Dynamics of a polymer in a quenched random medium: A Monte Carlo investigation

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Abstract. – We use an off - lattice bead - spring model of a self - avoiding polymer chain immersed in a 3-dimensional quenched random medium to study chain dynamics by means of a Monte - Carlo (MC) simulation.

The chain center of mass mean-squared displacement as a function of time reveals two crossovers which depend both on chain length $N$ and on the degree of Gaussian disorder $\Delta$. The first one from normal to anomalous diffusion regime is found at short time $\tau_1$ and observed to vanish rapidly as $\tau_1 \propto \Delta^{-11}$ with growing disorder. The second crossover back to normal diffusion, $\tau_2$, scales as $\tau_2 \propto N^{2\nu+1} f(N^{2-3\nu} \Delta)$ with $f$ being some scaling function. The diffusion coefficient $D_N$ depends strongly on disorder and drops dramatically at a critical dispersion $\Delta_c \propto N^{2+3\nu}$ of the disorder potential so that for $\Delta > \Delta_c$ the chain center of mass is practically frozen.

The time-dependent Rouse modes correlation function $C_p(t)$ reveals a characteristic plateau at $\Delta > \Delta_c$ which is the hallmark of a non-ergodic regime. These findings agree well with our recent theoretical predictions.

Introduction. – Considerable progress has been made in understanding of the static \[1,2,3,4,5,6,7,8,9,10,11\] and dynamic \[12,13,14\] behavior of polymer chains in a quenched random medium. It was shown already in the paper by Cates and Ball \[2\] that for sufficiently large diffusion coefficient (so as the chain may sample the whole system) the quenched and annealed problems are equivalent. Indeed, since the chain always moves towards the deepest energy minimum, quenched and annealed problems can differ only for finite volume of the random medium \[10,11\].

In a recent publication \[15\] we have argued that dynamic aspects can significantly affect the problem in question. We have treated this problem \[15\] using the generating functional method which based on the Langevin dynamics. Within this method the averaging over

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the quenched disorder leads to coupling between different dynamic trajectories which in turn eventually results in a non-Markovian diffusional slowing down, i.e. anomalous diffusion, as well as in non-ergodic behavior for the Rouse modes of the polymer chain. The resulting equation of motion (which was derived within the Hartree approximation) has a memory kernel typical for the mode-coupling theory of the glass transition. Self-consistent treatment of this equation leads to the conclusion that in $d$-dimensional space the center of mass diffusion coefficient decreases according to the law:

$$D_N \approx D_R[1 - \text{const}(\Delta/b^d)N^\alpha],$$  

where $\Delta$ is the dispersion of the disorder potential, $b$ is the Kuhn segment length, and $\alpha = 2 - \nu d$ ($\nu$ is the Flory exponent). This differs remarkably from the earlier prediction,

$$D_N \approx D_R \exp\left[-(\Delta/b^d)N^\alpha\right],$$

based on a simple Markovian diffusion argumentation. As a result some critical disorder, $\Delta_c = b^d N^{-\alpha}$, exist such that at $\Delta > \Delta_c$ the chain center of mass is arrested by the random potential. In the case when the capture time $t_{\text{cap}} \gg t_{\text{eq}}$ (where $t_{\text{eq}}$ is the time of internal degrees of freedom equilibration) the quenched and annealed problems are not equivalent even for an infinite volume! Rouse modes of the chain also freeze at a common disorder strength $\Delta$, so that the non-ergodicity plateau shows up according the A-type (or continuous) transition. In the present letter we will mainly check these important predictions of the ref. [15] by the direct and vast MC-simulations. In the conclusion we also sketch some possible future developments.

