A Study on The Motion of Long Chain Molecules

Hsing-Mei HUANG (黃幸美)

Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, R.O.C.

and

Yu Ming SHIH (石育民)

Department of Physics, Taiwan Normal University, Taipei, Taiwan 11 7, R.O.C.

(Received 5 October 1984)

Employing the " coincidence counting" method proposed by Ma, we have studied the entropys of systems of long chain molecules with simple two dimensional lattice model. The entropy thus calculated is different from the direct counting of the available phase space volume as one might expect due to the effect of entanglement. However, we found that the difference in entropy essentially comes from the effect of percolation instead of the effect of entanglement.

1. INTRODUCTION

$\boxed{U}$ sing the concept of " entanglement" de Gennes[1] formulated a " reptation " theory to explain qualitatively some strange behavior of polymer metls in recent years. A strange subtance called " silly putty" , when given a bit of time, flows like a viscous liquid. Forced to respond quickly, it bounces like rubber de Gennes traces this " viscoelastic" behavior to the knotting of the chains of " monomers" that made up the polymers. Shearing forces tend to undo certain knots, but this takes a finite time τ. In a time greater than τ the original knots fade out, and the polymer melt flows., Over shorter times the original knots are all present, and the polymer melt behaves like an elastic network.

Eventually, there is a metastable state over a certain time scale. In the present case, this metastable state is more difficulty to handle theoritically than most of other cases. Strictly speaking, all the real systems which we regard as in equilibrium are metastable. Any solid under shear or tension is metastable. The very container which usually helps us define an ,"isolated" system is metastable. Some metastable states last very long and some short. As long as the period of observation is short enough, metastable systems have very welldefined thermodynamic properties. It seems clear that- time is a crucial consideration. Therefore a formulation of statistical mechanics which excludes time from its conceptual foundation is expected to have series difficulties. However, in most cases, the consideration of time is simple. Dynamical variables which do not change much over the observation period are considered fixed. Or in the other words, the limitation of the achievable region in the phase space of the system is clearly defined. However, in present

case, it is very difficult to define the restriction of the region in the phase space. The thermodynamic properties of this metastable state is not easy to find out by the simple working rule of statistical mechanics.

In 1980, Ma[2] proposed a method to evaluate the entropy of a system from data of motion, i.e. from the trajectory. This view is quite different from the traditional formulation. This method could be a suitable tool to deal with the " entangled polymers" problem. The reason will be clear later.

The method essential is a counting of coincidence (or repetition) of states along the trajectory. Let us spend a little time on the coincidence method. The famous Boltzmann formula for the entropy

$$S = \ln \Gamma (E)$$

is the foundation of statistical mechanics. Here E is the total energy of the system. $\Gamma(E)$ is the number of states with the energy E. It is the volume of aa region Ω in the phase space. Ma's idea is to define Ω and measure $\Gamma(E)$ from the trajectory alone. The basic idea is simple. Suppose that the trajectory is a set of n points randomly distributed in a region of Γ positions. Even if n is much smaller than Γ, there is a nonzero chance for coincidence. Since the probability for a point to fall in any given position is $1/\Gamma$, the number of coincidences is easily estimated :

$$N_c = \frac{n(n-1)}{2} * 1/\Gamma .$$

If the number of coincidences N_c and number of total points n are known, the volume Γ can be obtained. Thus, the entropy is determined from the trajectory.

Since the entropy is calculated from the trajectory a metastable state of the system. will show up itself in the proper time scale. This is why we would consider the coincidence method might be a good tool to deal with the " entangled polymers" which does not show the restriction of the region in the phase space explicitly.

In this paper, we will try to set up a model to simulate the entangled polymers. In Section II we will describe the model. The calculation method will be discussed in Section III. The result and discussion will be given in section IV.
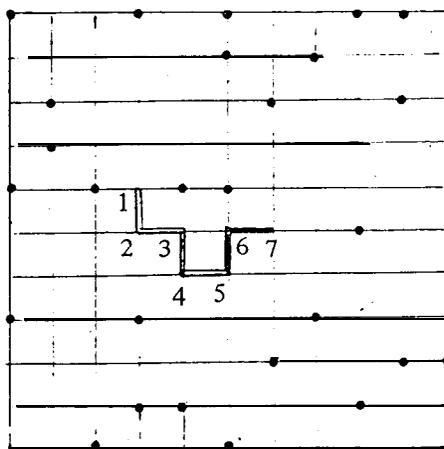

FIG. 1   Double solid line represents the polymer chain, • represents the fotbidden site.

