Crossover behavior for long reptating polymers

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We analyze the Rubinstein-Duke model for polymer reptation by means of density matrix renormalization techniques. We find a crossover behavior for a series of quantities as function of the polymer length. The crossover length may become very large if the mobility of end groups is small compared to that of the internal reptons. Our results offer an explanation to a controversy between theory, experiments and simulations on the leading and subleading scaling behavior of the polymer renewal time and diffusion constant.

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The study of the dynamical properties of polymers is a field of great interest, because of important applications ranging from material science to biophysics. The process of reptation, i.e. the motion of a polymer along its own contour by the diffusion of stored length, is generally believed to be one of the most important mechanisms for polymer dynamics \cite{rubinstein1986}. The simplest model for reptation is that introduced by Rubinstein \cite{rubinstein1986} and later extended by Duke \cite{duke1988} to include the effect of a driving field. In spite of its simplicity the Rubinstein–Duke (RD) model contains the essential physics of reptation and compares well with experiments \cite{van2011}. As very little exact results are available for the model one has to rely on numerical techniques to investigate its properties.

In this Letter we present results on the scaling behavior of the polymer renewal time and diffusion constant, which are obtained by the Density–Matrix Renormalization–Group (DMRG) technique \cite{white1992}. DMRG allows to compute stationary state properties for rather arbitrarily long polymers with unprecedented accuracy. We find a crossover behavior with two different regimes: for an intermediate range of lengths various quantities scale as a function of the polymer length with effective exponents that differ from the asymptotic ones. We also show that by tuning an appropriate parameter it is possible to increase or decrease considerably the crossover length, i.e. the characteristic length which separates the two regimes. The findings help to clarify controversial results between theory, simulations and experiments for the renewal time and diffusion constant. Crossover behavior for single polymer reptation has been suggested earlier on various occasions \cite{rubinstein1986, duke1988}. Our results are an articulation and proof of these suggestions. Moreover they enable us to pinpoint the crossover region precisely and to estimate the effective exponents for arbitrarily long polymers.

We consider here a $d$-dimensional version of the RD model on a hypercubic lattice (see Fig.1(a)). The polymer is divided in $N$ segments, or reptons, of the size of the order of the persistence length and each lattice site can accommodate an unlimited number of them. It is convenient to introduce a small driving external field $\varepsilon$, applied in a direction tilted by $45^\circ$ degrees with respect of the axes of the lattice: following previous work \cite{rubinstein1986} we assign a rate $B = \exp(\varepsilon/2)$ for moves of reptons in the direction of the field, while moves in the opposite direction occur with a rate $B^{-1}$. Here $\varepsilon$ is a dimensionless unit for the strength of the driving field. We focus here on the properties in the limiting regime of small $\varepsilon$, although the DMRG technique is not restricted to this regime.

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\begin{equation}
\frac{dP(y, t)}{dt} = \sum_{y'} [W(y|y')P(y', t) - W(y'|y)P(y, t)] = \sum_{y'} H_{yy'} P(y', t) \tag{1}
\end{equation}

in the limit $t \to \infty$. Here $P(y, t)$ indicates the probability of finding the polymer in a configuration $y$ at time $t$ and $W(y'|y)$ is a transition rate per unit of time from a configuration $y$ to a configuration $y'$. The matrix $H$ contains both the gain and loss terms and is stochastic in the sense that the sum over all columns vanishes, as required from the conservation of probability.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{(a) Configuration of a chain with $N = 8$ reptons embedded in a two-dimensional lattice. (b) One-dimensional projection of the configuration of (a) along the direction of the applied field identified by the sequence of relative projected coordinates $y = \{1, 0, 1, 1, -1, 1, 0\}$. The vertical arrows represent the allowed moves for the reptons.}
\end{figure}
Since the transition probabilities depend only on the projected coordinate along the field direction the RD model becomes essentially one dimensional (see Fig. (b)). The relative coordinates between neighboring reptons can assume only three values $y = \{-1, 0, +1\}$, therefore for a chain of $N$ reptons there are $3^{N-1}$ possible configurations. One should distinguish between moves for internal and end reptons. In terms of the $y$ coordinates the moves are: (a) Exchange of 0’s and 1’s for internal reptons, i.e. ±1, 0 ↔ 0, ±1, (b) end repton contractions ±1 → 0, (c) end repton stretchings 0 → ±1.

