New Biased-Reptation Model For Charged Polymers

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We study entangled charged polymers in an electric field with a new biased-reptation model. Two microscopic time scales are relevant: the usual tube disengagement time T_D, and a new chain stretching time constant τ_{str}. When $\tau_{str} < T_D$, i.e., for long chains and/or high electric fields, the chains are stretched in the field direction. As an example, we discuss DNA gel electrophoresis in terms of these results. Experimental and theoretical investigations are suggested.

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The motion of entangled polymers is widely considered to be explained, at least qualitatively, by the reptation mechanism.[1,2] Calculations based on this exceedingly simple model[1] have been reasonably successful in explaining the rheology of entangled polymer solutions. Discrepancies between experiments and the predictions of the reptation theory are believed to be due mainly to the dynamics of the entanglements.[3,4]

In order to study the entanglements, one should look for systems where their effects would be predictable. Charged polymers, in general, are good candidates since they usually involve time and length scales that are field dependent and therefore tunable. On the other hand, a gel matrix provides a fixed entanglement network for the reptating chains, and is therefore ideal to isolate the effects of the entanglements in the reptation theory.

In this paper, we introduce a biased-reptation model that we have developed recently in order to study the many aspects of the motion of uniformly *charged* polymers in an environment of *fixed* obstacles. This allows us to calculate the time duration and the size of the deformation of the chain caused by the field and the entanglements. As an example, this model is applied here to the case of DNA gel electrophoresis, but can be the starting point of future investigations in the science of ionomers and polyelectrolytes, which are polymers of great practical interest.

In the gel electrophoresis of DNA, an electric field forces long DNA chains to migrate through a gel in order to separate them according to their lengths (or masses). Recently, the reptating motion of DNA chains has been invoked both theoretically[5,6] and experimentally[7,8] to explain the behavior of the electrophoretic mobility (μ) of DNA fragments for which the expected radius of gyration exceeds the size of the gel pores. In this case, it has been proven[5,6] that μ should be inversely proportional to L, the contour length of the molecule. Experiments indicate that this is so,[8] although field-dependent mobilities[9,10] are observed for high fields and/or very long DNA chains. Moreover, the mobility[9,10] of very long DNA chains is measured to be almost length independent. These latter phenomena cannot be explained by the standard reptation approach to gel electrophoresis.

In the reptation theory, a chain is considered trapped in a tube (Fig. 1) which hinders any lateral movement. The tube is the result of the chain environment (entanglements with other chains, structure of the gel matrix, etc.). Only one-dimensional motion along the tube axis is allowed in the model. In the field-free case, the probabilities $p_{\pm}$ of forward (+) and back-

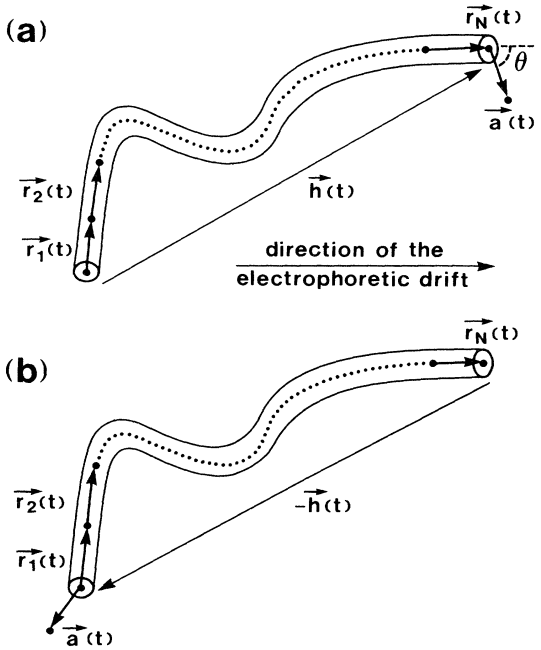

FIG. 1. The polymer chain is forced to move in a tube fixed by the entanglements of the surrounding gel matrix, which are separated by an average distance a. The chain is modeled by a series of N vector segments $\mathbf{r}_i$, each of constant length a. The direction of the electrophoretic drift is in the field direction for a positively charged chain. (a) During a forward jump at time t, the Nth segment leaves the tube. The result of this jump is the same as replacing the segment $\mathbf{r}_1(t)$ by the newly created segment $\mathbf{a}(t)$ at the other extremity of the chain; (b) similarly, during a backward jump, the segment $\mathbf{r}_N(t)$ is replaced by a new segment $\mathbf{a}(t)$ at the other extremity of the chain.

ward ($-$) motion of the chain are equal [$p_{\pm}(0)=\frac{1}{2}$], and the overall Brownian motion is seen as composed of jumps of length a (the average distance between entanglements along the tube), each taking time Δt, where the two parameters are related to the curvilinear diffusion coefficient D_c, and to the curvilinear friction coefficient ξ_c by (T is the temperature and k_B is the Boltzmann constant)

$$D_c = a^2/2\Delta t = k_B T/\xi_c. \tag{1}$$

During such a jump, the end segment of the chain that leaves the tube ($\mathbf{r}_1$ or $\mathbf{r}_N$; see Fig. 1) goes in a random direction $\mathbf{a}(t)$, while all the other $N-1$ segments $\mathbf{r}_i$, each of length a ($=L/N$), simply follow the tube.

