Collapse transition of short polymers on simple cubic lattice

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Abstract. Denatured proteins and polymers exhibit two types of conformations in solution. Extended coil conformation and compact globule conformation. There is a phase transition associated with these conformation change as a function of temperature or solvent concentration etc. These phase transition is usually studied using Self Avoiding Walk(SAW). We have generated Self avoiding walk using chain growth algorithm. Here we have compared our generated density of states with Exact enumerated data of the same. Also we have presented the Pseudo order parameter method to identify collapse temperature. The results are compared with Partition function zero analysis.

1. Introduction

Proteins are macromolecules of amino acids vital for almost all biological functions. There are about 10^5 proteins in human body[1]. Geometrical shapes of proteins are very important in their functions[2]. Linear chains of amino acids are called primary structure of proteins. Primary structures fold to form secondary structures through weak interactions and they in turn fold to form tertiary and quaternary structures. Secondary, tertiary and quaternary structures are together called native conformations. Native conformations are thermodynamically stable. Understanding the structure of proteins is very important in understanding their functions. Studying proteins using computational models have found significant attention from research community as the memory capacity and speed of computers have increased considerably. Several force fields have been used to simulate all atom conformations of specific proteins. but they are not very much useful in understanding thermodynamics of protein functions. Several measuring equipments are working in a time range that is beyond the reach of such models[3]. Therefore we are forced to remove some degrees of freedom from our model (e.g. intermolecular structures of amino acids, each amino acids are considered as a monomer). This reduction of degrees of freedom to increase relevant length scales is termed as coarse graining. Coarse grained models are further justified by the observation that protein topology has a grater role in their function than their atomistic details and interactions[4]. Coarse graining helps in understanding general problem of protein folding, we cannot make precise or specific predictions. Coarse grained models have been proposed in both continuum off lattice models and discreet lattice models. We are only going to see lattice models.

Most proteins are inside biological cell and are always surrounded by cytoplasm. Polymer physicists have been studying isolated polymers in solution for quiet considerable time. A poly-

mer or protein in solution is modeled via Self Avoiding Walks (SAW) . Random walks which does not cross itself are called Self Avoiding Walks (SAW). Self avoiding condition takes care of excluded volume interaction, i.e. two monomers cannot share same space. In lattice model SAW, polymers are considered as a long chain of rigid beads connected by bonds. Each bead represents a monomer, and they are sitting on a lattice point of a regular lattice (square lattice, triangular lattice etc in 2D and any of Bravais lattices in 3D). The effect of solvent is incorporated by considering Lattice points which are not occupied by polymer beads are occupied by solvent molecules. The monomers which are sitting in nearest neighbor lattice points and are not connected by bonds are having an attractive interaction of Lenard Jones type. This attraction gives rise to energy for each polymer. SAWs with the associated energy definition is called Interacting Self Avoiding Walk. The number of monomers in a polymer is denoted as walk length or chain length in SAW terminology.

From the previous studies it has been observed that isolated polymers in solution has mainly two types of conformations[5]. A random coil conformation and a comparatively ordered globule conformation. The pH, concentration or temperature of solvent can influence the conformational transition[6]. The temperature at which this transition happens is called Theta transition. But since polymers are finite size systems, they are some times termed as collapse transition. Collapse transition is a second order transition. Recent simulations shows a first order kind transition at a lower temperature and is called freezing transition. We will generate an ensemble of ISAWs to study these transitions.

2. Exact Enumeration and Monte Carlo Methods

Generating ensemble of walks is tedious task. We can exactly calculate the number of SAWs of chain length N by exhaustively Counting them using a computer. This becomes increasingly difficult since number of conformations increases exponentially with the increase in walk length. Each conformation has unique Energy. Number of conformations with same energy is called density of that state. Monte Carlo methods are also powerful method to generate ensemble of ISAWs. In chain growth method, growth starts by putting a monomer on some arbitrary lattice site and then next monomer is added to any of randomly chosen nearest neighbor site. This addition of monomers are repeated till we reach the specified number. We will generate an ensemble of walks to study the statistical mechanics of polymer system[7].

In a recent study J. H. Lee et al. has published exact enumeration studies of ISAWs on Simple Cubic Lattice up to chain length 24[8]. They have computed exact partition function zeros and analysis of zeros showed two different loci corresponding to two transitions. Earlier in 2007 T.Vogel et al. has done a Monte Carlo study using nPERMss and discussed collapse transition and freezing transition in detail[9].