II. THE MODEL

We consider a simple lattice model[3]. A polymer chain is represented as random walks on a lattice with definite length moving on a two dimensional square lattice (as Fig. I). a fraction of the lattice sites are chosen randomly to be forbidden sites. The polymer chain is not allowed to visit the forbidden sites or to cross itself[4].

For polymer chain with six units length, it occupies continuous sites. Denote the sites of the polyer chain as 1, 2, ..., 7 sequently. The polymer chain can take the following models of motion (as Fig. 2).
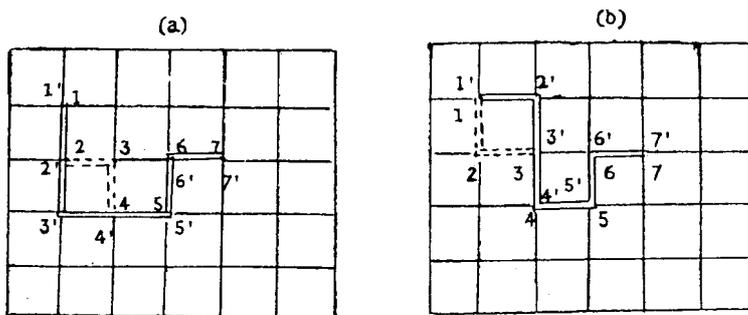
mode 1:
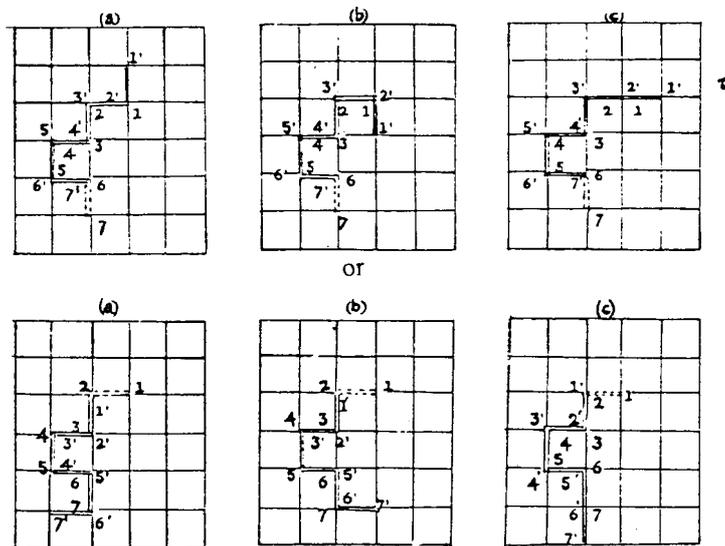
mode 2:
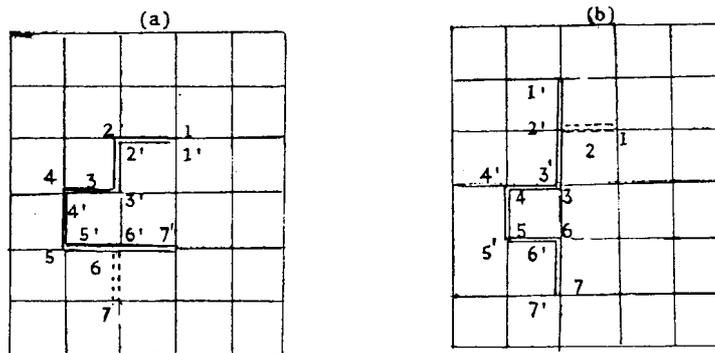
mode 3:

FIG. 2   The polymer chain with six units length can take the three modes of motion

1. Site 1 moves to one of its neighbor sites which is not occupied or forbidden. In this case, site 2 to site 7 follow to the original position of site 1 to site 6. Similar motion is allowed by replacing site 1 by site 7 and site 2 to site 7 by site 6 to site 1.

2. Site 1 moves to a site which is a neighbor of site 2 which is not occupied or forbidden. Site 2 to site 7 remain unchanged. Similar motion is allowed by replaceing site 1 by site 7. In this mode, site 1 to site 6, of course, remain unchanged.

