Electrophoresis of charged polymers: Simulation and scaling in a lattice model of reptation

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We report numerical results on the repton model of Rubinstein [Phys. Rev. Lett. **59**, 1946 (1987)] as adapted by Duke [Phys. Rev. Lett. **62**, 2877 (1989)] as a model for the gel electrophoresis of DNA. We describe an efficient algorithm with which we have simulated chains of N reptons with N several hundred in some instances. The diffusion coefficient D in the absence of an external electric field is obtained for $N \leq 100$; we find $N^2D = \frac{1}{3}(1+5N^{-2/3})$ for large N. The coefficient $\frac{1}{3}$ is in accord with the analytical results of Rubinstein and of van Leeuwen and Kooiman [Physica A **184**, 79 (1992)]. The drift velocity v in a static field of variable strength E is obtained for various N and NE up to $N=30$ when NE is as small as 0.01 and up to $N=400$ when NE is as large as 20. We find that v has a finite, nonzero limit as $N \to \infty$ at fixed E and that this limit is proportional to $|E|E$, in accord with the conclusions of Duke, Semenov, and Viovy [Phys. Rev. Lett. **69**, 3260 (1992)] for a different but related model. In a scaling limit in which $N \to \infty$ and $E \to 0$ the drift velocity in the repton model is fitted well by the formula $N^2v = NE[(\frac{1}{3})^2 + (2NE/5)^2]^{1/2}$ for all values of the scaling variable NE. We present a scaling analysis complementary to that of Duke, Semenov, and Viovy with which we rationalize the $|E|E$ behavior of the limiting drift velocity.

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I. INTRODUCTION

Rubinstein proposed a lattice model of the dynamics of entangled polymers that he termed the *repton* model [1,2], which Duke has adapted as a model for the gel electrophoresis of DNA [3–5]. It has been studied both analytically [1,2,6–11] and by Monte Carlo simulation [3–6].

The dynamics in the model is purely that of reptation; i.e., the polymer chain moves only along its own contour by the diffusion of stored length [12]. The model is most simply studied in its projected form in which it becomes that of a connected chain of N elements (reptons) that move by discrete steps on parallel tracks, each repton moving forward or backward on its track subject to certain dynamical rules [1,2]. If x_i (an integer-valued coordinate) is the location of the ith repton on its track, the chain connectivity requires that $|x_i - x_{i-1}|$ be only 1 or 0 for all $i = 2, 3, \ldots, N$. This condition of connectivity and the condition of reptation on the original three-dimensional lattice, before projection, are preserved by the move rules in the projected version: an end repton ($i=1$ or N) may move only forward (by one step) if its neighbor ($i=2$ or $N-1$) is one step ahead of it; only backward if its neighbor is one step behind it; and either forward or backward if its neighbor's x is the same as its own; while an interior repton ($2 \leq i \leq N-1$) may move only forward (by one step) if one of its neighbors is one step ahead of it and its other neighbor is at the same x as itself; only backward if one of its neighbors is one step behind it and its other neighbor is at the same x as itself; and otherwise may not move. These rules are exemplified in Fig. 1 for a chain of fifteen reptons (after Duke [3]). An arrow attached to a repton indicates an allowed move.

If there is an applied (static) electric field E, the reptons' tracks, and so the axis of the coordinates x, are chosen parallel to it, with x increasing in the direction of E as in Fig. 1. With every allowed move ↑ or ↓ of a repton there is associated a transition probability per unit time, B or B^{-1}, respectively, with

$$B = e^{E/2}, \tag{1}$$

thus favoring moves in the forward direction (that of increasing x) with the ratio e^E of forward to backward transition rates. (Here B and E are dimensionless; else-

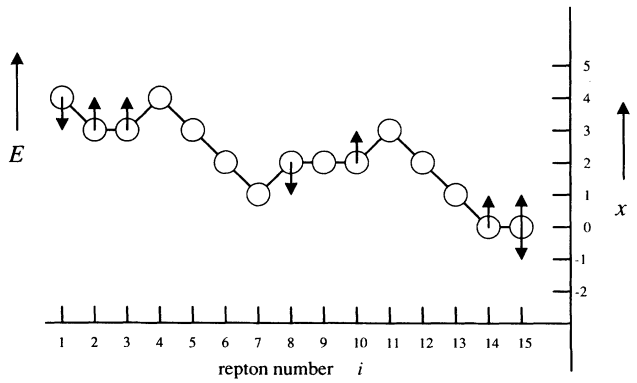

FIG. 1. Repton chain with $N=15$ in the projected representation in which there is a single discrete spatial coordinate x in the direction of an externally applied electric field E (after Duke [3]). The arrows attached to reptons represent allowed moves.

where [6] the transition rates are taken to be wB and wB^{-1} and the present E is called eEa/kT, where w and a are elementary rate and length parameters in the model, e the charge per repton, k Boltzmann's constant, and T the temperature.)

