# Relaxation length of a polymer chain in a quenched disordered medium

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(Received 22 March 1999)

Using Monte Carlo simulations, we study the relaxation and short-time diffusion of polymer chains in two-dimensional periodic arrays of obstacles with random point defects. The displacement of the center of mass follows the anomalous scaling law $r_{c.m.}(t)^2 = 4D^*t^\beta$, with $\beta < 1$, for times $t < t_{SS}$, where $t_{SS}$ is the time required to attain the steady state. The relaxation of the autocorrelation function of the chain's end-to-end vector, on the other hand, is well described by the stretched exponential form $C(t) = \exp[-(t/\tau^*)^\alpha]$, where $0 < \alpha \leq 1$ and $\tau^* \ll t_{SS}$. However, our results also obey the functional form $C(r_{c.m.}) = \exp(-[r_{c.m.}/\lambda]^2)$, implying the coupling $\alpha = \beta$ even though these exponents vary widely from system to system. We thus propose that it is $\lambda$, and not the traditional length $(D\tau^*)^{1/2}$, that is the relevant relaxation polymer length scale in disordered systems. [S1063-651X(99)10909-7]

PACS number(s): 36.20.Ey, 83.10.Nn, 87.15.He

## I. INTRODUCTION

The conformational and dynamical properties of polymers in (quenched) disordered media have attracted a lot of attention recently [1]. In particular, the possible collapse of the radius-of-gyration $R_g$ and the strong molecular size dependence of the diffusion coefficient $D$ have been studied using a variety of analytical and numerical tools [1]. Generally, it has been concluded that while $R_g$ is slightly reduced by disorder, the scaling law $R_g \sim (M-1)^\nu$, where $\nu = 3/(2+d)$ is Flory's exponent for a linear chain of $M$ monomers in $d$ dimensions, remains valid [1,2]. The scaling of $D$ with size $M$ is more system-dependent [1–3] because the disorder generates entropic barriers which hinder long-range diffusion of finite-size polymer chains with the resulting hoppinglike process being then governed by the connectivity of the voids. It is usually thought that the reptation model applies in cases where $R_g$ is much larger than the characteristic length scale(s) of the disordered medium [4]. The disorder is then a mean topological field which effectively rescales the polymer's mobility in its reptation tube (note that this has yet to be observed in computer simulations).

To our knowledge, polymer relaxation in disordered media has never been studied in detail. Scaling analysis indicates that the conformational relaxation times scale like $\tau \sim M^b$, with $b = 2\nu + 1$ and $b = 3$, in the Rouse and reptation limits, respectively [1]. In both cases, the simple scaling relationship $R_g \sim (D\tau)^{1/2}$ is satisfied since the polymer molecule diffuses over distances comparable to $R_g$ (the only relevant length scale) during relaxation. In a disordered medium, however, one can define several topological length scales such as the correlation length, the mean pore size, the mean distance between voids of size $a \geq R_g$, etc. Consequently, conformational relaxation and steady-state diffusion may no longer be directly related and the "relaxation length" $\lambda_0 \sim (D\tau)^{1/2}$ may become strongly system-dependent or even irrelevant [1,3]. On the other hand, diffu-

sion is often anomalous for short times in disordered media, while relaxation may be characterized by stretched exponentials. This paper proposes a way to link these different elements when studying entropic trapping systems.

We thus report a computer-simulation study of polymer relaxation in a two-dimensional ($d=2$) system. We find that relaxation is affected by the degree of disorder, leading to stretched exponential decay curves. The stretching exponent is shown to correspond directly with the anomalous (sub)diffusion transient regime, which in turn defines a new relaxation length scale $\lambda$.