**Model.** -- In the present study we employ an off-lattice Monte Carlo model of a bead-spring polymer chain, used in numerous investigations before [17]. During the simulation beads are chosen at random and displaced to a new trial position in their environment subject to a Metropolis procedure. Each polymer chain consists of $N$ beads, connected by anharmonic springs which are described by the finitely-extensible nonlinear elastic (FENE) potential

$$U_{\text{FENE}} = -\frac{KR^2}{2} \ln \left[1 - \frac{\left(l - l_0\right)^2}{R^2}\right],$$

where $l$ is the bond length which can vary in between $l_{\text{min}} < l < l_{\text{max}}$, and has the equilibrium value $l_0$, with $R = l_{\text{max}} - l$, $l_{\text{min}} = 2l - l_{\text{max}}$, and $K$ is the spring constant. As before [18], we take $l_{\text{max}} = 1$ as the unit length, $l_{\text{min}} = 0.4$, $l_0 = 0.7$, and $K/k_BT = 40$. The non-bonded interactions between the beads are described by the Morse potential [17]

$$U_M(r) = \varepsilon_M \exp[-2a(r - r_{\text{min}})] - \exp[-a(r - r_{\text{min}})],$$

where $r$ is the distance between the beads, $r_{\text{min}} = 0.8$, $\varepsilon_M = 1$, and $a = 24$ (since the potential has a very short range, the simulation code is rather fast [18]). The $\Theta$-temperature for the model is $k_BT_\Theta \approx 0.62$, so that at $k_BT = 1$, used throughout in this study, the chain is in a good solvent regime and all energetic variables are dimensionless.

The energetic disorder is created by dividing the simulation box into $64^3$ hypothetical subcells, each of size $l_{\text{max}} = 1$, which are ascribed a Gaussian-distributed local potential so that its dispersion is taken as a measure of the degree of disorder $\Delta$. Typically runs of length $10^8 \div 10^9$ MC steps (MCS) have been carried out and observables have been averaged over 500 different realizations of disorder.

**Results.** -- First of all we emphasize that the stochastic dynamics in the system under study is not time translational invariant (TTI) [19]. This means that in the time-dependent correlation function one should keep control on two times: the waiting time $t_w$, i.e. the time
elapsed after the system preparation (aging) before any measurement starts, and the actual measurement time \( t \). With this in mind we have studied the center of mass mean-square displacement (MSQD)

\[ g_4(t, t_w) = \langle \left[ r_{CM}(t) - r_{CM}(t_w) \right]^2 \rangle, \tag{4} \]

where the center of mass position \( r_{CM}(t) = \sum_{i=1}^{N} R_i(t)/N \) and the angular brackets denote an average over the realizations of disorder. In contrast, in cases of vanishing disorder TTI holds and the time correlation functions depend on a single variable \( \delta t = t - t_w \).

Fig. 1 – Mean-square displacement of a central monomer, \( g_1(t) \), of an end monomer, \( g_4(t) \), and of the chain center of mass, \( g_3(t) \) vs. time for \( N = 32 \) and \( \Delta = 0.95 \). Dashed lines with slope 1 denote normal diffusive behavior whereas the crossover times \( \tau_1 \) (from), and \( \tau_2 \) (back to) normal diffusion are marked by arrows. The mean squared radius of gyration of the polymer, \( R_g^2(t) \), appears as a horizontal line.

Fig. 1 shows a typical example for the chain length \( N = 32 \) the disorder strength \( \Delta = 0.95 \) and the MC-time interval \( t > 10^8 \). One can clearly distinguish three diffusional regimes. In the initial short interval \( 0 < t < \tau_1 \) a relatively fast normal diffusion shows up. The crossover time \( \tau_1 \) corresponds to the moment when disorder starts to effect the chain motion. In ref. [15] this moment was denoted by \( \tau_d \) and was defined as the point where the memory-friction term overwhelms the bare-friction term. After that the non-Markovian diffusion gets under way. In the interval \( \tau_1 < t < \tau_2 \) the MSQD manifests itself as anomalous diffusion with \( g_3(t) \propto t^{\beta} \), where the exponent \( \beta < 1 \). At time \( t > \tau_2 \) (which corresponds to the MSQD \( g_3(t) \gg R_g^2 \)) the diffusion goes back to normal albeit with a significant slowing down (see below).