3. If site 1, site 2 and site 3 do not form a straight line, they should occupy three corners of a unit square lattice. In this case, site 2 can move to the open site of this unit square lattice if the unit square is not occupied or forbidden. The other sites of the chain stay on its original position. Site 3 can have this kind of motion too. Eventually the mode is allowed for site 2 to site 6.

Obviously, the modes of motion stated above allow both "transverse", which is the lateral motion of the polymer, and "longitudinal", which is along the length of polymer, motions as well. In terms of the "reptation" picture, the polymer roughly moves in a tube defined by itself and the forbidden sites on both sides. The longitudinal motion is the motion sliding along the tube and the transverse motion is the motion perpendicular to the tube. Due to the effect of "entanglement" the relaxation time τ_ℓ for longitudinal motion is often much larger than the relaxation time τ_t for transverse motion, i.e., $\tau_\ell \gg \tau_t$.

If the observation period τ is

$$\tau_\ell \gg \tau \gg \tau_t$$

the calculated properties of this system would be that of the metastable state. We expect that the result would be very different from the long time $(\tau \gg \tau_\ell)$ average. In the case of no other metastable state exist, the long time average should equal to the ensemble average. More specifically, the entropy $\bar{S}$ calculated in the time scale $\tau_\ell \gg \tau \gg \tau_t$ by Ma's method would be much smaller than the entropy S_{en} by the standard ensemble average counting. S_{en} should be the same as that -of Ma' ·, calculation in the time scale $\tau \gg \tau_\ell$.

We did not consider the noncontact interaction between forbidden sites and polymers, and those between monomers of a polymer chain. However, the essential feature of entanglement should not depend much on the detail interactions. Ma's coincidence counting method enable us to calculate the entropy directly from the motion of polymer (in our model). The detail calculations will be presented in the next section. As we will see in later section the entropy is obviously different from direct counting the number of configurations.

111. THE CALCULATION

As a first step to attack this kind of problem. We consider a polymr chain with $N = 7$ unite length (i.e. $N + 1$ end to end sites) moving in a $L \times L$ square lattice ($L = 10, 12, 15, 20$). The whole numerical calculating procedure is as following:

1. Choose a definite dimension L of the square lattice. (We pick L= 10, 12, 15, 20).
2. Choose a definite percentage (10%, 20%, 30%, 40%, 50%, 60%, 70%) as the fraction f of the forbidden sites in the lattice.
3. Randomly distributed the forbidden sites in the lattice by a random number generator.
4. Place the polymer chain in a certain position.
5. Determine the mode of motion of each step by a random number generator. Let the polymer chain move step by step for about 20,000 steps.
6. Take the record of the position of the polymer chain every 50 steps. The total number of the recorded sample steps is 200.
7. After 20,000 steps, the moving is continuous step by step for 5,000 more steps.
8. Start to compare the present state of motion to the 200 recorded samples and count the number of coincidences.
9. Determine the probability of the coincidences. Therefore the volume Γ in the phase space is obtained.
10. For comparision, calculate the volume Γ in the phase space by direct counting the number of possible states of the polymer chain. The entropy calculated is denoted as S_{en}.

Repeat the procedure from step 3 to step 10 with same N and same percentage for about 10 times. Take the average of the volume Γ of different forbidden sites distribution (but with same percentage). We have the entropy $\bar{S}$ at a definite fraction f of forbidden sites. Both $\bar{S}$ and S_{en} are calculated.
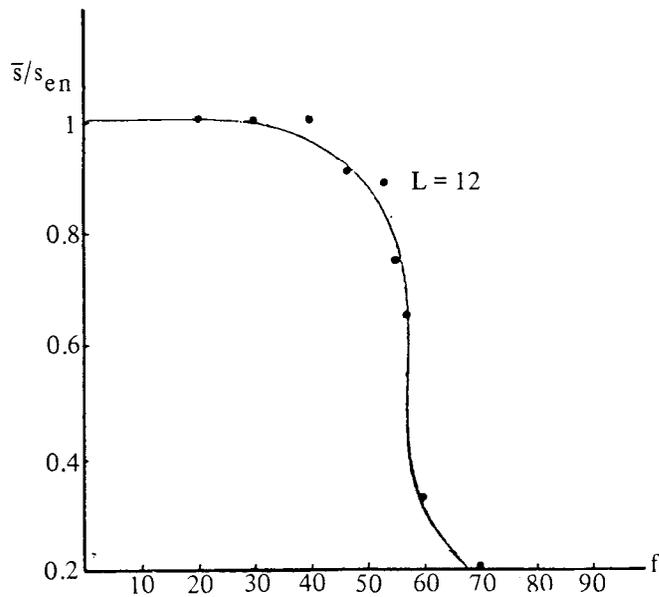