Formally exact but implicit formulas for the diffusion coefficient D at $E=0$ and for the drift velocity v are known [6]. (The present D and v are dimensionless and are what are elsewhere [6] called D/a^2w and v/aw.) D may be obtained by inversion of a sparse $3^{N-1}\times 3^{N-1}$ matrix; it is known analytically [6] for $1\le N\le 5$ and numerically [13], but exactly, for $6\le N\le 12$. Similarly, v is known analytically [6] for $1\le N\le 3$ for any E, and numerically but exactly for $N=4$ [6] and for $N=5,6,7$ [14], again for any E. For any fixed N these D, v, and E are related by the Nernst-Einstein relation

$$ND=\lim_{E\to 0}\frac{v}{E}\quad(\text{fixed } N)\ , \tag{2}$$

as required by general principles and as explicitly shown by van Leeuwen [7] for the present model.

It is characteristic of reptation in general [12], and of the repton model in particular, that D becomes proportional to $1/N^2$ in the asymptotic limit $N\to\infty$. From Rubinstein's analysis [1,2] as applied to the model with the present move rules, one expects the coefficient of the $1/N^2$ term in D to be $\frac{1}{3}$ (as quoted in [6]). Van Leeuwen and Kooiman [8–11] have made an important advance in the analysis of the model. Applying what they call periodic boundary conditions, and from a plausibility argument that the consequent alteration of the move rules for the end reptons should not affect the leading asymptotic behavior of D as $N\to\infty$, they, too, find the coefficient of the $1/N^2$ term in D to be $\frac{1}{3}$.

It was conjectured [6] that in a scaling regime defined by $N\to\infty$ and $E\to 0$ for any value of a scaling variable $u=\sqrt{N}E$ the drift velocity v would take the form $v=N^{-3/2}J(u)$ with $J(u)$ an odd function of u that is proportional to u for small u and to u^3 for large u. The small-u behavior of $J(u)$ would then give the required $D\sim\text{const}/N^2$, from (2); while its large-u behavior would imply that at fixed E the drift velocity approaches a finite, nonzero limit as $N\to\infty$, and that this limit is proportional to E^3 for small E. That v has a finite, nonzero limit as $N\to\infty$ at fixed E is a known phenomenon in electrophoresis—it is the loss of molecular-weight discrimination at high molecular weights—and, in particular, is a known property of the repton model [3]. This property, and the proportionality of the limiting ($N\to\infty$) drift velocity to E^3, are seemingly found also in other, related models of electrophoresis, by analytical and physical arguments (Refs. [15] and [16] and results quoted in Refs. [4] and [17]) and by simulation [18]. The analysis of Kooiman and van Leeuwen [9] is also in apparent agreement with the earlier conjecture [6] that for large N and small E the drift velocity is of the form $N^{-3/2}J(u)$ with $J(u)$ an odd function of the scaling variable $u=\sqrt{N}E$.

Recently, however, analyzing the different but related "biased reptation" model, but taking account of fluctuations not considered in earlier treatments [15,16], Duke, Semenov, and Viovy [19,20] have concluded that the drift velocity in the $N\to\infty$ limit would be proportional not to E^3 but to E^2 (or, more properly, to the nonanalytic $|E|E$, since v must be odd in E). This is also in better agreement with experiment [15,21].

We have performed Monte Carlo simulations of the repton model, which we describe in the next section, where we also present our results. We confirm that D is proportional to $1/N^2$ for large N, with the coefficient $\frac{1}{3}$ of Rubinstein [1,2] and of van Leeuwen and Kooiman [7–11]. We find the correction to be of order $1/N^{8/3}$. For any $N>\sim 20$ (we determined D for N up to 100) the data are fit well by

$$D=\frac{1}{3N^2}\left[1+\frac{5}{N^{2/3}}\right]\ . \tag{3}$$

We find, further, that there is indeed a scaling regime defined by the asymptotic limits $N\to\infty$ and $E\to 0$; but that, contrary to the earlier conjecture [6], the scaling variable u is NE rather than $\sqrt{N}E$,

$$u=NE\ , \tag{4}$$

and the scaling relation is of the form

$$v=N^{-2}J(u)\ , \tag{5}$$

with

$$J(u)\sim\begin{cases}\text{const}\times u\ , & u\to 0\\ \text{const}\times|u|u\ , & |u|\to\infty\ .\end{cases} \tag{6}$$

$J(u)$ is thus asymptotically proportional to u^2 (rather than to u^3, as conjectured earlier) as $|u|\to\infty$. With (2), this again implies that D is proportional to $1/N^2$ for large N, as expected, and it again implies that v approaches a finite, nonzero limit as $N\to\infty$, but it asserts that this limiting v is proportional to $|E|E$ rather than to E^3, in agreement with the conclusions of Duke, Semenov, and Viovy [19,20]. Specifically, we find the data to be fit well by

$$J(u)=u[(\tfrac{1}{3})^2+(\tfrac{2}{5}u)^2]^{1/2}\ , \tag{7}$$

which has the properties (6) in the limits of small and large u.

