Anomalous diffusion of ideal polymer networks

P. Licinio* and A. V. Teixeira

Departamento de Física, ICEx, UFMG, Caixa Postal 702, 30.123-970 Belo Horizonte/MG, Brazil

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Internal dynamics of swollen polymer arrays were investigated with Brownian dynamic techniques applied to regular Rouse networks. In all cases local or self-diffusion decayed as a power law with a power proportional to the given topological dimension. This behavior allows for the classification of three dynamic regimes: subcritical topologies accommodate power law anomalous diffusion; logarithmic anomalous diffusion occurs within the critical topological dimension $d_t = 2$; and upper-critical topologies siege bounded anomalous diffusion. [S1063-651X(97)13206-8]

Whenever particles in solution interact, their diffusion coefficient changes with time and eventually reaches an asymptotic simple behavior. Power law behavior has been often called anomalous diffusion and we use these words also in the same sense here. Particle diffusion in a fractal substrate is known to be anomalous and corresponding critical dynamic exponents have been estimated from theories as the effective medium approximation [1]. Diffusion of probe particles inside a static gel matrix close to percolation threshold have often been analyzed in this context [2]. Chain polymer liquids also display dynamic scaling, as given within the framework of many theories (see, for example, [3]). With this paper we bring attention to the often neglected dynamics of swollen gel networks themselves. Even homogeneous, nonfractal, polymer networks should display a broad scaling regime if one considers the entropic wandering of its flexible strands. This problem could be given the image of random walkers with links (three or more at each walker or knot to make a web). Neighbor interactions will give walkers a position persistence, i.e., their diffusion will be progressively hindered by the link topology in a nesting effect. Considering a lack of intrinsic coherence from the walkers action, their diffusion coefficient will decrease in time and with the size of the net. This kind of random walk with memory is already known to occur for linear polymers [4] and for the one dimensional lattice gas [5]. The resulting self-diffusion is anomalous with a Gaussian space-time distribution

$$P(r,t) \propto e^{-(d_e r^2)/[2\langle r^2(t)\rangle]}, \tag{1}$$

where d_e is the embedding space dimension and

$$\langle r^2(t)\rangle \propto t^{2/d_w}, \tag{2}$$

where d_w is the virtual dimension of the subdiffusive walk trace [6]. For the one dimensional lattice gas and the Rouse polymer $d_w = 4$, while for the Rouse-Zimm polymer $d_w = 3$. In concentrated regimes, reptation of polymers may occur at intermediate time scales with $d_w = 8$ [7,4]. The important class of random walks on percolation clusters is known to

have the fractal trace dimensions of $d_w = 2.87 \pm 0.01$ in two dimensions (2D) and $d_w = 5.0 \pm 0.2$ in 3D [8].

We have investigated the dynamic scaling hypothesis for networks by performing Brownian dynamics simulations, using the Langevin approach to generalized Rouse polymer gels of regular topology. The generalized Rouse gels are idealized by the ball and spring model, the balls taking place of sites and springs of bonds in the networks (Fig. 1). The spring constants are related to entropic polymer elasticity

$$k = \frac{3k_B T}{\xi^2}, \tag{3}$$

as one considers ideal phantom polymer chains of Flory radius ξ [9]. The balls (particles) concentrate the hydrodynamic drag
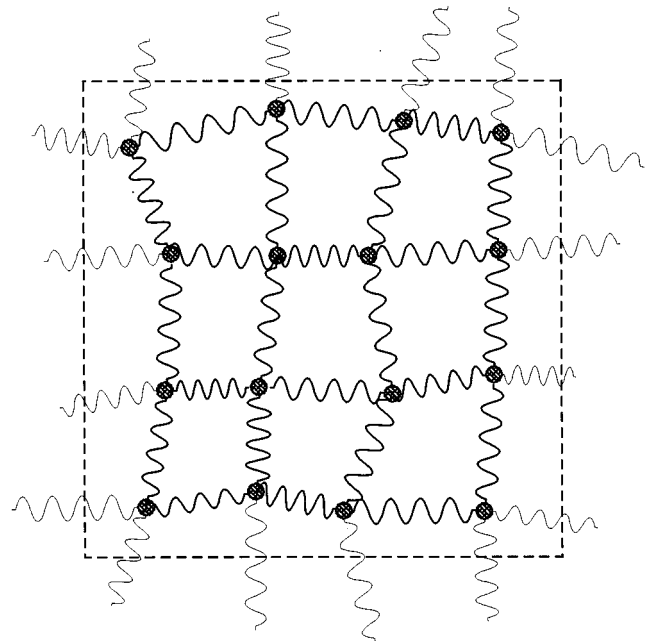

FIG. 1. Brownian dynamics of regular Rouse networks were implemented with periodic boundary conditions.

