

Density matrix renormalization group studies of the effect of constraint release on the viscosity of polymer melts

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The scaling of the viscosity of polymer melts is investigated with regard to the molecular weight. We present a generalization of the Rubinstein-Duke model, which takes constraint releases into account and calculates the effects on the viscosity by the use of the density matrix renormalization group algorithm. Using input from Rouse theory, the rates for the constraint releases are determined in a self-consistent way. We conclude that shape fluctuations of the tube caused by constraint release are not a likely candidate for improving Doi's crossover theory for the scaling of the polymer viscosity.

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I. INTRODUCTION

The viscosity of polymer melts has been investigated intensively [1]. The models for describing this behavior, however, are not yet satisfying. Experiments show that the viscosity η scales like $M^{3.3\pm 0.1}$, where M is the molecular weight. This behavior is valid for several decades of the molecular weight. An early approach was the reptation model by de Gennes [2] which yields $\eta \propto M^3$ in the limit of infinitely long polymers. For short polymers Doi [3] calculated the viscosity by taking tube length fluctuations into account and found a region of M where the scaling is of the correct size—but this region appears to be too small. A discrete model for reptation which includes tube length fluctuations is the Rubinstein-Duke (RD) model [4,5]. Recently it was shown [6] that this model does not only provide a region where a scaling of $M^{3.3\pm 0.1}$ can be found, as already shown by Rubinstein [4], but also that this model shows a crossover to the reptation exponent 3. But again the mass region where the correct exponent is valid does not exceed one order of magnitude. In this paper we extend the RD model in order to investigate whether constraint release (CR) broadens that region. While good models for the nonlinear regime of viscosity can be constructed by using CR [7,8], there was only little success in the linear regime [9].

II. THEORY

A. RD model

In order to investigate the role of tube length fluctuations in reptation theory Rubinstein introduced a discrete “repton” model that allows the description of three-dimensional reptation dynamics by a one-dimensional lattice gas [4]. Duke generalized the model to the case that an external electric field acts on a charged polymer [5] which allows a good description of the diffusion constant in gel electrophoresis experiments [10]. However, also in the absence of a field the generalization by Duke is useful insofar as it provides a reference axis along which the displacement of the polymer

chain as a whole can be monitored. This makes it possible to calculate the diffusion coefficient and the viscosity from the model, without resorting to independent hypotheses.

Rubinstein assumes that constraints of the other polymers divide space into cells which form a d -dimensional regular cubic lattice. The polymer occupies a series of adjacent cells, the “primitive path.” It is not possible for the polymer to traverse the edges of the cells (in two dimensions (2D): the lattice points) so that only the ends of the polymer can enter new cells. The polymer is divided into segments whose lengths are of the order of the lattice constant, the number of segments is proportional to the length of the polymer or the molecular weight. The orientation of the lattice is introduced by Duke in a way that the electric field is diagonal to the lattice, i.e., in three dimensions in the (111) direction.

A segment—called a “repton”—is allowed to jump into an adjacent cell according to the following rules.

- (1) The reptons in the bulk are only allowed to jump along the primitive path.
- (2) No cell in the interior of the primitive path may be left empty.
- (3) The ends move freely insofar as rule (2) is respected. If an end repton occupies the cell alone, it can only retract in the cell of the adjacent repton. If the adjacent repton is in the same cell, the end repton may enter any of the 2D surrounding cells. Reptons in the bulk jump with the same probability as reptons at the end into occupied cells.

Rule (1) ensures that the polymer does not traverse the edges of the cells. Rule (2) is motivated by the fact that the segments are of the size of the lattice constant. Finally rule (3) reflects the fact that there are more free adjacent cells for an end repton than occupied ones. If one considers a field $F \neq 0$ the ratio of the probabilities to jump in, respectively, against the direction of the field is proportional to the Boltzmann weight. In the following we will only focus on the case without field, we only need the reference axis.

