An Interesting Constrained Random Walk Problem

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ABSTRACT: Consider a set of n ideal polymer strands, each containing N_j segments, and each having a fixed end-to-end distance s. The N_j values are free to fluctuate subject only to the constraint $\sum N_j = n\bar{N}$. This would represent, for example, a single ring chain of total length $n\bar{N}$ constrained to pass through a series of slip-links. Rieger[1-3] has discussed the problem for the case $n = 2$, as well as the general implications for theoretical polymer science. Here we generalize his results to arbitrary n. The most probable distribution of N_j's exhibits a symmetry-breaking transition: At large s the most probable distribution is $N_j = \bar{N}$ for all j; at small s, one of the N_j's is much larger than all the others. The most probable distribution changes abruptly at a critical value of s. This is not true, however, of arbitrary statistical properties: Fluctuations about the most probable distribution are important and wash out the abrupt transition. Only through the application of an external field, as we demonstrate here with Monte Carlo calculations, can the transition be made first order.

1. Introduction

Rieger[1-3] has discussed an interesting constrained random walk problem, which can be described in the following way: The two ends of an ideal polymer are anchored at the two points $z = 0$ and $z = 2s$ along the z axis, and the polymer is constrained to pass through a grommet at the point $z = s$. The polymer chain is free to slip through the grommet. If there are respectively N_1 and N_2 segments in the two polymer sections on either side of the grommet, then N_1 and N_2 fluctuate subject to the constraint $N_1 + N_2 = 2\bar{N}$, since the total number of segments is conserved. The statistical weight of any particular configuration of N_1 and N_2 is

$$\left(\frac{3}{2\pi N_1}\right)^{3/2} \exp\left(\frac{-3s^2}{2N_1}\right)\left(\frac{3}{2\pi N_2}\right)^{3/2} \exp\left(\frac{-3s^2}{2N_2}\right) \quad (1)$$

as is well-known. Rieger has shown that the configuration of N_1 and N_2 with maximum statistical weight exhibits a symmetry-breaking bifurcation: When s is large, $(N_1,N_2) = (\bar{N},\bar{N})$ is the configuration with maximum weight. As s decreases, the configuration of the maximum weight bifurcates. At very small s, either N_1 is likely to be much greater than N_2, or vice versa.

In this paper we generalize the problem to n strands. To be precise, we examine the statistical properties of a set of n variables, N_1, N_2, N_3, ..., N_n, given the free energy function

$$F(N_1,N_2,\ldots,N_n) = \frac{3}{2}\sum_{j=1}^{n} f(N_j); \quad f(N) = \ln N + \frac{s^2}{N} \quad (2)$$

and subject to the constraint

$$\sum_{j=1}^{n} N_j = n\bar{N} \quad (3)$$

Note that (2) is the expected free energy given a statistical weight such as (1), up to a neglected additive constant. Rieger has also considered[3] the generalization to $n > 2$; in this paper we extend his results.

2. Most Probable Sequence of N_j's

In this section we determine the global minimum of the function F given in eq 2 subject to the constraint 3. Obviously, this represents the most probable sequence of N_j's.

By the method of Lagrange multipliers, we determine that an extremal point of F is any set of N_j's satisfying

$$g(N_j) = \lambda \quad \text{for all } j \quad (4)$$

where

$$g(N) = f'(N) = N^{-1} - s^2N^{-2} \quad (5)$$

and where λ is the Lagrange multiplier. The function $g(N)$ behaves as $-(s/N)^2$ for small N and as $1/N$ for large N. It goes through a maximum at $N^* = 2s^2$; $g(N^*) = (4s^2)^{-1}$. A graph of $g(N)$ appears in Figure 1. $g(N)$ has a zero at $N_0 = s^2$. If $\lambda < 0$, eq 4 has only one solution. Call this $N_\beta(\lambda)$. If $0 < \lambda < (4s^2)^{-1}$, then eq 4 has two solutions, which we call $N_\alpha(\lambda)$ and $N_\beta(\lambda)$, with $N\alpha(\lambda) > N_\beta(\lambda)$. Note that $N_\beta(\lambda)$ for $\lambda > 0$ is just the continuation of $N_\beta(\lambda)$ as defined for $\lambda < 0$. In other words, $N_\beta(\lambda)$ always refers to the left branch of the $g(N)$ curve, and $N_\alpha(\lambda)$ always refers to the right branch.

