Diffusion of a polymer in a gel is studied within the framework of de Gennes’ model for reptation. Our results for the scaling of the diffusion coefficient \( D \) and the longest relaxation time \( \tau \) are markedly different from the most recently reported results, and are in agreement with de Gennes’ reptation arguments: \( D \sim N^{-2} \) and \( \tau \sim N^{3} \). The leading exponent of the finite-size corrections to the diffusion coefficient is consistent with the value of \(-2/3\) that was reported for the Rubinstein model. This agreement suggests that its origin might be physical rather than an artifact of these models.

In the theory of reptation as formulated by de Gennes, it is predicted that the asymptotic behavior of the diffusion coefficient \( D \) of an entangled polymer scales with the chain length as \( D \sim N^{-2} \), and that the longest relaxation time \( \tau \) scales as \( \tau \sim N^{3} \). Evans and Edwards were the first to present numerical studies of de Gennes’ reptation model, which describes a single reptating polymer, and their results were in agreement with theoretical expectations. Recent simulations of the short-time behavior of this model are also in agreement with reptation arguments. However, the simulations of the long-time behavior of this model by Deutsch and Madden contradict de Gennes’ predictions with, instead, \( D \sim N^{-2.5 \pm 0.04} \) and \( \tau \sim N^{3.14 \pm 0.14} \).

This paper presents simulation results on the same model as that studied by Deutsch and Madden. The advance in computers combined with a highly optimized multispin coding technique allows us to simulate over time scales that are several orders of magnitude longer than previous simulations, yielding more accurate data points for longer chains, which in turn allows for a data analysis that includes corrections to the leading power-law behavior.

An alternative model for reptating polymers was proposed by Rubinstein, and has been studied numerically by one of us. It was found that the diffusion coefficient \( D \) scales as \( D \sim N^{-2} \), and the exponent of the leading finite-size correction was found to be close to \(-2/3\). In an analytical work by Prähofer and Spohn the \( N^{-2} \) behavior was derived rigorously with a variational method, and the leading exponent of finite-size corrections was shown to be between \(-1/2\) and \(-1\), with the former the more likely. This paper will show that de Gennes’ model for reptation and Rubinstein’s repton model have the same length-dependence of the diffusion coefficient, both the leading and the subleading part in the long-length limit; such agreement between two different models enhances the credibility that these results are physical.

In this paper, we will first describe the model considered and then motivate the computational method used for the simulations. This part will be followed by the calculation of the diffusion constant and the results for the longest relaxation times.

\section{I. De Gennes’ Model for Reptation}

We simulate a model for a polymer in a gel that was introduced by de Gennes. In this model, a polymer of length \( N \) is represented by \( N + 1 \) monomers on a 3D cubic lattice, connected by a sequence of \( N \) steps on lattice edges. One elementary move in this model is made by randomly selecting one monomer, and attempting to move it. If this monomer is an endpoint of the polymer, or if its two steps are located on the same edge, it will randomly move to one of the six possible lattice sites (the site it is already in, and five new ones). The time scale involved with one such an elementary move is \( \Delta t = 1/(6N + 6) \), so that the rate of any monomer to move to any allowed lattice site is one time unit.

A configuration of the polymer in the two-dimensional version of this model is illustrated in Figure 1. In this configuration, monomers 1, 5, 11, 12, and 15 can move to three other locations, the other monomers are frozen. Note that all our simulations were done in the three-dimensional model.

![FIG. 1. Two-dimensional version of de Gennes’ model for a reptating polymer with length \( N = 14 \) steps.](image)
II. SIMULATION METHOD

Rather than storing the spatial coordinates all along the chain, it is for simulation purposes more convenient to store the spatial coordinates of only the endpoints, and the sequence of steps from one of them to the other.

In one elementary move in a direct implementation of the dynamics, the first step, the last step, or a pair of neighbouring steps is randomly selected and proposed to move. For the first and last step, this involves simply a replacement by a random step; a pair of steps in the middle of the chain can only move if the steps are opposite, and in that case it is replaced by a randomly selected pair of opposite steps. Every possible change in the configuration should be proposed once per unit time, and therefore \(6N+6\) such elementary moves should be performed per unit of time. As we will see in section \(\ref{sec:diffusion}\), the typical correlation time is approximately \(0.13N^2\), and thus around \(N^4\) elementary moves have to be performed to obtain a statistically independent configuration. Finite-size effects disappear only if \(N\) is well above 100, requiring around \(10^9\) elementary moves per statistically independent configuration; an efficient implementation is crucial for numerical accuracy.

To achieve such a high efficiency, we use multispin coding. Most of our results were obtained on a DEC alpha workstation with a 64-bit processor, allowing 64 simulations to be run in parallel. For each of the 64 simulations, we stored the coordinates of both endpoints as \(x_i^{(0)} \ldots x_i^{(63)}\) for the left ends, and \(x_r^{(0)} \ldots x_r^{(63)}\) for the right ends. The steps \(0 \ldots N-1\) are stored in \(3N\) long integers of 64 bits. Suppose that we denote the \(k^{th}\) bit of long integer \(w\) as \(w^k\), then step \(i\) of simulation \(k\) is stored in the three bits \(\{a[i]^k, b[i]^k, c[i]^k\}\); if the step is in the positive \(x\), \(y\), or \(z\)-direction, this triplet is equal to \(\{1,0,0\}\), \(\{0,1,0\}\), or \(\{0,0,1\}\), respectively; the negative directions are represented by \(\{0,1,1\}\), \(\{1,0,1\}\), and \(\{1,1,0\}\), respectively. Note that opposite steps are each other’s binary complement.