In the presence of an electric field, a longitudinal electric force F_l is applied to the charged chain, and this is expected to break both the symmetry of the backward and forward jumps and the possibility for the ends of the chain to choose a random orientation when they leave the tube. Together, these changes lead to a net velocity of the center of mass of the chain in the field direction. In the following, we will restrict ourselves to the case of uniformly charged chains in order to compare our results with those of DNA gel electrophoresis. The scalar force F_l is then simply given by[5]

$$F_l = \sum_{i=1}^{N} \frac{q\mathbf{E}\cdot\mathbf{r}_i}{a} = \frac{Q\mathbf{E}}{L}\cdot\sum_{i=1}^{N}\mathbf{r}_i = \frac{Q\mathbf{E}\cdot\mathbf{h}}{L}, \tag{2}$$

where q and Q ($=Nq$) are the effective charges of one chain segment and of the whole chain, respectively, $\mathbf{E}$ is the electric field, and $\mathbf{h}$ is the end-to-end vector of the chain. With $\mathbf{E}$ in the x directon, this leads to the curvilinear velocity v_l^E and to the center-of-mass (electrophoretic) velocity $\langle V^x_{\text{c.m.}}\rangle$ given by[5]

$$v_l^E = F_l/\xi_c = Q\mathbf{E}\cdot\mathbf{h}/L\xi_c, \tag{3a}$$

$$\langle V^x_{\text{c.m.}}\rangle = QE\langle h_x^2\rangle/L^2\xi_c. \tag{3b}$$

If we bias the probabilities $p_{\pm}(E)$ by writing

$$p_{\pm}(E) = \tfrac{1}{2}[1\pm\delta(E)], \tag{4}$$

where $\delta(E)$ is the field-dependent bias of the one-dimensional Brownian motion, it is clear that

$$v_l^E = \frac{a}{\Delta t}[p_+(E)-p_-(E)] = \frac{a\,\delta(E)}{\Delta t}. \tag{5}$$

By comparing Eqs. (3a) and (5), we then see that the bias must be given by

$$\delta(E) = (Q\mathbf{E}\cdot\mathbf{h}/2k_BT)a/L. \tag{6}$$

With this choice of $\delta(E)$, the biased jumps take into account the Brownian nature of the one-dimensional chain motion, and lead to the correct longitudinal velocity v_l^E as well.

The end segment that leaves the tube aligns itself preferentially in the field direction to minimize its potential energy. In our model, the probability of having a given angle θ between the field direction and the direction of this segment if proportional to a Boltzmann factor using the energy of a uniformly charged rod (having one end fixed) in an electric field, $\frac{1}{2}qEa\cos\theta/k_BT$. In this approach, the average angle $\langle\theta\rangle$ is given by (here we consider only the case for which $qEa/k_BT<1$; the normalizing factor is then of order unity)

$$\langle\cos\theta\rangle \simeq \int_0^{\pi}\tfrac{1}{2}\cos\theta\sin\theta\,d\theta\exp(qEa\cos\theta/2k_BT) \simeq qEa/6k_BT. \tag{7}$$

Equations (4), (6), and (7) define completely our biased-reptation model for a uniformly charged chain. We can now calculate the chain electrophoretic mobility, static structure factor, and elongation parameters.[11] Moreover, it allows simple computer simulations of the chain dynamics of noninteracting ionomers in an electric field, or of polymer gel electrophoresis. We calculate below the characteristic time constant of chain stretching, and the equilibrium surplus elongation (in the field direction) of a stretched chain; comparison is made with available results from DNA-gel-electrophoresis experiments.

