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Crossover behavior for long reptating polymers

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The Rubinstein-Duke model for polymer reptation is analyzed by means of density matrix renormalization techniques. It is found that the crossover in the scaling behavior of polymer renewal time (or viscosity) arises from the competing effect of the contribution due to tube length fluctuations and higher-order corrections, which are of opposite sign. Experiments which ought to emphasize both contributions are suggested. The exponent describing the subleading scaling behavior of the diffusion coefficient is also investigated.

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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 [1,2]. The simplest model for reptation is that introduced by Rubinstein [3] and later extended by Duke [4] 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 [5]. As very little exact results are available for the model, one has to rely on numerical techniques to investigate its properties.

In this Rapid Communication we study the scaling behavior as a function of the polymer length N, of the characteristic time for reptation τ (known as polymer renewal time), and of the diffusion constant D. These quantities are obtained by the density-matrix renormalization-group (DMRG) technique [6]. The reptation theory predicts that the diffusion constant and renewal time scale asymptotically as $D\sim N^{-x}$ and $\tau\sim N^{z}$, with $x=2$ and $z=3$, respectively [1]. While the scaling $D\sim N^{-2}$ is considered experimentally verified [7], a long debate [1,2] has been generated around the value of the exponent z, which was found experimentally to be systematically higher than 3: measurements of viscosity, which is essentially proportional to τ, of dense polymer mixtures yielded typically $z\approx 3.3-3.4$. It was suggested earlier [8,3] that this discrepancy is due to crossover effects that mask the correct asymptotic behavior and an analytic expression for the correction terms has been proposed. The aim of this paper is to investigate further this fundamental issue using the DMRG method, which allows us to compute stationary state properties of rather long polymers with an unprecedented accuracy. We find that crossover effects arise because of the competition between leading correction terms originating from tube length fluctuations [2] and higher-order terms, which are typically of opposite sign, and, to our opinion, cannot be neglected. The interplay between these two terms gives rise to the appearance of approximate power laws that are not the true asymptotic ones. Moreover we find that the crossover region is rather sensitive to a parameter describing the behavior of the endpoints of the chain. We suggest that by tuning this parameter in an experiment it would be possible to explore both types of contributions.

We consider 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 (here ''repton'' stands for the basic unit for reptation), 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 ε, applied in a direction tilted by 45° with respect to the axes of the lattice: following previous work [9], 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 ε is a dimensionless unit for the strength of the driving field. We focus here on the properties in the limiting regime of small ε, although the DMRG technique is not restricted to this regime.

The stationary state properties of the system can be derived from the solution of the Master equation

$$\frac{dP(y,t)}{dt}=\sum_{y'}\left[W(y|y')P(y',t)-W(y'|y)P(y,t)\right]$$

$$=\sum_{y'}H_{yy'}P(y',t) \qquad (1)$$

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

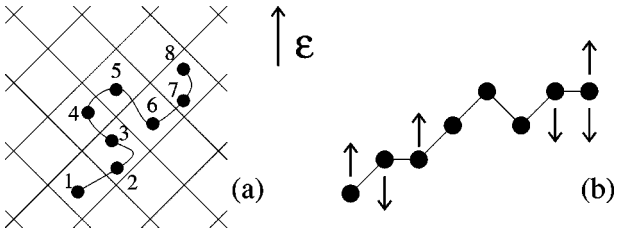

FIG. 1. (a) Configuration of a chain with $N=8$ reptons embedded in a two-dimensional lattice. (b) One-dimensional projection of the configuration of (a) along the direction of the applied field identified by the sequence of relative projected coordinates $y=\{1,0,1,1,-1,1,0\}$. The vertical arrows represent the allowed moves for the reptons.

gain and loss terms and is stochastic in the sense that the sum over all columns vanishes, as required from the conservation of probability.

Since the transition probabilities depend only on the projected coordinate along the field direction, the RD model becomes essentially one-dimensional [see Fig. 1(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: (i) Exchange of 0's and 1's for internal reptons, i.e., $\pm 1,0 \leftrightarrow 0,\pm 1$, (ii) end repton contractions $\pm 1 \rightarrow 0$, and (iii) end repton stretchings $0 \rightarrow \pm 1$.