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*Electronic address: pedro@fisica.ufmg.br

$$\zeta = \frac{k_B T}{D_0}, \tag{4}$$

where D_0 is the ball free diffusion coefficient. In the spirit of Rouse's original work, steric and hydrodynamic interactions were otherwise neglected. The latter, as given by the Zimm corrections with the Oseen tensor, should produce quantitative corrections to the dynamic scaling powers. Otherwise, in concentrated dispersions, hydrodynamic interactions become highly screened [10] and the Rouse approach applies well [11,4]. This should happen for most gels to which the present approach could give the most realistic results. Finally, as we are interested only in the long time, or Brownian regime, the Langevin equation is taken without inertial terms [12]

$$\zeta \frac{\partial \vec{r}_i}{\partial t} = -k \sum_{ni} (\vec{r}_i - \vec{r}_{ni}) + \vec{f}_i, \tag{5}$$

where $\vec{f}_i$ is a δ correlated force obeying Gaussian statistics with strength

$$\langle \vec{f}_i(t) \cdot \vec{f}_j(t') \rangle = k_B T \zeta \delta_{ij} \delta(t - t'), \tag{6}$$

and the ni sum runs over the neighbors of particle i as given by network topology. We have used periodic boundary conditions for linear configurations (topological or graph dimension $d_t = 1$) of $N = 200$ particles in the embedding dimension $d_e = 3$; and for 100×100 particles and $30 \times 30 \times 30$ particles square and cubic arrays in $d_e = d_t = 2$ and $d_e = d_t = 3$, respectively. In the following we express our results in terms of the unitary free diffusion coefficient $D_0 \equiv 1$ and Flory segment radius $\xi \equiv 1$.

The half mean squared displacement per degree of freedom $\langle r^2 \rangle / 2d_e$ obtained for the above mentioned networks are shown in Fig. 2 as a log-log plot. At short times, for small displacements, diffusion is normal, occurring with the free diffusion coefficient. Interactions progressively reduce the diffusion coefficient down and they will eventually reach the D_0/N long time limit value. The correct scaling for linear polymers Eq. (2) is immediately recovered from the slope of the corresponding data set. Nevertheless, 2D networks reach no clear power scaling and the mean squared displacement range of 3D network walks is bound to a limiting small range below 0.1. The situation can be clarified by plotting the differential diffusion coefficient

$$\widetilde{D} \equiv \frac{1}{2d_e} \frac{\partial \langle r^2 \rangle}{\partial t} \tag{7}$$

as shown in Fig. 3. A power scaling is now obtained for all the networks, with assimptotic functionality

$$\widetilde{D} = \left(\frac{t}{\tau} \right)^{-\alpha}, \tag{8}$$

with $\tau = 0.0285(2)$ and $\alpha = d_t/2$ within 1%. We note that Eq. (8) can be derived from the linear Rouse equation by the standard technique of overdamped phonon mode analysis with equipartition of energy. This result does not depend on the embedding dimension d_e, which appears only as a normalization in Eq. (7). The asymptotic regime is then obtained
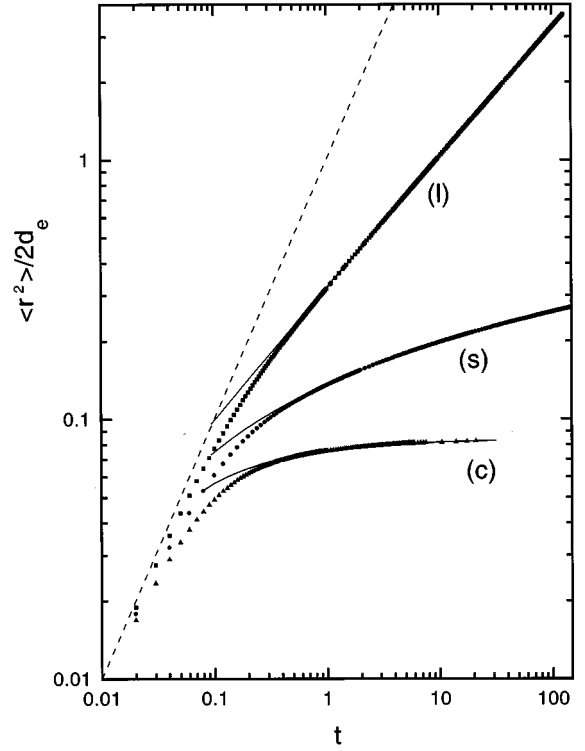