The quantities N_α and N_β can be computed as follows:

$$N_\beta(\lambda) = (2\lambda)^{-1}[1 - (1 - 4\lambda s^2)^{1/2}] = \frac{2s^2}{1+t} \quad (6)$$

$$N_\alpha(\lambda) = (2\lambda)^{-1}[1 + (1 - 4\lambda s^2)^{1/2}] = \frac{2s^2}{1-t} \quad (7)$$

In the above

$$t^2 = 1 - 4\lambda s^2 \quad (8)$$

To summarize: Any set of N_j's such that some m of them are equal to $N_\alpha(\lambda)$ while the remaining $n-m$ of them are equal to $N_\beta(\lambda)$ (all evaluated at the same λ) is an extremal point of the function $F(N_1,N_2,\ldots,N_n)$ subject to the constraint $\sum_j N_j = n\bar{N}$.

Once extremal points have been found, we must determine which of these are local minima. If there are m of the N_j's equal to $N_\alpha(\lambda)$ and $n-m$ equal to $N_\beta(\lambda)$, then the following three assertions can be proved:

(1) If $N_j = N_k = N_\beta(\lambda)$, then the infinitesimal exchange of segments $N_j \to N_j + \epsilon$, $N_k \to N_k - \epsilon$ always increases the free energy.

(2) If $N_j = N_k = N_\alpha(\lambda)$, then the infinitesimal exchange of segments $N_j \to N_j + \epsilon$, $N_k \to N_k - \epsilon$ always decreases the free energy.

(3) If $N_j = N_\alpha(\lambda)$ and $N_k = N_\beta(\lambda)$, then the infinitesimal exchange of segments $N_j \to N_j + \epsilon$, $N_k \to N_k - \epsilon$ always increases the free energy.

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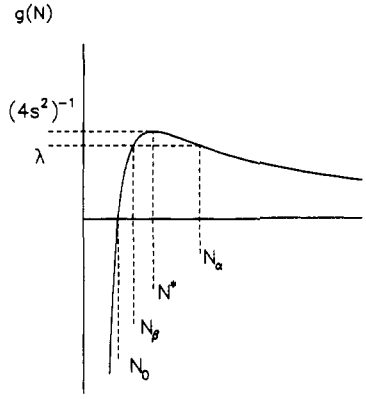

Figure 1. The function $g(N)$. It attains the maximum value $(4s^2)^{-1}$ at $N = N^* = 2$ and has a zero at $N = N_0 = 1$. $N_\alpha(\lambda)$ and $N_\beta(\lambda)$ are solutions of $g(N) = \lambda$.

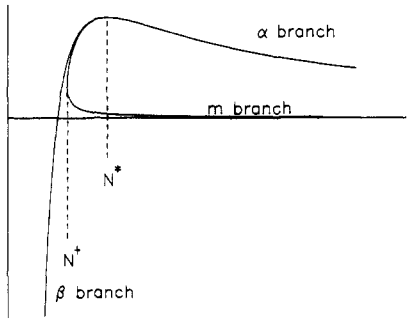

Figure 2. Two branches of the curve $g(\bar{N})$ α and β, for $\bar{N} > N^*$ and $\bar{N} < N^*$, respectively. A second curve, the "m branch," is constructed by combining $n-1$ parts of the β branch with 1 part of the α branch. The m branch turns about at $\bar{N} = N^\dagger$ and is therefore double-valued between $N^\dagger$ and N^*. All local minima in the $F(N_1,N_2,...,N_n)$ function occur on either the β or the m branch. The construction in this figure is for $n = 100$.

These three assertions imply that local minima of the free energy are of two classifications: (1) All n of the $N_j = N_\beta(\lambda)$. (2) $n-1$ of the $N_j = N_\beta(\lambda)$; the remaining one $= N_\alpha(\lambda)$.