3. Simulation and Density of States

In our study we have used chain growth algorithm, the simple RR walk[10]. By using the concept of atmosphere, which is a random variable we can calculate the density of states of any ensemble of walks[11]. Local atmosphere is the number of accessible nearest neighbor sites available for the walk to grow. Random variable 'atmosphere' for a complete walk is the product of all local atmospheres of each step. Atmosphere of a trapped walk is zero.

$$C_N^m = \frac{1}{M} \sum_{l=1}^{M_m} A_l \tag{1}$$

C_N^m is the estimated density of energy $-m$. M is total number of walks including trapped ones in ensemble. M_m is number of successful walks with energy $-m$. A_l is the atmosphere of lth

walk. Comparison of computed density of states with the same from exact enumeration shows they are almost same up to walk length 24 (24 is the maximum available exact enumeration data on Simple Cubic). Fig. 1 shows micro canonical entropy obtained from Simulation and Exact enumeration. Statistical error is less than the marker size. Statistical error is more for minimum energy conformations.
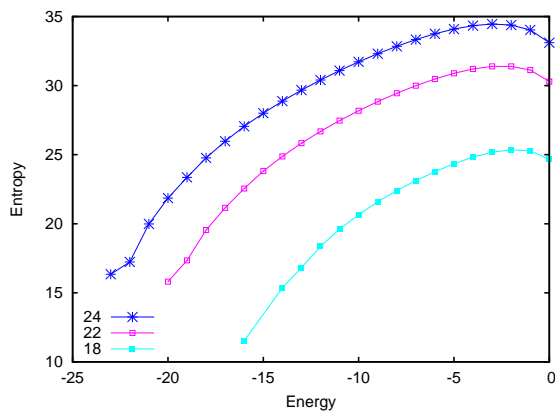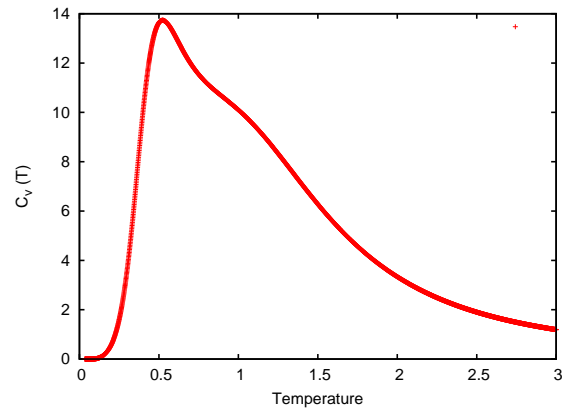

Figure 1. Entropy of walk lengths 18, 22 and 24

Figure 2. Specific heat capacity of walk length 24.

Looking at the specific heat curve in Fig: 2, we can clearly see a maximum followed by a shallow shoulder. Maximum corresponds to excitation transition, which is a pseudo effect only present in Simple cubic lattice[9]. The shallow shoulder denotes the collapse transition other wise known as coil globule transition. First order freezing transition is not visible in this plot, because of smaller walk length.

4. Partition Function Zeros and Pseudo order parameter

Partition function zeros are celebrated method for studying collapse transition. Characterization of phase transition using the zeros of partition function in the complex fugacity plane is introduced by Yang and Lee [12]. The method is generalized by Fisher [13] for treating the phase transitions in canonical ensemble. This is based on the analysis partition function zeroes on a complex temperature plane. The partition function can be computed from density of states,

$$C_N(\beta) = \sum_{m=0}^{m_N^{max}} C_N^m e^{-m\epsilon\beta} \tag{2}$$

Partition function is thus a polynomial of order m_N^{max} and will have same number of roots which are complex. It has been already observed that the zeros of partition function provide a good estimate of the collapse transition for ISAWs.Phase transition occurs if the roots intersect the positive real axis [14]. For a given finite sized ISAW, one can define first zeros as a pair of roots closest to the positive real axis. Fig 3 shows the first zeros from both exact and Monte Carlo estimate of density of states. First zeros of Monte carlo estimated DOS for even and odd walks are plotted using different color.

Further, density of states was used to find the canonical probability function. Phase transition was studied by plotting the canonical probability function for different inverse temperature.

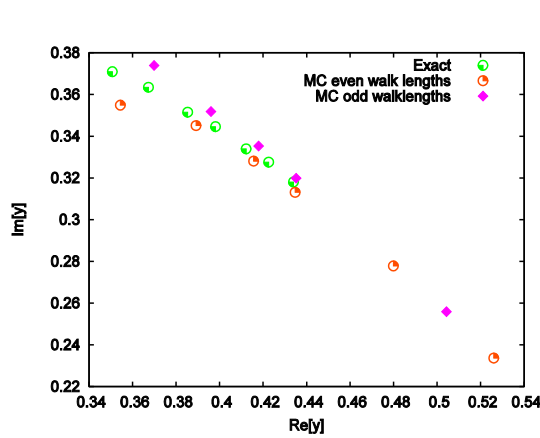$$P_N(\beta, m) = \frac{\sum_{m=0}^{m_N^{max}} C_N^m e^{-m\epsilon\beta}}{C_N(\beta)} \tag{3}$$

