

Random Walks and Polymers

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The idea of a random walk, where an object moves in steps and changes its direction randomly at each step, is very simple. But it is one of the most commonly encountered ideas in the study of a variety of natural phenomena, like diffusion of gases and conduction of heat. Many physical processes can be modeled as random walks of various kinds. In the following we shall discuss some quite simple problems about random walks and a very simple (but quite effective!) model of a polymer chain which can be modeled as a one-dimensional random walk.

1. Consider a random walker who sets out on a one-dimensional random walk from the origin. What is the probability that he is at the origin after N steps (regardless of whether he had come back earlier)? The right and left step are taken with equal probabilities.

To get back to origin the random walker has to take $N/2$ steps to the right. As we are considering one dimensional case, the other $N/2$ steps will obviously be to the left. A random walk of N steps can be done in 2^N different ways. Out of these, walks that have $N/2$ steps to right can be done in $\binom{N}{N/2}$ (binomial coefficient) different ways. Thus the probability that after N steps the random walker is at the origin is $\binom{N}{N/2}/2^N$. Notice that this probability monotonically decreases to zero as N increases. That is, the more the number of steps random walker has walked the less is the chance that he ever returns to the point of start. Some of us may have the impression that in a random walk the walker keeps shuffling around the point of start, because we know that *mean distance* covered in a random walk is zero. But this mean distance does not refer to the distance covered in a single random walk, but the mean of the distances moved in a large number of different walks of equal number of steps. What happens is that in a large number different random walks, the walker sometimes strays to the right (positive distance) and sometimes to the left (negative distance), and mean of these distances tends to zero. Loosely speaking, if you want to know the 'typical' distance moved by the random walker in a single random walk that is given by the *standard deviation* of net displacement to one side, which is \sqrt{N} steps away from the origin. See figure 1 for plots of some random walks generated on computer (A very simple task which can be done with a short program).

2. Find the number of ways in which a random walker can go a distance L to the right.

Suppose random walker takes n_R steps to right and n_L to left ($n_R > n_L$, $n_R + n_L = N$), so that the end-to-end length L is

$$L = (n_R - n_L)a = (2n_R - N)a \quad \dots (1)$$

where a is the length of a step. Note that L is different from the fully stretched length of the chain, which is Na . Just as we argued above in problem 1, n_R steps can be taken to right out of N total steps in $\Omega(n_R)$ ways, given by

$$\Omega(n_R) = \binom{N}{n_R} = \frac{N!}{(N-n_R)!n_R!} \quad \dots (2)$$

We can express Ω as a function of L by eliminating n_R using equation 1. How does this $\Omega(L)$ vary with L ? See the following problem.

3. Consider the following model of a one-dimensional polymer (See figure 2). One end of a polymer chain is fixed at the origin, and N monomers are linked to form a chain (say, along x-axis). Each link (i.e., monomer) in the chain can have one of the two orientations -0° or 180° , as shown in the figure. Each link takes an orientation randomly out of these two possibilities. The links have no energy of interaction, and one can lie on top of another. Find the entropy of this chain as a function of its end-to-end length.

This is a model of polymer as a random walk. The three-dimensional analogue of this is commonly used in polymer physics as an idealized model for real polymer chain in a good solvent.

We already have part the answer in equation 2 above. The polymer chain here is simply a random walk, the two steps to right and left replaced by two orientations of each link. Thus $\Omega(L)$ is the total number of different possible arrangements of N links (known as *conformations*) of the polymer chain for a given end-to-end length L . In other words $\Omega(L)$ is the total number of *microstates* of a polymer chain for a *macrostate* characterized by the end-to-end length L . Therefore the entropy is

$$S(L) = k_B \ln \Omega(L) = k_B \ln \left[\frac{N!}{(N-n_R)!n_R!} \right] \quad \dots (3)$$

where k_B is the Boltzmann constant. Using Sterling's approximation for the logarithm term in equation 3 and simplifying we get

$$S(L) = k_B [N \ln N - (N - n_R) \ln(N - n_R) - n_R \ln n_R] \quad \dots (4)$$

where $n_R = (L + Na)/2a$ (equation 1).

A plot of $S(L)$ against L is shown in figure 3. We can see that the entropy of the chain is highest $S = S_{\max} = N \ln 2$ (from equations 1 and 4) when the end-to-end length is zero, that is, both the ends of the chain are the same point. That is because in this case it is possible to arrange the N links in the largest number of configurations. As we start stretching the chain, the number of possible configuration goes on decreasing. Finally, when $L = L_{\max} = Na$, the chain is stretched into a straight line and there is only one possible configuration of N links for this. In this case there is no uncertainty about the microscopic state of the polymer and entropy is zero.