## II. MONTE CARLO METHOD

Details of the model can be found in Refs. [2], [3], and [5]. Briefly, the simulations use the four-site bond-fluctuation algorithm [6] on a square ($d=2$) lattice with periodic boundary conditions. The immobile obstacles are identical to the monomers and satisfy the same excluded volume rules. A polymer molecule is comprised of $M \geq 2$ monomers connected by $M-1$ bonds whose lengths are restricted to the range $\ell \in [2, 13^{1/2}]$ (in units of the lattice spacing); this constraint ensures the automatic compliance of the self-excluded volume effects. One Monte Carlo step consists of selecting a random monomer and attempting to move it one lattice spacing in a random direction ($\pm x$ or $\pm y$). A move is rejected if the newly chosen site is occupied, or if it results in violating the bond-length restrictions. In this model disordered system, the obstacles constitute a periodic (square) sublattice with lattice spacing parameter $p=4$ [2,3,5]. Imperfect lattices are created by randomly selecting and removing a fraction $(1-c)$ of the obstacles, thus creating pointlike defects in the obstacle sublattice. This model converges naturally towards Rouse and reptation dynamics in the appropriate limits $c = 0$ and 1, respectively. For intermediate concentrations, the chain spends long periods of time in the larger voids, and its dynamics is strongly affected by this "entropic trapping" [3]. The lattice size was at least $1260 \times 1260$; with such large system sizes, averaging over various realizations of the disorder was not necessary except when the concentration was in the narrow range $0.99 < c < 1.0$.

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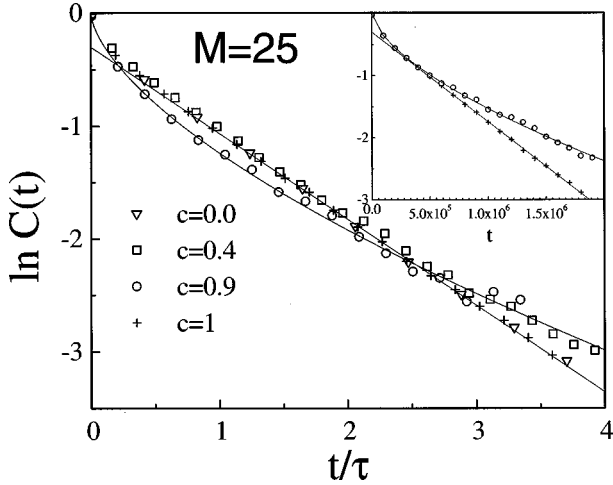*Author to whom correspondence should be addressed. Electronic address: gary@physics.uottawa.ca

FIG. 1. Correlation function $C(t)$ vs scaled time $t/\tau$ for various concentrations $c$. Inset: same data for $c=0.9$ and 1 with a normal time axis. In both figures, the solid lines are the best fits obtained using the form given by Eq. (3), with $\alpha=1$ for $c=1$ and $\alpha=0.66$ for $c=0.90$.

### III. RESULTS

The normalized autocorrelation function $C(t)$ of the chain's end-to-end vector $\mathbf{h}(t)$ is defined as (where $\langle\,\rangle$ signifies an ensemble average and $t$ is the time)

$$C(t)=\frac{\langle \mathbf{h}(t)\cdot\mathbf{h}(0)\rangle}{\langle h^2(0)\rangle}. \qquad (1)$$

In Fig. 1, we plot the $C(t)$ decay curves for an $M=25$ chain in the Rouse ($c=0$) and reptation ($c=1$) limits. In both cases, the curves become linear after a short time period ($t/\tau\approx0.4$) during which excluded volume effects and short length scale processes play a role (in fact, the two scaled curves are indistinguishable). For intermediate concentrations, however, the decays are clearly curved for all times. In each case, the time axis was rescaled by the (integral) relaxation time $\tau$, defined as

