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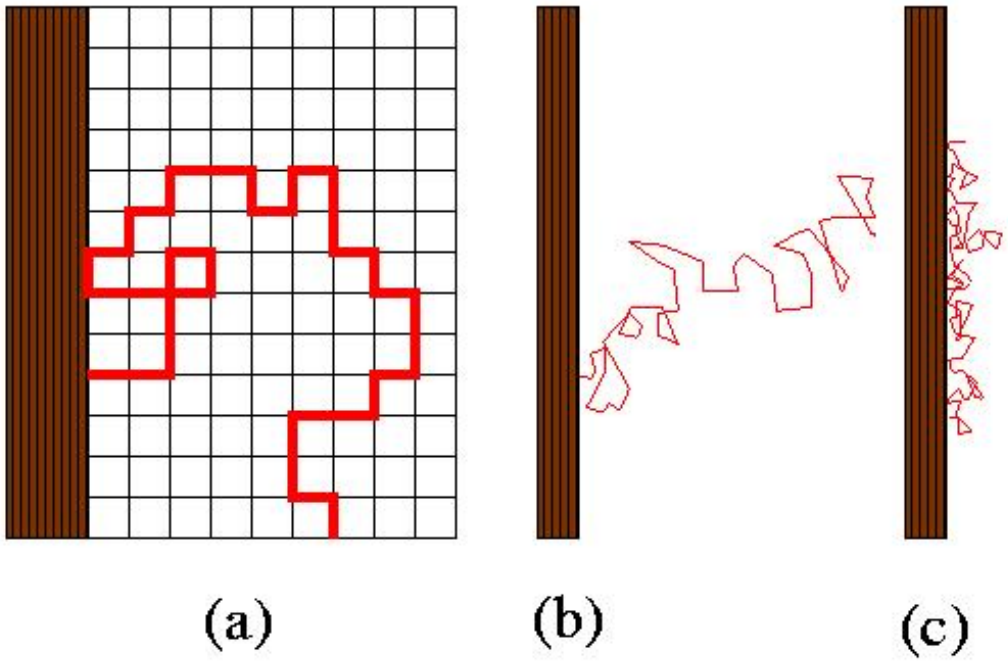
Question 09/02

POLYMER AT A WALL



One of the simplest idealizations of a flexible polymer chain consists of replacing it by a random walk on a cubic lattice in three-dimensional space or on a square lattice in two-dimensional space. (This walk is allowed to self-intersect, and it has no "bending energy", i.e. each step is independent of the previous one.) An example of such "polymer" is depicted by a red line in Fig. (a). Assume that one end of the polymer is tied to a surface (denoted by brown color in the Figure). The surface will be considered adsorbing, i.e. every time the polymer (or the random walk) touches the surface its energy decreases by V. E.g., the energy of the configuration in Fig. (a) is -3V, because the walk touches the surface three times.

A very long polymer will be either localized near the surface as depicted in Fig. (c), or will be delocalized as in Fig. (b), depending on the temperature T. (Figs. (b) and (c) have different scale from Fig. (a) and therefore the lattice is not shown.)

Describe the temperature-dependence of the "localization" of the polymer.

SOLUTION 09/02

Some comments before I start:
I will define the "localization" of the polymer as the maximal distance from the surface during the random walk and for shortness I'll call it length of the polymer. Other definitions are possible but I think this is the simplest and good enough for the description of the "localization" of the polymer. I'll assume that the polymer consists of $N>>1$ units and that random walk is defined on 2D square lattice.

Qualitative arguments:
1) At T=0 the system is in its ground state, i.e. all units are on the surface and its length is 0.

2) At low temperatures due to small random thermal fluctuations just a few units are out of the surface and the length is smaller than 1 or mostly 2 units.
3) At temperatures of the order kT=V random thermal fluctuations start significantly to compete with attracting force from the wall (they actually start to pull polymer from the wall) and length of the polymer becomes significant.
4) At high temperatures random thermal fluctuations do they best and length of the polymer tends to some constant value (One might expect that at infinite T the length will be N units, but it is not true since thermal fluctuations are random in direction and after they partly pull polymer from the surface they can't make it any more longer)
5) At infinite T the length of the polymer tends to some constant value mentioned above.