The MSQD-plot given in Fig. 1 has been obtained for waiting time \( t_w = 0 \). In the present report we shall not consider aging phenomena (i.e. the \( t_w \)-dependence of the time correlation functions as well as the violation of the fluctuation-dissipation theorem (FDT)) putting this off for a later publication. Nevertheless Fig. 2 clearly demonstrates the drift of the full energy \( E \) with time \( t \) which for \( N = 8 \) gets pronounced at \( \Delta > 0.9 \). Evidently in this case the TTI is violated for larger disorder. The age of the system also influences static conformational properties as the mean-squared radius of gyration \( R_g^2 \) of the polymer chain. Figure 3 shows that at small disorder, \( \Delta = 0.25 \), the \( R_g^2 \) versus \( N \) dependence has the same slope as in the pure (i.e. without any disorder) system. An inspection of the measured \( R_g^2 \) vs. \( N \) relationship yields \( \nu = 0.605 \pm 0.005 \) for the Flory exponent. At large disorder, \( \Delta = 1.00 \), however, the slope of \( R_g^2(N) \) is affected by the waiting time \( t_w \). The value of \( t_w \) which we have used in
Fig. 2 – Energy (per monomer) vs time of a chain with $N = 8$ for growing degree of disorder $\Delta$ (given as a parameter).

Fig. 3 – A scaling plot of the radius of gyration, $R_g^2$, with chain length $N$ for small, $\Delta = 0.25$, and large, $\Delta = 1.00$, degree of disorder.

Fig. 4 corresponds to the slow diffusion regime, i.e. $t_w > \tau_2$. In this case $\nu = 0.68 \pm 0.01$, i.e. $\nu > \nu_{\Delta=0}$ which is consistent with the results obtained on hierarchical lattices for the quenched problem. The quenched problem in ref. [7] corresponds to the case in which the one end of the chain is kept fixed. In this case the polymer stretches away from the fixed end in order to find a region with a minimal energy. The Imry - Ma arguments have been used in ref [6] to show that $\nu_{\text{quenched}} = 2/3$.

Now we go back to MSQD - plot (Fig.1) to discuss how the crossover times, $\tau_1$ and $\tau_2$, depend on $\Delta$. This is presented in Fig.4.

Fig. 4 – Crossover times $\tau_1$ and $\tau_2$ (inset) for chains of length $N$ at different degree of disorder $\Delta$.

The first crossover $\tau_1$ decreases whereas the second one $\tau_2$ increases with the disorder strength $\Delta$, so that the anomalous diffusion interval is extended. While for the relatively long chains, $N \geq 32$, the initial interval $\tau_1$ is getting progressively so short that a scaling
dependence on $\Delta$ is difficult to establish, for shorter chains (where the statistics is better too) the $\tau_1$ vs $\Delta$ relationship can be reasonably fitted by $\tau_1 \propto \Delta^{-11}$. In ref. [15] a theoretical prediction for $\tau_1$ was derived as:

$$\tau_1 \propto \Delta^{-1/(1-\beta)}$$

where the anomalous diffusion exponent $\beta = 1 - (2 - \nu d)/(2\nu + 1) < 1$. In the case of $d = 3$ and $\nu = 0.6$ one obtains $\beta = 0.9$ which leads to $\tau_1 \sim \Delta^{-10}$. This prediction agrees closely with the above-mentioned MC findings. As is clearly seen in the inset of Fig. 4, all data for the second crossover time $\tau_2$ follow a scaling law $\tau_2 \propto N^{1+2\nu} f(\Delta N^{2-3\nu})$ where $f$ is some scaling function.

As mentioned above, at $t > \tau_2$ the normal diffusion regime shows a significant slowing down. This extremely important result is depicted in Fig. 5 over a wide range of chain lengths.

![Figure 5](https://example.com/figure5.png)

**Fig. 5** – Variation of the normalized diffusion coefficient $D_N/D_R$ with scaled degree of disorder $x = \Delta N^{2-3\nu}$ for chains of length $8 \leq N \leq 256$. Dashed line denotes the simple Markovian diffusion prediction $ND_N \propto \exp(-x)$ [4, 15], a full line is a best fit with $ND_N \propto (x_c - x)^{0.8}$. Unscaled data is shown in the inset.