As can be seen in Fig. 1, a forward jump at time t can be thought of as equivalent to bringing the $\mathbf{r}_1(t)$ segment after the $\mathbf{r}_N(t)$ segment; the change of the end-to end vector $\mathbf{h}(t)$ is then $\Delta\mathbf{h}(t)=\mathbf{a}(t)-\mathbf{r}_1(t)$, where $\mathbf{a}(t)$ is the position that the segment vector $\mathbf{r}_N(t)$ takes once it has left the tube. Similarly, a backward jump replaces $\mathbf{r}_N(t)$ by the $\mathbf{a}(t)$ segment at the other extremity of the chain, and $\Delta\mathbf{h}(t) = -\mathbf{a}(t)-\mathbf{r}_N(t)$. For strong biases ($\delta\simeq 1$, i.e., $p_+ >> p_-$, but not necessarily $qEa/k_BT>1$) and small times, there will be mostly forward jumps, and the $\mathbf{r}_1(t)$ segment simply follows the initial random-walk tube. In this case, $\langle\mathbf{r}_1(t)\rangle\simeq 0$, $\langle\mathbf{r}_N(t)\rangle \simeq \langle\mathbf{a}(t)\rangle$, and we have ($\mathbf{i}_x$ is the unit vector in the x direction)

$$\frac{\partial\langle h_x(t)\rangle}{\partial t} = \frac{\langle p_+[\mathbf{a}(t)-\mathbf{r}_1(t)]+p_-[-\mathbf{a}(t)-\mathbf{r}_N(t)]\rangle}{\Delta t}\cdot\mathbf{i}_x$$
$$\simeq \frac{\langle\delta(E)\rangle\langle\mathbf{a}(t)\cdot\mathbf{i}_x\rangle}{\Delta t} = \frac{a\langle\delta(E)\rangle\langle\cos\theta\rangle}{\Delta t} = \frac{\langle h_x(t)\rangle}{\tau_{\text{str}}}, \tag{8}$$

where, with use of Eqs. (6) and (7), the chain stretching time constant τ_{str} is found to be[11]

$$\tau_{str}=\left(\frac{QEa\langle\cos\theta\rangle}{2Nk_BT\,\Delta t}\right)^{-1}=\frac{2\pi^2}{3}\left(\frac{QEa}{3k_BT}\right)^{-2}T_D, \tag{9}$$

and $T_D=L^2/D_c\pi^2$ is the disengagement time of de Gennes.[2] Other assumptions for the end-segment averages $\langle\mathbf{r}_1(t)\rangle$ and $\langle\mathbf{r}_N(t)\rangle$ lead to the same expressions for τ_{str}, apart from numerical coefficients of order unity.[11] The very strong dependence of τ_{str} ($\sim LE^{-2}$) on the electric field E shows that chain stretching is a combined effect of both of the biases given by $\delta(E)\sim E$ *and* $\langle\cos\theta\rangle\sim E$; we also note that it depends upon the average interobstacle distance a.

Since the chains are restricted to move in a tube, a chain with an end-to-end vector $\mathbf{h}$ is pulled in the field direction by an average force $F_l\langle\cos\theta\rangle$ (this force can be considered as applied by the $\mathbf{r}_N$ segment to the rest of the chain that is following it). The entanglements retard the $\mathbf{r}_1(t)$ segment by adding an eqivalent frictional force in the other direction; as a consequence, the force $F_l\langle\cos\theta\rangle$ leads to a net tension in the chain, and therefore to a net surplus elongation. The average steady-state surplus elongation of the chains, $\langle\Delta h_x\rangle$, can be estimated by use of the average chain tension $\langle F_l\rangle\langle\cos\theta\rangle$ and the well-known relation[12] for the average projection of one segment in the field direction [see, for example, (7)]

$$\langle\mathbf{r}_i\cdot\mathbf{i}_x\rangle/a=\langle\Delta h_x\rangle/L$$
$$=B\{a\langle F_l\rangle\langle\cos\theta\rangle/k_BT\}, \tag{10}$$

where $B\{x\}=\coth x-1/x$. With Eqs. (2), (7), and (10), we get, to first order in $QEa/3k_BT$ and in $\langle\Delta h_x\rangle$,

$$\langle\Delta h_x\rangle\simeq\frac{\langle h_x(E=0)\rangle}{N}\left(\frac{QEa}{3k_BT}\right)^2$$
$$\simeq\frac{\langle h_x(E=0)\rangle}{N}\frac{T_D}{\tau_{str}}, \tag{11}$$

where we have dropped numerical factors of order unity. The average end-to-end distance $\langle h_x\rangle$ increases by the minimal value $\langle h_x(E=0)\rangle/N$ (the average elongation per segment when $E=0$) only if $\tau_{str}>T_D$. This is reasonable since for $\tau_{str}>T_D$, the Brownian tube renewal would dominate any tube orientation (or stretching) driven by the electric field.[13]

Figure 2 shows $\langle\Delta h_x\rangle/\langle h_x(E=0)\rangle$ vs Q obtained by solving (10) numerically, for different values of E; we have put

$$\langle h_x\rangle\simeq\langle h_x(E=0)\rangle+\langle\Delta h_x\rangle$$
$$=(2La/3\pi)^{1/2}+\langle\Delta h_x\rangle$$

in the expression for $\langle F_l\rangle$ on the right-hand side of (10). The chosen parameters are typical for DNA electrophoresis. We see that appreciable elongation does indeed take place when $\tau_{str}<T_D$ (dotted parts of the curves).

