigenvalues of N^2 different $(s \times s)$ -matrices, evaluated for the N^2 values of \mathbf{k} , given in Eq. (6). Note that the derivation of Eq. (7) is very general and holds for arbitrary topological structures of the subunits between the lattice vertices. Also the 2D square lattice considered here is only a particular example of a regular lattice.

Our approach can be easily generalized to other lattice types and to higher dimensions. Given this remark, we now proceed with our study based on Eq. (7) and focus on small-world Rouse networks (SWRN) as lattice subunits.

IV. RELAXATION OF A 2D REGULAR LATTICE BUILT FROM SWRN

First of all, we recall some important properties of small-world networks (SWNs). A SWN is obtained by connecting sites of a regular lattice randomly through additional links (see Refs. 28–35). Thus SWNs are intermediate between regular lattices and random graphs.^{29,30} On the one hand, a SWN has well-defined local clusters, provided by the underlying regular lattice. On the other hand, already a small amount of additional links strongly reduces the minimal distances between the lattice points. One intriguing property³³ of SWNs built from linear chains consists in the appearance of a so-called “pseudogap” in the density of states, $\rho(\lambda)$, which goes as

$$\rho(\lambda) \sim \lambda^{-1/2} \exp\left(-\frac{\text{const}}{\lambda^{1/2}}\right) \quad (9)$$

for small λ 's. Equation (9) means that the probability to find eigenvalues of the SWN very close to $\lambda=0$ is extremely small.

Here we take such 1D SWRN to be our subunits and we study the stretching of a 2D lattice composed of such subunits; see Fig. 1. We follow the SWRN construction of Ref. 28, with the exception that we start from a linear Rouse chain, but not from a ring: The initial linear Rouse chain consists of n beads connected by elastic springs.^{26,27} Then we connect (by means of springs) with probability q/n each bead of the chain in a random way to some other bead. In this way beads distant from each other along the macromolecular backbone may get (due to the additional bonds) close in space. Finally, we insert these SWRN as subunits into a 2D square lattice.

The numerical procedure is as follows: We use as 2D lattice a $N \times N$ square, with $N=20$, and take for each lattice realization identical SWRN subunits consisting of $n=200$ beads. The SWRN then depends on q and on the specific realization of the SWN. In this way the matrix \mathbf{A} is known; however we need, according to the previous section, only to determine the corresponding $B_{ji}(\mathbf{k})$; see Eq. (8), and their eigenvalues for different \mathbf{k} . Using standard routines for diagonalization of symmetric matrices⁴⁴ we find $s=(2n+1)$ eigenvalues for each \mathbf{k} .

We are now ready to calculate the displacement $Y(t)$, based on Eq. (2), and we perform it for several situations. However, to get an idea of how differences in the SWRN realizations influence the results we start to calculate $Y(t)$ for isolated SWRN (not yet embedded in the lattice). We focus on $q=0.5$ and consider 10 different realizations of the SWRN. Then we use the two extremal $Y(t)$ plots to determine the “worst” SWRN realizations. These are then used as subunits of the 2D lattice, for which we again evaluate $Y(t)$.

In Fig. 2 we plot in double logarithmic scales the reduced (dimensionless) displacement $Y^*(t) = Y(t)\zeta/F\tau_0$ as a

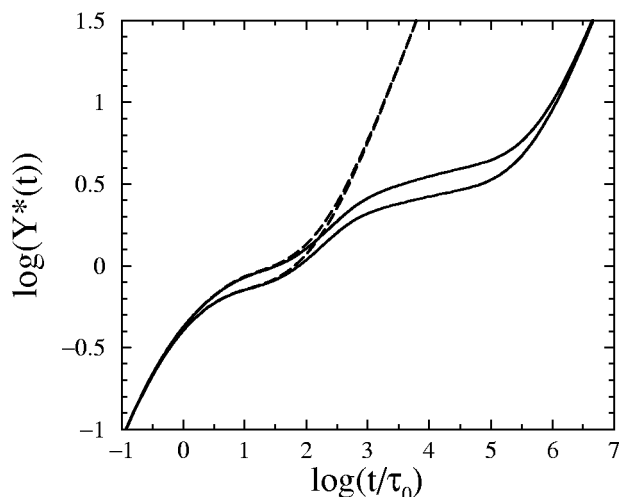


FIG. 2. The reduced average displacement $Y^*(t)$ plotted in double logarithmic scales vs the reduced time t/τ_0 . Shown are results for the two extreme realizations (from ten) for SWRN with $n=200$ and $q=0.5$; see text for details. The dashed lines give the situation for the individual SWRN (not embedded in the lattice), whereas the solid lines correspond to the full network (2D lattice with SWRN-subunits).