Obviously these two exhaust the possibilities for local minima, for if any two of the N_j's were equal to $N_\alpha(\lambda)$, then by the second assertion above, the free energy could be lowered further by exchanging segments between these two N_j's.

For the first class of local minima, we have

$$\bar{N} = N_\beta(\lambda) \tag{9}$$

For the second class, we have

$$\bar{N} = \frac{n-1}{n}N_\beta(\lambda) + \frac{1}{n}N_\alpha(\lambda) \tag{10}$$

Only one minimum of the first class exists, while the second class minima are n-fold degenerate, since any one of the N_j's could be selected to be equal to N_α.

The following geometrical construction permits determination of the local minima at any given value of $\bar{N}$. To the $g(N)$ curve of Figure 2, add one more curve that we call the m branch, representing the weighted average appearing in eq 10, and also relabel the ordinate of the plot $\bar{N}$. The m branch is constructed from $n-1$ parts of the β branch and 1 part of the α branch. (See Figure 2.) Then local minima lie on both the β branch and the m branch. For all $n > 2$, the m branch begins by moving toward the left, then turns about at some point $N^\dagger$, and finally moves to the right. For $\bar{N} < N^\dagger$, there is only one local minimum, a β-branch minimum. For $N^\dagger < \bar{N} < N^*$, there are three different classes of nonequivalent local minima. One is a β-branch minimum, while the other two are nonequivalent m-branch minima. For $\bar{N} > N^*$, the only local minima exhibited by the system are n degenerate m-branch minima.

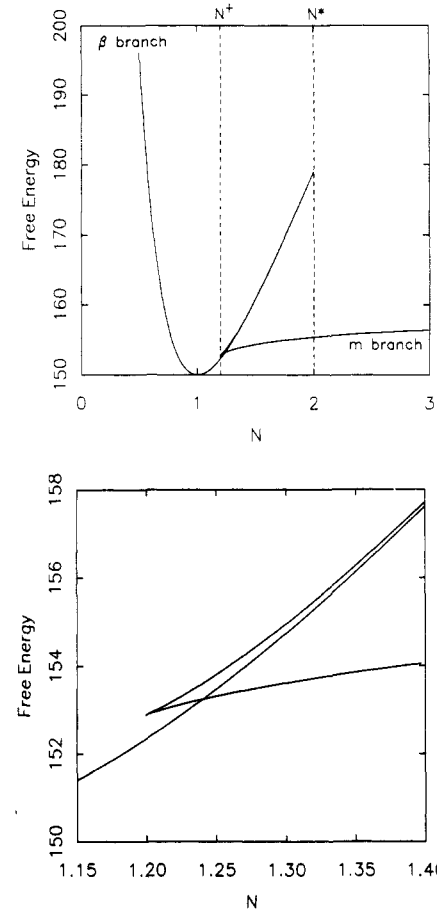

Figure 3. (a, top) Values of the free energy function $F(N_1,N_2,...,N_n)$ at all local minima. For $\bar{N} < N^\dagger$, there is only one local minimum, the β branch. For $\bar{N} > N^*$, there are n symmetry-equivalent local minima, the minima of the m branch. For $N^\dagger < \bar{N} < N^*$, there are three separate classes of local minima. Somewhere between $N^\dagger$ and N^*, the global minimum jumps abruptly from the β branch to the m branch. The construction in this figure is for $n = 100$. (b, bottom) Enlarged view of (a).

The global minimum is determined, of course, by comparing all local minima and selecting the lowest one. Obviously, somewhere in the interval $N^\dagger < \bar{N} < N^*$, the global minimum must shift from the β branch to the m branch. To see how this happens, we prepare a plot as follows. For all $\lambda \in (0, {}^1/_{4}s^2)$ compute $N_\alpha(\lambda)$ and $N_\beta(\lambda)$ according to eqs 6 and 7 and then $\bar{N}$ according to eq 10. Then draw a curve $F_m(\bar{N})$, depending parametrically on λ, according to

$$F_m(\bar{N}) = \frac{3}{2}[(n-1)\,f[N_\beta(\lambda)] + f[N_\alpha(\lambda)]] \tag{11}$$

Also, for all $\lambda < {}^1/_{4}s^2$, compute $N_\beta(\lambda)$ according to eq 6, and set $\bar{N} = N_\beta(\lambda)$. Then draw another curve, $F_\beta(\bar{N})$, also depending on λ parametrically, according to

$$F_\beta(\bar{N}) = \frac{3n}{2}f[N_\beta(\lambda)] \tag{12}$$

The resultant plot is shown in Figure 3a,b.