As the shape of the primitive path is not affected by the movement of the polymer and only the ends are created or annihilated this model can be mapped onto one dimension. To this end a particle is assigned to each bond between reptons; starting on one end, a bond into the direction of the field is identified with an A particle, against the field with a B particle and, finally, a bond without change of potential, i.e.,

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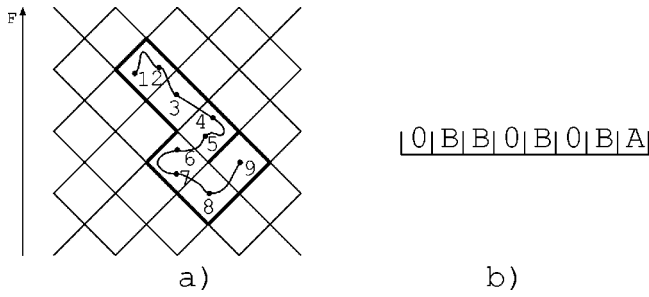


FIG. 1. (a) The repton model in two dimensions: the circles represent the reptons; the primitive path is marked by the bold lines. (b) Projection onto one dimension.

a bond between two reptons in one cell, by a vacancy \emptyset (Fig. 1) [18].

These particles are residing on a chain whose number of sites N is the number of bonds, thus the number of reptons minus one. As for each site three states are possible this model can be identified with a “quantum” spin-one chain [11,12]. We define

$$A \equiv \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \emptyset \equiv \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad B \equiv \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

We label this set of states with $X = \{A, \emptyset, B\}$. A state of a chain of length N can be considered as an element $|\eta\rangle$ of the tensor base $\mathbf{X} = X^{\otimes N}$; $|\eta\rangle$ is constructed by the tensor product of the three component vectors for the individual sites.

The dynamics of this one-dimensional model is

(1) A particles may exchange with vacancies \emptyset , $A\emptyset \rightleftharpoons \emptyset A$.

(2) B particles may exchange with vacancies \emptyset ; $B\emptyset \rightleftharpoons \emptyset B$.

(3) A particles may *not* exchange with B particles.

By these rules it is guaranteed that the shape of the primitive path is conserved. The following rules define the boundary dynamics.

(4) At the ends of the chain A particles may be annihilated, $A \rightarrow \emptyset$.

(5) At the ends of the chain B particles may be annihilated, $B \rightarrow \emptyset$.

(6) At the ends of the chain A particles may be created, $\emptyset \rightarrow A$.

(7) At the ends of the chain B particles may be created, $\emptyset \rightarrow B$.

The processes (1), (2), (4), and (5) take place with the same probability; the processes (6) and (7) are d times more probable.

In this way a stochastic interacting particle system on a one-dimensional chain has been defined. As the transitions are independent of the previous history this process is Markovian. It should be pointed out that the one-dimensional mapping is not able to reproduce the equilibrium statistics of the three-dimensional chain on length scales of the order of the tube diameter [13]. These length scales correspond to time scales much shorter than those investigated in this work

(the renewal of the primitive path whose dynamics is actually described in this model) and hence they need not taken into account.

B. Quantum Hamiltonian

A convenient way to describe the process mathematically is the quantum Hamiltonian formalism which we will present here shortly, for details see Ref. [11].

The probability to be in state $|\eta\rangle$ at time t is labeled by $P_\eta(t)$. These probabilities of the individual states can be combined to a vector: $|P(t)\rangle = \sum P_\eta(t) |\eta\rangle$. Due to the conservation of probability the entries of the vector $|P(t)\rangle$ sum up to 1 at any time t . With this definition the master equation can be written as

$$\frac{d}{dt} |P(t)\rangle = -H |P(t)\rangle \quad (1)$$

with the stochastic generator

$$H = - \sum_{\eta} \sum_{\eta' \neq \eta} w_{\eta' \rightarrow \eta} |\eta\rangle \langle \eta'| + \sum_{\eta} \sum_{\eta' \neq \eta} w_{\eta \rightarrow \eta'} |\eta\rangle \langle \eta'|. \quad (2)$$

Here $w_{\eta' \rightarrow \eta}$ is the transition probability from state $|\eta'\rangle$ to $|\eta\rangle$. In other words the off-diagonal elements of the matrix H are the negative transition rates between the respective states and the diagonal elements are the sum of the rates leading away from the respective state.