Equations (9) and (11) stress the fact that it is the total electric force $Q\mathbf{E}$ that is important here, and not only the field strength or the chain length. In gel electrophoresis, for instance, field-dependent mobilities and unexpectedly high mobilities for very long DNA chains are observed.[9,10] It is clear that since $\mu=\langle V_{c.m.}\rangle/E\sim\langle h_x^2\rangle$, the stretching predicted here gives additional length and field dependence to μ (see Ref. 11 for a quantitative study of both $\langle h_x^2\rangle$ and μ). For example, if the experimental conditions were such that $\tau_{str}\leqq T_D$, a field- and length-dependent correction term proportional to $\langle\Delta h_x\rangle$ [see (11)] would be added to $\mu(E=0)$: Since $\langle\Delta h_x\rangle\sim Q^{3/2}E^2$, this term would

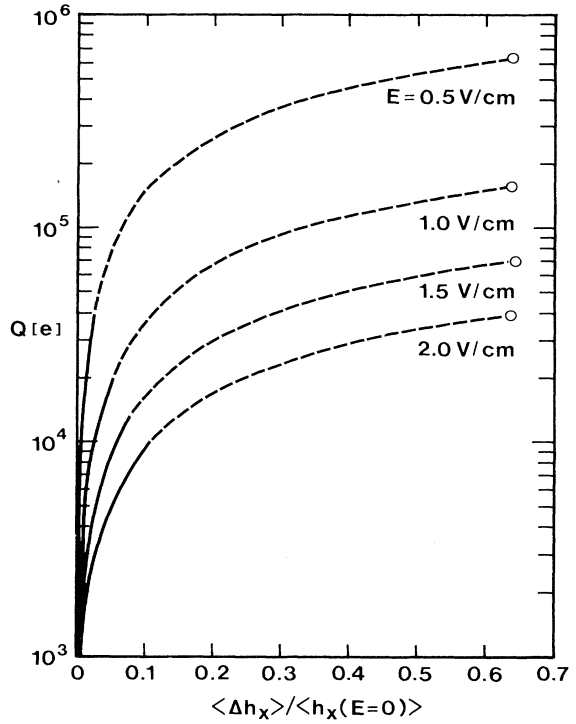

FIG. 2. Relative surplus elongation $\langle\Delta h_x(E)\rangle/\langle h_x(E=0)\rangle$ as a function of the total effective charge Q (in units of the electron charge e), for several values of the electric field E. The curves show little stretching in the field direction unless $\tau_{str}<T_D$ (dashed part of the curves). The parameters used are typical of DNA-gel-electrophoresis experiments: $a=1000$ Å, $T=300$ K, $q=300e$. The curves end at $\delta(E)=1$ (the circles) since the model is invalid for $\delta(E)>1$.

increase the actual mobility of long chains, and give field-dependent mobilities,[11] in agreement with experiments. Using Eq. (9) and the parameters indicated in Fig. 2, we see that the condition $\tau_{str} < T_D$ corresponds to about $Q > 10^4 e$, or to chains having more than about 20×10^3 bases (with one effective electronic charge e per base), in agreement with the experimental values for the size of the DNA chains for which such effects begin to be measurable.[9,10]

The DNA gel electrophoresis may not be the ideal system to verify the present theory since the size of the pores is rather large, and exceeds the transverse dimension of the DNA chain even for relatively small elongations. Systems with much smaller pores are certainly preferable. Although experiments involving DNA gel electrophoresis have their limitations, they should be excellent to test the low-stretching limit of our model. A complete study of the predictions of our model for DNA gel electrophoresis will be presented elsewhere.[11]

Considering that our theory explains most effects observed in the reptation regime of DNA gel electrophoresis,[11] it is tempting to use this generalizaton of the standard reptation model to study other systems of entangled polymers, such as polyelectrolytes and ionomers. In fact, the approach followed here could be modified easily to take into account various charge distributions along the chain; for example, we have calculated recently the nonequilibrium static structure factor of various charged chains in an electric field[14]; comparison with scattering experiments is expected to lead us to a better understanding of polymer chain dynamics, and hopefully to a better characterization of the effects of the entanglements. It is also a perfect model for computer simulations. We hope that this theoretical advance will stimulate research on entangled charged polymer systems, leading to an understanding of the role of the entanglements, new (better?) measurements of the reptation parameters, and progress in the dynamics of biologically important polyelectrolytes.

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