Obviously, the curves in parts a and b of Figure 3 represent the free energy of each one of the local minima existing at that particular value of $\bar{N}$. At some value of $\bar{N}$ between $N^\dagger$ and N^*, the global minimum jumps abruptly from a β-branch minimum to any one of the n-fold degenerate m-branch minima.

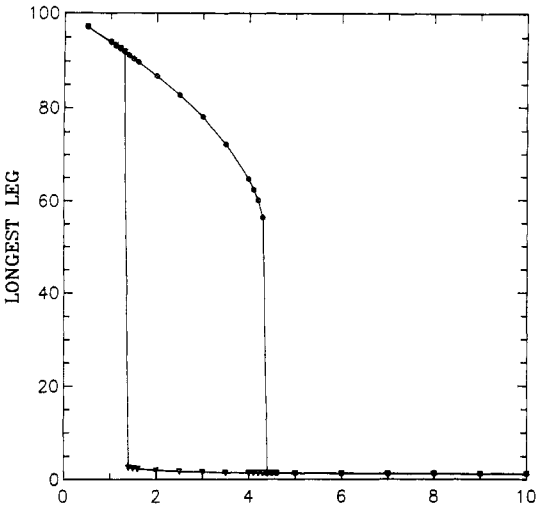

Figure 4. Average length of the longest leg in the presence of an external field.

The analysis changes somewhat in the case $n = 2$, as examined by Rieger.[1-3] Then $N^\dagger$ and N^* coincide, the m-branch curve of Figure 3 begins at $\bar{N} = N^*$ with infinite slope and curves to the right. The loop of Figure 3 shrinks to a point. Instead of jumping abruptly from one site in $(N_1,N_2,...,N_n)$ space to another, the global minimum bifurcates at $\bar{N} = N^*$. Rieger has discussed the properties of this bifurcation.

The loop-back of Figure 4 is a hallmark of a first-order phase transition. On the other hand, this analysis applies only to the most probable sequence of N_j's; if fluctuations about the global minimum are strong, then the system can pass smoothly through this symmetry-breaking transition. As one measure of the strength of the fluctuations, we compute the quantity

$$\Delta F^\dagger = F_m(N^\dagger) - F_\beta(N^\dagger) \tag{13}$$

This represents the free energy difference between the two classes of minima precisely at the point at which the m-branch minima first appear. We find, for large n

$$\Delta F^\dagger = \frac{3}{4}\ln M - \frac{15}{4} + 10M^{-1/2} + O(M^{-1}) \tag{14}$$

where $M = n - 1$. Note that for large n, $\Delta F^\dagger < \ln n$, which implies that the degeneracy of the newly appearing m-branch minima overwhelms the lower free energy of the global minimum. At the moment that these minima first appear as local minima, the probability of being found at one of these is greater than the probability of being found at the global minimum. This would imply that fluctuations about the most probable sequence of N_j's completely remove the first-order transition implied by the loop of Figure 3. This result is verified in the next section.[4]

3. Exact Statistical Results

We begin by calculating the partition function. It may be written

$$Q = \int_0^\infty dN_1 \int_0^\infty dN_2 ... \int_0^\infty dN_n\, e^{-F}\delta(n\bar{N} - \textstyle\sum_j N_j) \tag{15}$$

for F given by eq 2. Employing the Fourier integral representation of the δ function yields

$$Q = (2\pi)^{-1}\int_{-\infty}^{+\infty} dk\, \exp(ikn\bar{N})[G(k)]^n \tag{16}$$