All points in the reduced coordinates ($ND_N$ vs $\Delta N^{2-3\nu}$) lie on a single master curve. It appears that our MC-data nicely follows the best fit $D_N \propto N^{-1}(x_c - x)^{0.8}$ (where $x = \Delta N^{2-3\nu}$) which correlates well with the theoretical predictions for $D_N$ (see eq.(1)). A remarkable and strong systematic difference between the master curve (solid line) and the simple Markovian diffusion result (dashed line) can be seen, which grows progressively with increasing degree of disorder. The basis for this slowing down is the coupling between diffusional trajectories (or between different parts of the same trajectory) caused by the averaging over the disorder. This furnishes the non-Markovian slowing down regime, which mathematically shows up as a memory kernel term in the resulting equation of motion [16]. Such behavior is generic for the “schematic” mode-coupling theory of the glass transition [17]. The existence of such dynamic singularity for a finite chain is in principle questionable. More precisely one should better mean that the capture time of the center of mass, $t_{cap}$, is finite albeit astronomical, so that in the slowing down regime $t_{cap} \gg t_R \exp(\Delta N^{2-3\nu})$. This time scale goes beyond the scope of our present MC-simulation.

So far, we have focused mainly on the chain center of mass slow dynamics. We studied
also the time dependent correlation function of the Rouse modes [20]

\[ C_p(t, t_w) = \langle X_p(t)X_p(t_w) \rangle, \quad (6) \]

where the Rouse mode component with an index \( p \), \( X_p(t) = N^{-1} \sum_{i=1}^{N} r_i(t) \cos[(i - 0.5)p\pi N^{-1}] \), is measured at time \( t \). This correlation function reflects the dynamics of the internal degrees of freedom. It can be seen in Fig. 6 that at relatively large disorder strength \( \Delta \) a characteristic plateau appears which is reminiscent of a non-ergodic behavior for the so called \( A \)-type dynamical transition [16]. Figure 6 illustrates this non-ergodic plateau behavior for the first mode \( p = 1 \) and the chain length \( N = 16 \).

![Fig. 6 – Variation of the plateau height \( h \) with degree of disorder \( \Delta \) of the Rouse-mode correlation function \( C_1(t, 0) \) of a chain with \( N = 16 \). In the inset \( C_1(t, 0) \) are shown for the respective values of \( \Delta \).](image)

The height \( h \) of the plateau is found to be a continuous function of \( \Delta \), i.e. \( h \propto (\Delta - 1.06)^{2.5} \), which qualitatively agrees with the recent theoretical predictions [15]. It is interesting to note that the critical \( \Delta_c \approx 1.06 \) coincides with the critical value \( \Delta_c \) which is obtained for \( N = 16 \) from the diffusion results (see the Fig 5). The well-known \( F_1 \) model, which has been studied in ref. [16], provides a simple example of such kind of continuous transition.

**Conclusion.** – In this work an off-lattice model of a self-avoiding polymer chain in quenched random field is used to study the slow polymer dynamics. We examine the center of mass MSQD at different degree of disorder and find a broad regime of anomalous diffusion which starts at a crossover time \( \tau_1 \) and ends at a second crossover \( \tau_2 \) by going into normal diffusion regime. We have demonstrated that these crossover times are observed to scale in agreement with the theoretical predictions [15].

The diffusion coefficient \( D_N(\Delta) \) at \( t > \tau_2 \) drops dramatically at a critical value \( \Delta_c \propto N^{-2+3\nu} \). Simulation data for \( D_N \) of different polymer chain length and different degree of disorder is observed to collapse on a single master curve as predicted in a recent theory [15]. This significant slowing down effectively originates from the coupling between different dynamic trajectories of a polymer chain caused by the averaging over many disorder realizations. The Hartree approximation which has been used in [15] is close in spirit to the well-known mode-coupling approximation [10] and provides the basis for the treatment of non-Markovian regimes. In contrast, a treatment in terms of Markovian arguments yields an exponential
relationship between diffusion coefficient and reduced disorder which proves to be inadequate. The same reasons bring about the Rouse modes freezing at a common disorder strength $\Delta_c$, whereby the generic non-ergodicity plateau appears continuously. This is also in line with the theoretical predictions [15].

Finally we should stress that the system at issue does not satisfy TTI so that the waiting time $t_w$ is a very important parameter. Although $t_w$ has been controlled in the calculation of MSQD (eq.(1)) and the Rouse mode correlators, eq.(6), its impact on the dynamics is to be reported in a following communication. To this end the generating functional approach, which has been used in ref. [15], should be generalized to the out-of-equilibrium dynamics [19] where the influence of $t_w$ (or the aging) and FDT violation are the effects of a primary interest. We plan to consider these problems in a future publication.

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