To determine whether a hairpin is located in configuration \(k\) at steps \(i\) and \(j = i + 1\), we have to check whether the triplets \(\{a[i]^k, b[i]^k, c[i]^k\}\) and \(\{a[j]^k, b[j]^k, c[j]^k\}\) are complementary. This can be done with the following logical statement:

\[
h = (a[i] \oplus a[j]) \land (b[i] \oplus b[j]) \land (c[i] \oplus c[j]);
\]

the \(k^{th}\) bit of long integer \(h\) is one if there is a hairpin, otherwise it is zero. With this one statement, we have however determined the location of a hairpin in all 64 simulations! This is the power of multispin coding.

Of course it is not sufficient to determine the presence of a hairpin, we also have to replace hairpins by a random pair of opposite steps. Suppose we have available a triplet of long integers \(\{ra, rb, rc\}\) that represent 64 random steps, then the logical statement

\[
a[i] = (h \land ra) \lor (\neg h \land a[i]);
\]

and equivalent statements for \(b[i], c[i], a[j], b[j],\) and \(c[j]\) suffice to make one elementary move in all 64 simulations. In addition to these 24 logical operations some load- and store operations are required; altogether, we can make 64 elementary moves (one per simulation) in a fraction of a microsecond.

The endpoints require more care, since they involve keeping track of their spatial coordinates. For these, we needed a loop over the 64 simulations.

Since we perform long simulations, the generation of random numbers is a major concern. In our simulation, there are two places where random numbers are used: first, in the selection of the step \(i\), secondly in generating a random triplet of long integers \(\{ra, rb, rc\}\) that represent 64 random steps. For the first, we used the additive lagged Fibonacci generator proposed by Mitchell and Moore. For the second, we initially generated a set of \(M\) such triplets by building them up bit- by-bit with the Mitchell-Moore generator, and after using this set, a new set was generated from it by three operations:

- each triplet was permuted with 50\% probability
- each triplet was inverted with 50\% probability
- the list was reshuffled randomly.

For the first and second operation, we used a random bit generator proposed by Marsaglia. Note that we do not rely on the spectral properties of this generator, nor on the quality of each individual bit in the Mitchell-Moore generator. (Nor do we claim imperfections in these generators.)

III. THE DIFFUSION CONSTANT

To determine the diffusion constant \(D\), we started with 64 random polymer configurations, and let them evolve over a long time using the multispin approach outlined above. The coordinates \(\vec{r}_i\) and \(\vec{r}_r\) of the endpoints of each polymer were stored at regular time intervals. From their average \(\bar{r}_a \equiv (\vec{r}_i + \vec{r}_r)/2\) we calculate the function

\[
D(t) = \frac{(\bar{r}_a(t_0 + t) - \bar{r}_a(t))^2 - N/4}{6t};
\]

the long-time limit of this function gives the diffusion coefficient:

\[
D = \lim_{t \to \infty} D(t).
\]

The additional term \(N/4\) in Eq. \(\ref{eq:diffusion}\) corrects for the rapid fluctuations of the endpoints relative to the center of mass, that do not contribute in the long-time limit; it reduces the effects of the finiteness of the time interval significantly. As we will see in section \(\ref{sec:finite-size}\), the typical relaxation time scales as \(\tau \sim N^3\); we find that the long-time limit of \(D(t)\) is well reached at \(t = 6N^2\), and used
this time interval to measure $D$. Figure 2 illustrates the convergence of $D(t)$ as a function of $t$.

The results for the diffusion coefficient $D$ as a function of length $N$ are given in Table I. The length of the runs depends on the chain length $N$, and is also given in Table I. For $N = 150$ and $N = 200$, we used a 32-bit computer, all other results were obtained on a 64-bit computer.

In figure 3, the measured values for $DN^2$ are plotted as a function of $N^{-2/3}$; all measurements fall on a single straight line given by

$$DN^2 = 0.173 + 1.9N^{-2/3}. \quad (5)$$

This indicates that for long polymers, the asymptotic behavior of the diffusion is in agreement with reptation predictions of de Gennes: $D \sim N^{-2}$. Also, it gives strong indication that the leading exponent of the finite-size corrections has a non-integer value close to $-2/3$. This exponent has also been observed in the Rubinstein reptation model, another lattice model for diffusing polymers, and makes it plausible that it is not simply an artifact of the model.