4. Using the expression for the entropy in equation 4 above, obtain a relation between the end-to-end length L and the tension in polymer chain. Using this relation what can we say about elasticity and thermal expansion of this model polymer?

Suppose we apply a force f on the free end of the polymer chain so as to increase its end-to-in end length by dL . The work done on the chain is $dW = fdL$ (notice that this is positive, unlike the term $-pdV$ in the case of expansion of a gas). Applying first law of thermodynamics we have $dU = TdS + fdL$, where dU is the change internal energy and T absolute temperature. But there is no change in internal energy when the chain is stretched, because the monomers have no interaction energy. Thus $dU = 0$ and so

$$f = -T \left(\frac{\partial S}{\partial L} \right)_{U,N}$$

Using equation 4, after some simplification

$$f = -T \left(\frac{\partial S}{\partial n_R} \right) \left(\frac{\partial n_R}{\partial L} \right) = -\frac{k_B T}{2a} \ln \left(\frac{N-n_R}{n_R} \right) = -\frac{k_B T}{2a} \ln \left(\frac{Na-L}{Na+L} \right) \quad \dots (5)$$

This is a remarkable result. We have assumed that monomer links have no mutual interaction energy. But nevertheless this result shows that the chain can sustain tension – it resists extension. In the familiar solid objects like a metal wire the tension arises mainly due to mutual attractive forces between the atoms that make up the wire. But in the case of a polymer model considered above the tension arises entirely due to the entropy of the chain. We have seen that increasing the end-to-end length of the polymer decreases its entropy because it has fewer configurations adopt. But at finite temperatures (especially at higher temperatures) it has energy to go into higher energy configurations, which involve more doubled-up links. This obviously tends reduce its length and, if both ends of the chain are not free, a tension develops in the chain. This feature is not an artifact of a grossly simplified artificial model. More realistic 3-dimensional models also have this characteristic, and indeed the real polymers! As we are going see below the extraordinary thermal expansion and elastic properties of polymers are consequence of their entropy-dominated thermodynamics.

For the high temperature limit equation 5 can be simplified. Solving this for L we get

$$L = Na \left[\frac{1 - \exp(-2af/k_B T)}{1 + \exp(-2af/k_B T)} \right] = Na \left[\frac{\exp(af/k_B T) - \exp(-af/k_B T)}{\exp(af/k_B T) + \exp(-af/k_B T)} \right] = Na \tanh \left(\frac{af}{k_B T} \right)$$

For high temperatures $af/k_B T \ll 1$ and so we can approximate ($\tanh x \approx x$ for $x \ll 1$)

$$L = \frac{Na^2 f}{k_B T} \quad \dots (6)$$

Thus the length of the chain decreases with increasing temperature! Actually we can readily get thermal expansion coefficient from equation 6:

$$\alpha = \frac{1}{L} \frac{\partial L}{\partial T} = -\frac{1}{T} \quad \dots (7)$$

which is indeed negative. Contraction of a polymer with increasing temperature can be observed in a simple at-home experiment. Take a rubber band (which can be considered a bundle of large number of polymers chains) and suspend it vertically with a small weight attached to its lower end which keeps it straight. Warm it with a hot air blower and you can easily see it shorten.

Rewriting equation 6 as

$$f = \frac{k_B T}{Na^2} L \quad \dots (8)$$

we can see that the Hooke's law (tension is proportional to elongation) applies to this polymer. The term $k_B T/Na^2$ is the 'spring constant' of this chain which brings out another extraordinary feature of the polymer – it becomes *stiffer* with increasing temperature, unlike most other familiar materials, like metals, which become *softer* with increasing temperature.

