THERMODYNAMICS AND IDEAL GLASS TRANSITION ON THE SURFACE OF
A MONATOMIC SYSTEM MODELED AS QUASI “2-DIMENSIONAL”
RECURSIVE LATTICES

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Ran Huang
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THERMODYNAMICS AND IDEAL GLASS TRANSITION ON THE SURFACE OF A MONATOMIC SYSTEM MODELED AS QUASI “2-DIMENSIONAL” RECURSIVE LATTICES

Ran Huang

Dissertation

Approved: Purushottam D. Gujrati

Accepted: Ali Dhinojwala

Advisor

Department Chair

Committee Chair: Ali Dhinojwala

Dean of the College

Committee Member: Gustavo Carri

Dean of the Graduate School

Committee Member: Jutta Luettmer-Strathmann

George R. Newkome

Committee Member: Mesfin Tsige

Date
Two quasi 2-dimensional recursive lattices formed by planar elements have been designed to investigate the surface thermodynamics of monatomic Ising glass system with the aim to study the metastability of supercooled liquids and the ideal glass transition. Both lattices are constructed as hybrids of a Husimi lattice representing the bulk and lower dimensional recursive trees representing the surface. The coordination number, i.e. the number of neighbor sites surrounding one site, is designed to be 3 on the surface and 4 inside the bulk to mimic the 2D regular square lattice case. The recursive properties of recursive lattices were adopted to obtain exact thermodynamic calculations without approximation. The model has a strong anti-ferromagnetic interaction to give rise to an ordered phase identified as a crystal, and a metastable solution is also found to represent the amorphous phase. Interactions between particles farther away than the nearest neighbor distance are taken into consideration.

The calculations were done with C/C++ programs. A recursive calculation technique was employed to approach an exact description of the system with the ratio of partial partition functions (PPF) on each site of the lattice. Thermal properties including free energy, energy density and entropy of the ideal crystal and supercooled liquid state of the model on the surface are calculated by the PPF. By analyzing the free energies and entropies of the crystal and supercooled liquid state, we are able to identify the melting transition and the second order ideal glass transition on the surface. The effects of
different energy terms that produce competitions between crystallization and glass transition are studied. The results show that due to the coordination number change, the transition temperature on the surface decreases significantly compared to the transition temperature of the bulk system obtained in our previous research. Our theoretical calculation agrees with experiments and computer simulation results on the thermodynamics of surfaces and thin films conducted by others. Comparing to others’ work, there are two advantages in our approach: 1) in this work our model focuses on the small molecules system, it reveals the basic dimension origin of transition temperatures reduction without involving the long chain properties of polymer system; 2) the thermodynamics of systems are derived by exact calculation method, the computation time is much shorter than typical simulation methods, usually the calculation of one set of parameters in the interesting temperature region can be done in less than 100 seconds.
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CHAPTER I
INTRODUCTION

The phenomenon that the solid state of particular materials becomes brittle on cooling and soft on heating is referred as glass transition [1]. The temperature at which this transition happens is referred to as the glass transition temperature \( T_g \). Glass transition has been an interesting topic and studied for several decades. However, the properties of glass and of glass transition remain obscure. The significant thermodynamic, dynamic and mechanical property changes at the glass transition play important roles in many scientific and industrial fields like materials science and engineering [2-10].

Classical thermodynamics indicates that during the crystallization, with temperature decrease, a liquid will crystallize and turn into a solid, i.e. crystal [2, 3]. A crystal is an ordered state corresponding to the lowest possible free energy at a certain temperature. Nevertheless, in some cases, the crystal state cannot be achieved due to particular properties of the material and experimental conditions; the liquid will turn into a supercooled liquid below the melting transition temperature [4-6]. Unlike the discontinuous entropy drop during crystallization, the supercooled liquid has a continuous decreasing entropy. With continuous temperature decreasing, the supercooled liquid state will eventually turn to be another solid state, the glassy state. The transition between supercooled liquid and glass state is defined as the “glass transition”. Comparing to crystal which is the ordered state, glass is a metastable state with relatively higher entropy. Thus, instead of stating that the glass state is another solid state, it is more
suitable to treat the glass state as a “frozen liquid state” [4-10]. An entropy scheme of melting transition and glass transition is shown in figure 1.1.

In recent years it has been argued that glass transition is not a real thermodynamic phase transition; rather, it is a dynamic process which causes the property changes [11-20]. However, by exploring the thermodynamic behavior of supercooled liquid and the glass, Kauzmann proposed the entropy crisis and ideal glass transition in 1948, and the ideal glass transition is a thermodynamic transition. In this way, the ideal glass transition is believed to be the underlying thermodynamic reason for the glass transition, although the glass transition itself maybe merely a dynamic process [10, 21-23]. In this dissertation, we will always focus on the ideal glass transition instead of the glass transition.

Due to the structural properties, polymer systems often undergo a glass transition. Because the long molecular chain structure requires more energy, space and much longer time to rearrange its configuration to crystallize or reach 100% crystallization; supercooled liquids from the polymer melts form easily. Therefore, most studies of glass transition refer to polymers; however there exist many small molecule systems that undergo the glass transition [24]. In this paper we focus on the glass transition in theoretical small molecule alloy or monatomic systems. Nevertheless the model we constructed and the calculation method employed have the capacity to study either small molecules or polymer systems.
Figure 1.1. The scheme of entropy change of melting and glass transition
1) Entropy crisis and ideal glass transition

1.1) Configurational entropy and kinetic entropy

In classical statistical mechanics, in canonical ensemble, the partition function of a system of \( N \) structureless particles in a volume \( V \) at a given temperature \( T \), \( Z(T) \) can be expressed as a product of the configurational partition function \( Z_{\text{conf}}(T) \) and kinetic partition function \( Z_{\text{kinetic}}(T) \) [31, 32]:

\[
Z_{\text{total}}(T) = Z_{\text{conf}}(T) Z_{\text{kinetic}}(T) .
\] (1.1)

The first factor \( Z_{\text{conf}}(T) \) is the integration of the interaction energy weighted over all configurations:

\[
Z_{\text{conf}}(T) = \frac{1}{V_0^N} \int e^{-\beta E(r)} d^N \{r\},
\] (1.2)

where the \( E\{r\} \) is the potential energy of a particular configuration \( \{r\} \), which is determined by the particle position \( r_i, i = 1, 2, 3, \ldots N \) for \( N \) particles, \( \beta = 1/k_B T \) is the inverse temperature and \( k_B \) is the Boltzmann constant. The constant \( V_0 \) represents a small-scale volume, such as the volume of a particle, to make \( Z_{\text{conf}}(T) \) dimensionless. If we introduce an energy constant \( \varepsilon \), such as the average difference between the energy levels of a single particle in the two-body potential which determines the potential energy \( E \) of the system, we have the number of distinct configurations \( W(E)dE/\varepsilon \) with energy between \( E \) and \( E + dE \). Then the configurational entropy in microcanonical ensemble is determined by the number of configurations \( W(E) \) of energy \( E \):

\[
S_{\text{conf}}(E) = k_B \ln W(E).
\] (1.3)

Because the number of configurations cannot be smaller than 1, the configurational entropy must always be non-negative: \( S_{\text{conf}}(E) \geq 0 \).
In the canonical ensemble, the average potential energy is only a function of temperature. Therefore, the configurational entropy can be expressed as $S_{\text{conf}}(T)$.

The kinetic partition function in equation (1.1) represents the integration over momenta $\{p\}$:

$$Z_{\text{kinetic}}(T) = \left(\frac{V_0}{\hbar^3}\right)^N \int e^{-\frac{\beta K}{h} |p|^2} d^N\{p\},$$

where $h$ is the Planck’s constant. Similarly to the configurational entropy, from this partition function we may also derive the kinetic entropy $S_{\text{kinetic}}(T)$ depending on temperature, and the total entropy is the sum of kinetic entropy and configurational entropy:

$$S_{\text{total}}(T) = S_{\text{conf}}(T) + S_{\text{kinetic}}(T).$$

We will only focus on the configurational entropy in this dissertation for two reasons: firstly the kinetic entropy is a function that only depends on temperature but not on interaction; consequently the kinetic entropy of the crystalline and the metastable states shall be the identical at the same temperature if we assume it is equilibrium. And our work focuses on the thermal behavior of different states and the phase transition. Secondly we are using a lattice model and particles are well-confined on the sites; therefore, there is no kinetic part to consider in our study.

1.2) Kauzmann paradox and Ideal glass transition

The Kauzmann paradox was first proposed by Walter Kauzmann in 1948. In experiments, the glass transition temperature $T_g$ highly depends on the cooling rate, a slower cooling rate gives a lower $T_g$ and vice versa. In this way, for the same system a
series of \( T_g \) can be obtained by changing the cooling rate. Correspondingly, with the linkage of these \( T_g \) the entropy versus temperature curve of the supercooled liquid can be achieved. Thus, theoretically this entropy curve could continue to decrease without glass transition with sufficient slow cooling rate (i.e. infinitely slow). Kauzmann extrapolated the entropy of the supercooled liquid below its glass transition temperature, and found that the entropy of the supercooled liquid will be same as the entropy of the crystal, and even lower than crystal’s entropy with further extrapolation [10]. If we define the difference between the entropy of supercooled liquid and crystal as excess entropy:

\[
S_{ex}(T) = S_{SCL}(T) - S_{CR}(T),
\]

(1.6),

this excess entropy will become zero, and then negative with extrapolation, thus giving rise to an entropy crisis. The temperature where excess entropy becomes zero is called Kauzmann temperature. It is viewed as a paradox because it was believed that the ordered crystal phase should not have higher entropy than the disordered supercooled liquid state.

The entropy crisis implies that there must be a transition before the excess entropy becomes negative. Since the entropy crisis is from the extrapolation of glass transition with infinitely slow cooling rate, which is an ideal condition, this transition avoiding negative excess entropy is defined as ideal glass transition. This transition temperature is known as the *ideal glass transition temperature* \( T_K \). The glass transition temperature \( T_g \rightarrow T_K \) as the cooling rate \( dT/dt \rightarrow 0 \). Kauzmann paradox implies the underlying thermodynamic basis of glass formation instead of the result of fast cooling of liquid [10].

Kauzmann proposed that the entropy crisis occurs when the excess entropy becomes negative \( S_{ex}(T) < 0 \). However, in this paper we take the point where the configurational entropy of the supercooled liquid becomes negative \( (S_{conf,SCL}(T) < 0) \) as the entropy
crisis. The reason is, our system is confined in a lattice model, and the entropy is contributed only by the configuration entropy as mentioned above. And the configuration entropy of supercooled liquid is thermodynamically allowed to be lower than the entropy of crystal. Although there has no such supercooled liquid with entropy lower than crystal been found in nature, it is not necessary that the configuration entropy of supercooled liquid must be larger than corresponding crystal at the same temperature [23]. The entropy crisis introduced by Kauzmann and defined in this paper is shown in figure 1.2:
Figure 1.2. The ideal glass transition of original definition and being taken in this dissertation.
2) Ising model

The Ising model was proposed by Wilhelm Lenz and his student Ernst Ising in 1925. The Ising model was originally designed to describe the magnetic field and interactions between magnets. It is a discrete collection of variables called spins, and each spin has two possible values, which generally are assigned as up and down, or +1 and −1. Interactions exist between the two neighbor spins. The interaction has one value when two spins have the same value and the other value when the two spins have different value. In 1925 this model was solved by Ernst Ising for the one dimensional case in his PhD dissertation and he claimed there is no phase transition in this model [25]. However in 1944 Onsager solved the Ising model for the 2D case and the system undergoes phase transitions. Since then this model was utilized in various calculation and simulation methods in 2D, 3D and hyper-dimensional case [26, 27]. A standard Ising model on a 2D square lattice is shown in Figure 1.3

In the Ising model, each lattice site \(i\) (the blue circles in the figure 1.3) is occupied by a spin \(S_i\), which is + or −, (or we can mark it as up (↑) or down (↓)), i.e. each spin has two different states. For convenience, we denote \(S = +1\) as +, \(S = -1\) as −. The Ising model was designed to describe magnetization, though it can be used to represent various thermodynamic systems [28]. If we take one spin state as particle A and the other state as particle B, or particle and void, then the Ising model is also suitable to describe incompressible small molecules alloy systems or compressible monatomic systems. Many works have been done in our group to study small molecule thermodynamics by Ising model [21, 23, 29-38].
Figure 1.3. Ising model on a standard square lattice
The energy of the standard Ising model is:

\[ E = -\sum_{\langle i,j \rangle} J_{ij} S_i S_j - \sum_i H_i S_i, \]  

(1.7)

where \( \langle ij \rangle \) is the nearest-neighbor (nn) pairs of lattice sites \( i \) and \( j \). Notice that \( J_{ij} \) and \( H_i \) can be a constant in a uniform system or depend on the sites. In this paper we just consider the first situation:

\[ J_{ij} = J \text{ for all nn pairs of sites } \langle ij \rangle, \]

\[ H_i = H \text{ for all sites } i. \]

The product of spins can be either +1 if two spins are same (1×1 or \(-1\times-1\)), that is parallel, and \(-1\) if they are different \((-1\times1\)), that is anti-parallel. The coupling constant \( J \) is half the difference in energy (\(+J-(-J) = 2J\)) between two possibilities and can be of either sign. For each pair \( \langle ij \rangle \), \( J > 0 \) favors parallel arrangement, so that all spins tend to be in same state, such an interaction is called a ferromagnetic interaction. Anti-parallel arrangement is favored by \( J < 0 \), such an interaction is called an antiferromagnetic interaction. With \( J = 0 \), the spins are non-interacting. The parameter \( H \) is the external magnetic field and also can be of either sign.

In the ferromagnetic case, at low temperature all spins either point up or down. The model has a symmetry transformation \( S \rightarrow -S \), \( H \rightarrow -H \). It turns a particle into a void or particle A into particle B, and the magnetic field transformation changes the chemical potential. The transformation turns a liquid phase into gas state or vice versa. Thus the ferromagnetic case is suitable to describe liquid-gas or liquid-liquid transitions, with both phases different in density.
For the alloy system, the portion of different kinds of particles at any temperature must be constant, in this way the ferromagnetic case is not very useful because at zero temperature all the spins are either up or down. In contrast, the antiferromagnetic Ising model is appropriate to describe a crystal phase of alloy at low temperature since the two transition phases have distinct spins arrangement. In this case, $J < 0$, the ground state corresponds to all nearest-neighbor spins in opposite orientation at zero temperature and represents the ideal crystal state at zero temperature (figure 1.4).

With the temperature increasing, the spin arrangement becomes more disordered which corresponds to the liquid or supercooled state. Therefore, in this paper, the antiferromagnetic Ising model is adopted to study the supercooled liquid, glass and crystal states.

The standard Ising model only includes the interaction $J_{ij}$ between nearest neighbor spins. However it is not realistic that particles farther away than nearest distance do not interact with each other in real system. For a better approximation of a realistic system, more interaction energy terms will be considered in our calculation. Since our lattice is locally 2D with its basic unit similar to that of a square lattice, more interaction terms are introduced in our work. Interactions between second nearest sites, third nearest sites, and multi-spin interactions, i.e. interaction between three and four spins are employed in our model.
Figure 1.4. Antiferromagnetic Ising model on 1D and 2D lattice representing an ideal crystal state.
3) Review on glass transition on surface/thin film

Numerous works have been done [39-61] on glass transition on surface/thin film, due to both experimental and simulation/calculation aspects. Meanwhile, Ising spins glass has also been widely utilized to study the glass transition by simulation or calculation [28-33, 62-69]. However, the efforts on surface/thin film glass transition by Ising spin glass are relatively rare [34-38]. In this section we will briefly review the achievement and progress in this field.

3.1) Experimental

Glass transition on surface/interface/thin film has drawn many interests in the past decades. First reason is that, the finite-size-confined geometry is a good approach to understand the glass transition itself, especially to explore the dynamic aspect of glass transition due to the unique dynamic properties of thin film geometry. Secondly, the importance of surface and thin film in materials science and engineering requires a better understanding of its dynamic and thermodynamic properties, including glass transition.

Keddie and co-workers have done the early works on supported thin film of PS by ellipsometric measurements [39]. They prepared several PS films supported by silicon wafers with thickness from 3000 Å to 100 Å. The measurements indicated the decrease of the $T_g$ values, compared to the bulk $T_g$, with lower thickness under 400 Å. The results of samples with molecular weights from $120 \times 10^3$ to $2900 \times 10^3$ showed that the $T_g$ changes are independent of $M_w$. An empirical relationship between thickness and $T_g$ was given by Keddie:

$$T_g = T_g^{bulk} [1 - \left( \frac{a}{h} \right)^{\delta}]$$

(1.8)
where $T_g^{\text{bulk}}$ is the glass transition temperature of bulk PS. The $a$ and $\delta$ are the fitting parameters fitted to be 32 Å and 1.8 respectively, $h$ is the thickness of the film.

After Keddie’s work, many researchers have worked on different supported thin films for example PMMA, polycarbonate [40], poly(alpha-methylstyrene) and polysufone [41]. Different characterization methods other than ellipsometric measurements were employed like X-ray reflectivity, positron annihilation [42], and dielectric [43] techniques. Most of the results have demonstrated the same phenomenon that for liner polymer the $T_g$ decreases with the thickness of films under a certain thickness \(\sim 600\text{-}1000\ \text{Å}\), and consequently concluded that above that thickness the film is in bulk behavior.

Nevertheless, the supporting film has a considerable film-substrate interaction, which makes the conclusion controversial. One can argue that the substrate plays a critical role in the glass transition of thin films, and a much stronger attractive interaction between the substrate and thin film may increase the $T_g$ of thin film above the bulk $T_g$ [47]. van Zanten et al. measured $T_g$ for poly-2-vinylpyridine on oxide-coated Si substrates and found it larger than the bulk $T_g$, about maximum 50 K for a 77 Å film [44]. Therefore, experiments on supporting film were not sufficient to understand the size effects on glass transition and research focused on the free-standing films is prompted to avoid the weakness of supported films.

Forrest and co-workers have done pioneer work in measuring the $T_g$ of free-standing thin films [45-48]. They measured the $T_g$ of free-standing PS film with thickness from 200 to 2000 Å and different molecular weights by Brillouin Light Scattering (BLS) and transmission ellipsometry. Their research basically revealed two significant facts: 1) The $T_g$ decreases with the thickness of PS thin film however with a much larger magnitude; 2)
The $T_g$ variation shows a strong molecular weights dependence. Comparing to the supported-film measurements, regardless of molecular weights, the PS films show a much more dramatic $T_g$ decrease with smaller thickness, for example, the $T_g$ of 200 Å film with $M_w$ within 120 K to 378 K region reduces by 70 K below the bulk $T_g$, while this magnitude is around 10 K for supported films. Also, consistently the $T_g$ reduction of samples with various $M_w$ happens with larger film thickness up to 700 Å. These evidences indicate that the interaction between substrate and film strongly affect the film’s thermodynamic behavior, either in the positive or negative way. Thus, the study on free-standing film should be more convincible in reflecting the film’s own properties.

Forrest and co-workers’ results show a strong effect of $M_w$. The data divide into two regions of $M_w$. For the $M_w$ smaller than $378 \times 10^3$, the $T_g$ reductions are independent of $M_w$, or at least very weak. The dependence of $T_g$ on film thickness shows an intriguing non-linear behavior which is similar to the supported PS films, except the difference of the magnitude of reduction. The empirical equation (1.8) derived for supported film can be modified to describe the data for the low $M_w$ free-standing films. With $\delta = 1.8$, the parameter $\alpha$ was found to be 78 Å which is twice that found for supported films. This indicates that the mechanism of $T_g$ reduction maybe the same for both supported and free standing film. The free surface is the reason of $T_g$ reduction. While the $M_w$ is low and does not have a significant effect, the free standing film has two free surfaces corresponding to the twice length scale $\alpha$, i.e. twice effect on the $T_g$ reduction, of supported film, which has only one free surface. This comparison quantitatively suggests that the effect on $T_g$ reduction is proportional to the free surfaces.
The $M_w$ shows important effect when it is larger than $575 \times 10^3$. The larger the $M_w$, the thicker the film that the $T_g$ reduction happens. Models focusing on the effects on glass transition due to aspect of chain dynamics properties have been developed to explain the $M_w$ dependence [48]. However, in this paper, we will only investigate the glass transition on the surface/thin film of small molecular systems. Therefore, models involving $M_w$ effects are out of our concern. Although specific properties of polymer chain plays important role in glass transition on surface/thin film of polymer systems, our studies show that, a very basic dimension and coordination issue leads the $T_g$ reduction on surface/thin film, which will be discussed in Chapter 3&4.

3.2) Simulation and calculation

Along with the progress of experimental work, computer simulation and calculation have also been developed to investigate the glass transition on surface/thin film, and most of them are for polymer systems [49-61]. Two classical simulation methods, Molecular Dynamics (MD) and Monte Carlo (MC) are employed. Either simulation method with various modeling confirmed the $T_g$ decrease with thickness reduction for both supported and free standing film, or $T_g$ increase in some particular substrate-film interaction cases. The empirical equations derived from Keddie’s and Forrest’s results can also be validated by simulation results. Although the explanation for the mechanism of $T_g$ reduction is still a matter of debate.
3.2.1) MD simulation

MD simulation focuses on the physical movements of polymer chains modeled as a series of linked beads. The molecules are confined in a finite size by walls to represent the surface/thin film situation and allowed to interact for a period of time. Several models, such as bead-spring model [49], Bennemann (BE) model, and Rapaport’s model are used to represent the polymer chains. Usually non-bonded monomer–monomer interactions are described by Lennard–Jones (LJ) potential, and the covalent bond interaction in the polymer chain is described by harmonic spring potential. The \( T_g \) is indicated by either monitoring the mobility of polymer chains, or where the slope of film thickness \( h \) on cooling changes [50-57].

Most MD simulation verified the experimental observation (So far to the author’s knowledge, there is no MD simulation results contradicting the experimental results), that for supported film, a strong substrate-film interaction will increase the \( T_g \) above the value in the bulk, while the weak substrate-film interaction will give a \( T_g \) decrease, and free-standing film shows a much larger \( T_g \) reduction than supported film with weak substrate-film interaction. As an example, the result of a typical simulation reported by Torres, Nealey, and de Pablo is shown in figure 1.5 [58].