IV. THE LONGEST RELAXATION TIMES

The shape of the polymer at time $t_0 + t$ stays correlated to its shape at time $t_0$ for a long time, but eventually decays exponentially fast. This final decay sets the longest relaxation time; it is often related to the viscosity. The scaling of the longest relaxation time as a function of length is the topic of this section. To determine the longest relaxation time, we study the decay in the orientation $\vec{d} = \vec{r}_r - \vec{r}_l$. The function $\phi(t)$ is the two-time autocorrelation of this vector:

$$\phi(t) = \langle \vec{d}(t_0) \cdot \vec{d}(t_0 + t) \rangle. \quad (6)$$

We know that $\phi(0) = N$, since the expected end-to-end distance of the polymer is $\sqrt{N}$. The function $\phi(t)$ is expected to decay exponentially to zero as a function of $t$, with a typical length-dependent relaxation time $\tau_N$:

$$\phi(t) \approx N \exp(-t/\tau_N). \quad (7)$$

To determine the correlation time $\tau_N$, we have plotted in Figure 4 $(-1/t')\log(\phi(t)/N - \alpha_N)$ as a function of $t' = t/N^3$; $\alpha_N$ is an $N$-dependent parameter that removes partly the finite-time corrections but does not affect the scaling at large $t'$: since $\log(\phi(t))$ grows roughly linearly with $t$, it is the dominant term for longer $t$. The values

\begin{table}[h]
\centering
\begin{tabular}{cccc}
\hline
$N$ & $DN^2$ & #runs & $t$ \\
\hline
10 & 0.581 (0.001) & 64 & $3.2 \cdot 10^5$ \\
20 & 0.434 (0.001) & 64 & $2.6 \cdot 10^6$ \\
30 & 0.369 (0.001) & 64 & $8.6 \cdot 10^6$ \\
40 & 0.336 (0.002) & 64 & $4.1 \cdot 10^7$ \\
50 & 0.311 (0.002) & 64 & $8.0 \cdot 10^7$ \\
60 & 0.296 (0.003) & 64 & $1.4 \cdot 10^8$ \\
80 & 0.275 (0.002) & 64 & $3.3 \cdot 10^8$ \\
100 & 0.254 (0.005) & 64 & $3.2 \cdot 10^8$ \\
120 & 0.251 (0.005) & 64 & $5.5 \cdot 10^8$ \\
150 & 0.243 (0.004) & 32 & $6.8 \cdot 10^8$ \\
200 & 0.226 (0.010) & 32 & $2.8 \cdot 10^8$ \\
\hline
\end{tabular}
\end{table}
for $\alpha_N$ range from $\alpha_{20} = -0.62$ to $\alpha_{150} = -0.44$. The asymptotic values of the curves in figure 4 are equal to $N^3/\tau_N$.

![Graph](image)

**FIG. 4.** For several values of $N$, we have plotted $(-1/t')(\log(\phi(t)/N - \alpha_N)$ as a function of $t' = t/N^3$. All curves show convergence to a constant value, which is equal to $N^3/\tau_N$. From top to bottom, the curves correspond to $N = 20, 30, 40, 50, 60, 80, 100, 120, and 150.$

The values for $N^3/\tau_N$ that we obtained in this way are given in Table II, as well as their reciprocals; the errors are our estimates by eye.

| $N$  | $N^3/\tau_N$ | $\tau_N/N^3$ |
|------|---------------|---------------|
| 20   | 21.2 (0.2)    | 0.0472 (5)    |
| 30   | 18.0 (0.2)    | 0.0556 (6)    |
| 40   | 15.7 (0.2)    | 0.0637 (8)    |
| 50   | 14.2 (0.2)    | 0.070 (1)     |
| 60   | 12.9 (0.2)    | 0.078 (1)     |
| 80   | 11.3 (0.2)    | 0.088 (2)     |
| 100  | 10.4 (0.2)    | 0.096 (2)     |
| 120  | 9.8 (0.2)     | 0.102 (2)     |
| 150  | 9.3 (0.2)     | 0.107 (2)     |

It is expected from reptation arguments that in the limit of infinitely long chains, the product $D\tau$ scales linearly with $N$; as we found in the previous section that for long chains $D \sim N^{-2}$, this would mean that for long chains $\tau \sim N^3$. To check this, we have plotted $\tau/N^2$ as a function of $N$ in figure 5. For large $N$, the measurements are fitted well by a straight line with slope 0.13, indicating that for long polymers $\tau \approx 0.13N^3$.

**FIG. 5.** The longest relaxation time $\tau_N$ divided by $N^2$, as a function of $N$. The straight line is a fit given by $\tau_N = 0.13N^2 + c$, indicating that asymptotically $\tau \approx 0.13N^3$.

**V. CONCLUSIONS**

We have performed numerical simulations of de Gennes’ model for polymer reptation. For the diffusion coefficient $D$, we find $D = N^{-2}(0.173 + 1.9N^{-2/3})$. For the longest relaxation time $\tau$ of long polymers we find $\tau \approx 0.13N^3$. The leading-orders of the diffusion coefficient and the longest relaxation time are in agreement with theoretical arguments of de Gennes. There is no theoretical prediction for the leading exponent of the finite-size corrections for the diffusion coefficient; our value of -2/3 is identical to earlier reports of this exponent in the Rubinstein repton model.

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