The creation operators a^\dagger and b^\dagger are defined by $a^\dagger \emptyset = A$ and $b^\dagger \emptyset = B$, acting on any other state yields zero. The annihilation operators a and b are defined by $aA = \emptyset$ and $bB = \emptyset$, again acting on any other state yields again zero. Finally we define the number operators $n^A = a^\dagger a$, $n^B = b^\dagger b$, and $n^\emptyset = 1 - n^A - n^B$. By these definitions the stochastic generator H of the RD model reads [12]

$$H = b_1(d) + b_N(d) + \sum_{n=1}^{N-1} u_n \quad (3)$$

with

$$\begin{aligned} b_n(d) &= d[n_n^\emptyset - a_n^\dagger + n_n^\emptyset - b_n^\dagger] + n_n^A - a_n + n_n^B - b_n, \\ u_n &= n_n^A n_{n+1}^\emptyset - a_n a_{n+1}^\dagger + n_n^B n_{n+1}^\emptyset - b_n b_{n+1}^\dagger + n_n^\emptyset n_{n+1}^A \\ &\quad - a_n^\dagger a_{n+1} + n_n^\emptyset n_{n+1}^B - b_n^\dagger b_{n+1}. \end{aligned}$$

Again, d labels the lattice dimension. We have chosen the time scale such that the hopping rate in the bulk equals unity.

C. Calculation of the viscosity

The viscosity is proportional to the longest relaxation time of the stochastic generator H which is the inverse energy gap [3]. Due to the conservation of probability the ground state of a stochastic generator has the eigenvalue zero, so that we only need to calculate the first eigenvalue.

A very efficient algorithm to calculate the lowest excitations of quantum spin chains is the density matrix renormal-

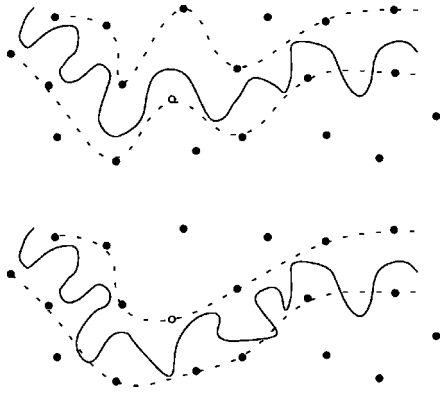


FIG. 2. A constraining polymer vacates for a short time its site and thus makes a constraint release event possible.

ization group (DMRG) algorithm [14,15]. For the standard RD model the usefulness of this algorithm has been demonstrated [6], so that we employ this algorithm as well for the modifications of the RD model, to be introduced in what follows. The Hilbert space of the spin chain grows exponentially with the number sites N ; the number of states is 3^N , so that for $N=50$ —the maximum number of sites considered in our calculations—the number of states is of the order 10^{23} . By this it is reasonable to project all quantities onto a subspace consisting of the most important states. The difficulty is to find out which states are the “most important.” The DMRG algorithm is a method that provides a choice of states which is optimal in terms of a maximum of the probability with which the states contribute to the target state [14,16]. This probability is gained by diagonalizing the density matrix. As the diagonalization of the density matrix for the whole system would be as laborious as the direct diagonalization of the Hamiltonian the system is built up stepwise. Starting with a small system (e.g., 2 states) one adds iteratively two states until the system has reached the searched size. In each step the Hilbert space is reduced to the subspace of the most probable states, so that the system size increases while the dimension of the matrices remain constant.

D. Constraint release

The RD model as well as standard reptation theory is based on the assumption that the polymer moves in a fixed network formed by the surrounding polymers. This assumption is at best justifiable for a single polymer immersed in a gel. But for polymer melts, for which the viscosity is measured, it should be taken into account that the surrounding polymers reptate themselves. In terms of the Rubinstein model this means that the lattice itself is subjected to fluctuations.

We consider the following model of lattice fluctuations: Imagine that a constraining polymer moves so far that the constraint for the investigated polymer is released so that it can move freely in this region. After a short time the constraining polymer returns or an other polymer has taken its place so that the free movement in this region is again prevented. The lattice has regained its original structure but the

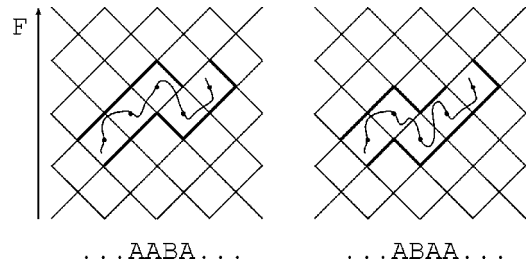


FIG. 3. Constraint release by AB permutation in the RD model.

primitive path may have changed in the bulk (Fig. 2). This is what we call a CR event.