3.2.2) Monte Carlo Simulation

Comparing to the MD simulation, very few Monte Carlo simulation works have been done on the glass transition of surface/thin film. Mattice and co-workers have done some MC simulation works in this field [59, 60], de Pablo et al. reported a MC simulation on Free-standing films of both linear and cyclic polymeric chains [61].
Figure 1.5. Apparent glass transition temperature vs film thickness by MD simulation.

(Graph is re-made from the data in Torres, Nealey, and de Pablo’s [58])
Basically the $T_g$ reduction with smaller thickness was confirmed in the above investigations. In de Pablo and co-workers’ work, the relation between $T_g$ and bulk $T_g$ can also be fitted as

$$T_g = T_g^{bulk} \left[ 1 - \left( \frac{a}{b} \right) \frac{\delta}{h} \right],$$

which is exactly the same equation (1.8) derived from experiments. Slight difference between linear and cyclic chains has been indicated that the ring polymers show a slower bond relaxation than the linear chains; and for a given film thickness, ring polymers has a higher glass transition temperature than linear polymers with the same molecular weight. Therefore it supports that chain ends are not important in the $T_g$ reduction, and the reduction of the glass transition temperature arises mainly from the fast dynamics in the surface region. It is found that both linear and ring polymer thin films exhibit a fluid-like interfacial region where the mobility is higher than in the bulk. The MC simulation results indicate that segmental mobility is a function of position of the chain in the film; segments in the “semi-fluid” interfacial region tend to move faster than the rest of the molecule in the bulk region.

Nevertheless, the simulations progress reviewed above can only be weak references to our research. Firstly, most simulation works are to be applied on polymer systems, even though the glass transition is not a unique property of polymers. Comparing to the amount of works done on glass transition of polymer systems, the works on small molecule systems are very rare. Secondly, the simulation results are very dependent on modeling method and artificial parameters setups. It is difficult to summarize different groups’ results together and compare with each other since each of them has a particular way to relate their fitting parameters to experimental parameters. For instance the
generalized temperatures used in different simulation are not directly comparable to each other, and more fits are necessary to convert these generalized temperatures to real temperatures. However, the basic principles revealed by various simulations should agree with each other, and help to examine our investigation.

4) Research on glass transition by Ising spin glass model

By different lattices adopted and interactions setup the Ising model is capable to describe various systems, such as gas, liquid, crystal and glass, and consequently the phase transitions, like melting and glass transition [28]. The so-called Ising spin glass has been used to study the glass transitions for a long time. Exact calculation, MC and MD simulation are adopted to study the glass transition of spin glass [29-33, 62-69]. The Kauzmann temperature can be indicated by many properties like density function, thermodynamic functions like internal energy, or kinetic properties. Putting the details aside, the general idea that the unacceptable negative excess entropy is the underlying thermodynamic reason of the ideal glass transition is agreed by most researchers using different calculation or simulation methods.

On the other hand, the glass transition of a spin glass on surface/thin film is very rare. This maybe because the glass transition on surfaces is mostly considered for application area and people mainly focus on the polymer systems, while spin glass itself is a very theoretical model and difficult to describe polymers. This field had been explored by Chhajer in our group by applying Ising model on a modified Bethe lattice to describe the thermodynamics of polymer systems near surface [34-38], which we follow in this dissertation. Although the glass transition was not specifically addressed in his
work, Chhajer’s results show the dramatic density profile changes and entropy increase near surface, which supports our expectation of the free surface effects on $T_g$ reduction.

5) Recursive lattice geometry

The Ising model on a standard lattice can be exactly solved in 1D, and in 2D if $H = 0$ (i.e. the Onsager solution) [25, 26]. For other cases, approximation methods such as mean-field approximation are usually employed. Although many efforts to obtain better accuracy and less crudeness have been made time by time [70, 71], the exact calculation methods, if possible, undoubtfully have the very merit in dealing with modeling and computation of thermodynamic systems. The recursive lattice adopted in our work can provide an exact calculation. On a recursive lattice, the interactions between particles are well confined and countable in a certain unit. The unit only interacts with other units on upper or lower level. There is no correlation between units on the same level, thus no approximation is needed to treat the combinatorics when summing over all the states. Implementation of this technique has proved its capacity to give accurate and reliable result [21, 23, 29-38, 69].

Three kinds of recursive lattices, Bethe lattice, Husimi lattice and Cubic Recursive lattice (CRL), are shown in figure 1.6 [69]. The unique property of these recursive lattices is that a certain number of independent lattice units joint at one site. The basic unit can be any artificial geometrical structure containing many sites. One unit is only related to a neighbor unit by a common site, and the neighbor unit relates to the next neighbor unit by the next common site, and so on in a recursive fashion. For example, in figure 1.6, the basic unit in the Bethe lattice is a line segment with two particles on the ends interacting
with each other. The unit in Husimi lattice is a square formed by four sites. We can also see that the units on one level do not interact with each other, and only correlate to the units on the above and next level.

The Husimi lattice is based on a 2D square local geometry and contains more correlations than a Bethe lattice. Thus the Husimi lattice is more suitable to approximate the standard square lattice to study many thermal systems with the same coordination number $q = 4$. Similarly, the CRL is based on local 3D structure of a cubic lattice which is more complex than Bethe lattice and Husimi lattice and more interaction terms can be introduced for calculation. In this work, we will use the Husimi lattice with $q = 4$ to represent a 2D bulk and a Bethe-like structure with $q = 3$ to represent the surface. Obviously, to mimic a 3D system with a 2D surface, a hybrid of Husimi lattice and CRL can be used for the modeling.
Figure 1.6. Bethe lattice (a), Husimi lattice (b) and Cubic Recursive Lattice (c)
In this chapter, we are going to construct two kinds of recursive lattices (#1 and #2), to describe the surface/thin film. Both lattices are to mimic the 2D case, i.e. the 2D bulk with 1D surface outside. The #1 lattice is integrated of formal square units representing the bulk and single bond representing the surface, the structure is made to have the same coordination numbers with regular 2D square lattice. The #2 lattice adopts a trick to diagonally cutting the square unit to mimic a surface, which is basically integrated by triangle unit with coordination number 3. Ising spins will be applied on the lattices to represent a small alloy system. The exact calculation on both lattices will be introduced and the solutions will be discussed. Principally, the thermodynamics can be calculated based the exact solutions achieved on the lattices.

1) Finite-size recursive lattice #1

1.1) Structure

As mentioned in the previous chapter, the recursive lattice is believed to be a good approximation of regular lattice due to the same coordination number. Therefore, we firstly need to explore the coordination number and interactions of a regular lattice of surface/thin film to construct a recursive lattice to represent the surface/thin film.

The figure 2.1 shows a regular 2D square lattice of a thin film with thickness = 5. The red line is the surface of that lattice. Here we label the central layer to be 0th level,
and the layer next to 0th layer is level 1st. The surface layer is labeled as level $S$. It is clear that sites on the surface have coordination number of 3, while inside the bulk the coordination number is 4. That is, a hybrid lattice with $q = 3$ and 4 is required to describe surface/thin film.

![Figure 2.1. A regular 2D square lattice of a thin film with thickness = 5](image)

Now we take out the basic unit inside the bulk and on the surface to construct a recursive lattice. The two units are shown in figure 2.2:

![Figure 2.2. The basic unit in the bulk and on the surface of a regular 2D square lattice](image)

Inside the bulk we can simply use square unit of $q = 4$ like bulk system, and consequently the recursive lattice would be the well-studied Husimi lattice which is
shown in figure 1.8. For the surface structure, we can see here a single bond presenting in
the surface unit, linked on a square unit then we can have sites with $q = 3$. However we
cannot simply adopt this unit to construct a recursive structure, because the recursive
calculation (will be discussed later) requires an origin point where the contribution from
the entire tree goes to, then if we draw an axis with the origin point and the unit on it, the
basic unit must be symmetrical to that axis. For the unit shown in figure 2.3, wherever we
determine the origin is (point A or B), the unit is not symmetrical to that point. In this way,
we have to modify the surface unit by replacing one square by another artificial single
bond at one lower corner. Although this unit differs from the regular lattice we want to
approximate, the coordination numbers on the surface square still accords to our design
and the calculation in the following chapters will show that this approximation is
practical. The modification is shown in figure 2.3.

Then we can put the bulk and surface unit (figure 2.2 and 2.3) together to make a
recursive lattice, which approximate the regular thin film lattice. The structure of a
thickness $= 5$ lattice is shown in figure 2.4.

From surface A to B, we have a finite bulk portion with a thickness $= 5$, and these
five layers are labeled as $S$, 1, and 0 like the regular film lattice in figure 2.1. On the
surface, the red surface single bond links two identical bulk trees together. In this
example, one bulk tree $T_B$ is linked overall with another 36 trees (only one bulk tree is
drawn in above figure), while they are all identical and independent with each other,
except a single surface bond connection. Recursively, each of these 36 trees is also linked
with another 35 trees by single surface bonds. This lattice gives us an infinite size tree
integrated by finite size bulk portions and infinite large surfaces. If we look at the surface
integrated by red surface bonds indicated by the arrow at the right lower corner in the figure, we can see the surface goes through the bulk trees \( T_B \) is infinitely large with a coordination number 3 everywhere. A stretched surface is shown in figure 2.5 to provide a more obvious view of the surface.

With this structure, we have an infinitely large surface with the repeating contribution from bulk tree \( T_B \) to the surface. Comparing to the regular lattice surface, the main difference is that one surface also receives contribution from other surface structure, which is caused by the surface unit modification shown in figure 2.3. But this is an approximation we have to take to achieve the recursive calculation. It is clear that we have infinite number of bulk trees and surfaces in this lattice, however since they are independent and identical, it does not impact the thermodynamic properties of a local region we are going to investigate. Moreover, this infinitely arranged structure will enable us to apply the recursive calculation.
Figure 2.3. The modification of surface square unit.

The bulk square on lower right corner is replaced by a single bond. In this way the modified structure is symmetrical to an imaginary axis links point A and the center of square unit S.
Figure 2.4. An example lattice #1 bulk tree structure with thickness = 5
Figure 2.5. The stretched view and the contribution direction of one surface in lattice #1
1.2) The sites labeling on bulk and surface unit

We label each site $S_i$ in a square as shown in figure 2.6:

![Figure 2.6 Sites index on a square unit in lattice #1](image)

The site in a square unit is labeled as $S_{a,b}$, where $a$ is the index of the square unit in the bulk tree, and $b$ is the index of site. Therefore, one site $S_{a,b}$ actually has two labels depending on which square unit we refer to. For example, the site $S_{a,4}$ is $S_{(a+1),1}$ in the higher level unit. When we are only focusing on one unit, the site $S_{a,b}$ may also be denoted as $S_b$ for convenience. In a square unit, the base site is determined to be the site closest to the bulk tree origin (the 0th square) and labeled as $S_{a,1}$. Therefore, in the above circle, the base site is the lowest site, while in the lower circle, the base site is the left one. The labeling in origin unit is a special case which will be discussed later. The interactions are also sampled in the above unit: $J$ is the interaction between nearest sites, $J_p$ is the interaction between second-nearest sites, i.e. the diagonal sites.
For surface calculation, we label the surface sites as shown in figure 2.7. Due to our calculation method, only two labels are necessary in surface labeling. The site close to the bulk site is labeled as $\bar{S}_0$, and the site diagonal to the bulk site is labeled as $\bar{S}_1$.

![Figure 2.7 The surface sites labeling in lattice #1](image)

1.3) The interactions and energy in bulk square unit

We consider four kinds of interactions in our model: $J$ the interaction energy between the nearest sites, $J_p$ the interaction energy between the second nearest sites, $J'$ the interaction energy of three sites (triplet), and $J''$ the interaction energy of four sites (quadruplet).

We now introduce following variables to count the interactions and magnetic fields of one square unit:

- $A_{\text{mb}} = S_1 \times S_2 + S_1 \times S_3 + S_2 \times S_3 + S_3 \times S_4$;

- $A_d = S_1 \times S_4 + S_2 \times S_3$;

- $A_{\text{tri}} = S_1 \times S_2 \times S_3 + S_1 \times S_2 \times S_4 + S_1 \times S_3 \times S_4 + S_2 \times S_3 \times S_4$;
\[ A_{\text{qua}} = S_1 \times S_2 \times S_3 \times S_4; \]
\[ A_{\text{mag}} = S_2 + S_3 + S_4. \]

Note that the base site \( S_1 \) is not included in the magnetic term \( A_{\text{mag}} \); instead we just count the contribution from the sites of the unit cell above the site \( S_1 \). The site \( S_1 \) plays a special role in our calculation. Simply to say, our calculation has a recursive fashion the energy of one unit is included in the contribution to the next level’s unit, and the base site of one will be counted in the next level’s energy equation, thus we need to exclude it here to avoid double counting. The details of the calculation will be discussed later.

Then, for a particular cell \( \alpha \) with a certain spin conformation \( \Gamma \), the energy of the Ising model in one cell is:
\[ e_\alpha = -J \cdot A_{\text{nt}}(\Gamma) - J_p \cdot A_d(\Gamma) - J' \cdot A_{\text{tri}}(\Gamma) - J'' \cdot A_{\text{qua}}(\Gamma) - H \cdot A_{\text{mag}}(\Gamma). \]

The total energy of the Ising model mentioned above is the sum of the energy of all cells on our recursive lattice:
\[ E_{\text{total}} = \sum_\alpha e_\alpha(\Gamma). \]

Each square unit has four sites and the Ising spin on each site has two possible states, the number of possible states of one square unit is \( 2^4 = 16 \). In table 1 we list all the 16 states from \( S_i = +1 \) to \( S_i = -1 \) and the corresponding energy.

For the anti-ferromagnetic Ising model, the 7th and 10th states correspond to ideal ordered crystal conformation, which have the largest weight comparing to other conformations at the same temperature, while the 1st and the 16th states are the most unstable conformations with the highest energy, which represent the disordered phase.
The base site of 1st to the 8th states is \( S_i = +1 \), and the 9th to the 16th states are with base site \( S_i = -1 \).

Then the Boltzmann weight \( \omega(\Gamma) \) of state \( \Gamma \) is given by

\[
\omega(\Gamma) = \exp(-\beta e(\Gamma)),
\]

where \( \beta \) is the inverse temperature, \( \beta = 1/k_B T \), and here we set the Boltzmann constant \( k_B = 1 \) to make the temperature to be generalized temperature in the units of energy.

Hence, we have

\[
\omega(\Gamma) = \exp(\beta (J \cdot A_{nb}(\Gamma) + J_p \cdot A_{d}(\Gamma) + J' \cdot A_{tri}(\Gamma) + J'' \cdot A_{qua}(\Gamma) + H \cdot A_{mag}(\Gamma))).
\]

Then the partition function of a finite lattice with \( \alpha \) cells is the sum over products over the Boltzmann weight:

\[
Z(T) = \sum_{\{S=\pm1\}} \left[ \prod_{\alpha} \omega_{\alpha}(\Gamma) \right].
\]

1.4) The interactions and energy on surface

In figure 2.5, there are two kinds of units, the single bond unit and the square unit alternatively appearing on the surface structure. The interactions and energy of the square unit is similar to the bulk square unit as we discussed in the previous section. However, here we would like to assign a different nearest neighbor interaction \( \bar{J} \) on the surface bond (the red bond), to distinguish it with the nearest neighbor interaction \( J \) in the bulk. This enables us to set more complex surface properties. And similarly we may also have a different diagonal interaction \( \bar{J}_p \), triplet interaction \( \bar{J}' \) and quadruplet interaction \( \bar{J}'' \):
On the surface single bond unit, the interaction is much simpler since there is only one nearest neighbor interaction:

\[ e_{\alpha} = -\vec{J} \cdot (S_2 \cdot S_4 + S_3 \cdot S_4) - J \cdot (S_1 \cdot S_2 + S_1 \cdot S_3) - \vec{J}_p \cdot A_d(\Gamma) - \vec{J}' \cdot A_{tri}(\Gamma) - \vec{J}'' \cdot A_{qua}(\Gamma) - \vec{H} \cdot A_{mag}(\Gamma) \]

(2.6)

On the surface single bond unit, the interaction is much simpler since there is only one nearest neighbor interaction:

\[ e = -\vec{J} \cdot (\vec{S}_1 \cdot \vec{S}_0) - \vec{H} \cdot \vec{S}_1 \]

(2.7)

Similar to the role of base site in bulk calculation, here the magnetic field of \( \vec{S}_0 \) is not included because that site will be counted in the next level’s energy equation. The ‘level’, in this statement, is indexed by taking the direction indicated by the arrow in figure 2.5, and employing an imaginary origin point infinitely far away from the region we concern. Since the surface is infinitely large, the selection of ‘origin point’ does not affect us to achieve the solutions on surface.

By the setup of values of interaction energies (\( J, J_p, J', J'' \), and \( H \)), we can simulate various systems with particular interactions and energy to study their thermodynamic properties and phase transition with the determination of the partition function. The effect of energy parameters will be discussed in Chapter V. Generally we set \( J = -1 \) to determine the temperature scale for our antiferromagnetic model. The solution based on \( J = -1 \) and all other parameters to be 0 is called the reference solution.

2) General recursive calculation technique

To discuss the calculation of our model, we first need to introduce the idea of sub-tree contributions. As mentioned above, for our finite bulk tree, we have an origin at the center of the tree. For each square unit, the base site is the closest site to the origin, and
Table 1. List of conformations of square unit in the bulk and on the surface

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$-4J - 2J_p - 4J' - J''' - 4H$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>$-0J - 0J_p + 2J' + J''' - 2H$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$-0J - 0J_p + 2J' + J''' - 2H$</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$-0J + 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>$-0J - 0J_p + 2J' + J''' - 2H$</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$-0J + 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$+4J - 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>$-0J - 0J_p - 2J' + J''' + 2H$</td>
</tr>
<tr>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$-0J - 0J_p + 2J' + J''' - 2H$</td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>$+4J - 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$-0J + 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>12</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$-0J - 0J_p - 2J' + J''' + 2H$</td>
</tr>
<tr>
<td>13</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>$-0J + 2J_p - 0J' - J''' - 0H$</td>
</tr>
<tr>
<td>14</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$-0J - 0J_p - 2J' + J''' + 2H$</td>
</tr>
<tr>
<td>15</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$-0J - 0J_p - 2J' + J''' + 2H$</td>
</tr>
<tr>
<td>16</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>$-4J - 2J_p + 4J' - J''' + 4H$</td>
</tr>
</tbody>
</table>
there are three sub-trees coming from the other three sites. The sub-trees could either be three identical portions of the bulk tree, or three surface trees linked by the single surface bond if it is the square unit on the surface. For convenience, we index the sites in one unit as shown in figure 2.8.

By this index, the sites on the level \( m \) is represented as \( S_m \). The sub-tree coming to the site on level \( m \) is marked as \( T_m \). In this way, we can introduce a partial partition function \( Z_{m+1}(S_{m+1}) \) at the level \( m+1 \) to represent the contribution of the branch \( T_{m+1} \) with spin \( S_{m+1} \) as its base site to the lower level \( m \), and \( T_m \) to the lower level \( m-1 \), etc. Therefore, we can start from the highest level, count the contribution of sub-trees on each level and recursively go to the lower level unit the origin point, where it gives the contribution of the entire lattice, and the thermodynamics of whole system can be obtained.

It is clear that the contribution of one sub-tree \( T_m \) is integrated by two sub-trees at level \( m+1 \) \( T_{m+1} \), one sub-tree at level \( m+2 \) \( T_{m+2} \) and the weight of a local square unit. Thus, the partial partition function at level \( m \) \( Z_m(S_m) \) must be a function of the partition functions at higher level \( Z_{m+1}(S_{m+1}) \), \( Z_{m+2}(S_{m+2}) \) and the local weight. The partition function \( Z_0 \) of the entire lattice can be represented by the contribution to the origin site \( Z_0(S_0) \):

\[
Z_0 = Z_0^2(\uparrow)e^{\beta H} + Z_0^2(\downarrow)e^{-\beta H}. \tag{2.8}
\]

The square of partial partition functions, \( Z_0^2(\uparrow) \), is to count the two symmetric trees with base spin \( S_0 = +1 \) meeting at the origin. Remember the weight of origin site is not
Figure 2.8. Level index in a square unit and the scheme of sub-tree contributions
contained in the energy equation of the unit at the previous level, the term $e^{-\beta H}$ is to count the contribution of the origin site with $S_0 = +1$. Similarly, $Z_0^2(\downarrow)$ is the contribution of two trees with $S_0 = -1$, and $e^{-\beta H}$ counts the contribution of origin with $S_0 = -1$.

Or, if the origin is a square unit, the total partition function is

$$Z_0 = \sum_{i}^4 (Z_i(S_i) \cdot \omega(\Gamma)),$$

where $S_i$ is one of the four spins on the origin square, $Z(S_i)$ is the partial partition function of the sub-tree coming to the site $S_i$, and $\omega(\Gamma)$ is the local weight of the origin square.

For the sub-tree $T_m$ the partial partition function $Z_m(\uparrow)$ is the sum of the configurations with the spin $S_m = +1$ over the product over the partial partition functions on higher levels with the local weight $\omega(\Gamma)$. For a square unit, $Z_m(\uparrow)$ has 8 terms with $S_m = +1$ and $Z_m(\downarrow)$ is the sum of the other 8 configurations with $S_m = -1$:

$$Z_m(+) = \sum_{\Gamma=1}^8 \prod_{\{m+1\}}^{2} Z_{m+1}(S_{m+1})Z_{m+2}(S_{m+2})\omega(\Gamma),$$

$$Z_m(-) = \sum_{\Gamma=1}^8 \prod_{\{m+1\}}^{2} Z_{m+1}(S_{m+1})Z_{m+2}(S_{m+2})\omega(\Gamma).$$

In equation (2.10) and (2.11), the product over $\{m+1\}$ represents a product over the two branches on level $m+1$. The term $Z_{m+2}(S_{m+2})$ is the contribution of the branch on level $m+2$. The term $\omega(\Gamma)$ is the local weight of the square unit.

Then we can introduce the ratios

$$x_m = Z(+) / [Z(+) + Z(-)],$$

$$y_m = 1 - x_m = Z(-) / [Z(+) + Z(-)].$$
These two are the ratios of partial partition functions on the level \( m \); they indicate, although not exactly to be, the probability that the site on level \( m \) \( S_m \) is occupied by a plus spin \( (x_m) \) or a minus spin \( (y_m) \). Therefore, these two ratios are critical in our model and all the thermodynamic calculations are based on these ratios, which we call the solutions of the lattice.

