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Anomalous dynamics of model polymer systems

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Abstract

Anomalous dynamics has been extensively investigated, especially in modelling energy and charge transfer. In many cases the moving objects have been assumed not to possess internal degrees of freedom. In this work, we present models in which the anomalous dynamics is due to the internal modes of the moving particles; it is expected that such features may be easily determined experimentally through either fluorescent measurements or electronic energy transfer. Depending on the system considered, scaling behavior may show up during certain time scales. Thus the motion of simple polymeric chains in dilute solutions scales; the same holds true for fractal networks, whereas the dynamics for other connected structures, such as small-world networks (SWNs) does not scale. Combining SWNs into larger, more regular structures again leads to scaling at longer times; we display this by embedding SWNs into 2D regular superstructures. © 2001 Elsevier Science B.V. All rights reserved.

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Regular diffusion is characterized (in the absence of external fields) by a linear increase of the mean-square displacement with time. For anomalous diffusion the temporal evolution of the mean-square displacement is non-linear, often obeying the scaling (algebraic) law [1–4]

$$\langle R^2(t) \rangle \sim t^\gamma \quad (1)$$

with $\gamma \neq 1$. In the presence of a constant, external field (say, oriented along the y -axis), Eq. (1) is often equivalent to [5–7]

$$\langle Y(t) \rangle \sim t^\gamma, \quad (2)$$

where we put $\mathbf{R} = (X, Y, Z)$. In the case $\gamma < 1$ one denotes the behavior as subdiffusive. For point-

like, moving objects Eqs. (1) and (2) are often due to disorder [1–3]; for polymeric materials—modelled as beads (monomers) connected by springs—the motion of the beads often obeys Eq. (1), even in the absence of disorder; this fact is related to internal relaxation processes of the structure [4,5,8]. Furthermore, also non-scaling behavior, which does not obey Eq. (2), may show up. We depict this aspect based on small-world networks (SWN), which we introduce in the following. We also consider embedding such SWNs into regular, larger scale structures. First, however, we discuss generalized Gaussian structures (GGS).

For simplicity, we describe polymeric materials through the Rouse model [5,8,9] and its extension to GGS [10–15]. A GGS consists of beads immersed in a fluid and hence subject to friction

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

$$\zeta \frac{d\mathbf{r}_l(t)}{dt} + K \sum_{m=1}^N A_{lm} \mathbf{r}_m(t) = \mathbf{F}_l(t) + \zeta \mathbf{w}_l(t), \quad (3)$$

where $\mathbf{A} = \{A_{lm}\}$ is the connectivity matrix of the GGS ($A_{lm} = 0$ if l and m are not connected, see Refs. [10–15] for details), $\zeta \mathbf{w}_l(t)$ is the thermal noise (here assumed to be Gaussian, with zero mean-value), and N is the total number of GGS beads. The linear system of Eq. (3) is solved by determining both the eigenvalues λ_i and the eigenfunctions of \mathbf{A} . Now we let a constant force F act (from $t=0$ on) on one of the GGS beads in the y -direction. The displacement $Y(t)$ of the bead, averaged over all possible points of attack of F and over the thermal noise is [11,12,16]

$$\langle Y(t) \rangle = \frac{F}{\zeta N} t + \frac{F\tau_0}{\zeta} \frac{1}{N} \sum_{i=2}^N \frac{1 - \exp(-\lambda_i(t/\tau_0))}{\lambda_i}. \quad (4)$$

In Eq. (4) $\tau_0 = \zeta/K$, and we took the zero eigenvalue to be λ_1 . Now $\lambda_1 = 0$ is associated with the motion of the centre of mass, $\langle Y_{\text{CM}}(t) \rangle = Ft/(\zeta N)$. Evidently, from Eq. (4) at very long times $\langle Y(t) \rangle = \langle Y_{\text{CM}}(t) \rangle$, whereas at very short times, $\langle Y(t) \rangle \simeq Ft/\zeta$. These features are very general and independent of the spectrum of the eigenvalues; the particular GGS structure under consideration (and thus information about its structural matrix \mathbf{A}) shows up only at intermediate times. Both $\langle Y(t) \rangle$ and also the stretch $\langle \delta Y(t) \rangle = \langle Y(t) \rangle - \langle Y_{\text{CM}}(t) \rangle$ can be amenable to study using fluorescent techniques, $\langle Y(t) \rangle$ by tracking, $\langle \delta Y(t) \rangle$ by energy transfer between fluorescent groups attached to the polymer. In this way one has mesoscopic probes for the microscopic dynamics of the GGS under study.