In the concluding Sec. III we summarize our results, and we present a scaling argument, complementary to that of Duke, Semenov, and Viovy [19,20], with which we are able to understand why the appropriate scaling variable is $u=NE$ [Eq. (4)], why the drift velocity scales as N^{-2} multiplied by a scaling function $J(u)$ [Eq. (5)], and why $J(u)$ is proportional to u^2 when u is large [Eq. (6)]. We discuss the connection to the earlier version of the biased reptation model [15,16], before it was extended by Duke, Semenov, and Viovy [19,20]. We conclude with a discussion of some still open questions.

II. NUMERICAL SIMULATION OF THE REPTON MODEL

Numerical simulations of the repton model have been previously carried out [3–6], but statistical errors have

prevented a definitive study of its scaling properties. In Sec. II A, we discuss a multispin coding scheme for the repton model that, when implemented on a powerful SP-1 parallel computer, has allowed us to obtain many new results.

In Sec. II B we discuss our results for the diffusion of a polymer in the repton model with no electric field. We find the usual $1/N^2$ diffusion constant behavior, but in addition we are able to determine the numerical prefactor and corrections to leading scaling for large N. In Sec. II C we consider small electric fields ($EN<1$, $E\ll 1$), and we are able to verify the Nernst-Einstein result. Section II D presents the drift velocity in a stronger field ($EN>1$, but still $E\ll 1$). Finally in Sec. II E we demonstrate that, for large N, our weak- and strong-field results can be described by a scaling function dependent only on EN.

A. Multispin coding for the repton model

For computational efficiency, we have used "multispin coding:" the computationally intensive part of the code is written in bit operations, which allows one to run 32 independent simulations in parallel by applying AND and OR operations to four-byte integers of which each bit corresponds to an independent simulation. The reptons in a chain have one-dimensional coordinates $(x_1,\ldots,x_N)$. The demand that the chain is not "broken" requires that, given x_i, only three options are left for x_{i+1},

$$x_{i+1}=x_i+s_i \ , \tag{8}$$

in which s_i equals -1, 0, or 1. In our simulation we keep track of x_1 and $s_1,\ldots,s_{N-1}$. The states $s=-1$, 0, and 1 are bitwise represented as $(s^l,s^r)=(1,0)$, (1,1), and (0,1), respectively. In each step of the algorithm, a repton i and a direction *up* is selected. If *up* equals 1, the proposed move is upward; otherwise it is downward. If the selected repton is not an end point of the chain, the new value for x_i is determined by s_{i-1}, s_i, and *up*, which in its turn determines the new values for s_{i-1} and s_i. By examining all the possible moves, we deduce that

$$\begin{aligned} s_{i-1}^l=&(s_{i-1}^l\wedge s_i^l)\vee(\neg\mathrm{up}\wedge s_{i-1}^l)\\ &\vee(\neg\mathrm{up}\wedge s_i^l\wedge s_i^r)\vee(\neg s_{i-1}^r) \ , \end{aligned} \tag{9}$$

$$\begin{aligned} s_{i-1}^r=&(s_{i-1}^r\wedge s_i^r)\vee(\mathrm{up}\wedge s_{i-1}^r)\\ &\vee(\mathrm{up}\wedge s_i^l\wedge s_i^r)\vee(\neg s_{i-1}^l) \ , \end{aligned} \tag{10}$$

$$\begin{aligned} s_i^l=&(s_{i-1}^l\wedge s_i^l)\vee(\mathrm{up}\wedge s_i^l)\\ &\vee(\mathrm{up}\wedge s_{i-1}^l\wedge s_{i-1}^r)\vee(\neg s_i^r) \ , \end{aligned} \tag{11}$$

$$\begin{aligned} s_i^r=&(s_{i-1}^r\wedge s_i^r)\vee(\neg\mathrm{up}\wedge s_i^r)\\ &\vee(\neg\mathrm{up}\wedge s_{i-1}^l\wedge s_{i-1}^r)\vee(\neg s_i^l) \ . \end{aligned} \tag{12}$$

For the left end point we derive in a similar way:

$$s_1^l=(\mathrm{up})\vee(\neg s_1^r) \ , \tag{13}$$

$$s_1^r=(\neg\mathrm{up})\vee(\neg s_1^l) \ , \tag{14}$$

and for the right end point,

$$s_{N-1}^l=(\neg\mathrm{up})\vee(\neg s_{N-1}^r) \ , \tag{15}$$

$$s_{N-1}^r=(\mathrm{up})\vee(\neg s_{N-1}^l) \ . \tag{16}$$

One step in the program consists of randomly selecting a repton i, generating a four-byte random number *up*, and applying the appropriate operations outlined above. If $i=1$, x_1 also has to be updated.