Hence the effect of constraint release acts on the tube itself or in terms of the RD model on the primitive path, whose dynamics is simulated. This is why the effects can be easily adopted in this model. Again, it should be mentioned that the equilibrium statistics are only reproduced on the long time scale we are interested in. A straightforward implementation of this mechanism is shown in Fig. 3. The turning of the bend of the primitive path equals to the permutation of an AB pair. At the ends of the path A particles can be transformed into B particles and vice versa which corresponds to a CR event at the ends.

To construct the extended Hamiltonian that takes these mechanisms into account, we introduce an operator that transforms B particles into A particles,

$$c = a^\dagger b; \quad c^\dagger = b^\dagger a, \quad (4)$$

the adjoint operator effects the reversed process. The corresponding diagonal elements are build up by n^B , respectively, n^A . Now the new Hamiltonian can be written as

$$H^{CR} = H + g_1(\alpha) + g_N(\alpha) + \sum_{n=1}^{N-1} v_n(\alpha),$$

$$g_n(\alpha) = \alpha [n_n^B - c_n + n_n^A - c_n^\dagger], \quad (5)$$

$$v_n(\alpha) = \alpha [n_n^B n_{n+1}^A - c_n c_{n+1}^\dagger + n_n^A n_{n+1}^B - c_n^\dagger c_{n+1}]$$

with the Hamiltonian H from Eq. (3), and α labels the rate for the CR process.

III. CALCULATIONS AND RESULTS

In order to investigate the dependence of the viscosity on the CR rate α we performed DMRG calculations for the rates $1/N$, $1/N^2$, and $1/N^3$. The choice of these rates is based on two estimates. The first is very simple: A constraint is released when an end repton retracts back into the tube. The probability that the constraint is exerted by an end repton is $2/N$, provided that the probability for the presence of a segment is equally distributed. The hopping of a single repton is a process of rate one and so we find that the rate for a CR is of the order of $1/N$. For the second estimate we assume that a CR is caused by a tube renewal. Later in this paper we will show the calculation of this estimate within the Rouse model, which leads to the result that the rate α is propor-

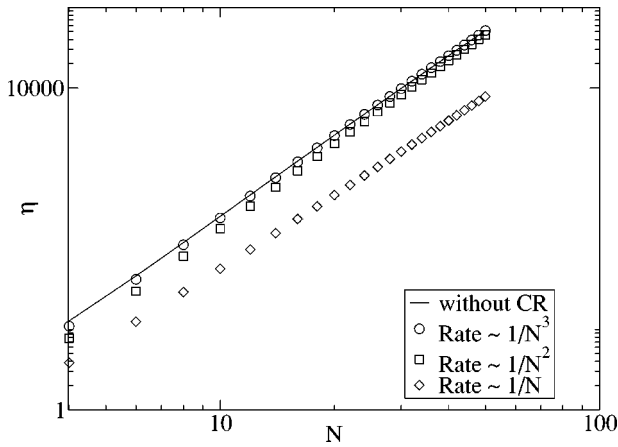


FIG. 4. The viscosity ($\eta \propto E_N^{-1}$) for several CR rates of *AB* permutation. The solid line shows the result for the standard RD model without CR.

tional to the inverse relaxation time and scales therefore with $1/N^3$.

The viscosity which was calculated with these rates for the mechanism of *AB* exchange is plotted in Fig. 4. It can be seen that the viscosity decreases with increasing CR rate that is reasonable because the relaxation of the tube is accelerated by this process. For the investigation of the scaling it is more useful to plot the local slope or the effective exponent

$$z_N = \frac{\ln \tau_{N+1} - \ln \tau_{N-1}}{\ln(N+1) - \ln(N-1)} \quad (6)$$

against $1/\sqrt{N}$ as introduced in Ref. [6]. The choice of the abscissa is motivated by the formula of Doi [3] which predicts a correction to the N^3 scaling in the order of $1/\sqrt{N}$ by taking tube length fluctuations into account. It should be mentioned that in this paper N labels the number of segments which is proportional to the length of the polymer while in Ref. [6] it labels the number of reptons that is the number of segments plus one. Surprisingly the latter interpretation shows a better agreement with the Doi formula while the former shows a better agreement with the experiments since the range where $z_N \approx 3.3 \pm 0.1$ is much broader.