FIG. 2. Half mean square displacement per degree of freedom for the linear (l), square (s), and cubic (c) networks. Asymptotic fits to Eq. (9) gave, respectively, $\Delta_1 = -0.004(4)$; $\Delta_2 = 0.0395(2)$; and $\Delta_3 = 0.0842(3)$. Dotted line corresponds to free diffusion.

with $\tau = 1/12\pi \simeq 0.026\,53$. This general and simple result can be readily integrated to yield the long time mean square displacements for the $d_t = 1$, 2, and 3 networks, respectively,

$$\frac{\langle r^2 \rangle}{6} = \Delta_1 + 2(\tau t)^{1/2}, \tag{9a}$$

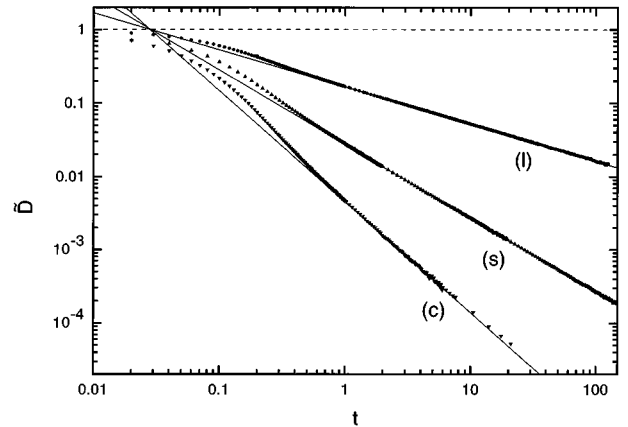$$\frac{\langle r^2 \rangle}{4} = \Delta_2 + \tau \ln(t/\tau), \tag{9b}$$

FIG. 3. Differential diffusion coefficient for the linear (l), square (s), and cubic (c) networks. Asymptotic fits to Eq. (8) gave, respectively, $\alpha_1 = 0.506(4)$, $\tau_1 = 0.0285(1)$; $\alpha_2 = 1.01(1)$, $\tau_2 = 0.0287(1)$; and $\alpha_3 = 1.52(6)$, $\tau_1 = 0.0283(5)$. Dotted line corresponds to free diffusion.
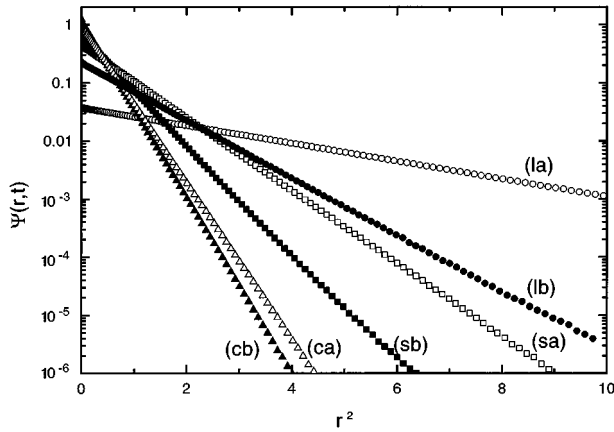
FIG. 4. Distribution functions $\Psi(r,t)$ for the linear (l), square (s), and cubic (c) networks at times $t=0.5$ (a) and $t=5$ (b) are shown to be Gaussians in this linearized log-square plot.
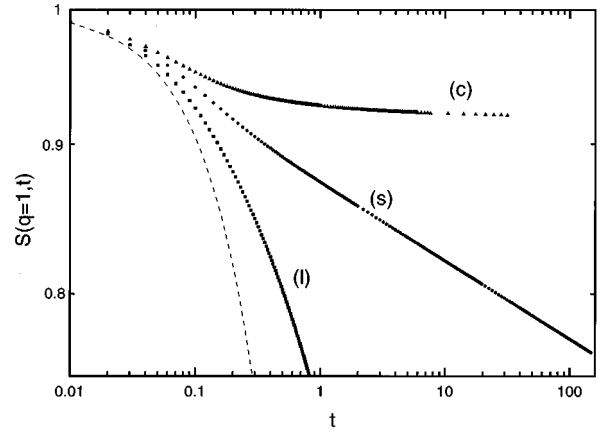