In a simulation, we frequently calculate the center of mass of the chain,

$$x_{\mathrm{c.m.}}=\frac{1}{N}\sum_{i=1}^{N}x_i \ . \tag{17}$$

Initialization of the chain is done by selecting s_i randomly from $\{-1,0,1\}$. As each of these values is equally likely to occur in the absence of an electric field, no thermalization is required if $E=0$.

Upward and downward moves are no longer equally likely if an external electric field is present. In our computer program, with a probability $1-1/f$ we assign a random number to *up*, and with a probability $1/f$ we assign the logical OR of two random numbers to *up*. Because of this, our upward transition probability equals $T_{\mathrm{up}}=(\omega'/2N)(1+f/2)$, and our downward transition probability $T_{\mathrm{down}}=(\omega'/2N)(1-f/2)$. This method yields transition rates that are equal to the transition rates as defined in Sec. I, if we choose a dimensionless $\omega'=(B+B^{-1})N$ and $f=2(B-B^{-1})/(B+B^{-1})$.

B. Results for diffusion constant with zero electric field

The diffusion constant was measured by measuring how far the centers of mass of chains moved in a given time, in the absence of any electric field. The square of the center-of-mass distance moved, divided by the elapsed time, gives the diffusion constant. Since all allowed configurations occur with equal probability, thermalization is not necessary if a random initial condition is chosen.

We performed simulations with $N=20$, 30, 50, 60, 70, and 100. For each value of N we performed 256 simulations (8 SP-1 processors, 32 simulations per processor), each consisting of 5×10^8 steps. During each simulation we kept track of the center of mass, and we calculated the diffusion constant D, given by

$$D=\sum_{i=1}^{256}x_{\mathrm{c.m.}}(i)^2/\Delta t \ , \tag{18}$$

in which Δt is given by $5\times 10^8/(2N)$.

We anticipate that the behavior of D for large N is given by $D\sim N^{-2}$ (Sec. I). In Fig. 2, DN^2 is plotted as a function of $N^{-2/3}$, and a straight line fit through the points obtained by the simulations results in $\lim_{N\to\infty}(DN^2)=0.34(1)$, which is in agreement with the coefficient $\frac{1}{3}$. If we assume that the asymptotic value is indeed $\frac{1}{3}$, we find $D=\frac{1}{3}N^{-2}+bN^{-8/3}$, with $b=1.66(3)$; in this paper, we take $b=\frac{5}{3}$. The circles in Fig. 2 indicate the exactly known values for D, obtained from [6] and [13].

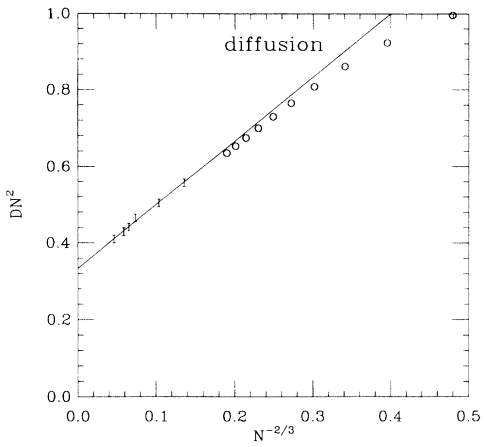

FIG. 2. Finite-size scaling of the diffusion constant. The scaled diffusion constant DN^2 is plotted as a function of $N^{-2/3}$. Circles indicate analytic results from Widom *et al.*; points with error bars indicate numerical results. The straight line is given by $N^2D=\frac{1}{3}(1+5N^{-2/3})$.

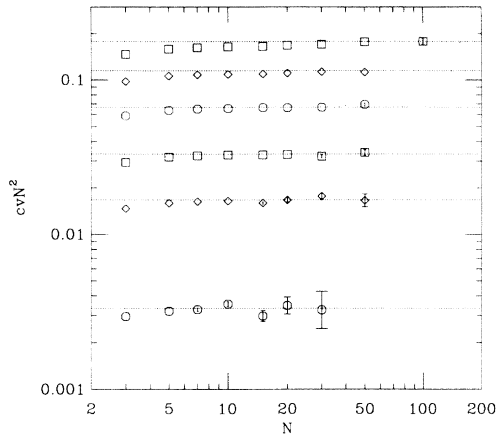

FIG. 3. Rescaled drift velocity cvN^2 as a function of polymer length N, for fixed values of NE. Asymptotic values for cvN^2 in the limit $N\rightarrow\infty$ are indicated by dotted lines. From top to bottom, curves correspond to $NE=0.5$, 0.33, 0.2, 0.1, 0.05, and 0.01. Error bars are omitted if they are much smaller than the symbol size.