$$\tau\equiv\int_0^\infty C(t)\,dt. \qquad (2)$$

Figure 2 shows how $\tau(c,M)$ varies as a function of size $M$ for different concentrations $c$. Our $c=0$ results are consistent with the scaling law $\tau(c=0,M)\sim M^{5/2}$, in agreement with Downey [7]. In the case $c=1$, however, the convergence towards the predicted reptation scaling law $\tau\sim M^3$ is rather slow over this size range, and a $\tau\sim M^{3.36}$ line provides an acceptable fit (not shown). This is not surprising since strong finite-size corrections are expected for finite sizes $M$ due to tube length fluctuations, which scale like $M^{-1/2}$ [8]. In fact, the form $\tau(M)=71M^3[1-1.14/M^{1/2}]^2$ provides a better fit (see Fig. 2; the last term is the correction factor for finite-size effects [8]). Because of these strong $c=1$ finite-size effects, it is more appropriate to refer to our molecules as oligomers. For intermediate concentrations, empirical scaling laws $\tau\sim M^\gamma$ are also found. We note that $\gamma$ increases quickly from 2.55 to 3.28 between $c=0$ and $c=0.2$, and attains a maximum value of 4.14 at $c=0.9$. Surprisingly, the longest
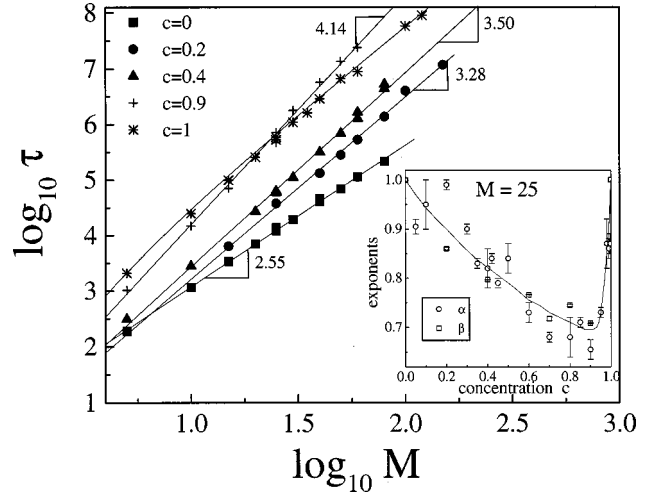


FIG. 2. Log-log plot of the integral relaxation time $\tau$ vs molecular size $M$ for various concentrations $c$. The slopes of the straight line fits are shown. The fit for $c=1.0$ is the theory-motivated function $\tau(M)=71M^3[1-1.14/M^{1/2}]^2$. Inset: exponents $\alpha$ and $\beta$ vs concentration $c$ for $M=25$.

relaxation times (as measured by the integral times $\tau$) are not found at $c=1.0$ here (for $M>20$). Clearly, disorder has a major impact on oligomer chain relaxation.

As can be seen in the inset of Fig. 1, the $c=1$ and $c=0.9$ decay curves are almost identical for $t<4\times10^5$, but diverge for later times. Therefore, polymers take more time to *fully* relax in the presence of a *small* degree of disorder, despite the lower density of obstacles. The decay curves conform well to the stretched-exponential or Kohlrausch-Williams-Watts (KWW) relation [9,10]

$$C(t)=\exp\left[-\left(\frac{t}{\tau^*}\right)^\alpha\right], \qquad (3)$$

where $0<\alpha\le1$ (see, e.g., $c=0.9$ in Fig. 1). Note that Eqs. (2) and (3) are simply related through $\tau=[\Gamma(1/\alpha)/\alpha]\times\tau^*$, where $\Gamma$ is the gamma function. Of course, it is because the stretched exponent $\alpha$ is much lower in the range of concentrations where strong entropic trapping occurs (approximately $0.6<c<0.95$ for our system [2–5]) that relaxation is anomalously slow in these cases.

In previous studies on disordered systems [1,5,11], it was remarked that the displacement $r_{c.m.}$ of the center of mass (c.m.) often follows anomalous subdiffusive scaling $r^2_{c.m.}=4D^*t^\beta$ (with $\beta<1$), where $D^*$ is the anomalous diffusion coefficient. Figure 3 shows that it is the case here for short times. Steady state (i.e., $r^2_{c.m.}=4Dt$) is achieved for longer times. The transition from anomalous to steady-state diffusion defines the steady-state time $t_{SS}=(D^*/D)^{1/(1-\beta)}$. For $c=0$ and 1, however, diffusion is normal over the whole range of times and $t_{SS}$ is ill-defined. The inset of Fig. 2 shows that the anomalous exponent $\beta$ corresponds rather well with the stretched exponent $\alpha$ when plotted versus the concentration $c$. In fact, the two are essentially indistinguishable given the scatter in our data.