The only effect of the dimensionality appears on the rates for moves (iii), which are dB (dB^{-1}) for moves in the direction of (opposite to) the field, as the end repton can move to d unoccupied new sites. Rates for the moves of types (i) and (ii) are not affected by d. Rather than linking d with the dimensionality (or even the coordination number) of the lattice, we prefer to see d as a parameter for the properties of the endpoints of the polymer which influences the asymptotic behavior in an important way. This allows us to also consider values $d<1$. The limit of small d corresponds to the case where the motions of type (iii) are suppressed, while for d large the polymer is stretched.

Renewal time. As can be deduced from Eq. (1) the renewal time corresponds to the inverse of lowest gap of the matrix H, which we calculate by DMRG setting $\varepsilon=0$. We recall that the DMRG method, although approximate, provides extremely accurate results [6,11]; in the present computation gaps are obtained for polymers of the order of $N \approx 100$ reptons and with a typical accuracy of six to seven significant digits; therefore, results can be considered, for practical purposes, numerically exact.

Doi [8] argued that the discrepancy between theoretical predictions and experimental results on the scaling of the polymer renewal time is due to finite size effects (due to length fluctuations) and proposed the following expression:

$$\tau_N \sim N^3[1-\sqrt{N_0/N}]^2, \tag{2}$$

with N_0 a characteristic length such that only for $N \gg N_0$ the right asymptotic behavior can be observed. Rubinstein [3] showed that a numerical calculation in the RD model (for chains up to $N \approx 100$ reptons) yielded $\tau_N \sim N^{3.4}$; however, the asymptotic behavior N^3 was not observed.

To analyze the scaling behavior of τ_N, we considered

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

which converges to z ($\tau_N \sim N^z$) in the limit $N \rightarrow \infty$.

In Fig. 2(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. (2). 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 $\tau \sim N^3$ [1]. Figure

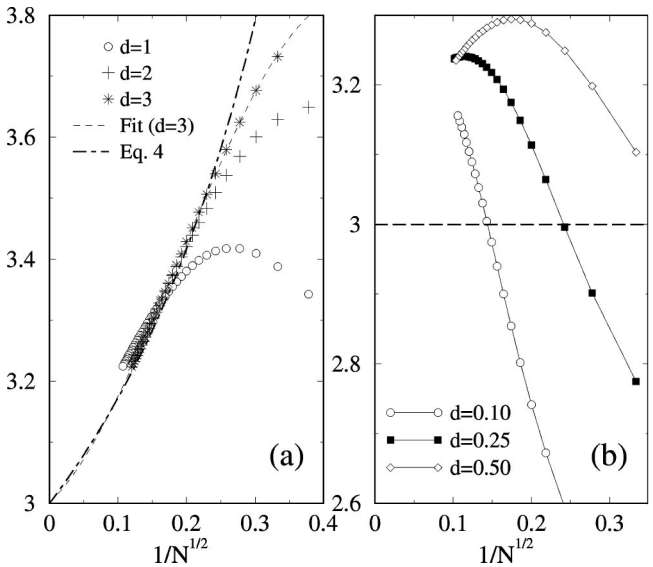

FIG. 2. (a) Plot of z_N as function of $N^{-1/2}$ for $d=1,2,3$; the dashed line is a cubic fit in powers of $N^{-1/2}$ for the $d=3$ case and the dotted-dashed line is Eq. (4). (b) As in (a) for $d=0.10,0.25,0.50$. Here and in all the other figures error bars, unless explicitly shown, are smaller than symbol sizes.

2(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) (dotted-dashed), which yields

$$z_N = 3 + \frac{\sqrt{N_0/N}}{1-\sqrt{N_0/N}}. \tag{4}$$

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. Typically, the DMRG data for z_N are charaterized by a maximum, which in a plot of $\ln \tau_N$ versus $\ln N$ 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 $z_{\text{eff}} = \max_N z_N$. Our analysis indicates that, for an appropriate description of the crossover region, one needs to include further correction terms beyond those given in Eq. (2). It would be desirable to have some analytical insight on the physical origin of these terms.