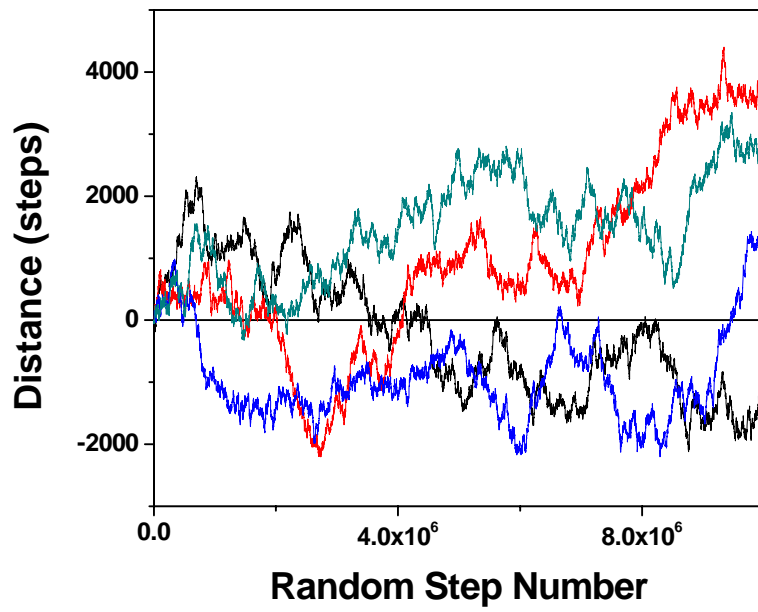


Figure 1. Four random walks generated on a computer, each of 10^7 steps.

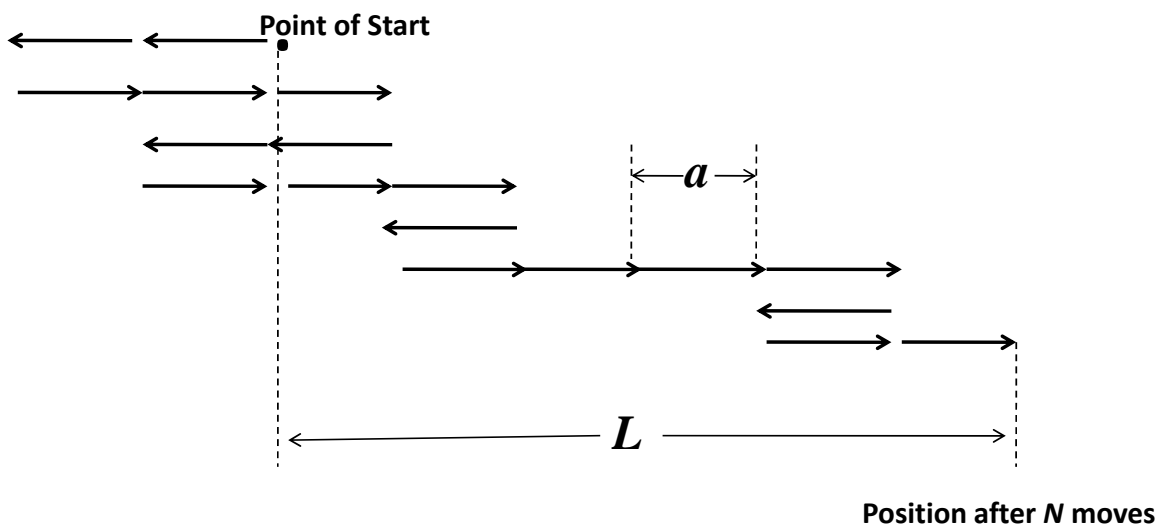


Figure 2. Polymer chain as one-dimensional random walk. Each arrow shows a monomer link pointing left or right. There is no vertical motion; arrows are shifted vertically only for visibility. The length of each link is a and end-to-end length L .

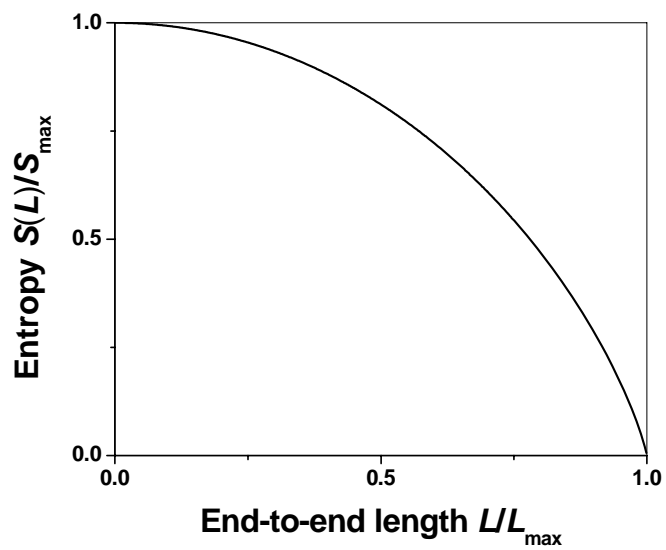


Figure 3. Entropy of a one dimensional random-walking polymer chain as a function of end-to-end length. $L_{\max} = Na$ and $S_{\max} = N \ln 2$ (see equations 1 and 4)