C. Results for drift velocity in weak fields

In small nonzero fields, the center of mass of the polymer will drift a distance proportional to the elapsed time of the simulation; the ratio of these two quantities gives the drift velocity. We have chosen random configurations (i.e., $E=0$ equilibrium configurations) as initial conditions, and we have simply run for sufficient time for the chain to move a distance of many times $N^{1/2}$. We have checked that our results are not biased by the short equilibration period at the start of our runs by verifying that within our statistical errors, the first and second half of the runs lead to the same drift velocity.

During our study, we observed that for fixed NE, vN^2 approached a constant for large N. Thus we are presenting data for N varied with EN fixed. We performed simulations for $N=5$, 10, 20, and 50, each for $NE=0.01$, 0.05, 0.1, 0.2, 0.33, and 0.5.

We measured the drift velocity v, and we have plotted vcN^2 as a function of N in Fig. 3. The factor $c=(\frac{1}{3}N^{-2})/(\frac{1}{3}N^{-2}+\frac{5}{3}N^{-8/3})$ is the correction for finite N that arises from the finite-size scaling of the diffusion constant as discussed in the previous section. Note that if $N\rightarrow\infty$, $c\rightarrow 1$; however, without the correction c, a believable extrapolation to $N\rightarrow\infty$ is not possible with the range of N studied here.

Figure 3 shows that for fixed NE, vN^2 approaches a constant value as $N\rightarrow\infty$. This indicates that vN^2 is a function only of NE for large N. The extrapolated value of vN^2 as a function of NE is plotted in the left half of Fig. 5 (squares), in which one can see that $vN^2\approx EN$ for $N\rightarrow\infty$ and $NE\ll 1$, which is precisely the Nernst-Einstein behavior discussed in Sec. I.

D. Results for drift velocity in strong fields

For EN larger than order unity, we carried out the same sort of measurements of drift velocity described in Sec. II C. We performed simulations for $N=30$, 40, 50, 60, 70, 80, 100, 200, 300, and 400, each for fixed $NE=1$, 2, 3, 4, 5, 10, and 20. The resulting drift velocities are shown in Fig. 4, in which we plot vN^2 as a function of N for fixed NE. For large NE we have found that we can extrapolate vN^2 to $N\rightarrow\infty$ to extract the large-N limiting behavior.

From Fig. 4 we conclude that vN^2 is a function of NE alone for large N. The extrapolated values for vN^2 are shown as a function of NE in the right half of Fig. 5 (circles) where we see that $vN^2\approx(NE)^2$, or $v\approx E^2$ for $N\rightarrow\infty$ and $NE\gg 1$.

E. One-parameter scaling of drift velocity

Figure 5 shows the extrapolation of vN^2 to infinite N at fixed NE obtained from the numerical results described in

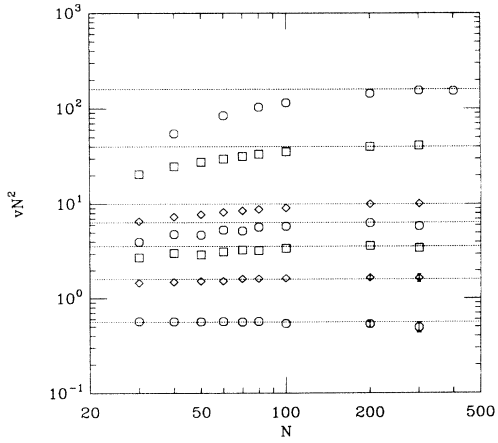

FIG. 4. Rescaled drift velocity vN^2 as a function of polymer length N, for fixed values of NE. Asymptotic values for vN^2 in the limit $N\rightarrow\infty$ are indicated by dotted lines. From top to bottom, curves correspond to $NE=20$, 10, 5, 4, 3, 2, and 1. Error bars are omitted if they are much smaller than the symbol size.

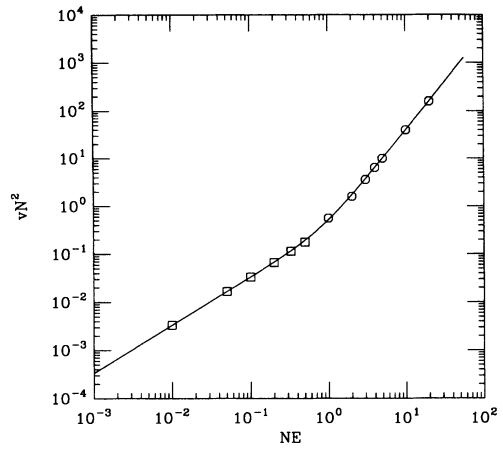

FIG. 5. Rescaled drift velocity vN^2 as a function of the rescaled electric field NE, in the limit $N\to\infty$. Squares are obtained from Fig. 4; circles from Fig. 5. The straight line is given by $N^2v=NE[(\frac{1}{3})^2+(2NE/5)^2]^{1/2}$.