To solve the solutions \( x \) and \( y \), here we define a compact notation

\[
z_m(S_m) = \begin{cases} x_m & (S_m = +1) \\ y_m & (S_m = -1) \end{cases}
\]

for convenience to use instead of \( x_m \) and \( y_m \). Then \( z_m(S_m) \) equals to \( x_m \) when \( S_m = +1 \), and \( y_m \) when \( S_m = -1 \).

By introducing \( B_m = [Z_m(\uparrow) + Z_m(\downarrow)] \), we then have \( Z_m(\uparrow) = B_m \cdot x_m \) and \( Z(\downarrow) = B_m \cdot y_m \). We substitute these two equations into (2.10) and (2.11) to obtain

\[
z_m(S_m) = \frac{B_{m+1}^2}{B_m} \sum_{\Gamma} \left[ \prod_{\{m+1\}}^2 z_{m+1}(S_{m+1}) \right] z_{m+2}(S_{m+2}) \omega(\Gamma), \tag{2.14}
\]

where the sum is over \( \Gamma = 1, 2, 3, \ldots, 8 \) for \( S_m = +1 (\uparrow) \), and over \( \Gamma = 9, 10, 11, \ldots, 16 \) for \( S_m = -1 (\downarrow) \). It is clear that the solution (ratios) on one level is a function of solutions on higher levels in a recursive fashion.

For convenience, we introduce the polynomials:

\[
Q_{m+}(x_{m+1}, x_{m+2}) = \sum_{\Gamma=1}^{8} \left[ \prod_{\{m+1\}}^2 z_{m+1}(S_{m+1}) \right] z_{m+2}(S_{m+2}) \omega(\Gamma), \tag{2.15}
\]

\[
Q_{m-}(y_{m+1}, y_{m+2}) = \sum_{\Gamma=9}^{16} \left[ \prod_{\{m+1\}}^2 z_{m+1}(S_{m+1}) \right] z_{m+2}(S_{m+2}) \omega(\Gamma). \tag{2.16}
\]
\[ Q_m(x_{m+1}, x_{m+2}) = Q_m^+(x_{m+1}, x_{m+2}) + Q_m^-(y_{m+1}, y_{m+2}) = \frac{B_m}{B_{m+1}^2 B_{m+2}}. \]  

(2.17)

Then the ratio \( x_m \) is just as function of the ratios on higher level \( x_{m+1} \) and \( x_{m+2} \):

\[ x_m = \frac{Q_m^+(x_{m+1}, x_{m+2})}{Q_m(x_{m+1}, x_{m+2})}. \]  

(2.18)

3) Fix-point solution

From the recursive relation shown in eqn (2.18), we may expect a repeating solution, which has the form:

\[ x_1, x_2, \ldots, x_\nu (\nu \geq 1) \] 

and \( x_k = x_{\nu+k} \) for some value of \( \nu \geq 1 \), so that eqn (2.18) holds.

Such a solution can be called a \( \nu \)-cycle solution that repeats after \( \nu \)-th the application of the recursive relation equation.

For example, for a 1-cycle solution \( x \), we simply have the same ratio \( x \) on all the levels:

\[ x = \frac{Q_m^+(x, x)}{Q_m(x, x)}. \]

For a 2-cycle solution \( x_1, x_2 \) we have

\[ x_1 = \frac{Q_m^+(x_2, x_1)}{Q_m(x_2, x_1)}, \]

\[ x_2 = \frac{Q_m^+(x_1, x_2)}{Q_m(x_1, x_2)}. \]

That is, two solutions alternatively appear level by level.
In this way, for a particular recursive relation, we can start from a set of initial seeds \( x_1 \) and \( x_2 \) to calculate the solutions on lower levels until we reach the recursively repeating solutions, which is called fix-point solution.

Usually many initial seeds are tried to obtain all the possible solutions for a particular recursive relation. According to our experience, solutions with \( \nu \geq 3 \) were never obtained, while solutions with \( \nu = 1 \) and \( \nu = 2 \) (1-cycle and 2-cycle solutions) are almost always available. Based on the property of \( x \), which is determining the probability that one site is occupied by the spin \(+\), a cycle solutions with \( \nu \geq 3 \) is hard to imagine.

An example 1&2-cycle solutions of an infinite Husimi lattice, with \( J = -1 \), \( J' = 0 \), \( J'' = 0 \) and \( H = 0 \) on a wide temperature range is shown in figure 2.9.

In figure 2.9 the temperature is the generalized temperature with Boltzmann constant \( k_B = 1 \) and has the units of energy. We can see that at high temperature, both 1-cycle and 2-cycle solutions are 0.5. That is, every site in the lattice has a 50% probability to be occupied by a \(+\) spin. This obviously represents a disordered state. At low temperature, the 1-cycle solution is still 0.5, while the 2-cycle solution occurs a transition and gives two branches, one of which goes to 1 and the other goes to 0 with temperature decrease. This indicates, for 2-cycle solution, two neighbor sites will prefer to have different spin states. In the region close to zero temperature, with one site has 100% (\( x = 1 \)) probability to be occupied by \(+\) spin, its neighbor sites have 0% (\( x = 0 \)) probability to be occupied by \(+\) spin (i.e. 100% probability to be occupied by \( -\) spin). Therefore, at zero temperature we will have a plus and minus spins alternative arrangement on the lattice. Recalling the anti-ferromagnetic model we introduced and the energy of each states in table 1, this 2-
Figure 2.9. An example 1&2-cycle solutions of an infinite Husimi lattice, with $J = -1$, $J_p = 0$, $J' = 0$, $J'' = 0$ and $H = 0$
cycle arrangement corresponds to the perfect ordered state (crystal) and the lowest energy (the most stable state). Then the one-cycle solution at the same temperature refers to the metastable state, that is, it is still a stable solution, however has a higher energy. The temperature where the 2-cycle solution appears is called critical temperature. At this temperature the amorphous state turns to be ordered state, or it can also continue as metastable state, the analog of three states here with liquid, crystal and supercooled liquid implies that it is the melting transition. The details will be discussed in Chapter III.

4) Calculations on lattice #1

4.1) The calculation in the bulk

For an infinite Husimi lattice, the calculation to get the fix-point solution is quite straightforward and has been discussed in our previous work [29, 69], we can simply start with two artificial initial seeds and recursively calculate the solutions by eqn (2.18) many times until we reach the fix-point solution. While for the surface/thin film lattice we developed in this paper, the bulk tree is finite and confined within surface trees, we need to carefully monitor the calculation on each specific site.

Let us take a lattice with thickness = 2m + 3, we label the surface square as S, then the square next to S is labeled as m-th level, then origin square is labeled as 0. Firstly we start from two initial guesses $\vec{x}_1^-, \vec{x}_2^-$ on the surface sites as shown in figure 2.10. The calculation through the surface square S will give us the solution on the top site of level m-th square $x_{m+1}$. On the other two surface squares labeled as $S'$ and $S''$ we again use the same initial guess seeds, however rotate their position by putting $\vec{x}_1^-$ on the top site and $\vec{x}_2^-$ on two side sites, then the calculation based on $S'$ or $S''$ will give us the solution $x_{m+1}'$ and
Figure 2.10. The initial seeds calculation scheme starting from the surface in lattice #1
on the side site of level $m$-th square. This is because by the anti-ferromagnetic Ising model and the properties of 2-cycle solution introduced above, we expect a 2-cycle style solution on our lattice (and the 1-cycle solution is just a special case when the two 2-cycle solutions are the same), thus the rotation avoids us to get the same results on neighbor sites, which makes the 2-cycle solution impossible.

Consequently, with the solutions $x_{m+2}$ and $x_{m+1}$ we obtain $x_m$ on the top site of square level $m-1$, and on the other branch the rotation of $x_{m+2}$ and $x_{m+1}$ will give us $x_{m-1}$, then we can continue the calculation to the origin square 0 as shown in figure 2.11 (a).

Once we reach the origin square, the solution $x_1$ and $x_1'$, if they have reached the fix-point solution, represent the state inside the bulk. This part of calculation is called downward calculation, which is from the surface to the bulk origin. However, this set of bulk solutions is from the initial guesses on the surface; it may not be the solution of real state. We still have to find the fix-point solution on the surface, and the bulk calculation from the surface fix-point solution is then the final result we are looking for. To find the fix-point solution on the surface, we start from the bulk origin and trace back to the surface (upward calculation), which provides a constant bulk contribution $T_B$ to the recursive calculation on the surface.

The upward calculation is shown in figure 2.11 (b). At the origin square, from the contributions from three identical trees and the local weight of the origin square, we can calculate the solution on the lower site, which is labeled as $x_{U1} = f (x_1, x_1', x_1'', w(\Gamma))$. The index $U$ means this upward. Then from $x_{U1}, x_{U2}, x_{U''}$ we can get $x_{U2}$ and so on. The
Figure 2.11 The calculation direction through the bulk tree: (a) start from surface to the bulk origin, (b) start from the bulk origin and go back to surface
upward calculation will obtain the solution $x_{m+1}^U$ at the base site of the surface square unit. This solution will be used as $x_B$ representing the bulk effect to surface in the surface calculation.

4.2) The calculation along the surface

The situation on surface is more complicated than in the bulk. From the previous introduction on downward and upward calculation, we can see a hint that depending on the direction of calculation, the solutions might be different on the same site, for example the $x_m$ and $x_{m+1}^U$ are different even they are on exactly symmetric sites. This direction issue does not affect us to explore the solutions describing the bulk, however it is critical in surface calculation. Therefore, we firstly classify two directions on the surface with specific labeling, as shown in figure 2.13:

![Figure 2.13. Two calculation directions on the surface of lattice #1](image)

In figure 2.13, the labeling on the surface is in this way: the solution on the base site is $x_B$, i.e. the solution from the bulk, and it is the $x_{m+1}^U$ in upward calculation; the solution
on the sides of the square is label as $\overline{x}_1$, and on the top is $\overline{x}_2$; the prime marks the direction that goes out from the square, while the label without prime is the direction going into the square. Therefore, the scheme A shows a “side-to-top” direction: the solution going out from the top site, $\overline{x}_2'$, is calculated from the solution going into the side top $\overline{x}_1$ and the base site solution $x_B$. Then from $\overline{x}_2'$ we go through a single bond to get the next $\overline{x}_1$. The scheme B shows a “side&top-to-side” direction: the solution going out from the side site, $\overline{x}_1'$, is calculated from the solution going into the side site $\overline{x}_1$, the solution going into the top site $\overline{x}_2$, and the base site solution $x_B$. Again from $\overline{x}_1'$ we then go through a single bond to get the next $\overline{x}_2$. Only after we have done the calculations in both directions, we can get the surface solutions pair, the solution going into the top site $\overline{x}_2$, and the solution going into the side site $\overline{x}_1$, to do the subsequent bulk calculation. (Note that initially this pair is a guess we made to do the first iteration’s bulk calculation). The surface calculation scheme is shown in figure 2.14.

The upward bulk calculation provides us the bulk tree contribution and the solution $x_B$ ($x_{m+1}^U$) on the base site of surface square. This solution is constant in the surface recursive calculation. In figure 2.14, we start from the $x_B$ and the initial seed $\overline{x}_1$ we have made to do two calculations as mentioned. The recursive calculation in process A will eventually give us a fixed $\overline{x}_1$, while the process B will give us a fixed $\overline{x}_2$. This new fixed set of $\overline{x}_1$ and $\overline{x}_2$ is then the seeds we are going to use for the next iteration’s bulk calculation. Note one difference in process A and B, in process A, we only need $\overline{x}_1$ for calculation, which is updated step by step, however in process B after each step we will
Figure 2.14. Surface calculation scheme along the surface of lattice #1
only have a updated $\bar{x}_1'$, while $\bar{x}_1$ is a constant in calculation. Thus, in the program, we always do the process A first to get a fixed $\bar{x}_1$, then use this $\bar{x}_1$ as a constant in the calculation of process B.

The calculation on the square unit, for example, $\bar{x}_1' = f(\bar{x}_1, \bar{x}_2, x_B)$ in process B, is the same as the bulk calculation. The calculation through the single surface bond, for example, $\bar{x}_2 = f(\bar{x}_1')$ in process B, is also similar with square. The only difference is that the partial partition functions only have two terms since there are 4 configurations for a single bond structure:

$$Z_m(+) = \sum_{\Gamma=1}^{2} Z_{m+1}(S_{m+1})\omega(\Gamma),$$  \hspace{1cm} (2.19)

$$Z_m(-) = \sum_{\Gamma=3}^{2} Z_{m+1}(S_{m+1})\omega(\Gamma).$$  \hspace{1cm} (2.20)

$$z_m(S_m) = \frac{B_{m+1}}{B_m} \sum_{\Gamma} z_{m+1}(S_{m+1})\omega(\Gamma). \hspace{1cm} (2.21)$$

where the sum is over $\Gamma = 1$ and 2 for $S_m = +1 (\uparrow)$, and over $\Gamma = 3$ and 4 for $S_m = -1 (\downarrow)$. Then we have the polynomials:

$$Q_{m+}(x_{m+1}) = \sum_{\Gamma=1}^{2} z_{m+1}(S_{m+1})\omega(\Gamma),$$

$$Q_{m+}(y_{m+1}) = \sum_{\Gamma=3}^{2} z_{m+1}(S_{m+1})\omega(\Gamma),$$

$$Q_m(x_{m+1}) = Q_{m+}(x_{m+1}) + Q_{m-}(y_{m+1}).$$  \hspace{1cm} (2.22)
Then the ratio \( m \) is just as function of the ratio on higher level \( x_{m+1} \):

\[
x_m = \frac{Q_m(x_{m+1})}{Q_m(x_{m+1})}.
\]

To summarize, the calculation scheme we reach the fix-point solutions both on the surface and inside the bulk is shown in figure 2.15.

As shown in figure 2.15, we actually do an embedded recursive calculation to get the final solutions on surface and in the bulk. The \( n \) iterations give us recursive updated solutions in the bulk until we find the fix fix-point solution, and a small recursive calculation only on the surface is embedded in one iteration to take the effect of updated bulk contribution each time. This complicated process is to make sure that we counter the mutual effects from surface to bulk and from bulk to surface, and the final solutions exactly describe the situations on the surface and in the bulk. Another necessity is that, the bulk tree has a finite size thus the fix-point solution is not guaranteed to be reached during one downward calculation. Nevertheless with updated surface solutions we start from at each iteration, the bulk fix-point solution is easier to obtain. According to our experience, for the structure with thickness \( \geq 19 \), we can always obtain the fix-point solution at bulk origin. Although on the first several layers close to surface we can only have numerical calculations instead of exact solutions.

5) Finite-size recursive lattice #2

5.1) Structure

The lattice #1 is consistent with our group’s investigation on the recursive lattice modeling like Husimi lattice and Bethe lattice. By specific modification and construction, this lattice provides an exact method to describe the surface situation, i.e. the hybrid of
Figure 2.15. The overall calculation scheme of lattice #1
structures with different coordination numbers. And it has the potential to extension to high dimensions, for instance, we can integrate a cubic recursive lattice as the bulk and a Husimi lattice as the surface to describe the 3D surface, by similar technique. However, we still have several drawbacks on this method: Firstly, the most concern of lattice #1 is that, it actually can only simulate the thin-film, but not a general surface with an infinite bulk. In the lattice #1, the bulk tree is confined within surface trees. Due to the recursive property, the increase of thickness, i.e. the size of bulk will cause a comparable increase of surface portion. The ratio of surface sites to the total number of sites will approach to 0.5 with an infinite bulk portion, while for a regular lattice the portion of surface sites approach to zero with an infinite bulk size, that is, the surface effect on the entire system will always play a critical role no matter how large the lattice is. Secondly, the modification on the surface unit shown in figure 2.3 actually makes a hyper-branched surface structure, which is not realistic in real system. Although the thermodynamic calculation has verified that this modification is acceptable to get reasonable results, it is still better if we can avoid this modification. Thirdly, since we need to track the calculation on each site in the bulk calculation, the computation on lattice #1 is complex.

The lattice #2 is invented to be a simpler surface modeling and to avoid the disadvantages mentioned above. Traditionally, for a regular square lattice, the surface is just the one dimensional line confining the bulk with coordination number = 3. However, we can also cleave a bulk as shown in figure 2.16, to make a zigzag surface. This kind of surface has a coordination number = 2, which is different to the regular surface we discussed above. Since it still has the identity of surface, we expect the modeling based on this zigzag form should also provide practical results.
The figure 2.16 shows a zigzag surface indicated by a red line. Since we take the diagonal interaction $J_p$ into the consideration, the neighbor surface sites are interacting with each other, although the coordination number is 2.

Now, to construct a recursive lattice we need to figure out the basic unit in the regular lattice. For the bulk part, we can still use Husimi lattice with the square units like in lattice #1. On the surface, the basic unit is a triangle, linked by two identical triangles and a bulk square, as shown in figure 2.18:
In this way, the construction of recursive lattice becomes very simple. We can just use a straight connection of triangle units to represent the surface, this triangle chain is infinite, and has the recursive property required for calculation. On each triangle unit, an infinite Husimi lattice is attached to represent the bulk part. The entire lattice is shown in figure 2.19:

The solutions on the surface is marked as $\bar{x}$, the solution on the base site of triangle unit is $x_B$. Imagine we start from a site far enough away from the surface, then approach
to the surface, then the $x_B$ is just the fix-point solution of Husimi lattice. In this way we can simply take count of the contribution of the infinite large bulk to the surface, and focus on the surface thermodynamics. Obviously this lattice is better to describe the behavior of one single surface, unlike the lattice #1, which is just for thin film case. Of course we can also make the bulk tree finite and put on other surfaces to describe the film case. The lattice #2 is simpler, rougher but more versatile than lattice #1.

5.2) Calculations on lattice #2

The interactions and sites labeling is shown in figure 2.20:

![Diagram](image.png)

Figure 2.20. The interactions, sites labeling and origin of the surface of lattice #2

The sites on the surface in a triangle unit are labeled as $S$ and $S'$, where $S'$ marks the site closer to an imaginary origin point on the surface, following the direction of the calculation. The triangle units also have levels due to the origin point. Thus, the $S'$ in one triangle is the $S$ in the lower level’s triangle. The base site is labeled as $S_B$. In the triangle unit we have two neighbor interactions $\bar{J}$, one diagonal interaction $\bar{J}_P$, and like the square unit, we can also add a three spins interaction $\bar{J}'$. The energy of the triangle unit is
\[ e_\alpha = -\bar{J}(S_B \cdot S + S_B \cdot S') - \bar{J}_P \cdot S \cdot S' - \bar{J}' \cdot S \cdot S' \cdot S_B - H(S + S_B). \quad (2.23) \]

Similarly, the magnetic field of \( S' \) is not included in the last term, since it will be counted in the next level’s energy equation.

The triangle unit has \( 2^3 = 8 \) possible configurations, four of them are with \( S' = +1 \) and four are with \( S' = -1 \). We can derive the two partial partition functions of the triangle on level \( m \) from the higher level’s partition function, the contribution from bulk and the local weight:

\[ Z_m(+) = \sum_{\Gamma=1}^{4} Z_{m+1}(S_{m+1}) Z_B(S_B) \omega(\Gamma) \quad , \quad (2.24) \]

\[ Z_m(-) = \sum_{\Gamma=5}^{8} Z_{m+1}(S_{m+1}) Z_B(S_B) \omega(\Gamma) \quad . \quad (2.25) \]

Again, with the ratios

\[ \overline{x_m} = Z(+)/[Z(+)+Z(-)], \quad (2.26) \]

\[ \overline{y_m} = 1 - \overline{x_m} = Z(-)/[Z(+)+Z(-)], \quad (2.27) \]

\[ \overline{z_m}(S_m) = \begin{cases} \overline{x_m}(S_m = +1) \\ \overline{y_m}(S_m = -1) \end{cases} \]

we have \( Z_m(\uparrow) = B_m x_m \) and \( Z(\downarrow) = B_m y_m \) with \( B_m = [Z_m(\uparrow) + Z_m(\downarrow)] \), then

\[ \overline{z_m}(S_m) = \frac{B_{m+1}B_B}{B_m} \sum_{\Gamma} \overline{z_{m+1}}(S_{m+1}) z_B(S_B) \omega(\Gamma) \quad . \quad (2.28) \]

By introducing

\[ Q_{m+}(\overline{x_{m+1}}, x_B) = \sum_{\Gamma=1}^{4} \overline{z_{m+1}}(S_{m+1}) z_B(S_B) \omega(\Gamma) \quad , \quad (2.29) \]
\[ Q_{m^-}(y_{m+1}, y_B) = \sum_{\Gamma=5}^{8} z_{m+1}(S_{m+1}) z_B(S_B) \omega(\Gamma) , \]
\[ Q_{m}(x_{m+1}, x_B) = Q_{m+}(x_{m+1}, x_B) + Q_{m-}(y_{m+1}, y_B) = \frac{B_m}{B_{m+1}B_B} . \]

we can derive the ratio \( x_m \) as a function of the ratios on higher level \( x_{m+1} \) and bulk solution \( x_B \):
\[ \overline{x_m} = \frac{Q_{m+}(x_{m+1}, x_B)}{Q_m(x_{m+1}, x_B)} . \]

Following the above equations we can calculate the solution on surface several iterations until we reach a uniform fix-point solution. The property of equation (2.32) implies that there is no 2-cycle solution possible on lattice #2. This can also be expected by the properties of triangle structure. The neighbor interaction \( \tilde{J} \) prefer to anti-align the \( S \) vs \( S_B \), \( S' \) vs \( S_B \) pair, unless we set the diagonal interaction also to be negative and very large, the system will always prefer the same spin on \( S \) and \( S' \), therefore, we should only have 1-cycle solutions on the surface.