Therefore, conformational relaxation, as described by $C(t)$, and center-of-mass anomalous diffusion appear to be related. This coupling implies a new expression for the correlation function,
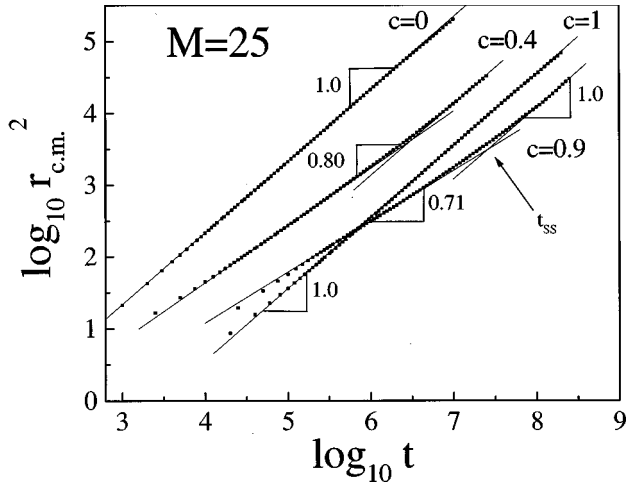
FIG. 3. Log-log plot of the mean-square displacement of the center of mass, $r_{c.m.}^2$, vs time $t$, for an $M=25$ chain and various concentrations $c$. The steady-state time $t_{SS}$ is defined at the transition between the short-time anomalous diffusion regime and the steady-state regime, as shown.

$$C(r_{c.m.}(t)) = \exp\left(-\left[\frac{r_{c.m.}(t)}{\lambda(c,M)}\right]^2\right), \qquad (4)$$

where $\lambda(c,M)$ is then the natural "relaxation length scale." In the Rouse and reptation limits ($c=0$ and 1, respectively) one has simply $\alpha=\beta=1$, $r_{c.m.}\sim t^{1/2}$, and $\lambda\sim R_g\sim M^{3/4}$, as discussed previously. For intermediate concentrations, Fig. 4 shows that plotting $\ln(C)$ versus $(r_{c.m.})^2$ indeed yields straight lines (except, again, for very short distances and times), indicating that $\alpha=\beta$ during relaxation. This is a novel way to investigate polymer relaxation in disorder systems.