Secs. II C and II D above. We have found that $vN^2=J(NE)$, where $J(u)$ is a universal function describing the crossover from the small-NE, $v\approx E/N$ behavior to the $v\approx E^2$ large-NE regime. For $u\ll 1$, $J(u)\propto u$, while for $u\gg 1$, we find that $J(u)\propto u^2$. Empirically, we find that the function $J(u)=u[(\frac{1}{3})^2+(2u/5)^2]^{1/2}$ runs through our data points, and is an accurate approximation to our extrapolated results.

III. DISCUSSION

We have carried out a study of the scaling properties of the Duke-Rubinstein model for an electrically charged polymer being driven through a fixed network by a constant electric field. At zero field, we obtain the original repton model of Rubinstein, and we find that the polymer diffuses with a diffusion constant of $1/(3N^2)$. The N dependence of the diffusion constant is as expected from reptation theory and as observed in previous simulations, and the numerical factor of $\frac{1}{3}$ matches the results of arguments of Rubinstein [1,2] and Kooiman and van Leeuwen and Kooiman [8-11]. However, in addition we have found that there are appreciable subleading power-law corrections to the diffusion constant which were not reported before.

Our numerical results for nonzero electric fields indicate that for large numbers of reptons N (proportional to molecular weight), but for small electric fields ($E\ll 1$), there is a simple one-parameter scaling behavior of the drift velocity of a chain in the repton model. The scaling variable describing the characteristic field strength was shown to be EN, and for low field strengths, the drift velocity is proportional to E/N as given by the Nernst-Einstein relation.

The E^2 dependence at larger fields ($EN>1$, but $E\ll 1$) has only recently been proposed by Duke, Semenov, and Viovy [19,20] for the case where the polymer is flexible at the network scale. The repton model should be in this class since many monomers may be stored at any one network node. Our numerical results strongly support this, showing a robust E^2 dependence of the drift velocity for $EN>1$.

Previous to the work of Duke, Semenov, and Viovy [19], the prevailing belief was that the velocity should behave as E^3 for $EN^{1/2}>1$, based on the original model of biased reptation studied by Lumpkin, Déjardin, and Zimm [15] and Slater and Noolandi [16]. Biased reptation turns out to be appropriate only when the polymer is inflexible at the network scale [19], which is not the case for the repton model as studied in this paper. However, there certainly may be experimental cases where the E^3 behavior may be observed, due to the polymer persistence length being comparable with the pore size. In what follows, we quickly summarize the scaling behavior of the repton model using some simple physical arguments, and then we briefly explain the relationship between the repton model as studied here, and the early version of the biased reptation model. Finally, we will mention some open questions that remain.

A. Drift velocity: small and large NE

We now present a physical argument for the E^2 behavior that we have observed in the repton model, based on ideas from the equilibrium statistical mechanics of stretched polymers. In this section we consider the three-dimensional chain conformations that correspond to the projected form of the repton model discussed above. Our argument arrives at the same results for the drift velocity as Duke, Semenov, and Viovy [19,20], but is somewhat simpler.

For small E, the Nernst-Einstein relation tells us that the drift velocity should be proportional to EN (the total force on the chain) times the $E=0$ diffusion constant. Since a reptating chain moves a distance $R\approx N^{1/2}$ in a time $\tau\approx N^3$ (the time required for diffusion of the chain out of its "tube" [12]), the diffusion constant of a reptating polymer is $D\approx R^2/\tau\approx 1/N^2$ [12], ignoring numerical prefactors. Thus for small enough E, we expect a drift velocity $v\approx END\approx E/N$.

The Nernst-Einstein estimate is invalid if the electric field significantly distorts the conformations of the drifting coil. The value of E at which this occurs can be determined by comparing stretching of the chain to its natural random-walk fluctuations. Consider the three-dimensional conformation of a chain of N reptons, numbered with an index ν. A weak external field which does not perturb the random-walk statistics appreciably will randomly point in the $+\nu$ and $-\nu$ directions, and thus the net force *along the tube occupied by the chain* will randomly push the polymer out of the $\nu=1$ and $\nu=N$ ends of its tube, and will have an amplitude which scales as $N^{1/2}E$. The stretching h of the chain along the tube (which can relax rapidly compared to the other, topologically constrained degrees of freedom of the chain) will be determined by the balance of this force against the entropic elasticity of the Edwards model [22], $h/N\approx EN^{1/2}$. Spontaneous fluctuations of the stretching along the tube for $E=0$ are of order $R=N^{1/2}$, and thus if $NE\ll 1$ we can expect the Nernst-Einstein result to be valid. For $NE>1$, the stretching along the tube exceeds the equilib-

rium fluctuations and the field must be considered "strong."