FIG. 5. Dynamic self-structure factor, $S_s(q,t)$ for the linear (l), square (s), and cubic (c) networks at $q=1$. Dotted line represents the decay due to free diffusion alone.

$$\frac{\langle r^2 \rangle}{6} = \Delta_3 - 2\tau^{3/2}t^{-1/2}. \qquad (9c)$$

The above relations were fitted to the $\langle r^2 \rangle$ data yielding $\Delta_1 = -0.004(4)$, $\Delta_2 = 0.0395(2)$, and $\Delta_3 = 0.0842(3)$. From the known diffusivity (internal modes) of linear Rouse chains [13] compared with Eq. (9a) one has $\Delta_1 = 0$. We are not aware of any estimates for Eqs. (9b) or (9c), although numerical analysis of the Rouse equation should be feasible. If Eq. (8) is universal and valid for fractal networks also, then $d_t = 2$ is a critical dimension for the dynamics of Rouse networks, which will have a logarithmic displacement. Topologies with higher graph dimensionality will bound the network to configurations around the equilibrium, and lower topologies should give rise to the usual unbounded anomalous diffusion.

We have also measured the distribution functions $\Psi(r,t)$, the probability for a given point in the network to have a displacement r in time t, to be Gaussians in the asymptotic regimes. Figure 4 shows, for instance, a linearized $\log[\Psi(r)]$ vs r^2 plot for the networks at times $t=0.5$ and 5. Since the Gaussian widths are given by the mean squared displacements one can also compute the dynamic self-structure factor decays to be $S_s(q,t) = \exp[-q^2\langle r^2(t)\rangle/2d_e]$. Dynamic structure factors are regularly measured in the context of gel studies. The interpretation of their often broad time spreading is controversial. For the ideal networks corresponding, respectively, to the subcritical, critical, and upper-critical regimes presented here one finds

$$S_s(q,t) \propto \exp[-(\Gamma_1 t)^{1/2}]; \quad \Gamma_1 = 4\tau q^4, \qquad (10a)$$

$$S_s(q,t) \propto t^{-\beta_2}; \quad \beta_2 = \tau q^2, \qquad (10b)$$

$$S_s(q,t) \propto \exp[(\Gamma_3 t)^{-1/2}]; \quad \Gamma_3 = (4\tau^3 q^4)^{-1}. \qquad (10c)$$

The subcritical decay is a stretched exponential, while the critical decay is characterized by a q-dependent power law. The bounded diffusion regime decays to the corresponding finite value $\exp(-q^2\Delta_3)$. These features are evident in Fig. 5 where we plot $\exp(-\langle r^2(t)\rangle/2d_e)$ from our measurements.

The structure factors are often more easily measured than mean squared displacements in scattering experiments. In the case of polymer gels, the dynamic light scattering technique (photon correlation) should apply well. The time domain of self-diffusion scaling $[t > (D_0\xi^2)^{-1} \approx 10^{-5}$ s$]$ is compatible with the apparatus resolution ($t > 10^{-6}$ s) [14]. Logarithmic correlators should present the appropriate time scales for studying these nonexponential decays. Gels should be washed to remove debris but should also be tagged with strong scatterers to display the true self-structure factor instead of the usual collective concentration decay. Such experiments should be able to give the first measurements of bounded anomalous diffusion and test the validity of the hydrodynamic screening approximation, implied in Eq. (10c).

This paper stresses the relation between anomalous self-diffusion of a polymeric network with its linking topology (graph dimension). It asks for further investigation on the effect of hydrodynamic interactions on relation (8) for the differential self-diffusion coefficient and possibly a general derivation of its universality. It also leads naturally into a division of anomalous diffusion phenomena in three classes with different qualitative behavior.

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