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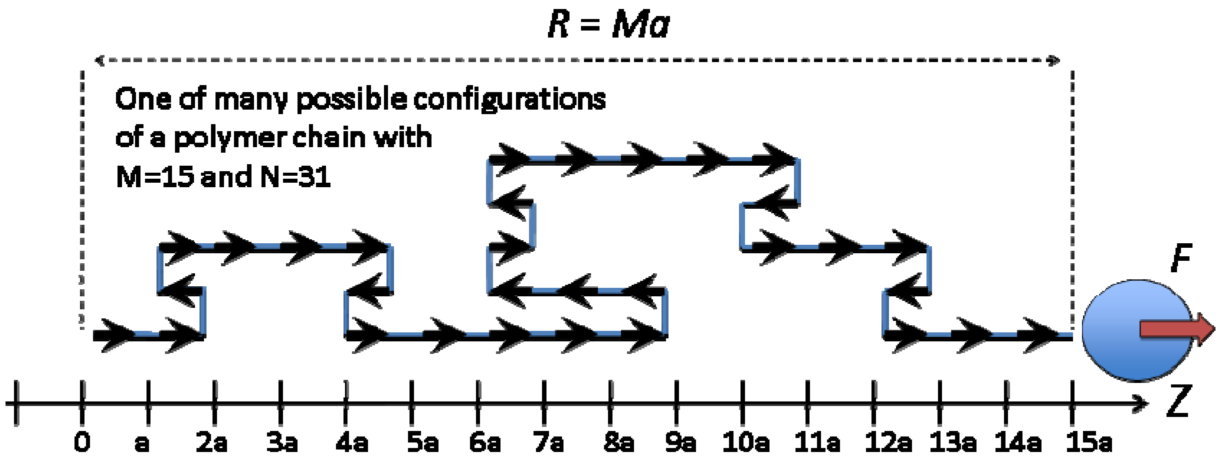
When you heat a rubber band, it contracts. If you only know about point particles and ideal gases, this behavior is perplexing. But, a simple classical statistical mechanics model of a chain provides some insight.



Model the rubber band as a single chain of N links, with each link having fixed length a. Treat the chain as a one-dimensional random walk along the Z axis. Let one end be pinned at the origin and let each link proceed to the left or the right with equal probability. Suppose the other end of the chain is located a distance $R= Ma$ from the origin, where M could range freely from $-N$ to $+N$ (both M and N are positive integer numbers). There are no interactions between links and the links can overlap at no cost, as shown in the figure.

In problems (a-c) no external force acts on the chain, but one end remains tethered at Z=0.

(a) Derive an exact formula for the number of configurations of the chain for given N and M. Call the result $\Omega(N,M)$.

(b) Using Stirling's approximation in the form $\ln(N!) \cong N\ln(N) - N$, show that for $N >> M$, $\Omega(N,M) \cong C(N)\exp(-M^2/2N)$, where $C(N)$ is a constant that you do not need to calculate.

(c) Using the above approximation for $\Omega(N,M)$, calculate the entropy of a polymer with N links and extent R, in the regime $Na >> R$. Write down the expression for the free energy of the chain (in the absence of external force) and calculate its equilibrium length.

In the remainder of this problem use the approximation in (b) for $\Omega(N,M)$. Now, suppose that a force F is applied to the free end of the chain in the $+z$ direction, using optical tweezers.

(d) Sketch the free energy of the chain subject to the force F vs. R at fixed T. Find the minimum of the free energy as a function of R and calculate the equilibrium length of the chain.

(e) Show that the chain extension R satisfies Hooke's law. Identify the temperature dependence of Hooke's coefficient. Explain, briefly, in what sense this result predicts that rubber bands contract when heated.