where

$$G(k) = \int_0^\infty dx\, e^{-ikx}x^{-3/2}\exp(-A^2/x) \tag{17}$$

and $A^2 = 3s^2/2$. This is transformed into

$$G(k) = 2\int_0^\infty dy \exp\left(-A^2y^2 - \frac{ik}{y^2}\right) \tag{18}$$

by the transformation $y = x^{-1/2}$. The integrand in (18) has antiderivative[5]

$$(4A)^{-1}\pi^{1/2}[\exp[+2A(ik)^{1/2}]\ \mathrm{erf}[Ay + (ik)^{1/2}y^{-1}] + \exp[-2A(ik)^{1/2}]\ \mathrm{erf}[Ay - (ik)^{1/2}y^{-1}]] \tag{19}$$

which means that we need the limits $\mathrm{erf}(\pm\infty)$ and $\mathrm{erf}[\pm i^{1/2}\infty]$, i.e., along both the real axis and the axis parallel to $i^{1/2}$. Now, along the real axis, $\mathrm{erf}(\pm\infty) = \pm 1$. Along the $i^{1/2}$ axis, erf is related to the Fresnel integrals:[6]

$$\mathrm{erf}(i^{1/2}x) = (2i)^{1/2}[C(t) - iS(t)];\quad t = (2/\pi)^{1/2}x \tag{20}$$

The fact that $C(+\infty) = S(+\infty) = {}^1/_2$ and the fact that erf is odd everywhere in the complex plane implies $\mathrm{erf}(\pm i^{1/2}\infty) = \pm 1$. Therefore

$$G(k) = \pi^{1/2}A^{-1}\exp[-2A(ik)^{1/2}] \tag{21}$$

Equation 16 becomes

$$Q = \pi^{n/2}A^{-n}(2\pi)^{-1}\int_{-\infty}^{+\infty} dk\, e^{ikn\bar{N}}\exp[-2An(ik)^{1/2}] \tag{22}$$

Equation 22 indicates that Q is to be had by taking the Fourier transform of a function of the same form as $G(k)$. Equation 17 indicates that we can write down that Fourier transform by inspection. Fourier inversion of eq 17 yields (writing α in place of A)

$$(2\pi)^{-1}\int_{-\infty}^{+\infty} dk\, e^{ikx}\exp[-2\alpha(ik)^{1/2}] = \alpha\pi^{-1/2}x^{-3/2} \times \exp(-\alpha^2/x),\ \text{if } x > 0 = 0,\ \text{if } x < 0 \tag{23}$$

Setting $x = n\bar{N}$ and $\alpha = An$ in eq 23 yields this expression for the partition function:

$$Q = n\left(\frac{2\pi}{3s^2}\right)^{(n-1)/2}(n\bar{N})^{-3/2}\exp\left(\frac{-3ns^2}{2\bar{N}}\right) \tag{24}$$

The distribution function obeyed by any one of the N_j's is

$$P(N) = Q^{-1}\int_0^\infty dN_1 \int_0^\infty dN_2 ... \int_0^\infty dN_n\, e^{-F}\delta \times (n\bar{N} - \textstyle\sum_j N_j)\delta(N_1 - N) \tag{25}$$

$$P(N) = (4\pi^2Q)^{-1}\int_{-\infty}^{+\infty} dk_1 \int_{-\infty}^{+\infty} dk_2 \exp(ik_1n\bar{N} - ik_2N) \times G(k_1 - k_2)[G(k_1)]^{n-1} \tag{26}$$

Integrating first over k_2 yields

$$P(N) = (2\pi Q)^{-1}N^{-3/2}e^{-A^2/N}\int_{-\infty}^{+\infty} dk\, e^{ik(n\bar{N}-N)} \times [G(k)]^{n-1},\ \text{if } N > 0 = 0,\ \text{if } N < 0 \tag{27}$$

Note that eq 27 is the statistical weight of a single leg of length N times the statistical weight of $n - 1$ legs of total length $n\bar{N} - N$. Equation 23 permits us to evaluate eq 27:

$$P(N) = \left(\frac{3s^2}{2\pi}\right)^{1/2}\left(\frac{n-1}{n}\right)\left[\frac{n\bar{N}}{N(n\bar{N}-N)}\right]^{3/2} \times \exp\left[\frac{-3s^2n(N-\bar{N})^2}{2N\bar{N}(n\bar{N}-N)}\right],\ \text{if } 0 \le N \le n\bar{N} = 0,\ \text{if } N < 0 \text{ or } N > n\bar{N} \tag{28}$$

