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## LETTER TO THE EDITOR

# Anomalous conformation of polymer chains: random walk of a random walk on a random walk

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**Abstract.** Conformation of polymer chains is analysed in the light of the results from the classical diffusion in random systems including fractals; the possibility of an anomalous conformation is conjectured.

The conformation of a polymer chain (Flory 1971, de Gennes 1979) depends mainly on two factors: (i) the nature of the chain (Gaussian, self-avoiding walk (SAW), rod, etc) and (ii) the medium in which it is embedded. For example, in dilute solution, it may be in a swollen state (SAW) in a good solvent, Gaussian at theta point and collapse in poor solvent while in melt it is Gaussian even in a good solvent (de Gennes 1979). In describing the viscoelastic properties of the chain polymers (Ferry 1980, Graessley 1982) one of the two conformations, namely the random walk and SAW, are mostly taken into consideration. Here we would like to point out that there may be an anomalous conformation of the chain in the semidilute to melt regime, which may give rise to anomalous properties for the polymeric systems.

In the dilute regime, since the concentration of the chain polymer is very small, the probability of their encounter in exploring their conformation is negligibly small (de Gennes 1979). The conformation of the chains (like random walk, SAW or rod) therefore depends mainly on the quality of the solvent in the dilute regime. Each chain explores its conformation in the available surrounding space which is equal to the volume of the whole system minus the volume of the chain (i.e. the volume occupied by the mobile solvent). On the lattice one may model this situation by placing the chains randomly on the lattice according to the nature of the chains (RW, SAW or rod); a site (bond) is occupied either by a point-like molecule (chain segment) or by a solvent molecule with probability $(1-p)$ and $p$ respectively $(0 \leq p \leq 1)$; a solvent molecule may exchange its position with a point-like molecule in the chain, like the interchange of the position of vacancies and electrons in the free electron gas diffusion problem (Kutner and Kehr 1983). Nevertheless, the movement of chain segments is restricted to a fraction $p$ of sites occupied by the solvent molecules.

For large $p$ ($\sim P_d$, dilute concentration regime) the chains feel practically no constraint in their movements in search of configurations of minimum free energy (entropic contribution) in their conformational phase space. Therefore, they (the chains) retain their original form (RW, SAW, etc). The radius of gyration of the conformation of the chain is proportional to the RMS displacement of a random walk (or SAW) (de Gennes 1979) in an inhomogeneous medium (the available space occupied

by solvent particles) resulting from the presence of random chains. The random medium may be quenched or annealed depending on the relaxation time of the chain conformations. In an annealed disordered medium there is no effect of randomness as far as the asymptotic power law behaviour of the end-to-end length (RMS displacement) of the chain (RW or SAW) is concerned (see Kutner and Kehr (1983) for the analogy with lattice gas diffusion). On the other hand, in a quenched disorder medium, the power law behaviour may change depending on the self-similar structure of disorder; for example, in a percolating system, the random walk (classical diffusion) behaviour on the sites occupied with concentration $p$, for $p > P_c$, changes into anomalous power law behaviour at $p = P_c$ where the range of self-similarity extends up to length scale infinite (as the percolation correlation length $\xi \to \infty$ at $p \to P_c$). Note that the asymptotic power law behaviour for the RMS displacement remains unchanged for $p > P_c$ even in quenched disorder systems; one may observe the anomalous behaviour (i.e. the change in the power law for the end-to-end distance considered here) only if end-to-end displacements are within the range of the validity of self-similar structure (i.e. fractal nature), even at $p < p_c$ in percolating systems. A more precise description of this crossover behaviour can be derived (Gefen *et al* 1983) using scaling arguments, according to which the end-to-end distance $R$ of an $N$-step random walk is given by

$$R \propto N^k \tag{1}$$

with $k = \frac{1}{2}$ for $p > P_c$ and $k = 0$ for $p < P_c$, but at $p = P_c$

$$k = (2\nu - \beta)/(2\nu + \mu - \beta) = d_s/2d_f \tag{2}$$

where $\nu$, $\beta$ and $\mu$ are the exponents for percolation correlation length, percolation probability and conductivity of the percolating network, respectively, and $d_s$ and $d_f$ are the spectral and fractal dimensionality of the random percolating cluster (Gefen *et al* 1983, Pandey *et al* 1984, Alexander and Orbach 1982). This relation for $k$ is valid even at $p < P_c$ if $R < \xi$.