Remember that bulk solution can be either a 1-cycle solution, or a set of 2-cycle solutions. For the 2-cycle solutions, we can substitute either fixed solution as \( x_B \) and it will affect the calculation on the surface to give us a different surface fix-point solution. For example, due to anti-ferromagnetic interaction, at zero temperature with \( H = 0 \), we will have “0 and 1” two-cycle solutions in the bulk (figure 2.9), then if we take \( x_B = 0 \), the surface solution will be \( \bar{x} = 1 \), and \( x_B = 1 \) will lead \( \bar{x} = 0 \). In next chapter we will see that the thermodynamics calculated based on both selections are identical, which in another way proves the consistency of our calculation method.
1) General free energy calculation method: the Gujrati trick

Since our lattices are infinitely large, it makes no sense to calculate the partition function or free energy for the entire lattice. However an exact treatment called Gujrati trick has been well developed to deal with the thermodynamic calculation on recursive lattices in our group. By this technique we can approach the thermal properties in a local area (per site) by the partial partition functions $Z(S)$ and solutions $x$ we discussed in the previous chapter.

The Helmholtz free energy is a function of the temperature and partition function $Z$:

$$F = -T \log(Z).$$

(3.1)

Therefore, we can derive the thermal properties by simply figuring out the partition functions. Let us take a regular Husimi lattice as an example. For an infinitely large Husimi lattice we have an artificial origin point, where we have reached the fix-point solutions. By the idea of sub-tree contribution, we have two sub-trees of level 0 contributing onto the origin point. Then for the next level, we have symmetrical two sets of three sub-trees contributing to the square unit of level 1, as shown in figure 3.1:
Figure 3.1. The origin of Husimi lattice and sub-tree contribution
Thus, depending on the spin state of the origin site, the two sub-trees’ contribution to the whole system is:

$$Z_0^2(\uparrow)\exp(\beta H) \text{ or } Z_0^2(\downarrow)\exp(-\beta H),$$  \hspace{1cm} (3.2)

where the magnetic term is to count contribution of origin site which is not contained in $Z_0(S_0)$. (Remember the base site is not included in the magnetic field term, eqn ()). The partition function of the system is:

$$Z_0 = Z_0^2(\uparrow)\exp(\beta H) + Z_0^2(\downarrow)\exp(-\beta H).$$  \hspace{1cm} (3.3)

Since $Z_0$ counts the contribution of the whole system, it must the sum of contributions of the six sub-trees on level 1 and 2, and the weight of the two square units. If we cut off the two sub-branches on level 2 and joint them together, we have an identical but smaller lattice. Similarly the partition function of this smaller lattice is:

$$Z_2 = Z_2^2(+)\exp(\beta H) + Z_2^2(-)\exp(-\beta H).$$  \hspace{1cm} (3.4)

Therefore we can also cut off the 4 sub-branches on level 1 and form two smaller lattices. Their partition function will be

$$Z_1 = Z_1^2(+)\exp(\beta H) + Z_1^2(-)\exp(-\beta H).$$  \hspace{1cm} (3.5)

The free energy is an extensive quantity; the free energy of the whole system $F(Z_0)$ is the sum of the free energies of these three smaller lattices and the two local squares:

$$F(Z_0) = 2F(Z_1) + F(Z_2) + F(Z_{local}).$$

This yields

$$F_{local} = -T\log\left(\frac{Z_0}{Z_1Z_2}\right)$$

as the free energy of the local two squares, i.e. four sites.
The free energy per site is:

\[ F = -\frac{1}{4} T \log \left( \frac{Z_0}{Z_1^2 Z_2} \right) \]  \hspace{1cm} (3.6)

By substituting

\[ Z_m(+) = B_m x_m \]

and

\[ Z_m(-) = B_m (1-x_m) , \]

we have

\[ F = -\frac{1}{4} T \log \left( \frac{B_0^2 \left[ x_0^2 e^{\beta H} + (1-x_0)^2 e^{-\beta H} \right]}{B_1^4 \left[ x_1^2 e^{\beta H} + (1-x_1)^2 e^{-\beta H} \right]^2 B_2^2 \left[ x_2^2 e^{\beta H} + (1-x_2)^2 e^{-\beta H} \right]} \right) , \]

recall that for either 1-cycle or 2-cycle fix-point solutions we have \( x_0 = x_2 \), and

\[ Q_0 = \frac{B_0}{B_1 B_2} , \]

It follows

\[ F = -\frac{1}{4} T \log \left( Q_0^2 \frac{x_0^2 e^{\beta H} + (1-x_0)^2 e^{-\beta H}}{x_1^2 e^{\beta H} + (1-x_1)^2 e^{-\beta H}} \right) . \]  \hspace{1cm} (3.7)

In the previous chapter we have discussed the calculation of \( Q_0 \) and fix-point solution \( x_0 \) and \( x_1 \), the free energy can be easily achieved.

In this way, for a recursive structure with an origin point, we can always do this “cut and rearrange” trick to yield the partition function and free energy of the local area (per site) around the origin point.

The entropy is the first derivative of the free energy with respect to the temperature:

\[ s = -\frac{\partial F}{\partial T} . \]  \hspace{1cm} (3.8)
With the free energy and entropy, by the thermodynamic definition we can simply obtain the energy per site (energy density) by

\[
E = F + sT,
\]

(3.9)

A typical thermodynamic behavior of a Husimi square lattice with \( J = -1 \) and all other parameters to be 0 is shown in figure 3.2:

In figure 3.2, the free energy of two solutions are the same at high temperature. At the melting temperature \( T_m \) the 1-cycle’s free energy differs from 2-cycle’s and is less stable. The continuous entropy at \( T_m \) of 1-cycle implies the supercooled liquid state, while the entropy of 2-cycle state decrease implies the crystallization. Although here the entropy decrease is not a discontinuous jump, which is the typical behavior of first order melting transition, we may still treat it as the coexisting phases point since the 2-cycle state is the most stable state here. Furthermore, the detailed discussion in Chapter 4 will shown that we are able to get a first order transition with discontinuous entropy change via the setup of energy parameters.

Another interesting entropy behavior can be observed if we continue to decrease the temperature. At \( T = 1.1 \), the 1-cycle state (supercooled liquid) quickly decrease to zero and become negative. This is the Kauzmann’s paradox and the ideal glass transition. The negative entropy is unphysical in nature, thus the metastable state must undergo a transition and change to the glass state at \( T_K \).

The thermodynamics of 1 and 2-cycle solutions agree with our anti-ferromagnetic model. As discussed in Chapter 1, the anti-ferromagnetic Ising model prefer to anti-align neighbor spins, therefore the 2-cycle state should have the lowest energy, i.e. crystal, while the 1-cycle solution represents the metastable state with higher energy.
Figure 3.2 The free energy, entropy and energy vs temperature curves of Husimi square lattice. The neighbor interaction $J = -1$ and all other parameters are 0.
2) The thermodynamics of lattice #1

We are following the Gujrati trick to solve the free energy and consequent thermal functions of the surface/thin film recursive lattice. Although the basic principle is the same, the asymmetrical structure on the surface of lattice #1 requires further tricks to do the calculation.

If we take a random site on the surface as the origin, to do the “cut and rearrange” trick, we need to select a local area around the origin, and find matching sub-trees contributing to the local area. Here the matching is more specific than it is in a homogeneous bulk lattice. For example in the Husimi lattice discussed in previous section, all the sites are identical, thus if two sites have the same ratios (solution $x$) on them, the sub-trees cut off from them can be hooked up together to make a new lattice. However, the sites on the surface of lattice #1 have three different situations: on the top of a surface square where the sub-tree’s contribution going out, on the side of a surface square where the sub-tree’s contribution coming in, and on the bottom of a surface square where the bulk tree’s contribution coming in. The matching must be done on sites with exactly the same situations to make an identical but small lattice, but the asymmetrical structure of lattice #1 makes the cutting and matching impossible. However we select an origin local area and cut the sub-trees, there will always be two sub-trees left and cannot be matched with each another. Two example cuttings are shown in figure 3.3.

Figure 3.3 shows two cutting schemes, with “1 square and 2 single bonds” area and “2 squares and 4 single bonds” area respectively. In the cutting scheme #1, by removing the local area surrounded by the blue curves, we have four sub-tree at the point A, A’, B and B’. The two sub-trees on A and A’ can be linked together to form a smaller lattice but
Figure 3.3 Two example cuttings on the surface of lattice demonstrating that the smaller tree matching cannot be done
with exactly the same structure. While the sub-trees on B and B’ obviously do not match with each other, since they are a bulk sub-tree on B and a surface sub-tree contributing the top site of a surface square.

In the cutting scheme #2, the local area of “2 squares and 4 single bonds” is bounded by the green curves. In this way the sub-trees on C and C’ can form a smaller lattice. The two bulk sub-trees on D and D’ also can be hooked up together since the two sites on D and D’ are identical. Although the new formation is not identical to the entire lattice, we can still count its partition function and handle the ratio calculation. However the same difficulty, as we encountered in scheme #1, presents on the sites E and E’. The E site is at the side of a surface square while the E’ site is on the top.

Therefore, either we choose odd or even numbers of basic units as local area around origin, the Gujrati trick cannot be done as the same as the two schemes discussed above. We have to somehow modify the origin structure to avoid the problem of asymmetry. As shown in figure 2.13, the single bond and square unit have a “head-to-side” connection, that is, following the calculation direction, the sub-tree coming from a single bond is always linked to the side site of next level’s square, or vice versa. This arrangement is designed to make the structure uniform on the surface, but it also causes the asymmetry. For the thermodynamic calculation at the origin, it is necessary to make one “head-to-head” connection as the origin of the surface, as shown in figure 3.4

In this way, we have two infinite and identical surface trees connected in a “head-to-head” style, this single bond is then the origin of our entire lattice, and except for this bond, all other surface single bonds are in “head-to-side” connection. Starting from the origin, the closest squares can be labeled as level 1; the second closest squares are on
Figure 3.4. The modification on the surface of lattice #1 and the cutting area around the origin
level 2 and so on. As shown in figure 3.4, by the selection of four squares and six single bonds as the local area, we can form one identical lattice on level 1 at the sites A and A’, two identical lattices on level two at the pairs B and B’, C and C’. The sub-trees cut at D, D’, E and E’ are identical bulk trees so we can pair them to form two bulk lattices. Now we can easily derive the free energy of the local area to be:

$$F_{loci} = -T \log \left( \frac{Z_1}{Z_2 Z_2 Z_B} \right).$$  \hspace{1cm} (3.10)

Unlike the point origin in Husimi lattice, here the origin is a single bond unit. The total partition function thus has four terms due to the four possible states of the single bond:

$$Z_0 = Z_0^U (+) Z_0^L (-) e^{-\beta J} + Z_0^U (-) Z_0^L (+) e^{-\beta J} + Z_0^U (+) Z_0^L (-) e^{\beta J} + Z_0^U (-) Z_0^L (+) e^{\beta J}.$$  \hspace{1cm} (3.11)

To specifically track the spins in the origin area and rematch the sub-trees we define the two sub-trees meeting at the origin bond as “upper” and “lower” parts. In equation (3.11), the superscript U or L is to indicate the upper or lower part of the lattice. Take the first term for example, if the upper site of the origin single bond is occupied by + spin and the lower site is occupied by − spin, then the partial partition function of the upper branch is $Z(\pm)$, while the PPF of the lower branch is $Z(\mp)$, the local weight here is $e^{-\beta E}$ where $E = -\bar{J}S_0^U S_0^L - \bar{H}(S_0^U + S_0^L)$ is the interaction of the single bond. For convenience here the magnetic field $H$ is set to be zero. With four possible states of the origin single bond, we have four terms in equation (3.11).

Similar integration can be employed to form the partition functions of smaller lattice we rearranged in equation (3.10). The ratio of partition functions can be represented by
the solutions and polynomials which have been achieved in Chapter II. However in Chapter II, we go along the surface and calculate the solution on each site and the polynomial ratios step by step, these detailed solutions are not necessary here and make it complicated to determine the equation (3.10). Here we redefine the basic unit as one square and two single bonds linked on its side as shown in figure 3.5:

By the selection of this rectangle basic unit, in the upper or lower branch we simply have two units contributing to the sides of next unit, and recursively the whole branch contributing to the origin bond, as indicated by the arrows in the lower part in figure 3.4. The contribution of bulk tree can be treated as a constant. The calculation based on this selection will provide only one solution as $x^L$ or $x^U$ on the output site, regardless of it is 1-cycle and 2-cycle solutions on the surface. This single solution is sufficient for us to determine the equation (3.10). For instance, if we look at the smaller lattices rearranged on points AA' in figure 3.4, we can see that for the calculation of this smaller tree, we will only need the solution $x^L$ and $x^U$ because they are on the output sites A and A'.

Similarly, for either $x^L$ or $x^U$, we define

$$z_m(S_m) = \begin{cases} x_m(S_m = +1) \\ y_m(S_m = -1) \end{cases},$$

and $Z_m(+) = B_m x_m, Z_m(-) = B_m y_m$ with $B_m = [Z_m(+) + Z_m(-)]$, then

$$z_m(S_m) = \frac{B_{m+1}B_B}{B_m} \sum_{\Gamma} \left[ \prod_{\{m+1\}} z_{m+1}(S_{m+1}) \right] z_B(S_B) \omega(\Gamma),$$

(3.12)

where the $S_B$ is the index of the site linked to the bulk tree.

With six spins the rectangle unit has 64 possible configurations thus we can introduce the polynomials:
Figure 3.5. The redefined unit on the surface tree of lattice #1
Then we can obtain the 1-cycle recursive relation:

\[ x_m = \frac{Q_m(x_{m+1})}{Q_m(x_{m+1})}. \]

And the fix-point solution is the one cycle solution \( x^L \) or \( x^U \), although the actual solution on the surface may be either 1-cycle or 2-cycle.

It is important to clarify that the solution \( x^L \) or \( x^U \) are exactly the same to the solutions we achieved on the surface in Chapter II. The reason we re-select the basic unit is to obtain a simple polynomial \( Q \) for the calculation in equation (3.13) and (3.14), otherwise it will be a much more complex form by being represented by the polynomials in equations (2.17) and (2.22).

Now we may rewrite equation (3.10)

\[
F_{local} = -T \log \left( \frac{(Q_m^U/Q_m^L)^2}{(x^U y^L e^{-\beta J} + y^U x^L e^{-\beta J} + y^U y^L e^{\beta J})^2 (x^R y^L e^{\beta H} + y^U y^R e^{-\beta H}) (x^L y^R e^{\beta H} + y^L y^R e^{-\beta H})} \right). \quad (3.15)
\]

This local area contains 14 sites, thus the averaged free energy on each site is

\[
F = \frac{1}{14} F_{local}.
\]
Figure 3.6. The free energy behaviors of 1-cycle and 2-cycle solution of lattice #1 with thickness =19, $J = -1$, $\bar{J} = -1$ and all other parameters to be zero.
An example free energy behaviors of 1-cycle and 2-cycle solution of lattice #1 with thickness =19, neighbor interaction $J = -1$, surface neighbor interaction $\tilde{J} = -1$ and all other parameters to be zero is shown in figure 3.6

An interesting phenomenon can be observed from figure 3.6. The free energy of 2-cycle solution (crystal state) is higher than the free energy of metastable state between $T = 1.7$ to 2.1. This is different from the bulk behavior in figure 3.2. The cross point of 1 and 2-cycle’s free energy at lower temperature can be determined to be the melting transition. Above the melting temperature, our results indicate that the anti-aligned spins arrangement is less stable than the 0.5 solution. This behavior has not been investigated, yet it is not clear whether it is simply unphysical or it implies a “super-heated crystal” state.

Below the melting temperature the behavior is similar to the bulk system. The 2-cycle solution represents the crystal state with a lower free energy and continues to decrease to the free energy of ideal crystal. While the free energy of 1-cycle solution, the metastable state, will reach a minimum point than bind back, this unphysical behavior implies the ideal glass transition.

With equations (3.8) and (3.9) we can easily calculate the energy density and entropy from the free energy. The figure 3.7 shows the thermodynamic behaviors derived from the free energy in figure 3.6:

In figure 3.7 the black line with arrow on the entropy and energy density show the melting transition at the cross point of free energies. The entropy of 1-cycle solution will step to 2-cycle solution’s entropy. The calculation program only provides two
Figure 3.7. The thermodynamic behaviors of lattice #1 with $J = -1, \bar{J} = -1$ and all other parameters to be zero
independent curves of 1 and 2-cycle solutions. The melting transition on entropy and energy density curves requires an artificial indication shown as the black arrows in figure 3.7.

The ideal glass transition temperature $T_K$ can be clearly observed by the negative entropy of 1-cycle solution. However, since the melting transition is indicated by the cross point of free energy curves, here the entropy and energy density shows a discontinuous gap between two solutions. Therefore at crystallization point the entropy must undergo a step drop indicated by the black arrows in figure 3.7. Comparing to the bulk system behavior, the melting transition is a first order transition on the surface because of the discontinues entropy jump. The detailed discussion on surface thermodynamics and the surface effect comparing with bulk system will be presented in Chapter IV.

3) The thermodynamics of lattice #2

Comparing to the lattice #1, the simpler structure and approximation property of lattice #2 make the thermodynamic calculation on the surface much easier. The figure 3.8 shows the surface structure and the cutting scheme around the origin of lattice #2:

![Figure 3.8. The cutting scheme around the surface origin of lattice #2](image)

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Due to the symmetrical structure and uniform solution on the surface of lattice #2, we can randomly select a site on surface as the origin point. The local area is chosen to be two triangle units joint on the origin point. In this way, we can put two sub-trees contributing to the point A and A’ together to make a identical lattice, and two bulk trees B and B’ together to make a whole bulk lattice. The free energy per site in the local area is given as:

\[
    F_{\text{local}} = -\frac{1}{3} T \log \left( \frac{Z_0}{Z_1 Z_2} \right). 
\]  

(3.16)

From the equations (2.28-2.31) we can calculate the ratio of partition functions as

\[
    F_{\text{local}} = -\frac{1}{3} T \log \left( \frac{Q_2^2}{x_B \beta H + (1 - x_B)^2 e^{-\beta H}} \right). 
\]

Then the entropy and energy density can be achieved by equations (3.8) and (3.9). An example thermodynamics behaviors of a triangle surface with \( J = -1 \) and other parameters to be 0 is shown in figure 3.9.

The free energy behavior similar to the lattice #1 can be observed in figure 3.11. The free energy of two solutions differs at \( T = 2.8 \), below which the 2-cycle solution free energy is unstable and unphysical until a cross point is reached at \( T = 1.33 \), which is the melting transition. With continuously decreased temperature, the entropy of 2-cycle solution approaches to zero while the entropy of 1-cycle becomes negative at \( T = 0.69 \), which is the ideal glass transition temperature.

In a short conclusion, both lattice #1 and #2 are constructed by particular approximations however the thermodynamics calculation on either lattice show the similar results, and the transition features are as expected. The strange behavior on the unstable 2-cycle solutions above the melting temperature implies the effect and the
uniqueness of surface. Very few reports on the super-heated crystal have been published, and they are all under certain conditions like the application of electric field. So far to the authors’ knowledge, no theoretical or simulation work has been done on this area. Thus we are unable to determine whether this observation is merely a mathematic existence of super-heated crystal or could imply something practical. Besides this part, the behaviors of both lattices show clear melting and ideal glass transition, this supports the practice of our construction and modeling methods. The details of surface effects, lattice structure effects and comparison, and the effects of variation of parameters will be discussed in Chapter IV.
Figure 3.9. The thermodynamics behaviors of the surface of lattice #2 with $J = -1$ and other parameters to be 0
CHAPTER IV
RESULTS AND DISCUSSION

1) Discussion on the solutions

As introduced in previous chapters, the thermodynamic calculations are mainly based on the solutions $x$, i.e. the ratio of partial partition functions on our lattice. The 1 and 2-cycle solutions of a simple anti-magnetic field Husimi case is presented in figure 2.9, and we have discussed how the melting transition, crystal state and metastable state can be indicated from the solutions. The typical 2-cycle solutions of lattice #1 with $J$ and $\bar{J} = -1$, other parameters as 0, and thickness = 19 are shown in figure 4.1.

The solutions of bulk Husimi lattice from figure 2.9 are also included in figure 4.1 for comparison. With increasing temperature, the solutions on surface converge to 0.5 at lower temperature than the Husimi bulk solution. This indicates a lower melting transition temperature on the surface, which is easy to understand with smaller coordination number and less interactions on the surface, the spins on the surface are easier to be anti-aligned with less energy. Also, unlike the symmetrical solutions we usually have, the 2-cycle solution on the surface is asymmetric. This is because of the hybrid structure on the surface, which defines two different circumstances on the surface square unit and single bond unit respectively. Naturally the spins on the surface square unit has the solution closer to the bulk solution, while the spins on the single bond unit has a less stable (closer to 0.5) solution due to the lower dimension. Depending on the initial seeds adopted for surface calculation, we may also have the other set of surface
solutions symmetric to the one in figure 4.1. The details will be discussed later in figure 4.3.

The 2-cycle bulk solutions \( x_{1\_bulk} \) and \( x_{2\_bulk} \) are the solutions at our bulk origin (figure 2.15). Since the Husimi lattice plays the bulk portion in our thin film lattices, we can expect the bulk origin solution to be identical to the solutions of Husimi lattice if the thickness is large enough to ignore the effects of surface to bulk, and this expectation is confirmed in the region \( T < 2 \). However the 2-cycle bulk solutions differ from the Husimi lattice solutions, and converge to 0.5 solution quickly above \( T = 2 \). Since the bulk solution comes to be almost steady with thickness larger than 19, this difference is not really caused by the surface effect. Our calculation requires a set of initial seeds for the recursive calculation, as the procedure described in figure 2.15, the bulk calculation takes the surface solution as its initial seed, in this way, once the surface solution reaches 0.5, the initial seeds of 0.5 will immediately affect the recursive calculation inside the bulk and converges the bulk origin solutions to be 0.5. The bulk origin solutions at converging point with different thickness are shown in figure 4.2. We can see the convergence occurs, with very slight differences, no matter how large the thickness is, while theoretically, we should have the bulk origin solutions to be identical with Husimi bulk solutions. Simple to say, because of the property of recursive calculation, the bulk origin solution will be lead away from the exact description by the effect of surface solution in the temperature region between surface melting and Husimi bulk melting transition temperatures, which is not really “surface effect” in nature.