Because $\tau\ll t_{SS}$, conformational relaxation occurs well within the transient anomalous diffusion regime in the presence of disorder; consequently, the simple scaling argument $\tau\sim R_g^2/D$ is not valid and the relaxation length scale is not $\lambda_0=(4D\tau)^{1/2}$. Instead, our finding suggests the existence of
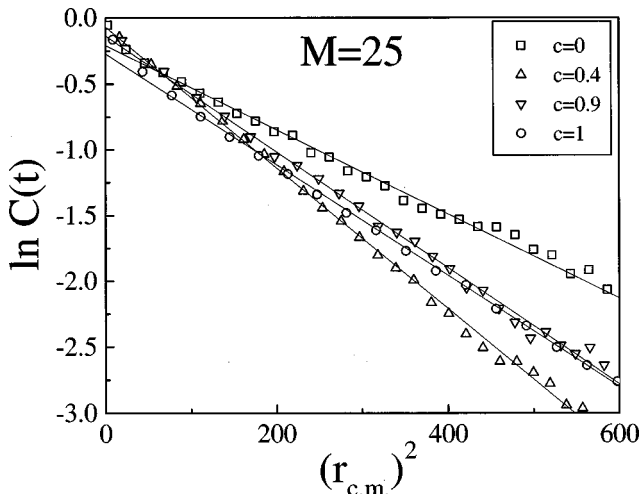
FIG. 4. Plot of $\ln C$ vs $r_{c.m.}^2$ for $M=25$ and different concentration $c$. Straight line fits are shown (the latter provides a good fit except when very close to $r_{c.m.}=0$). The slope gives $-1/\lambda^2$.
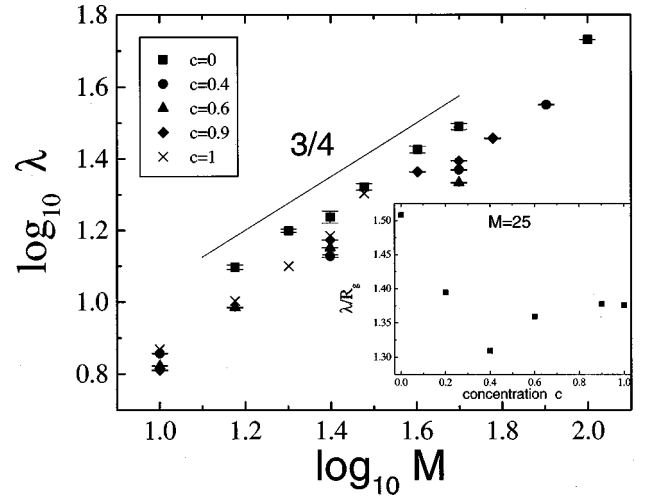
FIG. 5. Relaxation length scale $\lambda$ vs molecular size $M$ for different concentrations $c$. The $\nu=\frac{3}{4}$ slope corresponds to Flory's scaling law for the radius of gyration. Inset: ratio $\lambda/R_g$ vs concentration $c$ for $M=25$.

a new length scale $\lambda\geqslant\lambda_0$ defined as $\lambda^2=4D^*(\tau^*)^\beta$, with $\beta$ and $D^*$ characterizing anomalous diffusion and $\tau^*$ the relaxation process, respectively. Figure 5 shows that $\lambda$ scales approximately like $M^{3/4}$ for all concentrations (there is no clear deviation from this slope in our data, although we cannot rule out such deviations given the noise in the data). In other words, our data suggest that we have a relationship $\lambda=f(c)\times R_g$, where $f(c)>1$ is a numerical factor of order unity that decreases slowly with $c$ (inset of Fig. 5).

## IV. CONCLUSION

Our Monte Carlo simulations previously revealed that disorder dramatically affects polymer dynamics [2,3,5]. For example, we reported that the diffusion coefficient $D(M)$ and the radius-of-gyration $R_g$ both attain minimum values for $c\approx0.90$ in our model system. In this short paper, we found that polymer relaxation is also strongly affected. For instance, the relaxation of the end-to-end vector follows a stretched exponential, while the diffusion of the center of mass is anomalous for a period of time which greatly exceeds the relaxation time. Again, it is in the presence of a small amount of disorder (i.e., for $c\approx0.90$) that we find the slowest dynamics, e.g., the longest relaxation times. This is a good example of the impact of entropic traps on polymer properties. Large random voids can act as deep potential wells which trap the polymer chains and modify their dynamics.

Stretched exponentials have been reported in a wide class of materials, including polymeric substances and glasses [12], and have often been explained using the concept of dynamic heterogeneity [13]. Here, they result from the coupling between the relaxation process and the disorder-related anomalous diffusion, defining a new relaxation length scale $\lambda=[2dD^*\tau^\beta]^{1/2}$. We suggest that $\lambda$ is the fundamental parameter pertaining to polymer relaxation in quenched disor-

dered systems. For our model two-dimensional system, we find the approximate relationship $\lambda \sim R_g$, but this somewhat surprising result may in fact be system-dependent. It would be most interesting to examine, for example, how the lack of excluded volume effects (or the weaker excluded volume effects present in three-dimensional systems) would affect this apparent scaling law. We hope that this concept will

prove useful to understand polymer entropic trapping in quenched disordered media.

## ACKNOWLEDGMENT

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