The only effect of the dimensionality appears on the rates for the moves (c), which are $dB dB^{-1}$ for moves in the direction (opposite to) the field, as the end repton can move to unoccupied new sites (here dimension stands basically for the lattice coordination number $[3]$). Rates for the moves of type (a) and (b) are not affected by $d$. In general the dimensionality is believed to have no influence on the dependence of the properties on $N$, as far as the exponents of the asymptotic behavior are concerned. On a quantitative level, as we shall see, the influence of $d$ is however large. Higher dimensions stretch the polymer by giving a larger rate to the stretching processes (c). Not only integer values of $d$ are physically relevant, since the dimension enters in the RD model as the ratio between end–point stretching and end–point contraction. This allows to consider also values $d < 1$. The limit of small $d$ corresponds to the case where the motions of type (c) are suppressed. We will show that $d$ strongly influences the crossover behavior and the appearance of effective exponents.

In principle a direct numerical diagonalization of the matrix $H$ yields, for instance, the polymer drift velocity and the relaxation time $\tau$. In practice such calculations are restricted to polymers of rather short lengths ($N \leq 20$) as the dimensionality of the configurational space grows exponentially with the number of reptons $N$. This problem can be overcome by the DMRG technique $[4]$ that we apply here to the RD model. DMRG has been used for quite some time now and it is known for its accuracy and for the possibility of treating large systems using an efficient truncated basis set. Although originally introduced for hermitian matrices $[5]$, the DMRG method has also been applied to a series of non-hermitian problems $[6]$. In the latter case the results are known to be less accurate than in the hermitian case, however since we are primarily interested on the small field limit the matrices to be diagonalized are only weakly non-hermitian, therefore DMRG is expected to perform well in this case.

**Renewal time** - We set first $\varepsilon = 0$. In this limit the matrix $H$ is symmetric since moves in the direction and opposite to the field are equally probable. The longest relaxation time $\tau$, also known as polymer renewal time, is a quantity also accessible to experiments since it is related to viscosity. Theoretical arguments predict a scaling behavior as function of the chain length of the type $\tau \sim N^z$, with $z = 3 \quad [1]$. Various experiments yielded numerical values of the exponents systematically higher $z \approx 3.2 - 3.4$ (see, for instance, $[3] \quad [7]$ and references therein). This apparent disagreement has generated some discussions in the past years and quite some effort has been devoted to reconcile theory with experiments. Doi $[8]$ argued that the discrepancy is due to finite size effects and proposed the following expression

$$\tau \sim N^3 \left[ 1 - \sqrt{\frac{N_0}{N}} \right]^2,$$  \quad (2)

with $N_0$ a characteristic length such that only for $N \gg N_0$ the right asymptotic behavior can be observed. Rubinstein $[8]$ showed that a numerical calculation in the RD model (for chains up to $N \approx 100$ reptons) yielded $\tau \sim N^{3-\varepsilon}$, however the asymptotic behavior $N^3$ was not observed.

![FIG. 2. (a) Plot of $z_N$ as function of $N^{-1/2}$ for $d = 1, 2, 3$; the dashed line is a cubic fit in powers of $N^{-1/2}$ for the $d = 3$ case and the dotted-dashed line is obtained from Eq. $[10]$. (b) As in (a) for $d = 0.10, d = 0.25$ and $d = 0.50$. Here and in all the other figures error bars, unless explicitly shown, are smaller than symbol sizes.](image)

The renewal time is the inverse gap of the matrix $H$, a quantity which is easily accessible in the DMRG calculation. To estimate the exponent $z$ we considered:

$$z_N = \frac{\ln \tau_{N+1} - \ln \tau_{N-1}}{\ln (N+1) - \ln (N-1)},$$  \quad (3)

which converges to $z$ in the limit $N \to \infty$.