function of the reduced time t/τ_0 for these two “worst” cases. The dashed lines in Fig. 2 give $Y^*(t)$ for the isolated SWRNs and the solid lines the $Y^*(t)$ corresponding to the full networks. As is evident, the differences between the curves of the extremal cases are rather small and the shapes of the curves are very similar for the two realizations. Moreover, the curves for $Y^*(t)$ for isolated SWRNs reproduce very closely the results obtained in Ref. 28. The curves corresponding to the full networks (GGs) clearly show the existence of several domains: these are related to the motion of single beads, to the motion of individual SWRN, to an intermediate domain, and to the dynamics of the underlying lattice, followed by the motion of the whole network. As usual, the very short-time (very high-frequency) dynamic behavior of the network is determined by the motion of single beads which do not yet “feel” the connectivity of the GGS. The very long-time (very low-frequency) dynamics is given by the displacement of the GGS as a whole, $Y_{CM}(t) = Ft/\zeta N^2 s$. The plots in Fig. 2 make it possible to differentiate clearly the purely SWRN-dynamics (dashed lines) from the dynamics of the networks of which they are subunits (solid lines); the dashed lines show at longer times the drift motion of individual SWRN. Due to the fact that n , the number of beads in SWRN, is the same in both realizations, these curves merge at large t . The same holds true for the full network dynamics, whose curves merge at extremely long times. Also very clear to see from Fig. 2 is that the spread in the network’s $Y^*(t)$ -curves can be directly attributed to the individual SWRN-realizations underlying the particular GGS. Now the spread in the individual SWRN’s $Y^*(t)$ -curves is due mainly to the difference in the number of additional links introduced in each realization of the SWRN (remember that q fixes only their *average* number). For Fig. 2 we counted the additional links of the SWRN involved and found that the top (bottom) curves correspond to SWRN with 89 (108) additional links; it is clear therefore

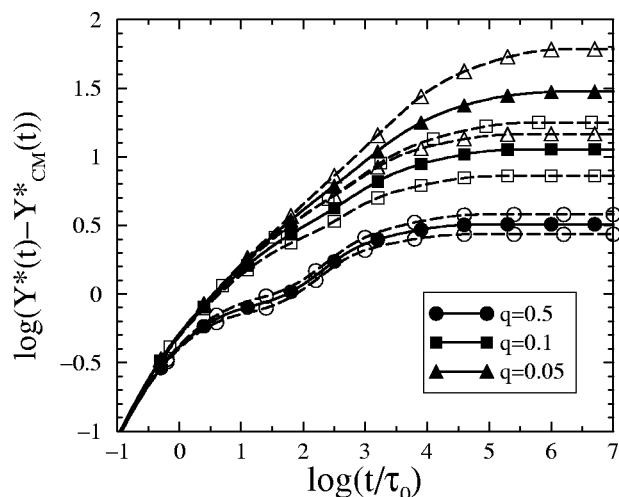


FIG. 3. The dimensionless displacement $Y^*(t) - Y_{CM}^*(t)$ vs the reduced time t/τ_0 in double logarithmic scales for several GGS. The networks are built from SWRN-subunits where the parameter q is 0.5 (circles), 0.1 (squares), and 0.05 (triangles). The dashed lines exhibit the spread given by the extreme cases; see text for details.

that these two SWRN subunits have different rigidity. Note from Fig. 2 that the spread between the two solid curves is larger in the domain of the lattice modes than in the isolated SWRN-domain (note the logarithmic scales); through the embedding into the lattice such differences are enhanced.^{15–18}

In Fig. 3 we plot the “stretch”⁴⁵ $Y^*(t) - Y_{CM}^*(t)$ of the GGS considered here for the two “worst” cases out of 10 SWRN realizations, while we vary q from 0.05 to 0.5. With decreasing q the curves become smoother, but the spread due to different SWRN realizations increases. This finding reflects the growing importance of fluctuations for small q . Furthermore, since with decreasing q a SWRN becomes more flexible, the global network relaxes more slowly, so that the stretch increases.