The influence on the effective exponent z_N is plotted in Fig. 5. The influence is nonmonotonic in α : While the rate $1/N$ causes an obvious shift down in comparison with the data without CR, the data of rate $1/N^2$ is located above the curve without CR. The data of rate $1/N^3$ is also located above the curve without CR but at a smaller distance.

We remark that from a theoretical point of view also the rate $\alpha = 1$ is interesting. If *A* and *B* particles exchange with the same rate as particles with vacancies, the particle can diffuse freely, as they no longer feel restrictions. This means that the reptation model transforms into the Rouse model as the tube can change its form freely. This is why rate $\alpha = 1$ represents a possibility to verify the model: The relaxation time should scale in the limit $N \rightarrow \infty$ as N^2 . But the DMRG calculation of the effective exponent with this rate yields a diverging curve. On the other hand, if the second excitation is considered, one can see that it scales as N^{-2} . This sug-

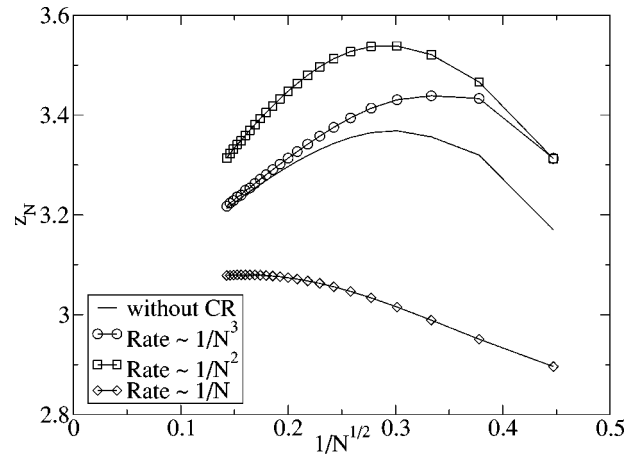


FIG. 5. The effective exponent z_N for several CR rates of *AB* permutation. The solid line shows the result for the standard RD model without CR.

gests that the first excitation is caused by an other relaxation mechanism and the second excitation yields the desired time, which scales with the expected exponent whereby the transition to Rouse dynamics is verified.

The bounds $1/N > \alpha > 1/N^3$ are rather weak and a self-consistent approach is needed for determining the appropriate scaling of the rate α . As a CR event is caused by the tube renewal of a polymer, this process is not independent of the relaxation time. The relaxation time itself is affected by the CR rate. So the rate is physical, if the relaxation time, which is calculated using this rate, yields the same CR rate.

To calculate the self consistent rate α_{SC} we proceed as follows: The dependence of the CR rate on the relaxation time $\alpha(\tau)$ is estimated by an analytical calculation using Rouse dynamics. The DMRG calculation with the rates mentioned above yields directly the dependence of the relaxation time on the CR rate $\tau_N(\alpha)$ for the respective chain lengths. The inverse function of $\alpha(\tau)$, $\tau(\alpha)$, is compared with $\tau_N(\alpha)$: The intersection of the curves yields the self-consistent rate α_{SC} in first approximation.

First we calculate the dependence of the CR rate on the relaxation time. The polymer whose relaxation time we want to calculate finally is hindered in his free movement by an other polymer. The position that exerts the constraint may have the distance s from one end of the constraining polymer. So, the constraint is released when the polymer moves either the distance s into one direction or the distance $N-s$ into the other direction, where N labels the length of the polymer. In Ref. [3] an expression is presented which provides the distribution $\psi(s, t)$ of the probability that the tube segment s was at time t not yet reached by the ends

$$\psi(s, t) = \sum_{p, \text{odd}} \frac{4}{p\pi} \sin\left(\frac{p\pi s}{N}\right) e^{-p^2 t / \tau} \quad (7)$$

with the relaxation time τ . The calculation of this formula bases on the assumption that the polymer diffuses in between the tube due to Rouse dynamics. The complementary prob-