When we add more chains in the system (lattice) (i.e. when we increase the concentration of polymer) the concentration $p$ of the available sites decreases; the chains may therefore start feeling the presence of each other due to the constraint of limited exploring space. The chains may still be able to explore all their conformations, but their exploration time (i.e. the relaxation time) $\tau_{ch}$ may increase. Had the available sites of concentration $p$ been quenched, the increase in relaxation time to attain an equilibrium conformation of a chain would have been similar to the relaxation time for a random walk (or SAW) motion on a random (percolating) system at $p > P_c$, where $P_c$ is the critical concentration (percolation threshold) at which the range of correlation in the concentration fluctuation $\langle \Delta P_i \Delta P_j \rangle$ between two sites $i$ and $j$ becomes infinity. In analogy with the relaxation in percolating systems, one may expect $\tau_{ch}$ to increase as

$$\tau_{ch} \sim (p - p_c)^{-x}$$

where $x$ is some unknown exponent. The exploring space, which we call a cage to be consistent with the polymer terminology (Graessley 1982), may not be quenched as the presence of other chains may act like an annealed impurity. Since the chains are exploring their conformations, the sites occupied by them (with concentration $1 - p$) are not quenched and neither are the available sites (with concentration $p$), i.e. the cage, as both depend upon each other. One may associate a characteristic time for the cage $\tau_r$ (known as tube renewal time (Graessley 1982)) in which the cage may

change its principal form completely on the length scale of the chain. $\tau_r$ depends on the conformational motion of the chains in a cooperative fashion which makes the whole situation very complex; one may assume

$$\tau_r \sim (1-p)^{-y}$$

where $y$ is some unknown exponent. Conformation of the chains may depend upon $\tau_{ch}$ and $\tau_r$ in an important way. However if the polymer concentration $(1-p)$ is still small so that the chains barely touch each other, the situation is not too bad, and the chains may attain their equilibrium conformation in a fair amount of time. This concentration lies in the semidilute regime, where extensive studies have been made using scaling arguments (de Gennes 1979).

On increasing the concentration of polymer chains from the dilute concentration both relaxation times $\tau_{ch}$ and $\tau_r$ increase. At the concentration $P_a$ of the cage sites (i.e. at the polymer concentration $(1-p_a)$, if the correlation length $\xi_p$ of the fluctuation of the cage sites (of concentration $p$) is larger than the chain length $R_{ch}$, then the chain cannot distinguish between the random shape of the cage at this concentration $p > P_c$ and at concentration $P = P_c$ where $\xi_p \to \infty$. Secondly, if the cage relaxes in such a way that the cage retains a certain random form over the length of the chain during its conformational exploration, then the cage may be treated as a random self-similar (i.e. fractal) space over the length scale of the chain. Let us assume that the chain is Gaussian in the dilute concentration where its radius of gyration $R_{ch} \sim N^{1/2}$. On extending the arguments of anomalous diffusion on the percolating network (Gefen *et al* 1983) to the chain polymer system considered here in the concentration regime $P_a$ where the cage is self-similar and $R_{ch} < \xi_p$, we obtain

$$R_{ch} \sim N^k \qquad P_d > P_a > P_{up}$$

where $k$ is given by equation (2) in that $d_s$ is the spectral dimensionality of the cage and $d_f$, its fractal dimensionality; $P_{up}$ is an upper cut-off for the concentration of the cage sites. One must note that the precise identification of the concentration regime and dependence of the relaxation times on it is a complex problem in itself as it involves both statics and dynamics of the whole random system. The above results apply strictly under the validity of the assumptions invoked.

Doi and Edwards (1978), in a study of the dynamic properties, particularly in deriving the power law for reptation, modelled the cage as Gaussian. However, if we model the cage (for the concentration regime where the self-similar arguments are valid) as a fractal formed by the random walk (Havlin *et al* 1984) then in $d = 3$, we obtain $k \simeq 0.29$ (as $d_s = \frac{8}{7}$, $d_f = 2$). On the other hand, if one assumes the cage as a simple percolating (site or bond) fractal (Stauffer 1985) then we get $k \simeq 0.20$ (Gefen *et al* 1983, Pandey *et al* 1984). In either case, one obtains an anomalous power law for the conformation of the chain, as long as the cage is self-similar on the chain length scale. It does not seem unreasonable to model the cage as a fractal formed by the random walk (Havlin *et al* 1984) and therefore the result $k \simeq 0.29$ appears to be a good possibility to describe the conformation of the chain; thus the random walk of a random walk on a random walk may give rise to an anomalous conformation of polymer chain. Since most of the conformational and dynamic properties of chain polymers depend upon how the radius of gyration of the chain varies with the number of chain segments $N$, we conjecture that these properties may show anomalous behaviour arising from the anomalous conformation of the chains.

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