In the limit $s \to \infty$, $P(N)$ tends to a Dirac δ function centered

at $\bar{N}$, since $P(N)$, as defined in eq 25, has unit integral over the interval $0 \le N \le n\bar{N}$, yet the exp term in (28) ensures that $P(N) \to 0$ at every $N \neq \bar{N}$ as $s \to \infty$.

Likewise, in the limit $s \to 0$, $P(N)$ tends to a pair of Dirac δ functions, one of strength $(n-1)/n$ centered at 0^+, the other of strength $1/n$ centered at $(n\bar{N})^-$. To see this, consider the integrals

$$I_1 = \int_0^{q\bar{N}} dN\, P(N) \qquad I_2 = \int_{(n-q)\bar{N}}^{n\bar{N}} dN\, P(N) \quad (29)$$

where we assume that q is arbitrarily small, yet much larger than s^2. To evaluate these integrals, make the transformations $x = N/\bar{N}$, $y = x(n-x)$, and $t = y^{-1/2}$. If we assume q to be sufficiently small, these integrals become

$$I_1 = (n-1)n^{-1}\,\mathrm{erfc}\left[\left(\frac{3s^2}{2\bar{N}q}\right)^{1/2}\right]$$
$$I_2 = n^{-1}\,\mathrm{erfc}\left[\left(\frac{3s^2(n-1)^2}{2\bar{N}q}\right)\right] \quad (30)$$

for erfc the complimentary error function. In the limit $s \to 0$, we have

$$I_1 \to \frac{n-1}{n} \qquad I_2 \to \frac{1}{n} \quad (31)$$

In other words, all the probability density "piles up" at one of the two limits 0 or $n\bar{N}$, which obviously means that $P(N)$ tends to a pair of δ functions.

As s changes from very large to very small, the system exhibits the symmetry-breaking transition discussed by Rieger. However, the transition is only abrupt if we consider the most probable distribution of N_j's. All statistical averages transform smoothly.

4. Effect of an External Field

It is interesting to ask if the model can be altered in any way to make the symmetry-breaking transition abrupt. Consider the case of a chain in a uniform external potential, which could be realized in practice by placing the chain in a uniform flow or, for a charged chain, by placing it in a uniform electric field. The statistical weight $(G(\mathbf{r},N)$ of an ideal chain stepping from the origin to the point $\mathbf{r} = (x,y,z)$ in N steps is given approximately as a solution of the Schrodinger equation in imaginary time:[7]

$$\frac{\partial G}{\partial N} = \frac{a^2}{6}\nabla^2 G - U(\mathbf{r})G \quad (32)$$

subject to the boundary conditions $G(\mathbf{r},N=0) = \delta(\mathbf{r})$. Here $U(\mathbf{r})$ is the external potential and a is the segment size. The solution to (32) for the case $U = -cx$ has been given elsewhere.[8] It is

$$G(\mathbf{r},N) = \left(\frac{3}{2\pi Na^2}\right)^{3/2} \exp\left(\frac{a^2c^2N^3}{18}\right) \times \exp\left[\frac{-3}{2Na^2}[(x-x')^2 + y^2 + z^2]\right] \quad (33)$$

where

$$x' = a^2cN^2/6 \quad (34)$$

We now set $(x,y,z) = (0,0,u)$, which is equivalent to assuming that the grommets are evenly spaced by a distance u at right angles to the direction of the external force. The free energy as a function of the N_j's is $-\sum_j \ln$