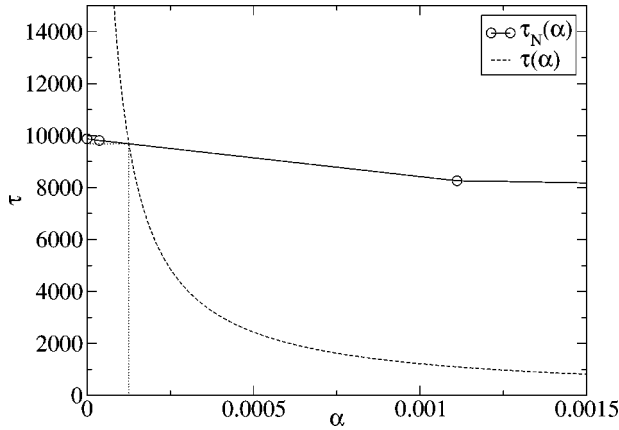


FIG. 6. Relaxation time versus CR rate α ; α_{SC} is given by the intersection point of the curves τ_N and τ (here exemplified for $N=30$).

ability distribution $\phi(s,t)$, which indicates the probability that at time t the segment s is already reached by one of the ends is then

$$\phi(s,t) = 1 - \psi(s,t). \quad (8)$$

The derivate with respect to time

$$f(s,t) = \frac{\partial \phi}{\partial t} \quad (9)$$

is the first passage time density, i.e., the probability per time that the segment s is reached by one end just at time t . Now we can specify the mean first passage time

$$\bar{\mu}(s) = \int_0^\infty dt t f(s,t), \quad (10)$$

which indicates how long it takes in average until segment s is reached by an end. Finally we average over all s provided that each segment builds up an entanglement with the same probability

$$\mu = \frac{1}{N} \int_0^N ds \bar{\mu}(s). \quad (11)$$

This is the desired time: In average the release of a constraint will take the time μ , the CR process takes place with rate $\alpha = \mu^{-1}$. The calculation of the integrals is elementary mathematics and we only show the result

$$\mu = 0.822\tau \Rightarrow \alpha = 1.22\tau^{-1}. \quad (12)$$

This calculation is based on a continuous description of the polymer. However, we are considering a lattice model of reptation so that boundary effects might not be taken into account correctly by the continuum expression (11). Therefore we performed the above calculation as well for the discrete case. As the result for the discrete case converges quickly to the continuous case but consists of only numerical

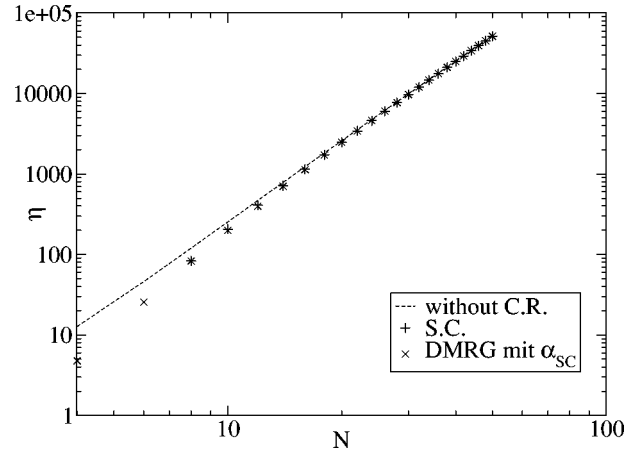


FIG. 7. The new DMRG calculation of viscosity—a good coincidence with the data of the intersection points can be seen.

evaluable series, we restricted ourselves to the continuous case here. There is an error of less than 2% for as little as 10 reptons.

Figure 6 shows the curve $\tau(\alpha) = 1.22\alpha^{-1}$ and the relaxation times for the CR rates $\alpha = 1/N^3$ and $1/N^2$ exemplified for $N=30$, the data point for $\alpha = 1/N$ is out of the plotted range. In order to investigate the dependence of the relaxation time on the CR rate we interpolated the data points linearly by fitting them with splines. The data points are well approximated by this interpolation in the region where the intersection point is expected. In this way we determined the self-consistent relaxation times and rates for the lengths $N=8, \dots, 50$. As the lengths $N=4$ and $N=6$ do not lead to reasonable intersection points we did not take them into account. To verify the self-consistence a new DMRG run was done with a fit of the determined rates; as can be seen in Fig. 7 the resulting relaxation times coincide well with the ones determined by the self-consistence condition, so that the linear interpolation represents a sufficiently good approximation.