This is also a reason we are not interested in calculating the thermodynamics of the whole lattice #1. Theoretically, the solution on each site of the lattice #1 can be
approached and therefore we can calculate the thermal properties. Nevertheless, there are three facts make this calculation unreliable. First, as mentioned above, in the temperature region between surface melting and Husimi bulk melting transition, the bulk origin solution is affected by the seeds of 0.5 solutions on the surface. Second, the recursive calculation technique requires several steps to reach the fix-point solutions. This implies the calculations on the first few layers closing to the surface are numerical instead of exact calculation. Although for large thickness bulk this error can be neglected, the thermal behaviors associated with exact different layers is not useful. Third, the recursive structure of lattice #1 proportionally generates more surfaces with increasing thickness. Unlike the regular lattice, in which the contribution of surface will be neglected with a sufficient large bulk, the lattice #1 will have half sites on the surface with infinitely large bulk trees. In this way, the thermodynamics on each site is just the averaged value of surface and bulk values. For a short summary, our approach of lattice #1 is good to track the thermal behaviors on the surface with the account of bulk contributions, but not to discover the thermal behaviors change with various thicknesses.
Figure 4.1 The typical 2-cycle solutions of lattice #1 with $J$ and $\bar{J} = -1$, other parameters as 0, and thickness = 19.
Figure 4.2. The bulk origin solutions (upper branch) at converging point with different thickness. The curves of thickness = 19 and 33 almost overlap and cannot be distinguished in the graph.
An important thing to notice is that, the solutions in figure 4.1 do not reflect the whole situation on the surface of lattice #1. Recall the calculations in figure 2.14, the process A and B actually provides two sets of solutions depending on the directions. And recall the calculations in figure 3.5, our origin structure only adopted the solutions from process A to calculate the thermal properties in the local origin area. However in figure 3.5, the origin single bond requires the two spins on it to be preferred with different states, i.e. $x^U$ and $x^L$ to be different at low temperature, although they have the same roles in process A in figure 2.14. Remember that depends on how we assign the initial seeds on the surface, the calculation going into the bulk and going back to the surface in figure 2.11 can give two different seeding back to surface. This raise another two sets of solutions from process A and B in figure 2.14, where we label this set of solutions as “c” (counterpart). To summarize, there are four sets of solutions on the surface of lattice #1, and we only adopt two of them to do the thermal calculations. We also have checked that by either adoption of the other four sets solutions we still have the same thermal behaviors, because these solutions are symmetrical to their counterparts. The four sets of solutions with reference setup (thickness = 19, $J$ and $\tilde{J} = -1$, other parameters = 0) are shown in the figure 4.3.
Figure 4.3. All four sets of solutions with reference setup (thickness = 19, $J$ and $\bar{J} = -1$, other parameters = 0) on the surface on lattice #1.
This in another way demonstrates the complication of lattice #1. Comparing to the rougher but much simpler lattice #2, in the programming practice, lattice #1 costs much longer calculation time, and program bugs like memory overflow often happen. Although the lattice #1 provides a more precise description on the surface, the lattice #2 with triangle surface approximation has a particular merit in practice. The solutions of lattice #2 with reference condition are shown in figure 4.4:

From equation (2.32), the lattice #2 only has a 1-cycle solution on the surface in normal conditions. Or with different seeds from bulk, we may also have another symmetrical 1-cycle solution. This choice does not affect the thermal properties. Similar to lattice #2 we still have a 1-cycle 0.5 solution to describe the metastable state, which is not shown in figure 4.4. For convenience, we are still going to call the stable solution and corresponding thermodynamics “2-cycle” in the following discussion (as the index used in figure 3.11). Although it is important to keep in mind that both stable and metastable solutions are actually in 1-cycle form for lattice #2. Unlike the solutions of lattice #1, this 1-cycle form stable state solution itself does not give out any signal of phase transition, however the thermodynamic calculation based on it can be used to analyze the thermal behaviors of system, in a similar fashion of lattice #1.

In this work, for lattice #2 we are also only going to focus on the surface behaviors with the contributions from bulk, instead of the properties of few layers under surface, which, similar to Lattice #1, involves the non-exact numerical calculation.
Figure 4.4. The solutions of lattice #2 with $J$ and $\bar{J} = -1$, other parameters = 0
2) The transition temperature reduction

In Chapter I we have reviewed recent observation that the presence of a free surface dramatically decreases the transition temperatures of bulk system. By comparing the thermodynamics on the surface/thin film we achieved in Chapter II and III and in the bulk system, our calculations also clearly indicate the reduction of both melting and ideal glass transitions temperature on the surface. Figure 4.5 and figure 4.6 show the free energy comparison of Husimi bulk system and lattice #1 and #2 respectively:

![Figure 4.5. The free energy comparison of Husimi bulk system and lattice #1](image)

Figure 4.5. The free energy comparison of Husimi bulk system and lattice #1
Figure 4.6. The free energy comparison of Husimi bulk system and lattice #2
In both lattice #1 and #2, the melting and ideal glass transition temperature are dramatically decreased comparing to bulk system. In Chapter I we introduced the empirical equation to describe the temperature reduction with the change of the thickness. Since the thickness dependence of transition temperature reduction is not available in our methods, and our calculations focus on the transitions right on the surface, we may compare our results to the ratio of glass transition temperatures of bulk and the thinnest free-standing film in others’ works, either experimental or simulation results.

The $T_K$ reduction ratio of lattice #1 is $0.89/1.1 = 0.809$, and of lattice #2 is $0.688/1.1 = 0.625$. In Forrest and co-workers’ work, the $T_g$ of the thinnest PS film they made is 300K and the $T_g$ of bulk PS is 369K, the reduction ratio is 0.813 [48]. In Torres and co-workers’ MD simulation, this ratio of a free standing film is $0.24/0.3 = 0.8$ [58]. In de Pablo and co-workers’ MC simulation, this ratio is $0.85/1.08 = 0.79$ [61].

By the comparison to above results, we may conclude several things. Firstly, because our results are from the reference case, which is very simple without any particular artificial parameters setup, the fact that our ratios are close to others’ results may only verify the validity or practice of our method. To particularly describe a real system, the setup of energy parameters is the most critical issue. The effects of energy parameters in our model will be discussed in later section. Secondly, the ratio of $T_K$s of lattice #2 is less consistent to other results; this is easy to be expected because lattice #2 was designed with a rough and simple approximation to gain the benefits of easy calculation. Nevertheless it does not dismiss any utility of lattice #2 because the transition temperature can be adjusted by the setup of energy parameters. It only implies that lattice #2 requires some different modification to describe the real system than lattice #1.
Thirdly, The fact that similar reduction can be observed in our small molecular model implies that the lower transition temperature on surface/thin film basically originates from the dimension reduction and less interaction constraints. The unique properties of polymer chain may not be the main reason for transition temperature reduction, although they do play important roles to affect the transition properties.

3) The effects of energy parameters

3.1) Lattice #1

In this section we are going to study the effects of different energy parameters in lattice #1 by the variation of one parameter with other parameters fixed. The thickness is always set to be 19 for providing a fix-point solution guaranteed tree size and relatively shorter calculation time consumption.

In equation (2.6) we specified the diagonal interaction energy parameter on the surface to be $J_p$, differed from the diagonal interaction $J_p$ inside the bulk. And similarly we have $J$, $J'$ and $J''$. This specification is to enable us setup different interaction circumstance on the surface and provide more versatility in our model. However the effect role played by either $J_p$ or its counterpart on the surface $J_p$ are the same. Thus in this section, which is only to discuss the effects of energy parameters, we are going to simplify the case and setup $J_p$ and $J_p$, $J''$ and $J''$ to be the same. In the following sections, for example the notation $J_p = 0$ means $J_p$ is also set to be 0. Nevertheless, a variation with fixed $J$ will be discussed in details, because the nearest-neighbor interaction $J$ and $J$ have a much larger weight in the Hamiltonian and play more critical roles in the system. The
difference setup of $J$ and $\bar{J}$ provides the simulation of surface tension which is critical to the surface properties. The case is different with $J'$ and $\bar{J}'$, which will be discussed later.

3.1.1) The diagonal interaction $J_p$

In the Hamiltonian equation (2.1), since the nearest-neighbor interaction $J$ is also to be negative by the definition of anti-ferromagnetic Ising model, the system prefer an anti-aligned spins arrangement to obtain a lower energy with a negative first term, similarly the second term will contribute to even lower energy as negative, or compete with the first term and lift the energy if it is positive. We can also observe that for an anti-aligned spins arrangement, the diagonal spins pairs are in the same state. Therefore, unlike the nearest-neighbor interaction $J$, a positive diagonal interaction will make the second term to be negative, which encourages the alternating arrangement and increases the transition temperatures (i.e. the crystal is more stable to melt). On the other hand, a negative $J_p$ will compete with the $J$ and trend to destroy the ordered state, which decreases the transition temperature. Because we have four nearest-neighbor and two diagonal interactions in a square unit, the nearest-neighbor interaction outweigh the diagonal interaction. Also, there is no diagonal interaction in the surface single bond unit, which also lowers the contribution of $J_p$. The variation of $J_p$ will only moderately change the transition temperatures on the surface; the overall thermal behaviors are similar to reference condition. We also found that $J_p$ cannot be larger than $\pm0.5$ otherwise stable solutions can not be reached.

The thermal behaviors with four different $J_p$ values 0.2, 0.4, $-0.2$, and $-0.4$ are shown in figure 4.7-10, note that the black arrows between the entropy and energy
density of two states is manually added to indicate the melting transition, i.e. the cross point of free energy of two states:
Figure 4.7. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $\bar{J} = -1$, $J_p = 0.2$ and other parameters = 0
Figure 4.8. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $\tilde{J} = -1$, $J_p = 0.4$ and other parameters = 0
Figure 4.9. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $\bar{J} = -1$, $J_p = -0.2$ and other parameters = 0
Figure 4.10. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and

$$\tilde{J} = -1, J_p = -0.4 \text{ and other parameters} = 0$$
It is obvious that positive $J_p$ will make the system more stable and increase the transition temperatures, or vice versa. The melting and ideal glass transition change with $J_p$ variation is summarized in figure 4.11 and table 2.

Figure 4.11. The transition temperature variations with different $J_p$
Table 2. The transition temperature variations with different $J_p$

<table>
<thead>
<tr>
<th>$J_p$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1.95</td>
<td>1</td>
<td>1.950</td>
</tr>
<tr>
<td>0.2</td>
<td>1.82</td>
<td>0.95</td>
<td>1.916</td>
</tr>
<tr>
<td>0</td>
<td>1.7</td>
<td>0.89</td>
<td>1.910</td>
</tr>
<tr>
<td>-0.2</td>
<td>1.55</td>
<td>0.88</td>
<td>1.761</td>
</tr>
<tr>
<td>-0.4</td>
<td>1.38</td>
<td>0.8</td>
<td>1.725</td>
</tr>
</tbody>
</table>

Another intriguing observation in figure 4.9 and 4.11 can be found: With a negative $J_p$, the unstable part of 2-cycle thermodynamics above the melting temperature is lower, i.e. smaller gap between 1-cycle and 2-cycle solutions. Even we have no clue on this unstable part to be either unrealistic or super-heated crystal; this smaller gap can still be explained by the role of $J_p$. Since the negative $J_p$ will compete with $J$ and make the overall system less stable, in this way the stable state must have a lower energy gap to the metastable states, which is reflected by a smaller difference in free energy or entropy behavior of 1-cycle and 2-cycle solutions.
3.1.2) The quadruplet interaction $J''$

The quadruplet interaction $J''$ is a complicated term. By simply analyzing the fourth term in Hamiltonian eqn. (2.1), it is difficult to give out a clear expectation on the effects of $J''$ since both system preferred or defective structures can give out either positive or negative values of fours spins product, then consequently either positive or negative values of $J''$ can against the crystallization. Trials of $J'' = \pm 0.2, \pm 0.4, \pm 0.6, \pm 0.8$, and $\pm 1.0$ with other parameters fixed are shown in figure 4.12-21:
Figure 4.12. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = -0.2$ and other parameters = 0
Figure 4.13. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = -0.4$ and other parameters = 0
Figure 4.14. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = -0.6$ and other parameters = 0
Figure 4.15. The surface thermodynamics of Lattice #1 with thickness = 19, \( J \) and \( J'' = -0.8 \) and other parameters = 0
Figure 4.16. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = -1.0$ and other parameters = 0
Figure 4.17. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $ar{J} = -1, J'' = 0.2$ and other parameters = 0
Figure 4.18. The surface thermodynamics of Lattice #1 with thickness = 19, \( J \) and \( J'' = 0.4 \) and other parameters = 0

\[ \bar{J} = -1, J'' = 0.4 \text{ and other parameters} = 0 \]
Figure 4.19. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = 0.6$ and other parameters = 0
Figure 4.20. The surface thermodynamics of Lattice #1 with thickness = 19, \( J \) and \( \tilde{J} = -1, J'' = 0.8 \) and other parameters = 0
Figure 4.21. The surface thermodynamics of Lattice #1 with thickness = 19, $J$ and $J'' = 1.0$ and other parameters = 0
From the graphs above, we can see that the parameter $J''$ has a similar effect to $J_p$: positive $J''$ will make the system more stable and increase both transition temperatures, and vice versa. We also found that, unlike the limited value of $J_p$, $J''$ can be assigned with large value such as ± 1.0 without destroying the stable solutions. The transition temperatures variation with different $J''$ are summarized in figure 4.22 and table 3.

![Graph showing transition temperature variations with different $J''$.](image)

Figure 4.22. The transition temperature variations with different $J''$
Table 3. The transition temperature variations with different $J''$

<table>
<thead>
<tr>
<th>$J''$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.89</td>
<td>1.00</td>
<td>1.89</td>
</tr>
<tr>
<td>0.8</td>
<td>1.88</td>
<td>0.98</td>
<td>1.92</td>
</tr>
<tr>
<td>0.6</td>
<td>1.84</td>
<td>0.96</td>
<td>1.92</td>
</tr>
<tr>
<td>0.4</td>
<td>1.78</td>
<td>0.94</td>
<td>1.89</td>
</tr>
<tr>
<td>0.2</td>
<td>1.76</td>
<td>0.92</td>
<td>1.91</td>
</tr>
<tr>
<td>0</td>
<td>1.70</td>
<td>0.89</td>
<td>1.91</td>
</tr>
<tr>
<td>-0.2</td>
<td>1.64</td>
<td>0.86</td>
<td>1.91</td>
</tr>
<tr>
<td>-0.4</td>
<td>1.56</td>
<td>0.80</td>
<td>1.95</td>
</tr>
<tr>
<td>-0.6</td>
<td>1.46</td>
<td>0.76</td>
<td>1.92</td>
</tr>
<tr>
<td>-0.8</td>
<td>1.36</td>
<td>0.69</td>
<td>1.97</td>
</tr>
<tr>
<td>-1.0</td>
<td>1.26</td>
<td>0.62</td>
<td>2.03</td>
</tr>
</tbody>
</table>
One important difference between the effects of $J_p$ and $J''$ can be observed in table 2 and 3: Although both parameter act similar in changing the transition temperature, with the $J''$ variation the ratio of $T_m/T_K$ is relatively constant unless $J''$ is assigned with extraordinary values like ±1.0, while with the $J_p$ variation the ratio of $T_m/T_K$ also changes dramatically. This difference could be very useful in modifying the parameters setup to describe the real systems or experimental results. For a real system, factors affecting the thermodynamics can act in different ways, some of them may lift/reduce both transition temperatures but keep the supercooled liquid region constant, or some may change the window size of supercooled liquid state. In this way, if our model is utilized to describe a particular real system, the experimental parameters effects can refer to different parameters setup.
3.1.3) The surface nearest-neighbor interaction $\bar{J}$

As mentioned above, for convenience we setup the energy parameters in the bulk and on the surface, such as $J_p$ and $\bar{J}_p$, to be the same, because due to the aspect of effects on thermodynamics these parameters should be the same. Nevertheless, our lattice has a fixed bond length (this length is unit 1 in Ising model) between neighbor sites on the surface and in the bulk, and we also know that the asymmetric interaction circumstance and the surface tension are the main reason of unique properties of surface. Therefore with a fixed bond length, we have to somehow modify the surface interaction circumstance to mimic the surface tension or asymmetric interactions. This can only be made possible with different $J$ and $\bar{J}$ setup. Thus in this section we are going to fix the bulk nearest-neighbor interaction parameter $J$ to be $-1$, and observe how the variation of surface bond interaction $\bar{J}$ affect the thermodynamics on the surface. The surface thermal behaviors with $\bar{J} = -0.5, -0.7, -0.9, -1.1, -1.3$ and $-1.5$ are shown in figure 4.23 – 28:
Figure 4.23. The surface thermodynamics of Lattice #1 with thickness = 19, \( J = -1 \),

\[ \bar{J} = -0.5, \text{ and other parameters} = 0 \]
Figure 4.24. The surface thermodynamics of Lattice #1 with thickness = 19, $J = -1$, $\bar{J} = -0.7$, and other parameters = 0
Figure 4.25. The surface thermodynamics of Lattice #1 with thickness = 19, $J = -1$, $\bar{J} = -0.9$, and other parameters = 0
Figure 4.26. The surface thermodynamics of Lattice #1 with thickness = 19, $J = -1$, \[ \bar{J} = -1.1, \] and other parameters = 0
Figure 4.27. The surface thermodynamics of Lattice #1 with thickness = 19, $J = -1$, $\bar{J} = -1.3$, and other parameters = 0
Figure 4.28. The surface thermodynamics of Lattice #1 with thickness = 19, $J = -1$, $\bar{J} = -1.5$, and other parameters = 0
From graphs above we can conclude that larger absolute value of negative $\bar{J}$ makes the system more stable and increases both melting and ideal glass transition temperatures. It also dramatically changes the free energy at low temperature closing to absolute zero, i.e. shift the whole curves up or down. This is different from $J_p$ and $J''$, which only do small shift on thermal curves otherwise their value will be too large to maintain the stable solutions. The variation of $\bar{J}$ revealed that the surface is more stable with large surface tension ($-\bar{J} > -J$), or easier to undergo transitions than in the bulk with small surface tension ($-\bar{J} < -J$). Positive $\bar{J}$ was also been tested however no stable solutions can be reached. This is because the positive $\bar{J}$ will prefer ferromagnetic-aligned spins arrangement which only has 1-cycle solution available. On the other hand it is also hard to imagine a homogeneous system with particles attractive to each other in the bulk but repulsive on the surface. Nevertheless, this situation, even difficult to be related to a real system, can still be studied in lattice #2, which provides natural 1-cycle solution on the surface. The details will be discussed in later sections.

The transition temperatures change with variation of $\bar{J}$ is summarized in figure 4.29 and table 4:
Figure 4.29. The transition temperature variations with different $\bar{f}$
Table 4. The transition temperature variations with different $\bar{J}$

<table>
<thead>
<tr>
<th>$\bar{J}$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.5</td>
<td>1.12</td>
<td>0.55</td>
<td>2.04</td>
</tr>
<tr>
<td>-0.7</td>
<td>1.38</td>
<td>0.7</td>
<td>1.97</td>
</tr>
<tr>
<td>-0.9</td>
<td>1.6</td>
<td>0.82</td>
<td>1.95</td>
</tr>
<tr>
<td>-1</td>
<td>1.7</td>
<td>0.89</td>
<td>1.91</td>
</tr>
<tr>
<td>-1.1</td>
<td>1.8</td>
<td>0.94</td>
<td>1.91</td>
</tr>
<tr>
<td>-1.3</td>
<td>2</td>
<td>1.05</td>
<td>1.90</td>
</tr>
<tr>
<td>-1.5</td>
<td>2.18</td>
<td>1.14</td>
<td>1.91</td>
</tr>
</tbody>
</table>
3.1.4) The triplet interaction $J'$ and magnetic field $H$

It is easy to understand that we have 0.5 solutions at high temperature, and 2-cycle solutions symmetric to 0.5 at low temperature, is because that the magnetic field $H$ is 0, the system has no bias on either $+ \text{ or } -$ spins on a particular site. Thus at high temperature one has 50% probability to be occupied by either $+$ or $-$ spin. Then if a non-zero value of magnetic field $H$ is set, we can expect the 1-cycle solution off the central 0.5 line or asymmetric 2-cycle solutions. Due to energy equation of Ising model, a positive $H$ will prefer more $+$ spins and moves the 1-cycle solution higher than 0.5, or vice versa. In our previous research on bulk Husimi lattice and CRL, the three spins interaction (triplet) $J'$ plays a considerable role in thermodynamics; especially it acts similarly to magnetic field $H$ in changing the bias of spins. The effects of both $H$ and $J'$ were verified in bulk Husimi lattice and CRL.

However, in lattice #1 the $J'$ and magnetic field $H$ are not useful, although we still have them in our lattice model and energy equations. The reason is that, the uneven property of the surface on lattice #1 determines the 1-cycle solution can only be 0.5. If a non-zero magnetic field $H$ or triplet interaction $J'$ presents, the 1-cycle solution on the surface cannot be achieved. The single bond unit does not have triple interaction $J'$ and the effect of $H$ is much smaller than it is in the square unit, therefore the anti-aligning property of the single will always prefer to have different spins on it. In this way, if a 1-cycle solution can be achieved on the single surface bond, it must be the 0.5 solution. Even we can still calculate the thermodynamics of 2-cycle solution on the surface. We must have the corresponding 1-cycle solution to determine the melting and ideal glass transitions.
By the explanation above, we have to abandon the variation of $H$ and $J'$, which is a disadvantage of the lattice #1.

3.2) Lattice #2
3.2.1) The surface nearest-neighbor interaction $\tilde{J}$

By considering that the diagonal interaction parameter has a minor impact on the surface thermal behavior, the surface of lattice #2 is actually a zigzag surface, and the surface bond is just the upper bond of surface square unit. One surface site is linked with two surface bonds, which are both the surface itself and the connections between surface site and the bulk tree. Therefore, the interaction $\tilde{J}$ on this bond plays a critical part in lattice #2’s thermodynamics. The thermal behaviors with $J$ fixed to be $-1$, other parameters to be 0, and $\tilde{J} = -0.5, -0.7, -0.9, -1.1, -1.3, \text{ and } -1.5$ are shown in figure 4.30 - 35
Figure 4.30. The surface thermodynamics of Lattice #2 with $J = -1, \tilde{f} = -0.5$, and other parameters = 0
Figure 4.31. The surface thermodynamics of Lattice #2 with $J = -1, \bar{f} = -0.7$, and other parameters $= 0$
Figure 4.32. The surface thermodynamics of Lattice #2 with $J = -1, \bar{f} = -0.9,$ and other parameters $= 0$
Figure 4.33. The surface thermodynamics of Lattice #2 with $J = -1, \tilde{f} = -1.1,$ and other parameters $= 0$
Figure 4.34. The surface thermodynamics of Lattice #2 with $J = -1$, $\bar{f} = -1.3$, and other parameters $= 0$
Figure 4.35. The surface thermodynamics of Lattice #2 with $J = -1, \bar{J} = -1.5, \text{ and other parameters } = 0$
Similar to the $\tilde{J}$ in lattice #1, the larger absolute value of negative $\tilde{J}$ makes the system more stable and increases both melting and ideal glass transition temperatures. It also dramatically changes the free energy at low temperature closing to absolute zero. Except that the $\tilde{J}$ in lattice #2 act more severely when it is small. For $\tilde{J} = -0.5$, the ideal glass transition falls out of the calculation region and the supercooled liquid region becomes very small. The transition temperature changes with various $\tilde{J}$ are summarized in figure 4.36 and table 5.