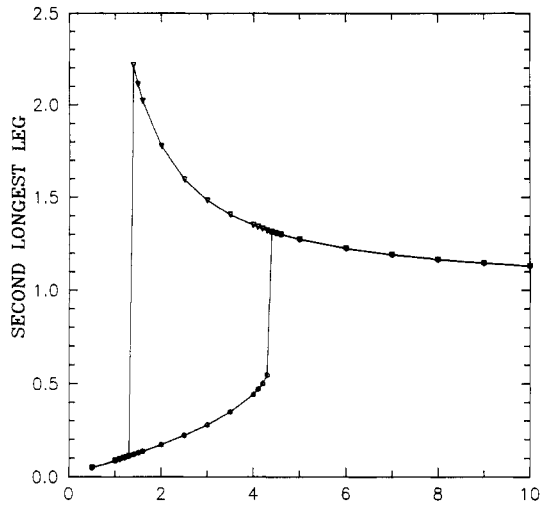

Figure 5. Average length of the second longest leg in the presence of an external field.

$G(\mathbf{r},N_j)$ or, with neglect of numerical constants

$$F(N_1,N_2,\ldots N_n) = \frac{3}{2}\sum_{j=1}^{n} f(N_j) \qquad f(N) = \ln N + \frac{s^2}{N} - q^2N^3 \quad (35)$$

where $s = u/a$ is a reduced distance between grommets, and $q = (108)^{-1/2}ac$ is a reduced field strength. Equation 35 is the generalization of eq 2 to the case of an external field.

The analysis of section 2 is not qualitatively affected by the presence of the q^2N^3 term. The geometrical construction leading to Figures 2 and 3 can still be formed, indicating that the most probable distribution of the N_j's still follows the same sort of symmetry-breaking transition: favoring equality among all the N_j's at large s, and one large N_j at small s.

However, with the generalization to nonzero q, we are unable to obtain any exact results for the statistical properties, as we had before in section 3. Therefore, a Monte Carlo calculation was performed to explore the statistical properties of the chain in the presence of the external field. This was done with Metropolis sampling in the space of the N_j's, using eq 35 as the Hamiltonian. The calculation was performed with $n = 100$, $\bar{N} = 100$, $q = 0.1$, and at various values of s between 0 and 10. The fundamental Monte Carlo step was an exchange of x segments between any two randomly chosen N_j's, for x a random variable satisfying $0 < x < 1$. In order to determine the sensitivity to the initial state of the system, independent calculations starting from two different initial states were performed at each value of s. These initial states were either the β minimum ($N_j = 1$ for all j) or in the vicinity of one of the m minima ($N_1 = 99.01$, $N_j = 0.01$ for all $j > 1$). The average lengths of the longest leg, the second longest leg, and the shortest leg were sampled, with results appearing in Figures 4–6. The results clearly indicate an abrupt structural transition as the chain becomes more stretched. At small s, the second longest leg is much shorter than the longest leg, agreeing with the prediction that one leg will be much longer than the others. At large s, all the legs tend toward the same constant length. Within the interval $1.4 < s < 4.4$, the results are dependent on starting conditions, clearly indicative of a nucleation barrier opposing the transition from one state to the other. This nucleation barrier appears to be large: Presumably, for very long simulations the two transitions near $s = 1.4$ and $s = 4.4$ would approach one another; nevertheless, a 10-fold increase in the simulation time was insufficient to

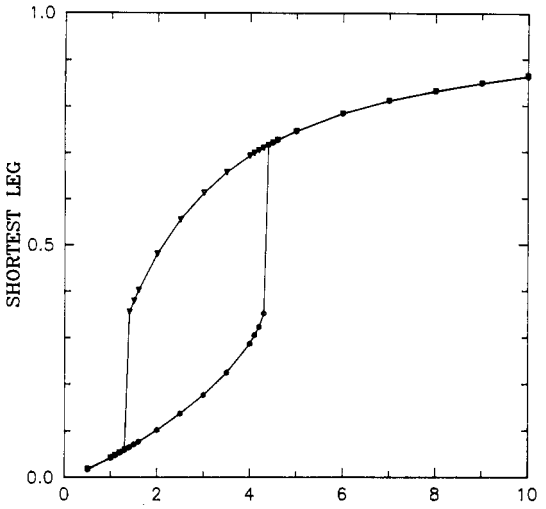

Figure 6. Average length of the shortest leg in the presence of an external field.

change the position of the transitions to a resolution in s of 0.1. This hysteresis phenomenon is indicative of a first-order symmetry-breaking transition between the m- and β-branch minima as s changes.