FIG. 3 $\bar{s}/S_{en}$ functiion of f. N = 7 and L = 12. $\bar{s}$ is the entropy averaged over initial (random) polymer configuration, and random forbidden site distributions. Sen is the Gibbs ensemble entropy.

IV. RESULT AND DISCUSSION

The numerical results did show the difference between $\overline{S}$ and S_{en} as expected. Fig. 3 shows $\overline{S}/S_{en}$ at varies fraction f for **L** = 12. There are no much difference for different L's. However, a more careful study shows that the difference in $\overline{S}/S_{en}$ here is not due to the entanglement. The time scale we employed in the calculation is long enough to reach equilibrium. We found no metastable state exists. The polymer chain may be not long enough to show the entangle effect.

Then why $\overline{S}$ and S_{en} are different? Take a closer look at Fig. 3, we can see that $\overline{S}$ becomes significantly smaller than S_{en} as f increases towards and beyond the percalation threshold f = 50%. Hence, we guess theat the difference in $\overline{S}$ and S_{en} comes from the percolation.   Near or beyond the percolation threshold, the forbidden sites block the square lattice into several isolated region.   The polymer chains is therefore localized The entropy is thus greatly reduced.

We can further plot a figure which shows the entropy $\overline{S}$ for different **L's.** Since the volume I' in phase space is larger for larger L, we would expect the entropy increase with L as Fig. 4 has shown. However, the entropy is practically the same when fraction f larger than 50%. The reason is not hard to see. When f is beyond the percolation threshold the space available for the motion of polymer chains is localized therefore is independent of size L.
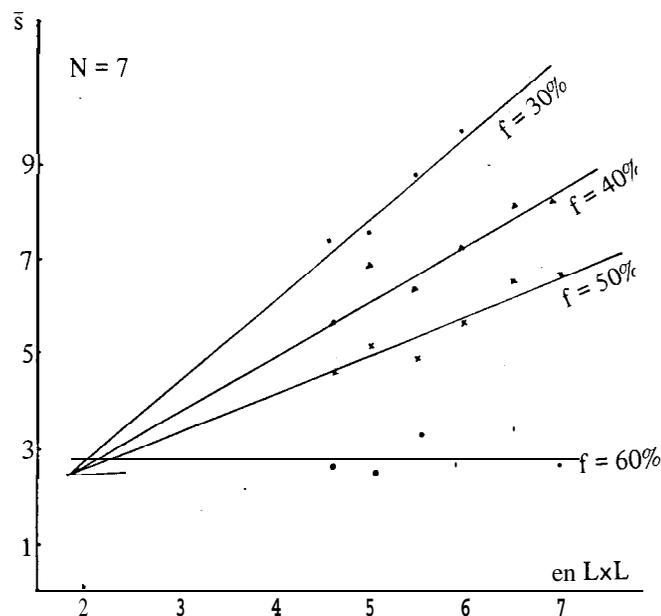

FIG. 4.   The entropy3 for different L' s function off.

Although the calculation in this paper does not show the entanglement, the method we proposed here did show the ability to deal with problems with different $\overline{S}$ and $S_{en}{}^{5}$. However, a little longer of polymer chain will cost a lot more computing work. In order to deal with the entanglement problem, a new feasible model is desperately needed. It is subjected to our next investigations.

REFERENCES

1. P.G. de Gennes, Scaling Concepts in polymer physics. Cornell University Press, Ithaca, N.Y., 1979.
2. Shang-Keng Ma, J. Stat. Phys. 26,221 (1981).
3. P. Flory, Statistics of China Molecules, Interscience Publishers, N.Y. 1969.
4. D.S. Mckenzie, Phys. Rept. 27C (2), 1976.
5. H.M. Huang et al., Sol. St. Comm. 51(3), 147, 1984.