Figure 4.36. The transition temperature variations with different $\tilde{J}$ in lattice #2
Table 5. The transition temperature variations with different $\tilde{J}$ in lattice #2

<table>
<thead>
<tr>
<th>$\tilde{J}$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.5</td>
<td>0.65</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>-0.7</td>
<td>0.92</td>
<td>0.6</td>
<td>1.53</td>
</tr>
<tr>
<td>-0.9</td>
<td>1.2</td>
<td>0.63</td>
<td>1.90</td>
</tr>
<tr>
<td>-1</td>
<td>1.33</td>
<td>0.69</td>
<td>1.93</td>
</tr>
<tr>
<td>-1.1</td>
<td>1.5</td>
<td>0.77</td>
<td>1.95</td>
</tr>
<tr>
<td>-1.3</td>
<td>1.8</td>
<td>0.9</td>
<td>2.00</td>
</tr>
<tr>
<td>-1.5</td>
<td>2.1</td>
<td>1.01</td>
<td>2.08</td>
</tr>
</tbody>
</table>
Comparing to the $\bar{J}$ in lattice #1, positive values is also possible here because we naturally have 1-cycle solutions representing ordered state in lattice #2. Although for a homogeneous system it is not likely to have attractive spins in the bulk while repulsive spins on the surface, we have tested a positive value $+1.5$ of $\bar{J}$ to explore its properties. With $\bar{J} = 1.5$ we have the exactly same behavior of $\bar{J} = -1.5$. It indicates that due to the 1-cycle solution nature, the sign of nearest-neighbor interaction parameter do not affect the thermodynamics, the transition is only affected by the magnitude of $\bar{J}$. (figure 4.37)
Figure 4.37. The surface thermodynamics of Lattice #2 with $J = -1, \bar{J} = +1.5$, and other parameters = 0
3.2.2) The diagonal interaction $J_p$

The role of $J_p$ in lattice #2 is different than in lattice #1. For the triangle unit, the two top sites are affected by the lower site, they are prefer to be occupied by the same state spins other than the state of lower site and that is why we only 1-cycle solutions on the surface. The diagonal interaction between the two top sites therefore is the only competition to the nearest-neighbor interaction $\tilde{J}$. Thus the different setups of $J_p$ and $\tilde{J}_p$ may provide something interesting behaviors. For the same value of $J_p$ and $\tilde{J}_p$ we may expect a similar effect of $J_p$ in lattice #1. The transition temperature changes of $\tilde{J}_p = J_p = \pm 0.2, \pm 0.4$ and $\pm 0.6$ are shown in figure 4.38 and table 6:

![Figure 4.38. The transition temperature variations with different $J_p$ in lattice #2](image)

Figure 4.38. The transition temperature variations with different $J_p$ in lattice #2
Table 6. The transition temperature variations with different $J_p$ in lattice #2

<table>
<thead>
<tr>
<th>$J_p$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
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<td>0.85</td>
<td>0.4</td>
<td>2.13</td>
</tr>
<tr>
<td>-0.2</td>
<td>1.1</td>
<td>0.6</td>
<td>1.83</td>
</tr>
<tr>
<td>0</td>
<td>1.33</td>
<td>0.69</td>
<td>1.93</td>
</tr>
<tr>
<td>0.2</td>
<td>1.54</td>
<td>0.75</td>
<td>2.05</td>
</tr>
<tr>
<td>0.4</td>
<td>1.73</td>
<td>0.85</td>
<td>2.04</td>
</tr>
<tr>
<td>0.6</td>
<td>1.9</td>
<td>0.92</td>
<td>2.07</td>
</tr>
</tbody>
</table>
An interesting graph (figure 4.39) can be obtained with the setup \( J_p = -0.5 \) and \( \overline{J}_p = 0.5 \), the unstable part of 2-cycle solutions above the melting transition disappears and we have a similar behavior to the Husimi bulk lattice, that the free energies of two solutions start to differ from each other at the melting temperature. Although the unstable region of 2-cycle solutions have not been studied, we yet know it is simply unphysical or implies superheated crystal, this phenomenon could be a clue to investigate this unrevealed problem. In contrast, \( J_p = -0.5 \) and \( \overline{J}_p = 0.5 \) gives a much longer unstable part of 2-cycle solutions. (figure 4.40)
Figure 4.39. The surface thermodynamics of Lattice #2 with $J = -1, \bar{J} = -1, J_p = 0.5, \bar{J}_p = -0.5$ and other parameters = 0
Figure 4.40. The surface thermodynamics of Lattice #2 with $J = -1, \bar{J} = -1, J_p = -0.5,$

$\bar{J}_p = 0.5$ and other parameters $= 0$
3.2.3) The triplet interaction $J'$

Unlike the lattice #1, the homogeneous triangle surface in lattice #2 can have stable solutions with various setups of $J'$ because there is no single bond on the surface and all the spins are within the triplet interaction. The thermal behaviors with $J' = \pm 0.1$ and $\pm 0.3$ are shown in figure 4. 41 - 44:
Figure 4.41. The surface thermodynamics of Lattice #2 with $J = -1$, $J' = -1$, $J'' = -0.3$, and other parameters $= 0$
Figure 4.42. The surface thermodynamics of Lattice #2 with $J = -1, \tilde{J} = -1, J' = -0.1,$ and other parameters = 0
Figure 4.43. The surface thermodynamics of Lattice #2 with $J = -1$, $\bar{J} = -1$, $J' = 0.1$, and other parameters = 0
From graphs above we can conclude that negative $J'$ increases the transition temperatures or vice versa. Comparing to the effect of $J'$ in lattice #1, the $J'$ here has an impressive effect on the thermodynamics, i.e. a sight change will dramatically change the overall thermal behaviors. The transition temperature changes are summarized in table 7:

Since the $J'$ plays a more dominant role in lattice #2, the value setup of $J'$ is limited to be relatively small. Two abnormal behaviors can be observed with the setup $J' = 0.3$ and $J' = -0.5$. In the first case, the 2-cycle solutions will never have a lower free energy than 1-cycle solution. Even it has a lower entropy at low temperature we still cannot determine the transition between two solutions since there is no cross point. On the other hand the 1-cycle solution still undergoes Kauzmann paradox. Thus the only reasonable understanding is that under this condition the crystal state is not achievable. With temperature decreasing, we will only have supercooled liquid and glassy state (figure 4.44). Similarly in the second case, the free energy of 2-cycle solution still has an unstable part but the cross point disappears, the free energy undergo an unphysical curvature and jumps to an ordered state. The melting transition cannot be determined (figure 4.45).
Table 7. The transition temperature variations with different $J'$ in lattice #2

<table>
<thead>
<tr>
<th>$J_p$</th>
<th>$T_m$</th>
<th>$T_K$</th>
<th>$T_m/T_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3</td>
<td>1.90</td>
<td>0.76</td>
<td>2.50</td>
</tr>
<tr>
<td>-0.1</td>
<td>1.55</td>
<td>0.7</td>
<td>2.21</td>
</tr>
<tr>
<td>0</td>
<td>1.33</td>
<td>0.69</td>
<td>1.93</td>
</tr>
<tr>
<td>0.1</td>
<td>1.05</td>
<td>0.69</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Figure 4.44. The surface thermodynamics of Lattice #2 with $J = -1$, $\tilde{J} = -1$, $J' = 0.3$, and other parameters $= 0$
Figure 4.45. The surface thermodynamics of Lattice #2 with $J = -1, \bar{J} = -1, J' = -0.5,$ and other parameters $= 0$
CHAPTER V

CONCLUSION

The glass transition has been studied for several decades and still remains a challenging topic today. Especially the glass transition on the surface/thin film drew much interest in the past twenty years, since the finite size effects are believed to be helpful to reveal the properties of glass transition, and this research itself is critical in surface/thin film related industry. Both experimental and simulation/computation works have been done in this area, and almost all focus on polymer systems. On the other hand, the recursive lattice with Ising spins has been used to investigate the supercooled liquid state and ideal glass transition for bulk system in our groups’ early work. In this work, we applied recursive lattice technique to investigate the thermodynamics and ideal glass transition on the surface/thin film of small molecules system with a theoretical base.

Two recursive lattices were constructed to describe a regular finite size square lattice, with a 2D bulk surrounded by 1D surface. The lattice #1 utilizes the finite-sized Husimi lattice, which is integrated by 2D square units, to be the bulk part, and adopts single bond to connect the finite-sized bulk parts. These single bonds and the outsider bonds of bulk trees assemble the surfaces surrounding the bulk part and slipping through independent bulk parts. The lattice #2 originates from a diagonal cutting on the regular square lattice and approximates the zigzag cutting edge to be the surface. The zigzag structure can be considered to be a surface assembled by triangle units, and then infinite large Husimi trees are linked on the triangle units to represent the bulk parts. Both lattices are
constructed with particular approximations and compromises; however they are believed to be reliable approximation to the regular square lattice in the aspect of coordination numbers, i.e. the number of neighbor sites of one site. The coordination number is 4 inside the bulk and 3 on the surface in both lattices.

The Ising model consists of variables called spins. Each spin has two possible states + or −. In our work we assigned anti-ferromagnetic interaction in the model, the system will prefer different spin states in neighbor pairs. In this way the alternative spins arrangement represents the ordered states with the lowest energy at certain temperature. If we take one spin state as particle and the other state as void, or one state as particle A and the other as particle B, then the Ising language is very suitable to describe compressible monatomic system or small molecule alloy.

The partition function of a sub-tree with its base spin state fixed is defined as partial partition function (PPF). Based on the recursive properties, the PPF of one sub-tree can be expressed as a function of the PPFs of its sub-sub-trees and a local weight. This recursive relation enables us to derive the ratio of PFFs on one site. This ratio is called solution in our model, and it is related to the possibility of one site to be occupied by either + spin or −. Two kinds of stable solutions usually can be achieved by recursive calculation. One is in 2-cycle form and represents the ordered state, the other is in 1-cycle representing the amorphous/metastable state. For lattice #2, we do not have 2-cycle solution on the surface however there is another stable 1-cycle solution available to represent the ordered state.

With the solutions calculated on the surface sites, we can calculate the thermodynamics of the local area around the origin on the surface by Gujrati trick. The
integration of thermal behaviors of 2-cycle and 1-cycle solutions can indicate the melting transition by the cross point of free energies of two solutions, and the ideal glass transition by the negative entropy of 1-cycle solution. Our results agree with others’ work that the transition temperatures are dramatically reduced on the surface/thin film comparing to them in the bulk. Nevertheless our work shows that, regardless of specific properties of particular materials, either polymer or small molecules, this transition temperature reduction can be simply due to the dimension downgrade and lower interaction energy on the surface.

The effects of different interaction energy parameters other than nearest-neighbor interaction such as diagonal interaction, three spins (triplet) interaction and four spins (quadruplet) interaction were investigated. The variation of energy parameter could either increase or decrease the stability of system and change the transition temperatures according to the Hamiltonian. The parameters on the surface were specified in our program. Therefore we can setup different values in the bulk and on the surface to mimic the surface tension. The unique behaviors of energy parameters can be used to setup a certain model to describe the real system.

We have explored the basic theoretical properties of our model. However it is still a challenge to connect this abstract model to the real systems. For example, the relationship between the experimental parameters and the fitting energy parameters in our model must be specified for particular simulation. The spin particles in our research have a very simple attractive or repulsive interaction with unit 1, thus further modification will be necessary if more complicated interaction potentials are to be applied to simulate real systems. Nevertheless, with a rough comparison and agreement with others’ work, either
experimental or simulation, we are confident that our modeling is practical in principle and has an expectable potential in further applications.
REFERENCES


APPENDIX

In this appendix the codes of all the C++ programs used to obtain the results in the dissertation are presented. The program I is for multi-branch Husimi bulk calculation. The program II is to obtain the solutions on the lattice #1. The program III is to calculate the thermodynamics from the solutions of program II. The program IV is the calculation on lattice #2.

Program I

```cpp
#include <stdio.h>
#include <math.h>
#include <stdlib.h>

int B=3,R;//branch number of model
double a1,a2,a3,a4,a5,a6,a7,a8,a9,a10;
double Q1(double x0, double x1);
double Qtemp(double x0, double x1);
double Q11(double x00);
double Qtemp1(double x00);

int main() {
    FILE *fp;//define a file pointer to stand for file name out.txt
    if((fp=fopen("out.txt","w+b"))==NULL) {
        printf("can not create or open the file out.txt\n");
    } //if out.txt cannot be create or open,display error message
    FILE *fp2;//define a file pointer to stand for file name out.txt
```
if((fp2=fopen("out2.txt","w+b"))==NULL) {
    printf("can not create or open the file out2.txt\n");
} //if out.txt cannot be create or open,display error message

double x0,x1,x00,x11,k,kp,k1,k2,v,T1,T0,deltaT,J,Jp,J1,J2,h,FE0,FE,S,E;//FE1;
//FE is free energy; S is entropy; E is energy
double dFE,d2FE,rFE=0,rrFE=0,dFE1,d2FE1,rFE1=0,rrFE1=0;
double w1,w2,w3,w4,w5,w6,w7,w8,w11,w22,w33,w44,w55,w66,w77,w88,
FILE *fp3;
if((fp3=fopen("in.txt","r"))==NULL) {
    printf("can not open the file in.txt\n");
}

fscanf(fp3,"%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf",
      &T0,&T1,&deltaT,&J,&Jp,&J1,&J2,&h);
//printf("The number of branches\n");
//scanf("%i%c",&B);

R=B-1;
//printf("x0\n");
//scanf("%lf%c",&x0);
//printf("x1\n");
//scanf("%lf%c",&x1);
//printf("x00\n");
//scanf("%lf%c",&x00);
x0=0.51880162;
x1=0.48119811;
x00=0.99;
for (double T=T0;T<=T1;T=T+deltaT)
{
k=exp(-1/T*J);//neighborhood interaction
kp=exp(-1/T*Jp);//diagonal interaction
k1=exp(-1/T*J1);//three bodies interaction
k2=exp(-1/T*J2);//four bodies interaction
v=exp(1/T*h);//magnetic field

a1=1/(pow(k,-4)*pow(kp,-2)*pow(k1,-4)*pow(v,-3));
a2=1/(pow(k1,2)*pow(v,-1));
a3=1/(pow(k1,-2)*pow(v,3));
a4=1/(pow(k,4)*pow(kp,-2)*pow(v,1));
a5=1/(pow(kp,2)*pow(v,1));
a6=1/(pow(k1,2)*pow(v,-3));
a7=1/(pow(k,4)*pow(kp,-2)*pow(v,-1));
a8=1/(pow(k,-4)*pow(kp,-2)*pow(k1,4)*pow(v,3));
a9=1/(pow(k1,-2)*pow(v,1));
a10=1/(pow(kp,2)*pow(v,-1));
double x2,q1,q2,qtemp,xtemp,acc,ii,c1,c2,c3;
for(int i=2;i<=10000;i++)
{
q1=Q1(x0,x1);
qtemp=Qtemp(x0,x1);
\[ q_2 = q_1 + q_{temp}; \]
\[ x_2 = q_1 / q_2; \]

\[ ii = i; \]

\[ acc = \text{fabs}(x_2 - x_0); \]
\[ x_0 = x_1; \]
\[ x_1 = x_2; \]
\[ \text{fprintf}(fp2, "\n%.12lf", x_2); \]
\[ \text{if} \ (acc < 0.0000000000001) \ \text{break}; \]

\[ \text{if}(x_0 \geq x_1) \]
\[ \{ \]
\[ \text{xtemp} = x_0; \]
\[ x_0 = x_1; \]
\[ x_1 = \text{xtemp}; \]
\[ \} \]

\[ \text{printf}("\nT=%lf\n", T); \]
\[ \text{printf}("i=%lf\n", ii); \]
\[ \text{printf}("accuracy=%.12lf\n", acc); \]
\[ \text{fprintf}(fp, "\n%.12lf ", T); \]
\[ \text{for(int k=0;k<=1;k++)} \]
\[ \{ \]
\[ q_1 = Q_1(x_0, x_1); \]
\[ q_{temp} = Q_{temp}(x_0, x_1); \]
q2 = q1 + qtemp;

x2 = q1 / q2;

printf("Xm+%d=%.12lf\n", k, x2);
fprintf(fp, ".12lf ", x2);
x0 = x1;
x1 = x2;
}
q1 = Q1(x0, x1);
qtemp = Qtemp(x0, x1);
q2 = q1 + qtemp;

c1 = pow((pow(x1, B) * v + pow((1 - x1), B) * (1/v)), 2*(B-1));
c2 = pow((pow(x0, B) * v + pow((1 - x0), B) * (1/v)), (B-2));
c3 = log(pow(q2, B) / (c1 * c2));
FE0 = -T * 0.25 * c3;

printf("FE0=%.12lf\n", FE0);
fprintf(fp, ".12lf ", FE0);

// the first and second derivative of free energy

dFE = (FE0 - rFE) / deltaT;
printf("dFE/dt=%.12lf\n", dFE);
fprintf(fp, ".12lf ", dFE);
rFE = FE0;
\[ d2FE = \frac{(dFE - \text{rrFE})}{\text{deltaT}}; \]

\[ \text{printf(}"d2FE/dt2=\%.12lf/n",d2FE); \]

\[ \text{fprintf(fp","%.12lf",d2FE);} \]

\[ \text{rrFE} = \text{dFE}; \]

// energy calculation
\[ \text{w1} = \text{exp}(-1/\text{T}*(4*J+2*Jp+4*J1-3*h)); \]
\[ \text{w2} = \text{exp}(-1/\text{T}*(-2*J1+h)); \]
\[ \text{w3} = \text{exp}(-1/\text{T}*(2*J1+3*h)); \]
\[ \text{w4} = \text{exp}(-1/\text{T}*(-4*J+2*Jp+h)); \]
\[ \text{w5} = \text{exp}(-1/\text{T}*(-2*Jp+h)); \]
\[ \text{w6} = \text{exp}(-1/\text{T}*(-2*Jp+h)); \]
\[ \text{w7} = \text{exp}(-1/\text{T}*(-2*J1-h)); \]
\[ \text{w8} = \text{exp}(-1/\text{T}*(-2*J1-h)); \]
\[ \text{w11} = \text{exp}(-1/\text{T}*(-2*J1-3*h)); \]
\[ \text{w22} = \text{exp}(-1/\text{T}*(-4*J+2*Jp-h)); \]
\[ \text{w33} = \text{exp}(-1/\text{T}*(4*J+2*Jp-4*J1+3*h)); \]
\[ \text{w44} = \text{exp}(-1/\text{T}*(2*J1+h)); \]
\[ \text{w55} = \text{exp}(-1/\text{T}*(2*J1+h)); \]
\[ \text{w66} = \text{exp}(-1/\text{T}*(2*J1+h)); \]
\[ \text{w77} = \text{exp}(-1/\text{T}*(-2*Jp-h)); \]
\[ \text{w88} = \text{exp}(-1/\text{T}*(-2*Jp-h)); \]
\[ e_1 = w_1 \times (4J+2Jp+4J1-4h/B) \times x_0 \times (x_1R) \times (x_1R) \times (x_0R) \times v; \text{//energy term} \]

\[ e_2 = w_2 \times (-2J1-2h/B) \times x_0 \times (x_1R) \times (x_1R) \times (x_0R) \times v; \]

\[ e_3 = w_3 \times (2J1+2h/B) \times x_0 \times ((1-x_1)R) \times ((1-x_1)R) \times ((1-x_0)R) \times v; \]

\[ e_4 = w_4 \times (-4J+2Jp) \times x_0 \times ((1-x_1)R) \times ((1-x_1)R) \times (x_0R) \times v; \]

\[ e_5 = w_5 \times (-2Jp) \times x_0 \times (x_1R) \times ((1-x_1)R) \times ((1-x_0)R) \times v; \]

\[ e_6 = w_6 \times (-2Jp) \times x_0 \times (x_1R) \times ((1-x_0)R) \times ((1-x_1)R) \times v; \]

\[ e_7 = w_7 \times (-2J1-2h/B) \times x_0 \times (x_1R) \times (x_0R) \times ((1-x_1)R) \times v; \]

\[ e_8 = w_8 \times (-2J1-2h/B) \times x_0 \times (x_1R) \times (x_0R) \times ((1-x_1)R) \times v; \]

\[ e_{11} = w_{11} \times (-2J1-2h/B) \times (1-x_0) \times (x_1R) \times (x_1R) \times (x_0R) / v; \]

\[ e_{22} = w_{22} \times (-4J+2Jp) \times (1-x_0) \times (x_1R) \times (x_1R) \times ((1-x_0)R) / v; \]

\[ e_{33} = w_{33} \times (4J+2Jp+4J1+4h/B) \times (1-x_0) \times ((1-x_1)R) \times ((1-x_1)R) \times ((1-x_0)R) / v; \]

\[ e_{44} = w_{44} \times (2J1+2h/B) \times (1-x_0) \times ((1-x_1)R) \times ((1-x_1)R) \times (x_0R) / v; \]

\[ e_{55} = w_{55} \times (2J1+2h/B) \times (1-x_0) \times (x_1R) \times ((1-x_0)R) \times ((1-x_1)R) / v; \]

\[ e_{66} = w_{66} \times (2J1+2h/B) \times (1-x_0) \times (x_1R) \times ((1-x_0)R) \times ((1-x_1)R) / v; \]

\[ e_{77} = w_{77} \times (-2Jp) \times (1-x_0) \times (x_1R) \times (x_0R) \times ((1-x_1)R) / v; \]

\[ e_{88} = w_{88} \times (-2Jp) \times (1-x_0) \times (x_1R) \times (x_0R) \times ((1-x_1)R) / v; \]

\[
\begin{align*}
\text{double } cc, dd, ff, gg; \\
cc &= 4 \times q2 / B; \\
dd &= x0 \times x0 \times v; \\
ff &= (1-x0) \times (1-x0) / v; \\
gg &= e1 + e2 + e3 + e4 + e5 + e6 + e7 + e8 + e11 + e22 + e33 + e44 + e55 + e66 + e77 + e88; \\
printf("gg=%.12lf\n", gg); 
\end{align*}
\]
\[ E = \frac{gg}{cc \cdot (dd + ff)}; \]