We can now estimate the drift velocity for $NE > 1$, but still $E \ll 1$. There is a characteristic chain length $N_b \approx 1/E$ which defines the scale below which the polymer statistics cease to be perturbed away from the equilibrium (random-walk) ensemble. A portion of the chain of size N_b is therefore a roughly isotropic "blob" of size $\xi \approx N_b^{1/2} \approx E^{-1/2}$. The entire chain is made up of $n \approx N/N_b \approx NE$ such blobs arranged roughly end to end: beyond the blob scale, the polymer is fully stretched. Thus, we expect a cigarlike conformation of length $l \approx n\xi \approx NE^{1/2}$ and diameter $\xi \approx E^{-1/2}$.

We note that a roughly analogous "blob" scale is essential to problems where polymers have stretched equilibria (e.g., grafted polymers [23], polymers under traction [24], polyelectrolytes in low-salt solution [25], etc.) and is a consequence of the $n^{1/2}$ behavior of the Edwards model for a random walk, which always beats out an extension linear in n, as $n \to 0$.

The drift velocity follows by noting that the Nernst-Einstein argument can be applied *to each blob.* Each blob is acted on by a body force $N_b E$, and has a mobility given by the blob diffusion coefficient $D_b \approx 1/N_b^2$. At super-blob scales, the polymer smoothly drifts at a velocity $v \approx N_b E D_b$, or $v \approx E^2$. The dependence on molecular weight has disappeared due to the fact that the polymer is completely stretched at scales beyond N_b: thermal fluctuations are insufficient to alter the steady motion of the chain along the external field at super-blob scales.

B. One-parameter scaling of drift velocity

The identification of NE as a variable that characterizes the field strength, and its correspondence to the number of blobs for $NE > 1$, is consistent with our numerical result that the drift velocity can be written in terms of a universal function of NE. Our numerical results (see Fig. 5) indicate that for $N \gg 1$ and $E \ll 1$, the drift velocity v can be written in terms of a universal function $J(NE)$ as $v = N^{-2} J(NE)$, where we have the behaviors $J(u) \approx u$ as $u \to 0$, and $J(u) \approx u^2$ as $u \to \infty$.

The existence of one-parameter scaling follows from the assumption that $1/N$ is the only scale for E; this in turn follows from the universality of the Edwards model for long polymers. Thus we expect that such scaling should hold for any polymer in a network provided that it is sufficiently flexible, and that the network is sufficiently coarse for the chain to be described by an Edwards model *at the pore scale.* The repton model satisfies this requirement, and by the use of numerical simulations, we have been able to show that one-parameter scaling holds for the drift velocity.

Figure 5 shows the scaling function $J(u)$ calculated numerically for the repton model for $N \to \infty$; it smoothly interpolates between the linear small-u region (where the fluctuation-dissipation theorem holds) to the quadratic u^2 region, where the polymer is pulled out into an extended object. In other models, or in experiments, additional length scales due to rigidity, or due to strong orientational interactions between the pores and the polymer, may set additional scales for E. For the repton model in an electric field, the statement that one-parameter scaling of v holds at large N for any $E \ll 1$ is the major result of this paper.

C. Biased reptation model

It is worth commenting how one arrives at the E^3 behavior associated with the original version of the biased reptation model [15,16]. In this model, it is assumed that each segment along the polymer has an orientation with projection along the field axis that scales as E. Thus, the extension of the chain is assumed to be of order $h = EN$. This extension exceeds the spontaneous random-walk conformation fluctuations when $h > N^{1/2}$, or for $EN^{1/2} > 1$. This criterion replaces the stretching argument made above when the chain is inflexible at the network scale [19,20], circumstances under which the elasticity ideas of the Edwards model are obviously inapplicable. For $EN^{1/2} < 1$ we may continue to apply the usual reptation and Nernst-Einstein arguments to find a drift velocity $v = E/N$. As before, we suppose that $E \ll 1$ and that $N \to \infty$.

For biased reptation, we may use a blob argument to estimate the drift velocity for $EN^{1/2} > 1$. The blob molecular weight is $N_b \approx 1/E^2$; below this scale there is no appreciable stretching. Along a chain we thus have $n = N/N_b = NE^2$ blobs. The blob size is $\xi = N_b^{1/2} = 1/E$, and thus the total extension of the chain is $l = n\xi = EN$, while its diameter is ξ. Note that this total extension is consistent with the total extension *assumed* in the biased reptation model. We then estimate a drift velocity of $v = N_b E D_b$, and using the blob diffusion constant $D_b = 1/N_b^2$, we have $v = E^3$.