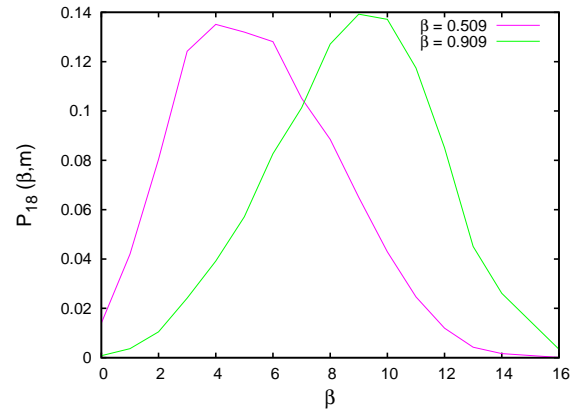**Figure 3.** First zeros of Partition function.

Figure 4. canonical partition function of walk lenth 18 above and below collapse temperature.

For any second order transition, we will be able to see an asymmetric shape with one long tail region for canonical partition function at any inverse temperature. This long tail shifts from side to the other as we vary temperature across collapse transition as in fig 4. This shifting can be used as a pseudo order parameter to find the theta transition[15].

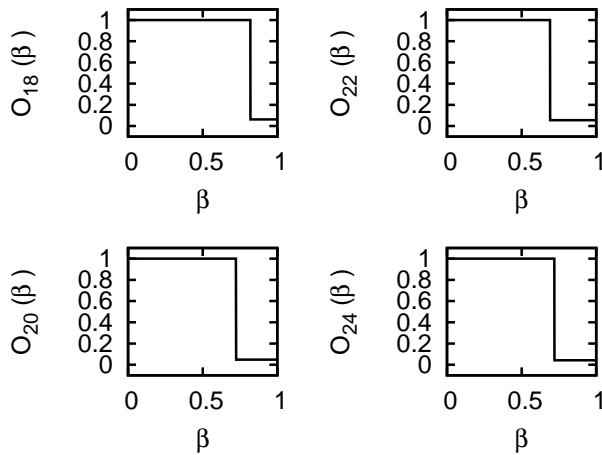$$O_N(\beta) = \frac{m(min[P_N(\beta, m)])}{m_N^{max}} \qquad (4)$$

Figure 5. Pseodo order parameter registers a jump from 1 to 0 across collapse temperature
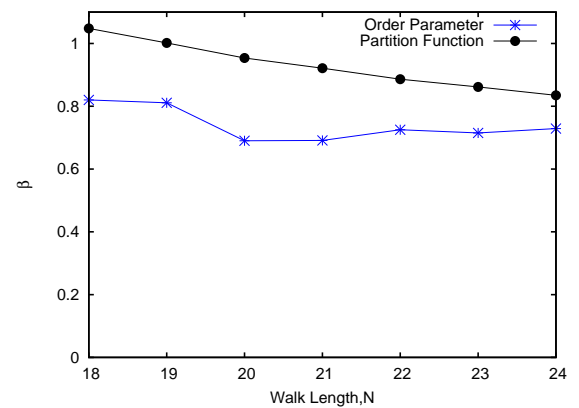

Figure 6. Fluctuation in collapse transition. Results from both PFZ analysis and pseudo order parameter is shown

Fig 5 shows pseodo order parameter defined above. Since this method gives a binary signal, estimation of collapse temperature is unmistakable. In Fig 6 we have plotted inverse collapse temperature (β_c) for walk lengths 18 to 24 from both PFZ method as well as from pseudo order parameter method.

T. Vogel et al. reported theta temperature is 3.72(1) ($\beta = 0.268$) [9]and J.H.Lee repoted same to be 3.76(32) ($\beta = 0.266$) and 3.03(12) ($\beta = 0.330$) with and without logarithmic correction[8].

Collapse transition for short walks are always smaller than that. In our simulation we got first zeros of partition function same as those from exact enumeration. Collapse temperature from pseudo order parameter is not same as those from first zeros of partition function. But our pseudo order parameter method gives collapse temperature slightly closer to theta temperature than partition function zero. This is not because of any artifacts from estimation of density of states. Pseudo order parameter calculated using exact enumeration data also show similar behavior. We still don't have an explanation for that.

5. Conclusion

Simulated density of states using chain growth algorithm are in good agreement with exact enumeration results for interacting Self Avoiding walk on Simple Cubic Lattice. Computed specific heat showed signatures of excitation transition and collapse transition. Collapse transition temperature is estimated using the analysis of partition function zeros and pseudo order parameter method.

Acknowledgment

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