// the formula of average energy calculation

\[ S = \frac{(E - FE0)}{T}; \]

printf("E=%.12lf\n",E);

fprintf(fp,"%.12lf ",E);

printf("S=%.12lf\n",S);

fprintf(fp,"%.12lf ",S);

// This shadow part is to check if the rotation of x1 and x0 affects

// q1 = Q1(x1, x0);

// qtemp = Qtemp(x1, x0);

// q2 = q1 + qtemp;

// c1 = pow(pow(x0, B) \cdot (1/v) + pow((1-x0), B) \cdot v), 2*(B-1));

// c2 = pow(pow(x1, B) \cdot (1/v) + pow((1-x1), B) \cdot v), (B-2));

// c3 = log(pow(q2, B)/(c1*c2));

// FE1 = -T*0.25*c3;

// printf("FE1=%.12lf\n",FE1);

// fprintf(fp,"%.12lf ",FE1);

// ================
// =for one cycle=
// ================

//
for(i=1;i<=10000;i++)
{
    q1=Q11(x00);
    qtemp=Qtemp1(x00);
    q2=q1+qtemp;
    x11=(q1/q2+2*x00)/3;
    acc=fabs(x00-x11);
    ii=i;//to check how many steps it used
    if (acc<0.0000000000001) break;
    x00=x11;
}

printf("nFor One Cycle\n");
printf("i=%lf\n",ii);
printf("accuracy=%.12lf\n",acc);
for(int kk=0;kk<=1;kk++)
{
    x00=x11;
    q1=Q11(x00);
    qtemp=Qtemp1(x00);
    q2=q1+qtemp;
    x11=q1/q2;
    printf("Xm+%d=%.12lf\n",kk+1,x11);
    fprintf(fp,"%.12lf ",x11);
}

c1=pow((pow(x00,B)*v+pow((1-x00),B)*(1/v)),2*(B-1));
\[ c_2 = \text{pow}(\text{pow}(x11, B) \times v + \text{pow}((1 - x11), B) \times (1/v), (B - 2)) \]

\[ c_3 = \log(\text{pow}(q2, B) / (c_1 \times c_2)) \]

\[ FE = -T \times 0.25 \times c_3; \]
\[ \text{printf}("FE=\%.12lf\n", FE); \]
\[ \text{fprintf}(fp,"\%.12lf ", FE); \]

\[ dFE1 = (FE - rFE1) / \Delta T; \]
\[ \text{printf}("dFE/dt=\%.12lf\n", dFE1); \]
\[ \text{fprintf}(fp,"\%.12lf ", dFE1); \]
\[ rFE1 = FE; \]

\[ d2FE1 = (dFE1 - rrFE1) / \Delta T; \]
\[ \text{printf}("d2FE/dt2=\%.12lf\n", d2FE1); \]
\[ \text{fprintf}(fp,"\%.12lf ", d2FE1); \]
\[ rrFE1 = dFE1; \]

\[ e1 = w1 \times (4 \times J + 2 \times Jp + 4 \times J1 - 4 \times h/B) \times x00 \times \text{pow}(x00, R) \times \text{pow}(x00, R) \times \text{pow}(x00, R) \times v; \]
\[ e2 = w2 \times (-2 \times J1 - 2 \times h/B) \times x00 \times \text{pow}(x00, R) \times \text{pow}(x00, R) \times \text{pow}((1 - x00), R) \times v; \]
\[ e3 = w3 \times (2 \times J1 + 2 \times h/B) \times x00 \times \text{pow}((1 - x00), R) \times \text{pow}((1 - x00), R) \times \text{pow}((1 - x00), R) \times v; \]
\[ e4 = w4 \times (-4 \times J + 2 \times Jp) \times x00 \times \text{pow}((1 - x00), R) \times \text{pow}((1 - x00), R) \times \text{pow}(x00, R) \times v; \]
\[ e5 = w5 \times (-2 \times Jp) \times x00 \times \text{pow}(x00, R) \times \text{pow}((1 - x00), R) \times \text{pow}((1 - x00), R) \times v; \]
\[ e6 = w6 \times (-2 \times Jp) \times x00 \times \text{pow}(x00, R) \times \text{pow}((1 - x00), R) \times \text{pow}((1 - x00), R) \times v; \]
e7=w7*(-2*J1-2*h/B)*x00*pow(x00,R)*pow(x00,R)*pow((1-x00),R)*v;
e8=w8*(-2*J1-2*h/B)*x00*pow(x00,R)*pow(x00,R)*pow((1-x00),R)*v;

e11=w11*(-2*J1-2*h/B)*(1-x00)*pow(x00,R)*pow(x00,R)*pow((1-x00),R)/v;
e22=w22*(-4*J+2*Jp)*(1-x00)*pow(x00,R)*pow(x00,R)*pow((1-x00),R)/v;
e33=w33*(4*J+2*Jp-4*J1+4*h/B)*(1-x00)*pow((1-x00),R)*pow((1-x00),R)/v;
e44=w44*(2*J1+2*h/B)*(1-x00)*pow((1-x00),R)*pow((1-x00),R)*pow(x00,R)/v;
e55=w55*(2*J1+2*h/B)*(1-x00)*pow(x00,R)*pow((1-x00),R)*pow((1-x00),R)/v;
e66=w66*(2*J1+2*h/B)*(1-x00)*pow(x00,R)*pow((1-x00),R)*pow((1-x00),R)/v;
e77=w77*(-2*Jp)*(1-x00)*pow(x00,R)*pow(x00,R)*pow((1-x00),R)/v;
e88=w88*(-2*Jp)*(1-x00)*pow(x00,R)*pow(x00,R)*pow((1-x00),R)/v;

cc=4*q2/B;
dd=x00*x00*v;
ff=(1-x00)*(1-x00)/v;

gg=e1+e2+e3+e4+e5+e6+e7+e8+e11+e22+e33+e44+e55+e66+e77+e88;
E=gg/(cc*(dd+ff));

S=(E-FE)/T;

printf("E=%.12lf\n",E);
fprintf(fp,"%.12lf",E);
printf("S=%.12lf\n",S);
fprintf(fp,"%.12lf",S);
printf("press enter to exit");
scanf("%*c");
fclose(fp); // close file fp

double Q1(double x0, double x1) {
    return a1*pow(x1,2*(B-1))*pow(x0,(B-1))
    +a2*pow(x1,2*(B-1))*pow((1-x0),(B-1))
    +a3*pow((1-x1),2*(B-1))*pow((1-x0),(B-1))
    +a4*pow((1-x1),2*(B-1))*pow(x0,(B-1))
    +2*a5*pow(x1,(B-1))*pow((1-x1),(B-1))*pow((1-x0),(B-1))
    +2*a2*pow(x1,(B-1))*pow((1-x1),(B-1))*pow(x0,(B-1));
}

double Qtemp(double x0, double x1) {
    return a6*pow(x1,2*(B-1))*pow(x0,(B-1))
    +a7*pow(x1,2*(B-1))*pow((1-x0),(B-1))
    +a8*pow((1-x1),2*(B-1))*pow((1-x0),(B-1))
    +a9*pow((1-x1),2*(B-1))*pow(x0,(B-1))
    +2*a9*pow(x1,(B-1))*pow((1-x1),(B-1))*pow((1-x0),(B-1))
    +2*a10*pow(x1,(B-1))*pow((1-x1),(B-1))*pow(x0,(B-1));
}

double Q11(double x00) {
    return a1*pow(x00,3*(B-1))
    +a2*pow(x00,2*(B-1))*pow((1-x00),(B-1))
    +a3*pow((1-x00),3*(B-1))
\begin{align*}
& \quad +a4*\text{pow}((1-x00),2*(B-1))*\text{pow}(x00,(B-1)) \\
& \quad +2*a5*\text{pow}(x00,(B-1))*\text{pow}((1-x00),2*(B-1)) \\
& \quad +2*a2*\text{pow}(x00,2*(B-1))*\text{pow}((1-x00),(B-1));
\end{align*}

\begin{align*}
\text{double Qtemp1(double x00) } & \{ \\
& \quad \text{return a6*\text{pow}(x00,3*(B-1))} \\
& \quad +a7*\text{pow}(x00,2*(B-1))*\text{pow}((1-x00),(B-1)) \\
& \quad +a8*\text{pow}((1-x00),3*(B-1)) \\
& \quad +a9*\text{pow}((1-x00),2*(B-1))*\text{pow}(x00,(B-1)) \\
& \quad +2*a9*\text{pow}(x00,(B-1))*\text{pow}((1-x00),2*(B-1)) \\
& \quad +2*a10*\text{pow}(x00,2*(B-1))*\text{pow}((1-x00),(B-1));
\}
Program II

#include <stdio.h>
#include <math.h>
#include <stdlib.h>

int S1[17],S2[17],S3[17],S4[17],S1bar[3],S2bar[3];//states series of each

double
a[17],as[17],as2[17],w[17],ws[17],ww[17],wws[17],e[17],es[17],abar[3],wbar[3],ebar[3];
//coefficient

double Q1(double x2,double x3,double x4);
double Qtemp(double x2,double x3,double x4);
double Q1s(double x2,double x3,double x4);
double Qtemps(double x2,double x3,double x4);
double Q1ss(double x2,double x3,double x4);
double Qtempss(double x2,double x3,double x4);
double Q1bar(double x1bar);
double Qtempbar(double x1bar);

int main(){
    FILE *fp;//define a file pointer to stand for file name out.txt
    if((fp=fopen("out.txt","w+b"))==NULL) {
        printf("can not create or open the file out.txt\n");
    }//if out.txt cannot be create or open,display error message

    FILE *fp2;//define a file pointer to stand for file name out.txt

if((fp2=fopen("out2.txt","w+b"))==NULL) {
    printf("can not create or open the file out2.txt\n");
} //if out2.txt cannot be create or open,display error message
FILE *fp3;//define a file pointer to stand for file name out.txt
if((fp3=fopen("Xin1.txt","w+b"))==NULL) {
    printf("can not create or open the file Xin1.txt\n");
} //if out2.txt cannot be create or open,display error message

int s1,s2,s3,s4,s1bar,s2bar,jj;//state of each site

double x2,x4,Rx2,Rx4,cx2,cx4,cRx2,cRx4,x1,cx1,xtemp,x[1000],cx[1000],xo1,xo2;//variables for recursive calculation

double x2i,Rx4i,cx2i,cRx4i;//initial seed

int anb,asd,atri,aqua,amag;//coefficient of each state

double q1,q2,qtemp,q1bar,q2bar,qtempbar;

double Js,Jp,Jps1,Jps2,J1,J1s1,J1s2,J1s3,J2,J2s,h,ks,k,kp,
    kps1,kps2,k1,k1s1,k1s2,k1s3,k2,k2s,v;

double amp1,amp2,bbar1,bbar2,zbarp[2],zbar[2];

double f,A=0,E;

double dFE,rFE=0;

int NS;

//interaction energy, J=neighborhood, Jp=surface diagnol, J1=3spins, J2=4spins...

double T1,T0,deltaT,Beta;//temperature

double B[100][2];

int m;//thickness

printf("The thickness\n");
scanf("%d%*c", &m);

FILE *fp4;
if ((fp4=fopen("in.txt","r"))==NULL) {
    printf("can not open the file in.txt\n");
}

fscanf(fp4,"%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,

    &T0,&T1,&deltaT,&x2i,&Rx4i,&cx2i,&cRx4i,&Js,&J,&Jp,&Jps1,&Jps2,
    &J1,&J1s1,&J1s2,&J1s3,&J2,&J2s,&h);

for (double T=T0; T<=T1; T=T+deltaT) {

    Beta=1/T;
    k=exp(Beta*J);//neighborhood interaction
    ks=exp(Beta*Js);//surface neighborhood interaction
    kp=exp(Beta*Jp);//surface diagnol interaction
    kps1=exp(Beta*Jps1);//surface diagnol interaction
    kps2=exp(Beta*Jps2);//surface diagnol interaction
    k1=exp(Beta*J1);//three spins interaction
    k1s1=exp(Beta*J1s1);//three spins interaction
    k1s2=exp(Beta*J1s2);//three spins interaction
    k1s3=exp(Beta*J1s3);//three spins interaction
    k2=exp(Beta*J2);//four spins interaction

\[ k_{2s} = \exp(Beta \cdot J_{2s}); / four \ spins \ interaction \]

\[ v = \exp(Beta \cdot h); / magnetic \ field \]

int i=1;
    for (s1=-1;s1<2;s1=s1+2)
    {
        for (s2=-1;s2<2;s2=s2+2)
        {
            for (s3=-1;s3<2;s3=s3+2)
            {
                for (s4=-1;s4<2;s4=s4+2)
                {
                    S1[i]=s1;
                    S2[i]=s2;
                    S3[i]=s3;
                    S4[i]=s4;

                    anb=s1*s2+s1*s3+s2*s4+s3*s4;
                    asd=s1*s4+s2*s3;
                    atri=s1*s2*s4+s2*s4*s3+s4*s3*s1+s3*s1*s2;
                    aqua=s1*s2*s3*s4;
                    amag=s2+s3+s4;

                    a[i]=\text{pow}(k,anb)*\text{pow}(kp,asd)*\text{pow}(k1,atri)*\text{pow}(k2,aqua)*\text{pow}(v,amag);
                }
            }
        }
    }

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as[i]=pow(k,(s1*s2+s1*s3))
    *pow(ks,(s2*s4+s3*s4))
    *pow(kps1,(s1*s4))
    *pow(kps2,(s2*s3))
    *pow(k1s1,(s1*s2*s3))
    *pow(k1s2,(s1*s2*s4+s1*s3*s4))
    *pow(k1s3,(s2*s3*s4))
    *pow(k2s,aqua)
    *pow(v,amag);

as2[i]=pow(ks,(s1*s2+s1*s3))
    *pow(k,(s2*s4+s3*s4))
    *pow(kps1,(s1*s4))
    *pow(kps2,(s2*s3))
    *pow(k1s1,(s1*s2*s3))
    *pow(k1s2,(s1*s2*s4+s1*s3*s4))
    *pow(k1s3,(s2*s3*s4))
    *pow(k2s,aqua)
    *pow(v,amag);

//printf("%lf \n%lf \n%lf \n",a[i],as[i],as2[i]);

w[i]=exp(Beta*(anb*J+asd*Jp+atri*J1+aqua*J2+amag*h));
ww[i]=exp(Beta*(anb*J+asd*Jp+atri*J1+aqua*J2+(amag+s1)*h));
e[i]=(-anb*J-asd*Jp-atri-J1+aqua-J2-(s1+amag)*h/2);
i++;

}}}}//loop for all bulk states by this bracket

i=1;
for (s2bar=-1;s2bar<2;s2bar=s2bar+2)
{
  for (s1bar=-1;s1bar<2;s1bar=s1bar+2)
  {
    S1bar[i]=s1bar;
    S2bar[i]=s2bar;
    anb=s1bar*s2bar;
    amag=s1bar;
    
    abar[i]=pow(ks,anb)*pow(v,amag);
    wbar[i]=exp(Beta*(anb*Js+amag*h));
    ebar[i]=(-anb*Js-(s2bar+amag)*h/2);
    i++;
  } //loop for all surface states by this bracket

for(int j=1;j<=300;j++)
{
  fprintf(fp,"\n%.12lf %.12lf",Rx4i,x2i);
  x2=x2i;
\[ x_4 = R x_4 i; \]

\[ q_1 = Q_1 s(x_2, x_2, x_4); \]
\[ q_{temp} = Q_{temp s}(x_2, x_2, x_4); \]
\[ q_2 = q_1 + q_{temp}; \]
\[ x_4 = q_1 / q_2; \]
\[ x[m] = x_4; \]

\texttt{fprintf(fp, "\n%.12lf %.12lf", cRx4i, cx2i);}
\texttt{cx2 = cx2i;}
\texttt{cx4 = cRx4i;}

\[ q_1 = Q_1 s(cx_2, cx_2, cx_4); \]
\[ q_{temp} = Q_{temp s}(cx_2, cx_2, cx_4); \]
\[ q_2 = q_1 + q_{temp}; \]
\[ cx_4 = q_1 / q_2; \]
\[ cx[m] = cx_4; \]

\texttt{fprintf(fp, "\n!x4=%.12lf cx4=%.12lf",x4,cx4);}

\texttt{for(jj=m-1;jj>=0;jj--)}
\{
\texttt{q1=Q1(cx4,cx4,x4);}
\texttt{qtemp=Qtemp(cx4,cx4,x4);}
\texttt{q2=q1+qtemp;}
\}
x[jj] = q1/q2;

q1 = Q1(x4, x4, cx4);
qtemp = Qtemp(x4, x4, cx4);
q2 = q1 + qtemp;
cx4 = q1/q2;

cx[jj] = cx4;
x4 = x[jj];
oxo1 = x4;
oxo2 = cx4;

// set the value back for new seeds
fprintf(fp, "\n!x4=%.12lf x2=%.12lf", x4, cx4);
}
} // down loop

x1 = x4;

cx1 = cx4;

for(jj = 1; jj <= m-1; jj++)
{
  q1 = Q1(cx[jj+1], cx[jj+1], x1);
  qtemp = Qtemp(cx[jj+1], cx[jj+1], x1);
  q2 = q1 + qtemp;
  x1 = q1/q2;
  fprintf(fp, "\n!!x1=%.12lf", x1);
}
\[ q_1 = Q_1(x_{jj+1}, x_{jj+1}, cx_1); \]
\[ q_{temp} = Q_{temp}(x_{jj+1}, x_{jj+1}, cx_1); \]
\[ q_2 = q_1 + q_{temp}; \]
\[ cx_1 = q_1 / q_2; \]
\[ \text{fprintf(fp,"\n!cx1=%.12lf",cx1);} \]
\[ \text{//uploop} \]

\[ \text{for (int sl=1; sl<60; sl++)} \]
\[ \{ \]
\[ q_1 = Q_{1ss}(x_{2i}, x_{2i}, x_1); \]
\[ q_{temp} = Q_{tempss}(x_{2i}, x_{2i}, x_1); \]
\[ q_2 = q_1 + q_{temp}; \]
\[ x_4 = q_1 / q_2; \]
\[ \text{fprintf(fp,"\n-x4=%.12lf",x4);} \]

\[ q_{1bar} = Q_{1bar}(x_4); \]
\[ q_{tempbar} = Q_{tempbar}(x_4); \]
\[ q_{2bar} = q_{1bar} + q_{tempbar}; \]
\[ x_{2i} = q_{1bar} / q_{2bar}; \]
\[ \text{fprintf(fp," -x2=%.12lf",x2i);} \]
\[ \} \]

\[ \text{for (sl=1; sl<=60; sl++)} \]
\{ \\
q1=Q1s(Rx4i,x1,x2i); \\
qtemp=Qtemps(Rx4i,x1,x2i); \\
q2=q1+qtemp; \\
Rx2=q1/q2; \\
fprintf(fp, "\n+x2=\%.12lf", Rx2); \\
\\nq1bar=Q1bar(Rx2); \\
qtempbar=Qtempbar(Rx2); \\
q2bar=q1bar+qtempbar; \\
Rx4i=q1bar/q2bar; \\
\\nfprintf(fp, "+x4=\%.12lf", Rx4i); \\
\\}

//No.1 surface forward and backward
for (sl=1; sl<=60; sl++)
{

q1=Q1ss(cx2i,cx2i,cx1); \\
qtemp=Qtempss(cx2i,cx2i,cx1); \\
q2=q1+qtemp; \\
\text{cx4}=q1/q2; \\
//fprintf(fp, "n-x4=\%.12lf", cx4);
q1bar=Q1bar(cx4);
qtempbar=Qtempbar(cx4);
q2bar=q1bar+qtempbar;
cx2i=q1bar/q2bar;

//fprintf(fp," -x2=%.12lf",cx2i);
}

for (sl=1;sl<=60;sl++)
{

q1=Q1s(cRx4i,cx1,cx2i);
qtemp=Qtemps(cRx4i,cx1,cx2i);
q2=q1+qtemp;
cRx2=q1/q2;
//fprintf(fp,"+n+x2=%.12lf",cRx2);

q1bar=Q1bar(cRx2);
qtempbar=Qtempbar(cRx2);
q2bar=q1bar+qtempbar;
cRx4i=q1bar/q2bar;

//fprintf(fp," +x4=%.12lf",cRx4i);
}

//No.2 surface forward and backward
}} // fix point

fprintf(fp2, "n%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf%.10lf", T, xo1, xo2, Rx2, Rx4i, x2i, x4, cRx2, cRx4i, cx2i, cx4);

fprintf(fp3, "n%.10lf%.10lf%.10lf%.10lf", T, x4, cx4, x1, cx1);

// partial partition fn

bbar1 = sqrt(1/(Rx4i*Rx4i+(1-Rx4i)*(1-Rx4i)));
zbarp[0] = bbar1*Rx4i;
zbarm[0] = bbar1-zbarp[0];
amp1 = log(bbar1);

bbar2 = sqrt(1/(x2i*x2i+(1-x2i)*(1-x2i)));
zbarp[1] = bbar2*x2i;
zbarm[1] = bbar2-zbarp[1];
amp2 = log(bbar2);

x2 = x2i;
x4 = Rx4i;

q1 = Q1s(x2, x2, x4);
qtemp = Qtemps(x2, x2, x4);
q2 = q1 + qtemp;
xtemp = q1/q2;
amp1 = (log(q2) + 2*amp2 + amp1);
```c
q1 = Q1s(x4, x4, x2);
qtemp = Qtemps(x4, x4, x2);
q2 = q1 + qtemp;
x2 = q1 / q2;
x4 = xtemp;
amp2 = (log(q2) + 2 * log(bbar1) + amp2);
// fprintf(fp2, "n%.12lf %.12lf", amp1, amp2);
for(jj = m-1; jj >= 1; jj--)
{
    q1 = Q1(x2, x2, x4);
    qtemp = Qtemp(x2, x2, x4);
    q2 = q1 + qtemp;
    xtemp = q1 / q2;
    B[jj][0] = (log(q2) + 2 * amp2 + amp1);
    q1 = Q1(x4, x4, x2);
    qtemp = Qtemp(x4, x4, x2);
    q2 = q1 + qtemp;
    B[jj][1] = (log(q2) + 2 * amp1 + amp2);
    x2 = q1 / q2;
    x[jj] = x2;
    x4 = xtemp;
    // xx[jj] = x4;
```
amp1=B[jj][0];
amp2=B[jj][1];