It is also interesting to investigate the effect of the endpoints stretching rate d on the scaling behavior of τ. As shown in Figs. 2(a) and 2(b), the maximum of z_N decreases when d decreases; we find $z_{\text{eff}} \approx 3.4$ ($d=1$) and $z_{\text{eff}} \approx 3.2$ ($d=0.5$). For d sufficiently small ($d=0.1$) the maximum disappears; assuming that asymptotic exponents do not depend on d, the turning point will be reached to much longer polymers than those considered here. Note that there is a range of lengths where z_N becomes even smaller than 3.

We recall that, although the reptation theory strictly applies to the motion of an isolated polymer into a fixed network of obstacles, it is also used to describe more complicated situations as concentrated solutions of flexible polymers [2]. The idea behind this assumption is that each polymer is topologically constrained by its neighbors, which

on the relevant timescale for the dynamics can be viewed as forming a frozen environment. It is not clear whether this simplifing assumption is always legitimate; for instance, it has been suggested that the discrepancy between theory and experiments on the polymer renewal time may be due to inter chain interactions [12], which are not included in the simple reptation theory.

If the RD model correctly describes dense polymer solutions, we expect that the exponent z found experimentally in viscosity measurements decreases when decreasing d. A way of exploring experimentally different d values would be that of coating the ends of the chains with some large molecules; if their size becomes comparable to that of the entanglement distance, the value of d could be substantially lowered. For sufficiently small d, endpoint fluctuations are suppressed and the system should enter in a different regime where corrections beyond Eq. (2) start to play a dominant role and $z_N < 3$, as seen from the curve with $d=0.10$ in Fig. 2(b). An experimental verification of these ideas would be rather useful to understand further the long debated issue of the polymer relaxation time.

Diffusion constant. Crossover behavior also appears in other quantities; for instance, in the scaling of the diffusion constant $D(N)$ as a function of the polymer length N. We calculated $D(N)$ by applying a small field ε and using the Nernst-Einstein relation [14]

$$D=\lim_{\varepsilon\to 0}\frac{v}{N\varepsilon}. \tag{5}$$

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

$$D(N)=\frac{1}{AN^2}\left(1+\frac{B}{N^{\gamma}}\right) \tag{6}$$

where the leading term N^{-2} is by now well-understood [1–3,15–18] and is considered to be experimentally verified [7]. In the RD model also the prefactor happens to be known exactly [16,17]: $A=2d+1$. The next to leading order term has been investigated as well. By relating the diffusion constant to the renewal time it was predicted [19] that the correction term would be anomalous, i.e., $\gamma=1/2$. This prediction is also supported by other theoretical arguments [17]. 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 [15] and also for another model of polymer reptation [18]. 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.

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 [10], and DMRG results which we extended up to $N=57$ [13]. 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

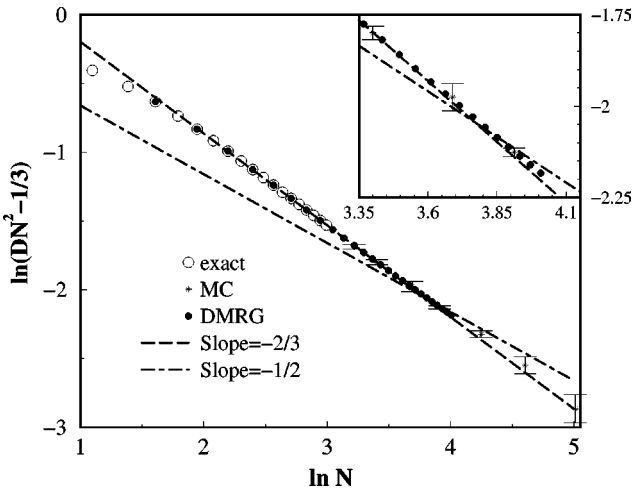

FIG. 3. Log-log plot of $DN^2-1/3$ vs N for $d=1$. The DMRG data are in good agreement with the exact ones and with the Monte Carlo results. Inset: blow up of the region for large N where the deviation of the DMRG data from the slope 2/3 starts being noticeable.

