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Kink Motion in a Chain Molecule Driven through a Pore

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Recently, in a very interesting paper, Kasianowicz et al.[1] showed that an electric field can be used to drive single-stranded RNA and DNA through a 2.6 nm diameter ion-channel. The theory of such translocation processes has been examined by Park and Sung.[2−4] They assume the reaction coordinate for the process to be the center of mass of the chain. On the basis of the results of the Rouse model,[7] they take the center of mass to diffuse with a diffusion coefficient proportional to $1/N$, where N is the total number of segments in the polymer (N is proportional to the length L of the polymer). As N segments have to cross the pore, the time of crossing (t_{cross}) is proportional to N^3. If there is a favorable difference in the chemical potential between the two sides, the time can be lowered to being proportional to N^2, while in unfavorable cases it is increased to being exponential in N.[5] In the experiments[1] it was found that t_{cross} is proportional to the length of the molecule and hence to N. In the following we suggest that the portion of the chain inside the pore is to be thought of as a kink and that translocation may be thought of as the motion of the kink on the chain, in the reverse direction. Our model leads to the prediction that t_{cross} is proportional to N, in agreement with the results of the experiment. We present the basic idea in the following, leaving out the detailed mathematical development to other publications.[6]

Under the conditions of the experiment, the DNA strand is negatively charged, and under the influence of a potential difference, it migrates from the side where the potential is negative (cis), to the side where the potential is positive (trans). We shall assume that the charge on the DNA is spread uniformly over all its segments. Then, a segment of DNA on the cis side has a higher free energy than on the trans side. As the segment passes through the pore, it would interact with the walls of the pore, which too are charged. So one expects the free energy per segment of the chain to change as shown in the Figure 1. It is possible that the pore could represent a region where the free energy is larger, and hence there is a barrier to the translocation process. This means that the process is activated. As this does not seem to be the situation in the experiments,[1] and as we have discussed this situation earlier,[6] we shall not discuss this case here.

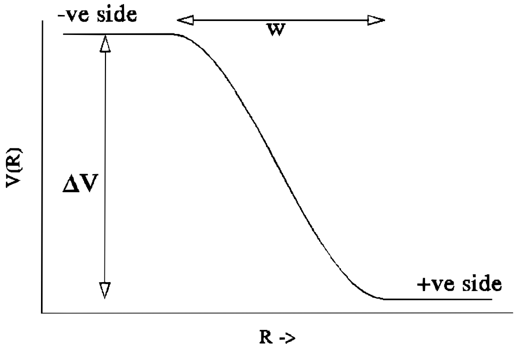

Figure 1. The free energy per segment of the polymer, shown as a function of the position of the segment. As the segment goes from the left (−ve) to right (+ve), the free energy changes by $-\Delta V$.

The pore is about 10 nm wide, and therefore, at any time, there should be more than 10 nucleotides in it. As this number is not small, we can adopt a continuum description for the dynamics, where instead of looking at the dynamics of individual units, one looks at the dynamics of a string (see the book by Doi and Edwards[7] for details). The dynamics of the string passing through the pore is governed by the equation (assuming the motion to be one-dimensional)

$$\zeta\partial_t R(n,t) = m\partial_{nn}R(n,t) - V'(R(n,t)) + f(n,t) \tag{1}$$

n denotes bead number along the chain. $m = 3k_BT/l^2$, where l is the Kuhn length.[7] ζ denotes the friction constant for the beads modeling the chain.[7] $R(n,t)$ denotes the position of the nth unit at time t, and $V(R(n,t))$ represents the free energy per unit length of the string, inside the pore. $V'(R) = \partial V(R)/\partial R$. $f(n,t)$ is the random thermal noise driving the chain. We take the width of the pore to be w and the potential inside the pore to be given by $V(R) = \Delta V(R/w)^2\,(2\,R/w - 3)$ for $0 < R < w$ while $V(R) = 0$ for $R < 0$ and $V(R) = -\Delta V$ for $R > w$. The free energy change in going from the left to right is $-\Delta V$. To analyze the translocation process, we consider the average motion of the chain by neglecting the fluctuating force $f(n,t)$ in eq 1. The resulting deterministic equation

$$\zeta\partial_t R(n,t) = m\partial_{nn}R(n,t) - V'(R(n,t)) \tag{2}$$

has a solution of the form $R(n,t) = R_s(\tau)$, where $\tau = n - vt$. It may be found by putting this functional form in to the equation 2, which leads to:

$$m\partial_{\tau\tau}R_s + \zeta v\partial_\tau R_s - 6\Delta V\,(R_s/w^2)\,(R_s/w - 1) = 0 \tag{3}$$

We find a kink solution[8] to this equation such that $R_s(-\infty) = 0$, $R_s(\infty) = w$. It is: $R_s(\tau) = w[1 + \exp(-\sqrt{\Delta V/m}(\tau - \tau_0)/w)]^{-2}$, where τ_0 is an arbitrary constant. This solution exists only if $\zeta v = -5\sqrt{m\Delta V}/w$. That is, the kink moves in the negative direction—this corresponds to the motion of the chain molecule in the reverse direction. As the kink is moving with a finite velocity, and as there are N segments to move across, the time t_{cross} has to be proportional to $Nw/(\zeta\sqrt{m\Delta V})$. Thus, we find that the traversal time is directly proportional to the number of units in the polymer, in agreement with the experiments of Kasianowicz et al.[1] Further, our analysis predicts that t_{cross} is inversely proportional to the square root of the applied potential difference, a prediction that is in variance with the results of ref 1. This difference can be due to: (a) in ref 1, only a limited range of potential differences were considered or (b) the form of the potential (see the Figure) that we have taken is not the correct one. A potential with a barrier leads to a more complex dependence on ΔV, in general. (c) There is also the possibility that the kink mechanism is not the correct one, but the transfer

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(1) Kasianowicz, J. J.; Brandin, E.; Branton, D.; Deamer, D. W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 13770.
(2) Park, P. J.; Sung, W. *Phys. Rev. Lett.* **1996**, *77*, 783.
(3) Park, P. J.; Sung, W. *J. Chem. Phys.* **1998**, *108*, 3013.
(4) Park, P. J.; Sung, W. *Phys. Rev. E* **1998**, *57*, 730.
(5) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989**, *22*, 1937. Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989**, *22*, 1941.
(6) Sebastian, K. L.; cond-mat 9907003, July, 1999. LANL reprint archive.
(7) Doi, M.; Edwards, S. F. *The theory of polymer dynamics*; Clarendon Press: Oxford, 1986.
(8) Rajaraman, R. *Instantons and Solitons*; North-Holland: Amsterdam 1982.

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occurs by movement of the few monomers inside the pore. This has been recently analyzed by Lubensky and Nelson.[9] Their predictions are in agreement with the data of ref 1. Clearly, more experimental work with a larger range of chain lengths and potential differences is needed.

Now, one may ask, what is the role of the random function $f(n,t)$? This term causes the kink to execute a random walk like motion, and plays a major role in the case where there is no free energy difference between the two sides.[6]

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[9] This possibility was pointed out by the reviewer. The mechanism has been discussed in a recent paper by Lubensky, D. K.; Nelson, D. R. *Biophys. J.* **1999**, *77*, 99005.