D. Further questions

Several questions have been raised by the results presented in this paper. First, we have found that there are strong subleading power-law corrections to the diffusion constant for finite N: $D = \frac{1}{3} N^{-2}(1 + 5N^{-2/3})$. The same corrections are observed in the drift velocity for weak fields ($EN < 1$), as one would expect from the Nernst-Einstein relation. We have not formulated a simple scaling argument to rationalize this correction to leading scaling. No such corrections are found in the exact results for the diffusion constant obtained by van Leeuwen and Kooiman [8–11] by analytical solution of the repton model with periodic boundary conditions. We speculate that this correction to leading scaling arises due to stress relaxation at the ends of the polymer, and that the different treatment of the ends of the polymer causes a different correction to leading scaling.

The diffusion constant may be related to the tube correlation time $\tau = R^2/D$, where $R = N^{1/2}$ is the size of the chain, giving a correlation time of the form $\tau \propto N^3/(1 + 5N^{-2/3})$. The time τ corresponds to the "terminal time" for entanglement release in a polymer melt, and is $\tau \approx N^3$ in the reptation theory of polymer melts. Experiments on polymer melts have long measured $d \ln\tau / d \ln N \approx 3.4$ [26]. It is amusing that the

correction term in the repton model leads to $d \ln\tau / d \ln N \approx 3 + (10/3)N^{-2/3}$, which for $N = 50$ gives 3.25. (Note that N in the repton model corresponds to the molecular weight in units of the entanglement molecular weight in a polymer melt.) Perhaps this type of correction is partially responsible for the rather slow convergence of observed scaling of the terminal time to N^3 behavior.

We have shown that the basic repton model does not show the E^3 drift-velocity dependence predicted by the original version of the biased reptation model for $EN^{1/2} > 1$. As discussed by Duke, Semenov, and Viovy [19,20] the E^3 drift-velocity dependence may still occur for chains which are sufficiently stiff at the scale of the network. An interesting question is what modification could be made to the repton model to obtain this behavior. Chain stiffness and a suppression of "piling up" of successive segments in the same pore could be introduced into the model, but it is not clear if this would be sufficient to change the universality class to that of biased reptation.

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[1] M. Rubinstein, Phys. Rev. Lett. **59**, 1946 (1987).
[2] M. Rubinstein, in *New Trends in Physics and Physical Chemistry of Polymers,* edited by L.-H. Lee (Plenum, New York, 1989), pp. 455–469.
[3] T. A. J. Duke, Phys. Rev. Lett. **62**, 2877 (1989).
[4] T. A. J. Duke, J. Chem. Phys. **93**, 9049 (1990).
[5] T. A. J. Duke, J. Chem. Phys. **93**, 9055 (1990).
[6] B. Widom, J. L. Viovy, and A. D. Défontaines, J. Phys. (France) I **1**, 1759 (1991).
[7] J. M. J. van Leeuwen, J. Phys. I (France) **1**, 1675 (1991).
[8] J. M. J. van Leeuwen and A. Kooiman, Physica A **184**, 79 (1992).
[9] A. Kooiman and J. M. J. van Leeuwen, Physica A **194**, 163 (1993).
[10] A. Kooiman and J. M. J. van Leeuwen, J. Chem. Phys. **99**, 2247 (1993).
[11] A. Kooiman, Ph.D. thesis, U. of Leiden, 1993.
[12] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971).
[13] R. H. Bisseling and I. Szleifer (unpublished).
[14] I. Szleifer (unpublished).
[15] O. J. Lumpkin, P. Déjardin, and B. H. Zimm, Biopolymers **24**, 1573 (1985).
[16] G. W. Slater and J. Noolandi, Biopolymers **25**, 431 (1986).
[17] J. L. Viovy, Electrophoresis **10**, 429 (1989).
[18] J. Batoulis, N. Pistoor, K. Kremer, and H. L. Frisch, Electrophoresis **10**, 442 (1989).
[19] T. A. J. Duke, A. N. Semenov, and J. L. Viovy, Phys. Rev. Lett. **69**, 3260 (1992).
[20] T. A. J. Duke, J. L. Viovy, and A. N. Semenov, Biopolymers (to be published).
[21] C. Heller, T. A. J. Duke, and J. L. Viovy, Biopolymers (to be published).
[22] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1989), Chap. 2.
[23] S. Alexander, J. Phys. (Paris) **38**, 983 (1977); P. G. de Gennes, Macromolecules **13**, 1069 (1980).
[24] P. Pincus, Macromolecules **9**, 386 (1976).
[25] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1988), Sec. XI.2.1.
[26] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1989), Chap. 7.