Quantitative arguments:

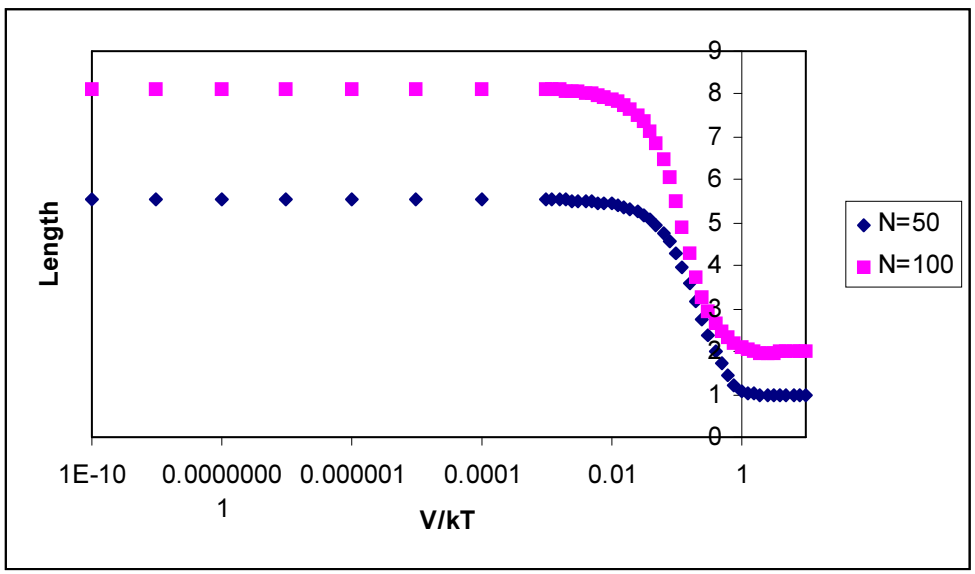
This is a system which has R states (i.e. R possible random walks) where $3^N < R < 4^N$ since in each step of random walk one decides between 3 (if one is on the surface) or 4 (otherwise) possibilities. Each state has its corresponding energy $-V \le E_j \le -(N+1)V$ and length $0 \le L_i \le N$. Mean length of the polymer is given by the well-known formula from statistical physics:

$$L = \frac{\sum_{i,j} g_{ij} L_i \exp(-\frac{E_j}{kT})}{\sum_{i,j} g_{ij} \exp(-\frac{E_j}{kT})}, \qquad (1)$$

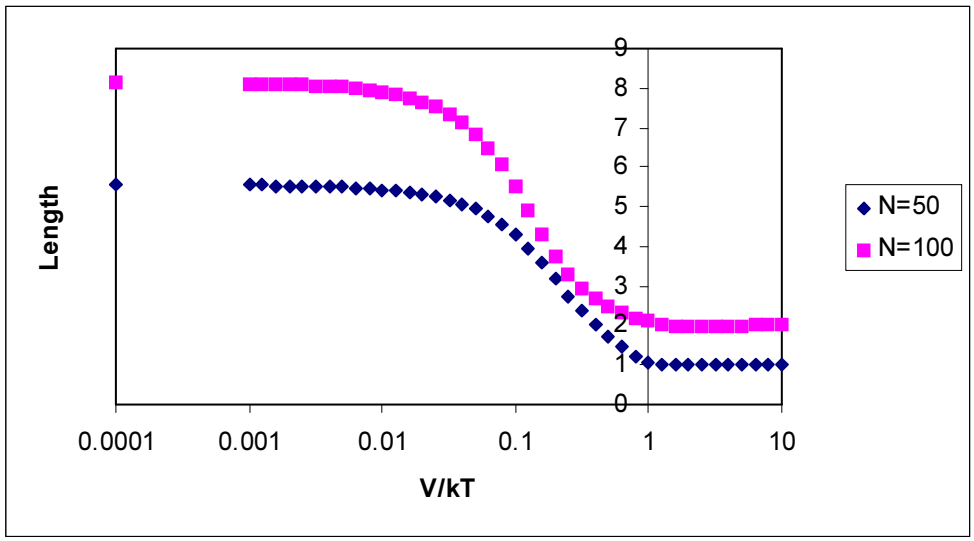
where g_{ij} is number of states with energy E_j and length L_i.

To perform an exact calculation of g_{ij} one should perform all possible random walks and calculate length and energy for each of them. This obviously can't be done numerically and I didn't find any theoretical method to do it, so I performed a Monte Carlo simulation. I used program package Mathematica to perform 1000000 random walks. Number of random walks in simulation with energy E_j and length L_i is obviously approximately proportional to g_{ij}. Once one gets numbers g_{ij} it is easy to calculate temperature dependence of L by putting them into the formula (1).

I performed 2 simulations, one for N=50 and one for N=100. The results are given by the following graph



This graph confirms all results obtained by qualitative arguments except for very low temperature behavior. From this graph it seems that L tends to some constant value different than zero as $T \to 0$. The reason for this is that 1000000 simulations are not enough to get those g_{ij} corresponding to low energies different from zero. However from formula (1) one gets that really $L \to 0$ when $T \to 0$,

since the ground state is the one with all units at the surface, (so $L = 0$) and its degeneracy is 2^N - obviously different from zero (one might say that this isn't small, but it is small comparing to other g_{ij}).

The following graph is the same as the previous. I just zoomed the interesting region around kT=V and that way I confirm that length starts to increase when kT reaches V.