5. Freeing the Two Ends

A crucial aspect of the problem becomes apparent when we consider the case in which the ends are free. We still imagine a chain free to slip through a set of grommets, but now the chain is held in place, not by pinning down the two ends, but by tying at each end knots that are too large to pass through the grommets. In other words, we now consider n strands, the jth strand having length N_j, and the total assembly having statistical weight

$$\prod_{j=2}^{n-1}\left(\frac{3}{2\pi N_j}\right)^{3/2}\exp\left(\frac{-3s^2}{2N_j}\right) \tag{36}$$

Contributions from N_1 and N_n are not present because these two strands have free ends, the integrated weight over all space for these two strands is unity. We therefore write the following for the total free energy:

$$F(N_1,N_2,...,N_n) = \frac{3}{2}\sum_{j=2}^{n-1} f(N_j) + \frac{3}{2}Q(N_1) + \frac{3}{2}Q(N_n) \tag{37}$$

where $(3/2)Q(N)$ is a potential introduced to enforce the constraints $N_1 > 0$, $N_n > 0$. $Q(N)$ is zero except for small values of N, at which time it rises sharply. We assume absence of an external potential, which means that the f function we consider is eq 2 rather than eq 35. The constraint, eq 3, still applies. The condition for an extremal point is now

$$\lambda = g(N_j) \text{ for } j = 2, 3, ..., n-1 \tag{38}$$

$$\lambda = Q'(N_1) = Q'(N_n) \tag{39}$$

where Q' is the derivative of Q and, therefore, some function that is zero everywhere except near zero, at which time it goes sharply negative. Q' is never positive. But then λ also is never positive, otherwise eq 39 could never be satisfied. There are two possibilities:

(1) $\lambda = 0$. Then $N_2 = N_3 = ... N_{n-1} = N_0$, and N_1 and N_n are both arbitrary. Then $\bar{N}$ is $(n-2)N_0/n \cong N_0$ or greater.

(2) $\lambda < 0$. Then $N_1 = N_n = 0$ and $N_2 = N_3 = ... = N_{n-1}$ are less than N_0. Then $\bar{N}$ is $(n-2)N_0/n \cong N_0$ or less.

The Lagrange multiplier λ can be thought of as proportional to the tension in the chain. With our particular sign convention, $\lambda < 0$ corresponds to the chain loaded in tension; each strand pulls on its two neighbors, and the tension is equilibrated when all strands have the same length. This is obtained in both cases of free and pinned ends when $\bar{N}$ is less than N_0. When $\lambda = 0$, there is no tension. This occurs in both cases when $\bar{N} = N_0$. When $\lambda > 0$, there is an excess of chain segments, and each strand tries to deliver segments to its two neighbors. A positive λ can only be maintained by pinning the two ends of the chain. When the ends are free, the excess in chain segments can be relieved completely by moving it into the free ends. When the ends are not free, the excess can be best relieved by selecting one of the strands to receive all of the excess, rather than by distributing the excess evenly among all strands. Therefore, the symmetry-breaking transition is a direct consequence of pinning down the two ends of the chain.

6. Conclusions

We have extended Rieger's study[1-3] of a constrained random walk problem in several ways. Rieger proved[3] the existence of a symmetry-breaking transition in the most probable distribution. In this paper, we describe geometrical constructions for determining the most probable distribution and show that the most probable distribution changes abruptly as the chain becomes less stretched. Then we demonstrate that the transition is not a true phase transition, but that it is smoothed out by fluctuations away from the most probable distribution. We show by Monte Carlo simulation that the transition can be made first order by applying an external potential to the chain. Finally we shown that the existence of the symmetry-breaking transition is intimately connected to the fact that the ends of the chain are pinned. Rieger[1-3] has discussed the consequences of this broken symmetry for theoretical polymer science; there is little we can add to his comments, except perhaps to temper them somewhat to emphasize the fact the the transition is only observed when the chain ends are pinned down.

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References and Notes

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