//fprintf(fp2,"%.8lf %.8lf",amp1,amp2);
//set the value back for new seeds
}

for (int n=0;n<16;n++)
{
    A=(x4*(S4[n]+1)/2-(1-x4)*(S4[n]-1)/2)
    *(x4*(S1[n]+1)/2-(1-x4)*(S1[n]-1)/2)
    *(x2*(S2[n]+1)/2-(1-x2)*(S2[n]-1)/2)
    *(x2*(S3[n]+1)/2-(1-x2)*(S3[n]-1)/2)
    *ww[n]+A;
}

NS=2*(pow(3,m+1)-1)-4*pow(3,m-1);

f=-T*(2*amp1+2*amp2+log(A))/NS;
//f=-T*(2*amp1+2*amp2+log(A));

fprintf(fp2," %d %.8lf",NS,f);

//the first and second derivative of free energy
dFE=(f-rFE)/deltaT;

rFE=f;

E=f-dFE*T;

fprintf(fp2," %.12lf %.12lf",-dFE,E);
printf("T=%lf",T);
} //temperature loop

printf("\npress enter to exit");
//scanf("%*c");
fclose(fp);
fclose(fp2);
fclose(fp3);//close file fp
}

double Qtemp(double x2,double x3,double x4) {
    double f=0;
    for (int n=1;n<9;n++)
    {
        f=f+a[n]*((x2-0.5)*(S2[n]+1)-x2+1)*((x3-0.5)*(S3[n]+1)-x3+1)*((x4-0.5)*(S4[n]+1)-x4+1);
        //printf("f=%.12lf\n",f);
    }
    return f;
}

double Q1(double x2,double x3,double x4) {
    double f=0;
    for (int n=9;n<17;n++)
double Qtemps(double x2,double x3,double x4) {
    double f=0;
    for (int n=1;n<9;n++)
    {
        f=f+a[n]*((x2-0.5)*(S2[n]+1)-x2+1)
            *((x3-0.5)*(S3[n]+1)-x3+1)
            *((x4-0.5)*(S4[n]+1)-x4+1);
        //printf("2 f=\%.12lf\n",f);
    }
    return f;
}

double Q1s(double x2,double x3,double x4) {
    double f=0;
    for (int n=9;n<17;n++)
    {
        f=f+a[n]*((x2-0.5)*(S2[n]+1)-x2+1)
            *((x3-0.5)*(S3[n]+1)-x3+1)
            *((x4-0.5)*(S4[n]+1)-x4+1);
        //printf("2 f=\%.12lf\n",f);
    }
    return f;
}
\[
f = f + a[n] \times ((x2-0.5) \times (S2[n]+1) - x2 + 1) \\
\times ((x3-0.5) \times (S3[n]+1) - x3 + 1) \\
\times ((x4-0.5) \times (S4[n]+1) - x4 + 1); \\
// \text{printf("s f=%.12lf\n",f); -}
\]

return f;
}

double Qtempss(double x2, double x3, double x4) {
    double f = 0;
    for (int n=1; n<9; n++)
    {
        f = f + as2[n] \times ((x2-0.5) \times (S2[n]+1) - x2 + 1) \\
        \times ((x3-0.5) \times (S3[n]+1) - x3 + 1) \\
        \times ((x4-0.5) \times (S4[n]+1) - x4 + 1); \\
        // \text{printf("2 f=%.12lf\n",f); -}
    }
    return f;
}

double Q1ss(double x2, double x3, double x4) {
    double f = 0;
    for (int n=9; n<17; n++)
    {
        f = f + as2[n] \times ((x2-0.5) \times (S2[n]+1) - x2 + 1) \\
        \times ((x3-0.5) \times (S3[n]+1) - x3 + 1) \\
        \times ((x4-0.5) \times (S4[n]+1) - x4 + 1); \\
    }
}
\[(x_3-0.5)(S_3[n]+1)-x_3+1\]
\[(x_4-0.5)(S_4[n]+1)-x_4+1\];

//printf("sf=\%.12lf\n", f);

return f;
}

double Q1bar(double x1bar) {
    double f=0;
    f=abar[3]*(1-x1bar)+abar[4]*x1bar;
    return f;
}

double Qtempbar(double x1bar) {
    double f=0;
    f=abar[1]*(1-x1bar)+abar[2]*x1bar;
    return f;
}
Program III

#include <stdio.h>
#include <math.h>
#include <stdlib.h>

int S12[65], S22[65], S32[65], S42[65], S52[65], S62[65]; // states series of each up spins
double a[65], e[65], w[65], V;
double Qtemp(double xB, double x2, double x3);
double Q1(double xB, double x2, double x3);
double energy(double xB, double x);

int main()
{
    FILE *fp;
    if((fp=fopen("Eout.c.txt","w+b"))==NULL) {
        printf("can not create or open the file Eout.c.txt\n");
    }

    FILE *fp2;
    if((fp2=fopen("in.txt","r"))==$NULL) {
        printf("can not create or open the file in.txt");
    }

    FILE *fp3;
    if((fp3=fopen("Xin1.txt","r"))==$NULL) {
        printf("can not create or open the file Xin1.txt");
    }
    return 0;
}
double deltaT,Beta;

//double x1,x2;

double J,Jp,J1,J2,h;

double k,kp,k1,k2;

double q1,qtemp,q2,q22;

double FE,rFE,E,S;

double c1,c2,c3,c4;

double x;

int s1,s2,s3,s4,s5,s6;

int anb,asd,atri,aqua,amag;

fscanf(fp2,"%lf,%lf,%lf,%lf,%lf",
 &J,&Jp,&J1,&J2,&h);

double shuttle[4000];

int j=1;

while(fscanf(fp3,"%lf",shuttle+j)!=EOF)
{
}
//fprintf(fp,"%.10lf\n",shuttle[j]);

j++;

}

for (int l=1;l<=175;l=l+5)
{

Beta=1/shuttle[l];

k=exp(Beta*J); //neighborhood interaction
kp=exp(Beta*Jp); //surface diagonal interaction
k1=exp(Beta*J1); //three spins interaction
k2=exp(Beta*J2); //four spins interaction
V=exp(Beta*h); //magnetic field

int i=1;

for (s1=-1;s1<2;s1=s1+2)
{

for (s2=-1;s2<2;s2=s2+2)
{

for (s3=-1;s3<2;s3=s3+2)
{

for (s4=-1;s4<2;s4=s4+2)
{


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for (s5=-1;s5<2;s5=s5+2)
{
    for (s6=-1;s6<2;s6=s6+2)
    {
        S12[i]=s1;
        S22[i]=s2;
        S32[i]=s3;
        S42[i]=s4;
        S52[i]=s5;
        S62[i]=s6;
        
        anb=s1*s2+s1*s3+s2*s4+s3*s5+s2*s6+s3*s6;
        asd=s1*s6+s2*s3;
        atri=s1*s2*s3+s1*s2*s6+s6*s3*s1+s2*s3*s6;
        aqua=s1*s2*s3*s6;
        amag=s2+s3+s4+s5+s6;

        a[i]=pow(k,anb)*pow(kp,asd)*pow(k1,atri)*pow(k2,aqua)*pow(V,amag);
        w[i]=exp(Beta*(anb*J+asd*Jp+atri*J1+aqua*J2+amag*h));
        e[i]=(-anb*J-asd*Jp-atri-J1+aqua-J2-(s1/2+s2+s3+s4/2+s5/2+s6/2)*h);
        i++;
    }
}
}  }}  }  }  }  }  //loop for all up bulk states by this bracket

q1=Q1(shuttle[l+3],shuttle[l+1],shuttle[l+1]);
\[
q_{\text{temp}} = Q_{\text{temp}}(\text{shuttle}[l+3], \text{shuttle}[l+1], \text{shuttle}[l+1]);
\]
\[
q_2 = q_1 + q_{\text{temp}};
\]
\[
x = q_1/q_2;
\]

```
//fprintf(fp4,"%lf,%12lf,%12lf,%12lf,%12lf\n",shuttle[l],shuttle[l+1],shuttle[l+2],shuttle[l+3],shuttle[l+4],x);
q_1 = Q_1(\text{shuttle}[l+4], \text{shuttle}[l+2], \text{shuttle}[l+2]);
q_{\text{temp}} = Q_{\text{temp}}(\text{shuttle}[l+4], \text{shuttle}[l+2], \text{shuttle}[l+2]);
q_{22} = q_1 + q_{\text{temp}};
```

\[
c_1 = \text{shuttle}[l+1]*(1-\text{shuttle}[l+2]) / k + (1-\text{shuttle}[l+1])*\text{shuttle}[l+2] / k + \text{shuttle}[l+1]*\text{shuttle}[l+2]*k + (1-\text{shuttle}[l+1])*(1-\text{shuttle}[l+2]) * k;
\]
\[
c_2 = \text{pow}((\text{shuttle}[l+3],2)/V + \text{pow}((1-\text{shuttle}[l+4]),2)*V;
\]
\[
c_3 = \text{pow}((\text{shuttle}[l+4],2)/V + \text{pow}((1-\text{shuttle}[l+4]),2)*V;
\]
\[
c_4 = \log(q_2*q_{22}*q_2*q_{22}/(c_1*c_1*c_2*c_3));
\]
\[
FE = -\text{shuttle}[l]*c_4/14;
\]

```
if (shuttle[l]==0.4||shuttle[l]==1.2)
{printf("\n%.12lf,%.12lf,%.12lf\n",q_2,q_{22},c_1*c_2*c_3);
}
```

```
//the first and second derivative of free energy
```

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deltaT = shuttle[l] - shuttle[l-5];
S = -(FE - rFE) / deltaT;
rFE = FE;
E = FE + S * shuttle[l];

// energy, entropy
// double dd, ff, gg;
// ff = (1 - shuttle[l+2]) * (1 - shuttle[l+2]) / V;
// gg = energy(shuttle[l+4], shuttle[l+2]);
// E = gg / (4 * q22 * (dd + ff));
// printf("E=%.12lf\n", E);
// fprintf(fp, ",%.12lf ", E);

// S = (E - FE) / shuttle[l];
// printf("S=%.12lf\n", entropy);
// fprintf(fp, ",%.12lf ", entropy);

// print out the thermo result
printf("FE0=%.12lf\n", FE);
// fprintf(fp, "%f %.12lf\n", shuttle[l], FE);
printf("S=%.12lf\n", S);
printf("E=%.12lf\n", E);
fprintf(fp, "%lf %.12lf %.12lf %.12lf\n", shuttle[l], FE, S, E);
double Qtemp(double xB, double x2, double x2bar) {
    double f=0;
    for (int n=1; n<33; n++)
    {
        f=f+a[n]*((xB-0.5)*(S62[n]+1)-xB+1)
            *((x2-0.5)*(S42[n]+1)-x2+1)
            *((x2-0.5)*(S52[n]+1)-x2+1);
        //printf("f=%.12lf\n",f);
    }
    return f;
}

} //end temperature loop

printf("\npress enter to exit");
//scanf("%c");
fclose(fp);
fclose(fp2);
fclose(fp3);
//fclose(fp4);
//close file fp

}
double Q1(double xB,double x2,double x2bar) {
    double f=0;
    for (int n=33;n<65;n++)
    {
        f=f+a[n]*((xB-0.5)*(S62[n]+1)-xB+1)*
        *((x2-0.5)*(S52[n]+1)-x2+1)*
        *((x2-0.5)*(S42[n]+1)-x2+1);
        //printf("ff=%.12lf\n",f);
    }
    return f;
}

double energy(double xB,double x) {
    double f=0;
    for (int n=0;n<=63;n++)
    {
        f=f+w[n]*e[n]*((xB-0.5)*(S62[n]+1)-xB+1)*
        *((x-0.5)*(S42[n]+1)-x+1)*
        *((x-0.5)*(S52[n]+1)-x+1)*
        *pow(V,S12[n]);
    }
    return f;
}
Program IV

#include <stdio.h>
#include <math.h>
#include <stdlib.h>

int S1[17], S2[17], S3[17], S4[17], S1s[9], S2s[9], S3s[9]; // states series of each

double a[17], as[9], w[17], ws[9], ww[17], wws[9], e[17], es[9]; // coefficient

double Q1(double x1, double x2);
double Qtemp(double x1, double x2);
double Q1s(double x1s, double xB);
double Qtemps(double x1s, double xB);

int main()
{
    FILE *fp; // define a file pointer to stand for file name out.txt
    if((fp = fopen("out.txt", "w+b"))==NULL) {
        printf("can not create or open the file out.txt\n");
    } // if out.txt cannot be create or open, display error message
    FILE *fp2; // define a file pointer to stand for file name out2.txt
    if((fp2 = fopen("out2.txt", "w+b"))==NULL) {
        printf("can not create or open the file out2.txt\n");
    } // if out2.txt cannot be create or open, display error message
    FILE *fp3; // define a file pointer to stand for file name out.txt
    }
if((fp3=fopen("Xin1.txt","w+b"))==NULL) {
    printf("can not create or open the file Xin1.txt\n");
} //if out2.txt cannot be create or open,display error message

int s1,s2,s3,s4,s1s,s2s,s3s;//state of each site

double J,Js,Jp,Jps,J1,J1s,J2,h;

double k,ks,kp,kps,k1,k1s,k2,v;

double anb,asd,atri,aqua,amag;

double xB1,xB2,x3,x1s,x2s,xtemps;xtemps;

double q1,qtemp,q2,q1s,qtemps,q2s;

double T0,T1,Beta,deltaT;

double FE,c1,c2,c3,rFE,E,S;

double OnecFE,OnecrFE,OnecE,OnecS;

FILE *fp4;
if ((fp4=fopen("in.txt","r"))==NULL) {
    printf("can not open the file in.txt\n");
}

fscanf(fp4,"%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf,%lf",
    &T0,&T1,&deltaT,&xB1,&xB2,&x1s,&J,&Js,&Jp,&Jps,
    &J1,&J1s,&J2,&h);

for (double T=T0;T<=T1;T=T+deltaT)
{

    Beta=1/T;

k = \exp(Beta \cdot J); // neighborhood interaction
ks = \exp(Beta \cdot Js); // surface neighborhood interaction

kp = \exp(Beta \cdot Jp); // diagonal interaction
kps = \exp(Beta \cdot Jps); // surface diagonal interaction

k1 = \exp(Beta \cdot J1); // three spins interaction
k1s = \exp(Beta \cdot J1s); // surface three spins interaction

k2 = \exp(Beta \cdot J2); // four spins interaction
v = \exp(Beta \cdot h); // magnetic field

int i=1;
for (s1=-1;s1<2;s1=s1+2)
{
    for (s2=-1;s2<2;s2=s2+2)
    {
        for (s3=-1;s3<2;s3=s3+2)
        {
            for (s4=-1;s4<2;s4=s4+2)
            {
                S1[i]=s1;
                S2[i]=s2;
            }
        }
    }
}
\[ S_3[i] = s_3; \]
\[ S_4[i] = s_4; \]

\[ \text{anb} = s_1 s_2 + s_1 s_3 + s_2 s_4 + s_3 s_4; \]
\[ \text{asd} = s_1 s_4 + s_2 s_3; \]
\[ \text{atri} = s_1 s_2 s_4 + s_2 s_4 s_3 + s_4 s_3 s_1 + s_3 s_1 s_2; \]
\[ \text{aqua} = s_1 s_2 s_3 s_4; \]
\[ \text{amag} = s_2 + s_3 + s_4; \]

\[ \text{a}[i] = \text{pow}(k, \text{anb}) \cdot \text{pow}(k_p, \text{asd}) \cdot \text{pow}(k_1, \text{atri}) \cdot \text{pow}(k_2, \text{aqua}) \cdot \text{pow}(v, \text{amag}); \]

\[ \text{w}[i] = \exp(\beta (\text{anb} J + \text{asd} J_P + \text{atri} J_1 + \text{aqua} J_2 + \text{amag} h)); \]
\[ \text{ww}[i] = \exp(\beta (\text{anb} J + \text{asd} J_P + \text{atri} J_1 + \text{aqua} J_2 + (\text{amag} + s_1) h)); \]
\[ \text{e}[i] = -\text{anb} J - \text{asd} J_P - \text{atri} J_1 - \text{aqua} J_2 - (s_1 + \text{amag}) \frac{h}{2}; \]

\[ \text{i}++; \]
\} \} \} \} // \text{loop for all bulk states by this bracket} \]

\[ \text{i} = 1; \]
\[ \text{for (s_1 s = -1; s_1 s < 2; s_1 s = s_1 s + 2) \} \]
\[ \{ \]
\[ \text{for (s_2 s = -1; s_2 s < 2; s_2 s = s_2 s + 2) \]
for (s3s=-1; s3s<2; s3s=s3s+2)
{
 S1s[i]=s1s;
 S2s[i]=s2s;
 S3s[i]=s3s;

 anb=s1s*s2s+s2s*s3s;
 asd=s1s*s3s;
 atri=s1s*s2s*s3s;
 amag=s2s+s3s+s1s;

 as[i]=pow(ks,anb)*pow(kps,asd)*pow(k1s,atri)*pow(v,amag);

 //printf(\"%lf \n%lf \n%lf \n\",a[i],as[i],as2[i]);

 ws[i]=exp(Beta*(anb*J+asd*Jp+atri*J1+amag*h));
 wws[i]=exp(Beta*(anb*J+asd*Jp+atri*J1+(amag+s1)*h));
 es[i]=(-anb*J-asd*Jp-atri*J1-(s1+amag)*h/2);

 i++;
}}}}//loop for all surface states by this bracket
for (int j=1;j<100;j++)
{
    q1=Q1(xB1,xB2);
    qtemp=Qtemp(xB1,xB2);
    q2=q1+qtemp;
    x3=q1/q2;

    xB1=xB2;
    xB2=x3;
    //fprintf(fp2, "%8.8lf %8.8lf\n", xB1, xB2);
}

//bulk calculation

if (xB1>xB2)
{
    xtemp=xB1;
    xB1=xB2;
    xB2=xtemp;
}

for (j=1;j<100;j++)
{
    xtemps=x1s;
    q1s=Q1s(x1s,xB1);
qtemps=Qtemps(x1s,xB1);
q2s=q1s+qtemps;
x2s=q1s/q2s;

q1s=Q1s(x2s,xB1);
qtemps=Qtemps(x2s,xB1);
q2s=q1s+qtemps;
x1s=q1s/q2s;

// fprintf(fp2, "%lf %lf
", x1s, x2s);
}

//along surface
fprintf(fp, "%lf %lf %lf %lf %lf", T, xB1, xB2, x1s, x2s);

//Thermo Calculation

c1=pow(x1s,2)*v+pow((1-x1s),2)*(1/v);

c2=(pow(x2s,2)*v+pow((1-x2s),2)*(1/v))*(pow(xB1,2)+pow((1-xB1),2));

c3=log(pow(q2s,2)*c1/c2);

FE=-T*c3/3;

//the first and second derivative of free energy
S=-(FE-rFE)/deltaT;
rFE=FE;
E=FE+S*T;

fprintf(fp," %.12lf %.12lf %.12lf",FE,E,S);

xB1=0.5;
xs1=0.5;
x2s=0.5;
q1s=Q1s(x2s,xB1);
qtemps=Qtemps(x2s,xB1);
q2s=q1s+qtemps;

//Thermo Calculation

c1=pow(xs1,2)*v+pow((1-xs1),2)*(1/v);

c2=(pow(x2s,2)*v+pow((1-x2s),2)*(1/v))*(pow(xB1,2)+pow((1-xB1),2));

c3=log(pow(q2s,2)*c1/c2);

OnecFE=-T*c3/3;

//the first and second derivative of free energy
OnecS=(OnecFE-OnecrFE)/deltaT;
OnecrFE=OnecFE;
OnecE=OnecFE+OnecS*T;
fprintf(fp," %.12lf %.12lf %.12lf\n",OnecFE,OnecE,OnecS);

} //temperature loop

printf("\npress enter to exit");
//scanf("%c");
fclose(fp);
fclose(fp2);
fclose(fp3);//close file fp
}

double Qtemp(double x1,double x2) {
    double f=0;
    for (int n=1;n<9;n++)
    {
        f=f+a[n]*((x1-0.5)*(S4[n]+1)-x1+1)*((x2-0.5)*(S3[n]+1)-x2+1)*((x2-0.5)*(S2[n]+1)-x2+1);
        //printf("f=%.12lf\n",f);
    }
    return f;
}
double Q1(double x1, double x2) {
    double f = 0;
    for (int n = 9; n < 17; n++)
    {
        f = f + a[n] * ((x1 - 0.5) * (S4[n] + 1) - x1 + 1) * ((x2 - 0.5) * (S3[n] + 1) - x2 + 1) * ((x2 - 0.5) * (S2[n] + 1) - x2 + 1);
        //printf("ff=%.12lf\n", f);
    }
    return f;
}

double Qtemps(double x1s, double xB) {
    double f = 0;
    for (int n = 1; n < 5; n++)
    {
        f = f + a[n] * ((xB - 0.5) * (S2s[n] + 1) - xB + 1) * ((x1s - 0.5) * (S3s[n] + 1) - x1s + 1);
        //printf("2 f=%.12lf\n", f);
    }
    return f;
}

double Q1s(double x1s, double xB) {
    double f = 0;
    //MORE CODEgettig...
for (int n=5; n<9; n++)
{
    f = f + as[n]*((xB-0.5)*(S2s[n]+1)-xB+1)
    *((x1s-0.5)*(S3s[n]+1)-x1s+1);
    //printf("sf=%.12lf\n", f);
}

return f;