In Fig. (a) we show $z_N$ for $d = 1, 2, 3$ plotted as a function of $1/\sqrt{N}$ since this type of correction-to-scaling term is predicted by Eq. $[4]$. Using a cubic fit in powers of $1/\sqrt{N}$ we find $z = 3.00(2)$ for $d = 3$, $z = 3.002(4)$ for $d = 2$ and $z = 2.99(1)$ for $d = 1$, in agreement with the
theoretical arguments leading to a renewal time scaling as \( \tau \sim N^3 \). Figure 3(a) shows also the fitting curve for \( d = 3 \) (dashed) and the prediction from Doi’s theory obtained by substituting Eq. (2) into Eq. (3) (dot-dashed). The latter compares very well with our data in the region of large \( N \), but fails to reproduce the change of curvature in \( z_N \), which is characteristic for the DMRG results.

While in the case \( d = 2, 3 \) the asymptotic value is approached monotonically from above, for \( d = 1 \) \( z_N \) shows a non-monotonic behavior. In a plot of \( \ln \tau_N \) vs. \( \ln N \) the maximum of \( z_N \) corresponds to an inflection point, where curvature is absent. Therefore in a range of lengths around the maximum the numerical data would be fitted rather well by an effective exponent \( z_{\text{eff}} = \max_N z_N \). This is particularly true in the case of data affected by small, but non-negligible error bars, as it happens in experiments or in computer simulations. A monotonic behavior is less harmful since in a \( \ln \tau_N \) vs. \( \ln N \) plot one should be able to distinguish always a non-vanishing curvature, although it may happen that the data are well fitted with effective powers in a range of values of \( N \) also in that case. We refer to the non-monotonic behavior as to a crossover effect. To investigate it more into details we considered also \( d < 1 \) (see Fig. 3(b)). For \( d = 0.5 \) and \( d = 0.25 \) again the data show a non-monotonic behavior in \( N \) and the turning point shifts to larger \( N \), i.e. crossover effects are more pronounced. For \( d = 0.1 \), the smallest value considered here, and for the range of \( N \) investigated, \( z_N \) increases monotonically. Assuming that the asymptotic exponents do not depend on \( d \), the turning point will be reached with much longer polymers than those considered here. It is also important to point out that the values for the effective exponent that we estimate from our data \( z_{\text{eff}} \approx 3.2 - 3.4 \) are exactly in the range of values which are found experimentally in measures of viscosity \( \eta \). Therefore our results strongly support the idea that the differences between theory and experiments are due to a crossover effect, as pointed out by some authors in the past \[13\]. The advantage of the DMRG calculations is here that they provide clear information of both the asymptotic and non-asymptotic regions. Moreover, in the case of \( d \) small, we find a range of lengths for which the renewal time scales with a local exponent smaller than 3 (see Fig. 3(b)). The crossover to the asymptotic regime where \( z = 3 \) is approached from above (as in Eq. 3) occurs only for extremely long polymers. We are not aware of any experiments showing this type of behavior; possible candidates could be concentrated polymer solutions with bulky endgroups in such a way that endpoint strechings are suppressed.

**Diffusion constant – Crossover behavior** appears also in other quantities, as for instance in the scaling of the diffusion constant \( D(N) \) as function of the polymer length \( N \). We calculated \( D(N) \) by applying a small field \( \varepsilon \) and using the Nernst–Einstein relation \[12\]

\[
D = \lim_{\varepsilon \to 0} \frac{v}{N\varepsilon}.
\] (4)