In Fig. 8 the effective exponent is shown for the self-consistent relaxation times and for the DMRG calculation.

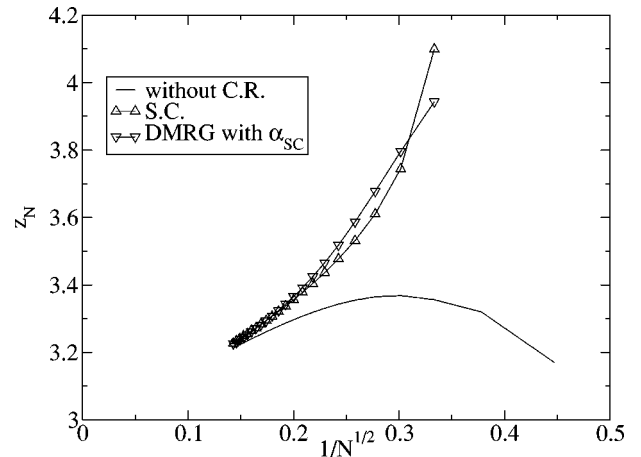


FIG. 8. The effective exponent z_N of the viscosity with self-consistent CR.

The exponent is shifted to higher values in the region of small N , but a broadening of the region where $z_N \approx 3.3$ could not be observed.

The Rubinstein model is not microscopic and hence there is some freedom in implementing microscopic process such as CR. A different mechanism [10] leads to the creation and annihilation of particles in the bulk. We performed similar analysis for this mechanism with qualitatively similar results [17].

We conclude that Rouse-based calculations do not lead to a proper description of crossover behavior in the viscosity of polymer melts when Rouse theory is used as a self-

consistency input in the mesoscopic and generally quite successful Rubinstein model for reptation. We cannot rule out that a fully self-consistent implementation of CR (without Rouse assumption) leads to a crossover regime closer to empirical evidence, but the broad range of CR rates studied here suggests that bulk shape fluctuations of the tube which result from constraint release do not significantly broaden the crossover range of the viscosity.

The anomalous scaling thus still is an open question. In the future it should be ruled out whether other relaxation mechanisms in the bulk can provide an explanation. A candidate would be whole loops that wriggle into new pores and by this form side branches of the primitive path.

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- [1] J.D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
- [2] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, London, 1979).
- [3] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [4] M. Rubinstein, Phys. Rev. Lett. **59**, 1946 (1987).
- [5] T.A.J. Duke, Phys. Rev. Lett. **62**, 2877 (1989).
- [6] E. Carlon, A. Drzewinski, and J.M.J. van Leeuwen, Phys. Rev. E **64**, 010801(R) (2001).
- [7] C.C. Hua, J.D. Schieber, and D.C. Venerus, J. Rheol. **43**, 701 (1999).
- [8] A.E. Likhtman, S.T. Milner, and T.C.B. McLeish, Phys. Rev. Lett. **85**, 4550 (2000).
- [9] N.A. Rotstein, S. Prager, T.P. Lodge, and M. Tirrell, Theor. Chim. Acta **82**, 383 (1992).
- [10] G.M. Schütz, Europhys. Lett. **48**, 623 (1999).
- [11] G.M. Schütz, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, London, 2000), Vol. 19.
- [12] G.T. Barkema and G.M. Schütz, Europhys. Lett. **35**, 139 (1996).
- [13] A. Baumgärtner, U. Ebert, and L. Schäfer, e-print cond-mat/0203218.
- [14] S.R. White, Phys. Rev. Lett. **69**, 2863 (1992).
- [15] R.M. Noack and S.R. White, in *Density–Matrix Renormalization, A New Numerical Method in Physics*, edited by I. Peschel and M. Kaulke (Springer, Berlin, 1999).
- [16] M. Henkel and G. Schütz, J. Phys. A **21**, 2617 (1988).
- [17] M. Paeßens, Diploma thesis, RWTH-Aachen, 2001.
- [18] In the Rubinstein model only two cases are distinguished; a bond between two cells is identified by a particle and a bond within a cell is identified by a vacancy.