slope is not the correct asymptotic one. Similar to the gap, this can be best seen from the discrete derivative

$$\gamma_N=-\frac{\ln g_{N+1}-\ln g_{N-1}}{\ln(N+1)-\ln(N-1)}. \tag{7}$$

A plot of γ_N versus $1/\sqrt{N}$ is shown in Fig. 4 for $d=1$, 2, and 3. As for the gap, we note a nonmonotonic behavior for $d=1$, where the maximum of γ_N is found at about 0.68, i.e., very close to the conjectured power $\gamma=2/3$. However, for sufficiently large N, γ_N clearly deviates from 2/3 to smaller

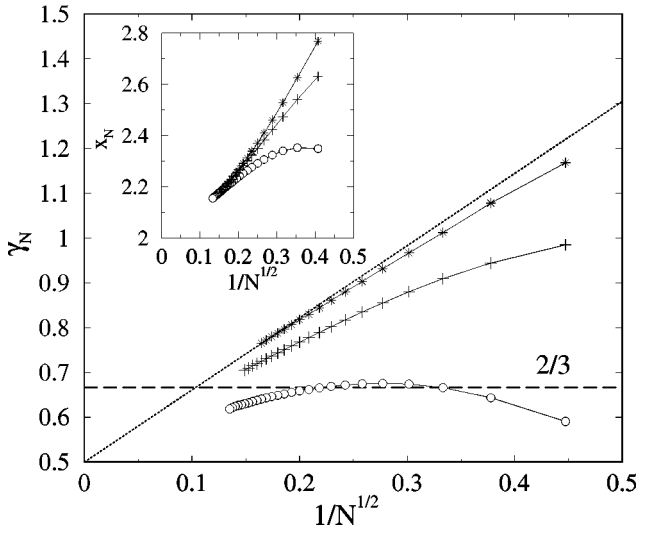

FIG. 4. Plot of the effective exponent γ_N as function of $1/\sqrt{N}$ for $d=1$ (circles), 2 (pluses), and 3 (stars). The horizontal dashed line indicates the value of the correction exponent $\gamma=2/3$ conjectured on the basis of Monte Carlo simulations for $d=1$. The dotted line is a guide for the eye. Inset: Plot of the effective exponent describing the scaling behavior of the diffusion constant, which converges asymptotically to $x=2$.

values. For $d=2$ and 3, γ_N is monotonic in N. As we did for the renewal time exponent z_N, we fit γ_N with a cubic curve containing powers of $1/\sqrt{N}$. 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 $\gamma=1/2$. The case $d=1$ nicely illustrates the effect of a maximum in the effective exponent (see Fig. 4), which produces an inflection point in the plot of Fig. 3, and data apparently closely follow a straight line in the log-log scale. Finally, the inset of Fig. 4 shows the effective exponent obtained from the logarithmic derivative of the diffusion constant, which is seen to converge asymptotically to $x=2$. Notice that the behavior is similar to the curves of Fig. 2, but the maximum of x_N, which starts to develop when d becomes smaller, is less pronounced than for z_N. This indicates that crossover phenomena for the scaling of the diffusion constant are less severe than those involving τ.

In conclusion, the above results show that the DRMG is powerful technique to investigate the properties of a reptating polymer. Although we have restricted ourselves to the renewal time and the diffusion coefficient, the DMRG calculations also yield a host of detailed information about the structure of the reptating polymer, for instance, on the drift velocity and correlation functions; these results will be presented elsewhere. Here we have shown that the large finite size corrections, characteristic for the reptation process, manifest themselves as effective exponents for the asymptotic behavior of the renewal time and the diffusion coefficient. We found that DMRG results reveal that while the leading correction terms, as given by Doi's theory [2] fit rather well the data for large N, they are not sufficient to cause a crossover behavior, and higher-order corrections need to be included. 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 a function of N, it shows up as an inflection point that can easily be mistaken for the asymptotic region in the case of insufficient data.

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