For the scaling behavior of \( D(N) \) one expects

\[
D(N) = \frac{1}{AN^2} \left( 1 + \frac{B}{N^\gamma} \right)
\] (5)

where the leading term \( N^{-2} \) is by now well-understood \[1–3,13–16\] and it is considered to be experimentally verified \[17\]. In the RD model also the prefactor happens to be known exactly \[4,11\]: \( A = 2d + 1 \). The next to leading order term has been investigated as well. By relating the diffusion constant to the renewal time it was predicted \[18\] that the correction term would be anomalous, i.e. \( \gamma = 1/2 \). This prediction is also supported by other theoretical arguments \[15\]. On the other side accurate Monte Carlo simulation results, done for \( d = 1 \), could be best fitted with a power \( \gamma \approx 2/3 \) both for the RD model \[13\] and also for another model of polymer reptation \[14\]. This issue is still unresolved. An exponent \( 2/3 \) is somewhat surprising since, as also seen above for the gap one naturally expects \( N^{-1/2} \) corrections.

\[
\text{FIG. 3. Log-log plot of } D N^2 - 1/3 \text{ vs. } N \text{ for } d = 1. \text{ The DMRG data are in good agreement with the exact ones and with the Monte Carlo results. Inset: blow up of the region for large } N \text{ where the deviation of the DMRG data from the slope } 2/3 \text{ starts being noticeable.}
\]

In Fig. 3 we show a plot of \( g_N = D(N)N^2 - 1/A \) as function of \( N \) on a log-log scale for \( d = 1 \). The figure shows results from exact diagonalization for small lattices, Monte Carlo simulations \[8\] and DMRG results which we extended up to \( N = 57 \). DMRG data are in good agreement with those obtained from other methods and follow rather nicely a slope \( -2/3 \) in the plot. Only a very close inspection of the region of large-\( N \) systems reveals (see inset) that this slope is not the correct asymptotic one. Similar to the gap, this can be best seen from the discrete derivative.
\[
\gamma_N = -\frac{\ln g_{N+1} - \ln g_{N-1}}{\ln(N+1) - \ln(N-1)}.
\] (6)

A plot of \(\gamma_N\) vs. \(1/\sqrt{N}\) is shown in Fig. 3 for \(d = 1, 2\) and 3. As for the gap, we note a non-monotonic behavior for \(d = 1\), where the maximum of \(\gamma_N\) is found at about 0.68, i.e. very close to the power \(\gamma = 2/3\). However for sufficiently large \(N\), \(\gamma_N\) clearly deviates from \(2/3\) to smaller values. For \(d = 2\) and 3, \(\gamma_N\) is monotonic in \(N\).

Like for the renewal time exponent \(z_N\), we fit \(\gamma_N\) with a cubic curve containing powers of \(1/\sqrt{N}\):

\[
\gamma_N = \gamma + \sum_{i=1}^{3} \frac{\alpha_i}{N^{i/2}},
\] (7)

where \(\gamma\) and \(\alpha_i\) are fitting parameters. Extrapolations yield \(\gamma = 0.51(1)\) \((d = 3)\), \(\gamma = 0.51(1)\) \((d = 2)\) and \(\gamma = 0.48(3)\) \((d = 1)\). These results strongly support a correction term with \(\gamma = 1/2\).

In conclusion, the above results show that DMRG is a very powerful technique to investigate the properties of a reptating polymer. In this Letter we have restricted ourselves to two aspects: the renewal time and the diffusion coefficient. The accurate values for a large set of lengths \(N\) make it possible to determine the corrections to scaling with great precision. In this way we find a natural reconciliation of the fairly strong theoretical arguments for a renewal time exponent \(z = 3\) and the equally pertinent experimental findings of values around \(z \approx 3.2 - 3.4\). Our analysis also shows that log–log plots to determine exponents are hazardous when such large corrections to scaling are present. In particular when the effective exponent shows a stationary point as function of \(N\), it shows up as an inflection point which can be easily mistaken for the asymptotic region in case of insufficient data. On the other hand the method of differential exponents is a very accurate indicator of the asymptotic behavior. However differential exponents require precision data for many values of the length \(N\), which neither in Monte Carlo simulations nor in experimental measurements are feasible.

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