To gain a better understanding of the dynamic processes going on in the network we plot in Fig. 4 for one specific SWRN realization with $q=0.8$ the average bead displacement $Y^*(t)$ for the particular SWRN, for the same SWRN but with fixed end points (clamped), and for the whole network (2D lattice with SWRN subunits). Parallel to it we also show the stretch $Y^*(t) - Y_{CM}^*(t)$ of the free SWRN. This allows us to sort out the different dynamic processes: Thus, after an initial time in which we see the individual motion of the beads, there follows a regime corresponding to the internal relaxation of SWRN, roughly up to times of about $\sqrt{10}\tau_0$. After this domain ends, the individual SWRN do not yet feel the 2D-lattice structure, fact giving rise to a “quasi-plateau” behavior. The existence of this domain is related to the previously discussed “pseudogap” in eigenvalues, only that now the “pseudogap” is between the minimal nonvanishing SWRN eigenvalue and the maximal eigenvalue of the 2D lattice modes. In this regime the GGS dynamics lies between that of the SWRN with free and frozen CM (given that through embedding the CM-displacement gets hindered), i.e., it tends to a flatter form. We note that the “pseudogap” situation renders the network dynamics here (where the sub-

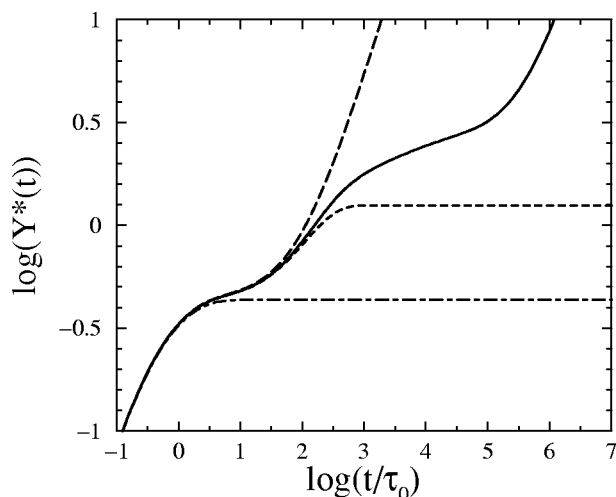


FIG. 4. The dimensionless displacement $Y^*(t)$ vs the reduced time t/τ_0 in double logarithmic scales for $q=0.8$. Displayed are: a single, free SWRN (long dashes), the same, but with fixed ends (short dashes), and the corresponding, 2D-decorated GGS (solid line). The dotted-dashed line corresponds to the stretch $Y^*(t) - Y_{CM}^*(t)$ of the same SWRN.

units are SWRN) drastically different from that of systems with Rouse-chain subunits; in that case the curves are quite smooth.^{17,18} Following this range (in Fig. 4 from times around $10^2 \tau_0$ to around $10^3 \tau_0$) there exists an intermediate regime corresponding to the combined dynamics of the SWRN subunits and of the 2D lattice. Now $Y^*(t)$ lies between the situation for the free and for the clamped SWRN, but closer to the latter. At longer times there appears a cross-over domain corresponding to the dynamics of the 2D lattice, a domain which extends up to the region of the pure CM-drift, at which times the whole internal information about the GGS is lost.

The discussion thus far has centered on $Y^*(t)$. As related quantities we mention now the dynamic moduli. Thus the characteristic regimes found here under stretching have their counterparts in the storage and loss moduli. For instance, due to the “pseudogap” discussed above, the storage modulus $G'(\omega)$ shows a plateau-type behavior in the frequency domain which extends from the highest lattice modes to the lowest modes of the SWRN.

V. CONCLUSIONS

Our main goal was to understand the role of strong structural inhomogeneities on the dynamic properties of materials. To this purpose we introduced generalized Gaussian structures (GGS), which make it possible to combine local disorder and mesoscopic order; we obtained the GGS by decorating regular lattices with subunits of arbitrary internal topology. As examples of such GGS we focused on the stretching of a 2D square lattice built from SWRN subunits. We found that the dynamic properties of such networks are very sensitive to disorder and that they differ from those found for regular structures built from simple Rouse chains.^{17,18} Thus for SWRN subunits we found for $Y^*(t)$ a plateau-type behavior in the time region lying between the internal SWRN modes and the modes of the lattice. This behavior is related to the appearance of the “pseudogap” in

the SWRN density of states. Related effects are also mirrored in the mechanical and dielectrical relaxation forms, whose detailed study we defer to a later publication.

On a cautionary note, we would like to stress that GGSs reflect the dynamics of polymer systems which are not very far from equilibrium; they cannot be used in treating nonlinear processes. Furthermore, a more realistic treatment must include excluded volume aspects, which lead to the problem of the role of entanglements, to be treated using tube-model ideas; see Ref. 46 for recent calculations. In the present work we wanted to stress the role of the local inhomogeneities, for which GGSs (being extensions of the Rouse model) offer a relatively easy, first-order access; nevertheless they also allow us to see interesting dynamical features, such as the ones related to the pseudogaps in the SWRN density of states.

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