In what $\langle Y(t) \rangle$ is concerned, we consider first two special GGS structures. A linear, finite chain obeys at short and medium times

$$\langle Y(t) \rangle \simeq \frac{F}{\sqrt{\zeta K}} t^{1/2}, \quad (5)$$

i.e. Eq. (2) with $\gamma = 1/2$. For GGS whose underlying structures are regular fractals of spectral dimension $d_s < 2$ one finds in the same time-range [6,17]:

$$\langle Y(t) \rangle \sim \frac{F}{\zeta^{1-d_s/2} K^{d_s/2}} t^{1-d_s/2}, \quad (6)$$

i.e., again scaling with $\gamma = 1 - d_s/2$ in Eq. (2).

Scaling, however, is not always obeyed; as previously shown for star polymers and for dendrimeric structures [7,12,18] in the intermediate time domain one may find complex $\langle Y(t) \rangle$ and $\langle \delta Y(t) \rangle$ behaviors, which reflect the topological structure of the GGS under study. To avoid repetition of these results, we focus here on other GGSs, namely on structures of much recent interest, the SWNs [16,19,20]. SWNs are obtained by attaching long-ranged additional links (AL) between the vertices (beads) of a regular lattice; in this way SWNs interpolate between regular and random lattices [19,20]. In Fig. 1 we display (inside the magnifying glass) such a SWN; the whole picture depicts a 2D lattice built from such SWNs. The SWN construction which we use here follows closely Ref. [16]: We take a finite chain and add to each bead with probability p an AL; the other end of the AL is connected to another bead of the

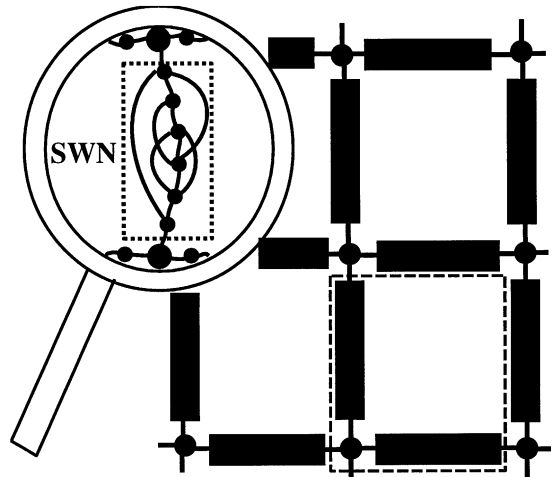


Fig. 1. Two-dimensional regular lattice built from subunits which connect the vertices of a regular lattice. Exemplarily, small-world networks (SWN) are shown as subunits (magnifying glass); a Bravais unit cell of the lattice is indicated by dashed lines.

chain, picked at random. Interestingly, the density $\rho(\lambda)$ of eigenvalues of such SWNs shows a “pseudogap” [20], i.e. the distance between the smallest non-vanishing λ_i (call it λ_2) and $\lambda_1=0$ is often fairly large. Now $\langle Y(t) \rangle$ depends via Eq. (4) directly on $\rho(\lambda)$, and the “pseudogap” situation is mirrored by $\langle Y(t) \rangle$, as we proceed to show.

To evaluate $\langle Y(t) \rangle$ we start from chains with $N=1000$ beads, and let p go from 0 (this being the simple Rouse chain) to 0.8. For each p we generate 100 SWN realizations and diagonalize the ensuing random connectivity matrices \mathbf{A} using standard routines [21]; then we compute as in Ref. [16] $\langle Y(t) \rangle$ and $\langle \delta Y(t) \rangle$ using the obtained sets of $\{\lambda_i\}$. In Fig. 2 we plot $\langle Y(t) \rangle$ for the above-mentioned set of p . For $p=0$ we recover the behavior of the Rouse chain; here $\langle Y(t) \rangle$ shows very clearly scaling domains, the subdiffusive one going as $t^{1/2}$, see Eq. (5). For $p \neq 0$ we stress that even a small departure of p from 0 affects $\langle Y(t) \rangle$; note that in the intermediate time domain $\langle Y(t) \rangle$ bends downwards from the $p=0$ case and that scaling gets lost. When p is large, $\langle Y(t) \rangle$ displays an almost flat portion, feature related to the “pseudogap” in the spectrum of \mathbf{A} ; this behavior should be readily detectable by fluorescent tracking.

To highlight the flexibility of the GGS-approach we address now the problem of large polymeric

networks, which are often heterogeneous at small distances and rather homogeneous at large ones. As a model for such networks we construct now GGSs based on regular lattices [22,23], whose connecting subunits are SWNs [24], see Fig. 1. The evaluation of the spectrum $\rho(\lambda)$ of the $\{\lambda_i\}$ is now quite straightforward because the underlying regularity allows to simplify the problem using Floquet’s (Bloch’s) theorem [24]. To fix the ideas we use finite, $M \times M$ square lattices, whose vertices are connected by subunits of n beads each; we let the $M \times M$ cells be labeled by $\Omega = (\alpha, \beta)$, and each cell consist of $s = 2n + 1$ beads. An in-depth analysis of the problem [24] shows that the eigenvalues $\{\lambda_i\}$ separate into subgroups $\lambda(\mathbf{k})$ according to $\mathbf{k} = (k_1, k_2)$, where $k_j = 2\pi m_j/M$ and $m_j \in \{0, M-1\}$; they fulfill:

$$\lambda(\mathbf{k})C_j(\mathbf{k}) = \sum_{i=1}^s B_{ji}(\mathbf{k})C_i(\mathbf{k}), \quad (7)$$

where the $B_{ji}(\mathbf{k})$ are related to the \mathbf{A} matrices discussed above through Fourier-transforms, and the $C_i(\mathbf{k})$ are the eigenvectors corresponding to the $\lambda(\mathbf{k})$. As in solid-state physics, the problem reduces from being sM^2 - to being s -dimensional. The network construction proceeds by taking a particular SWN of $n=200$ beads as subunit and setting $M=20$. We change the realization of the network by changing the particular SWN subunit; in this way the network depends on the specific SWN realization. For each network realization we determine the $B_{ji}(\mathbf{k})$ by transforming the corresponding matrix \mathbf{A} . The set of all eigenvalues is then determined using Eq. (7), by diagonalizing $\mathbf{B}(\mathbf{k})$ for M^2 different \mathbf{k} .

We are ready to calculate $\langle Y(t) \rangle$ and $\langle \delta Y(t) \rangle$, where the average includes now also the different network realizations. Now, the extension $\langle \delta Y(t) \rangle$ can be monitored, say, by attaching a fluorescent donor near the site on which the external force acts and an acceptor near the centre of the macromolecule. For short ranged interactions the change in the donor–acceptor distance while applying external forces would be clearly visible through changes in the temporal behavior of the energy decay of the donor. In Fig. 3 we depict $\langle \delta Y(t) \rangle$ for p going from $p=0$ to 0.8. Evident from Fig. 3 are

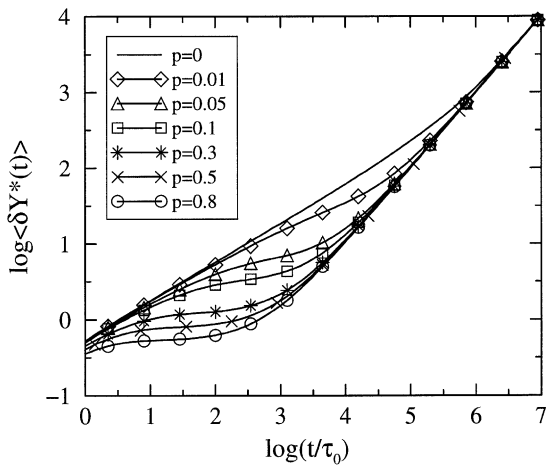


Fig. 2. Normalized displacement $\langle Y^*(t) \rangle = \langle Y(t) \rangle \zeta / (F\tau_0)$ plotted in double logarithmic scales versus the normalized time t/τ_0 , averaged over 100 SWN realizations. Here $N = 1000$ and p ranges from 0 to 0.8.

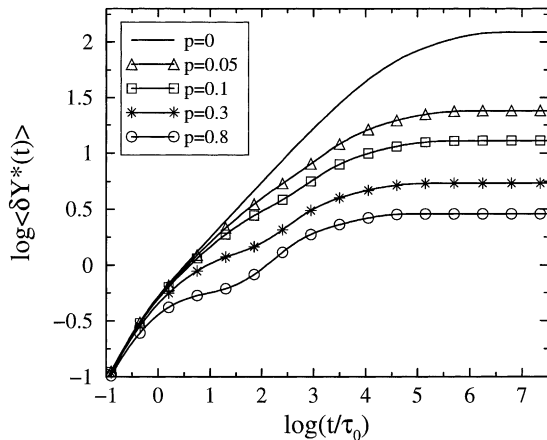


Fig. 3. Normalized stretch $\langle \delta Y^*(t) \rangle \equiv \langle Y^*(t) \rangle - \langle Y_{CM}^*(t) \rangle$ versus the normalized time t/τ_0 in double logarithmic scales, averaged over 100 realizations. The GGSs are 2D lattices built from SWN subunits, $M = 20$, $n = 200$, and p ranges from 0 to 0.8.

at short times the stretching behavior of the subunits, and at longer times the stretching of the lattice. From the many details connected to the picture, we want to stress that the “pseudogap” behavior again shows up; note with growing p the appearance of a plateau at intermediate times.

Summarizing, we have shown that the dynamics of polymers is particularly revealing of the topological connections between the monomers which form them. In several cases of wide importance, scaling behavior with time (related to anomalous diffusion) may show up. Other cases of importance do not obey scaling; the particular $\langle Y(t) \rangle$ and $\langle \delta Y(t) \rangle$ forms found for them are a mesoscopic signature of the microscopic structure. To unravel the situation, fluorescence-based techniques are very suitable; they definitely belong to the very modern instruments of the field.

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