

CARNEGIE MELLON UNIVERSITY

DOCTORAL THESIS

**Theoretical Study and Computer
Simulation of Generalized
Solid-on-solid Models**

Author:

Qi Fu

Supervisor:

Robert F. Sekerka

Robert H. Swendsen

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Abstract

The subject of this thesis is investigation of the morphology of a crystal surface by means of statistical mechanics and Monte Carlo simulations. We employ solid-on-solid models, modified to include the effects of corner and edge energies of faceted surfaces. We also account for surface configurational entropy associated with various surface configurations (colonies of facets). This is an extension of the work of Herring who ignored corner and edge energies and effectively treated periodic hill-and-valley structures, which have no configurational entropy. The excess energies from the corners and edges of a surface also affect the equilibrium shape of very small crystals. These and other related effects are studied on solid-on-solid models for nearest-neighbor forces with central symmetry and additive bond energies. We obtain theoretical formulae for configurational entropy and theoretical distributions of the heights and lengths of facets on one-dimensional crystal surfaces (two-dimensional crystals). These results are tested by comparison with simulation data and good agreement results. A modified solid-on-solid model with nearest neighbor energy proportional to the nearest neighbor height difference raised to a power p is used to account for effects of corner and edge energies for two-dimensional surfaces (three-dimensional crystals). On an initially flat (100) surface, a slight change of p -value has a significant effect on surface morphology. Especially for $p = 0.9$, which corresponds to positive corner energies, a “macroscopic smoothing” transition from a faceted surface at low temperatures to a non-faceted surface at high temperatures is observed. This transition is only evident for surfaces that are initially tilted with respect to a close-packed surface. We also develop a symmetric solid-on-solid model that preserves crystal symmetry. For this symmetric model, the “macroscopic smoothing” transition for $p = 0.9$ is still observed on (111) and (112) surfaces, but now the surface structure is consistent with crystal symmetry. We find a hysteresis effect in these transitions, which is less pronounced for large systems. We calculate the correlation time of the surface by several different measures to study the relaxation of the system. A discrete Fourier analysis of the surface is implemented and we verify that there exists a long-wave fluctuation in the surface. We also study the distribution of facet areas and facet heights, which turns out to be exponential. A histogram method is employed to extend results at a given temperature to nearby temperatures.

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Chapter 1

Background and Motivation

1.1 Crystals

Crystals are solids in which the elementary building blocks, the atoms, are arranged regularly in a space lattice with specific geometrical symmetry elements. There is no such thing as a “perfect crystal” in nature; although single crystals with a high degree of perfection can be grown, especially for semiconductors such as Si. For many practical applications, imperfections of the chemical and structural atomic arrangement are essential to obtain useful properties. Natural crystals have often been formed at relatively low temperatures by crystallization from solutions, sometimes for hundreds and thousands of years. Nowadays, crystals are produced artificially and rapidly to satisfy the needs of science, technology and other fields.

A crystal is a solid in which the atoms form a periodic arrangement, but not all solids are crystals. The first thing we often notice about a natural crystal is the presence of facets, which constitute its external boundaries. What distinguishes and defines a true crystal is that these facets develop spontaneously and naturally as the solid forms from a melt or from solution. When forces are applied to a crystal in certain directions, it will often break cleanly into two pieces along what is known as cleavage plane. The presence of facets is due to the ordered arrangement of lattice points at the microscopic level; however, growth conditions of a crystal ultimately determine its morphology, so many crystals do not display facets.

The underlying order of a crystalline solid can be represented by an array of regularly spaced points that indicate the locations of the crystal’s basic structural units, which contains a few atoms in a specific arrangement known as a basis. This array is called a Bravais lattice [1] and was studied by Auguste Bravais. Crystal lattices can be thought of as being built up from repeating units containing just a few atoms or molecules. Although

real crystals do not actually grow in this manner, this visualization is conceptually important because it allows us to classify a lattice type in terms of the simple repeating unit that is used to “build” it. The symmetry of a crystal is constrained by the requirement that the unit cells stack perfectly with no gaps. There are 219 possible crystal symmetries, called crystallographic space groups, and these are grouped into 7 crystal systems. In addition to their microscopic structure, large crystals are often identifiable by their macroscopic geometrical shape, consisting of flat faces with specific, characteristic orientations.

There are two extreme cases of the microstructure of crystal surfaces: atomically rough and atomically flat. Atomically rough surfaces are typical of many metallic systems and provide many sites for the attachment of atoms from the melt during crystal growth. Atomically flat interfaces are related to macroscopically flat, crystallographically well oriented surfaces or facets and are typical of complex molecular crystals. Atomic attachments on these interfaces are more difficult and require higher driving forces associated with nucleation of a new layer. Facets are oriented in a specific way relative to the underlying atomic arrangement of the crystal. This occurs because some surface orientations are more stable than others (lower surface free energy) or because of the growth kinetics associated with such surfaces. As a crystal grows, new atoms attach easily to the rougher and less stable parts of the surface, but less easily to the flat, stable surfaces.

1.2 Wulff Construction and Herring’s Theorem

Suppose that a crystal is cleaved and a surface is created. The creation of this surface adds energy, precisely surface free energy [2], which is proportional to the amount of surface area created. The surface free energy is defined as the excess of the grand potential per unit area due to a surface of a material as compared to the bulk. A surface free energy is necessarily positive, because otherwise bulk crystals would cleave spontaneously. It quantifies the disruption of intermolecular bonds and rearrangement of atoms that occurs when a surface is created. Surfaces must be intrinsically less energetically favorable than the bulk of a material for stability.

It is very desirable to measure the surface free energy of a solid interface because it is a fundamental quantity that emerges from calculation of the surface properties. The many theories of surfaces also benefit from a comparison to reliable experimental data. Theoretically, from a microscopic point of view, surface free energies will be different for surfaces of a crystal having various orientations. The number of bonds that have to be broken to generate a certain surface plane depends on surface orientation. Therefore, we can write the surface free energy with a dependence on orientation $\hat{\mathbf{n}}$, as characterized by a γ -plot, or mathematically $\gamma(\hat{\mathbf{n}})$, which can be represented by a polar plot of surface free energy as a function of orientation.

A small solid crystal at equilibrium with vapor or liquid can often have a shape for which a large fraction of the surface area is occupied by crystal planes having low surface free energies. More formally, such an equilibrium shape is the result of minimizing the total surface free energy [3], under the constraint of constant volume, over all possible orientations.

It was Wulff [4] who first made the connection between the microscopic and the macroscopic level. If the γ -plot for a given crystal is known, the equilibrium shape can be found by Wulff's construction. The procedure is simple: Draw vectors from the origin to every point on the γ -plot; then construct planes that are perpendicular to each vector at the point of intersection with the γ -plot; the inner envelope of these planes is the equilibrium shape of the crystal.

The equilibrium shape is of practical interest only for very small crystals because of the significant mass transport needed to change its overall shape. For large crystals, the free energy of a planar surface can possibly be lowered by rearranging the atoms into hills and valleys of a size large compared with atomic dimensions but still small from the macroscopic standpoint, as governed by Herring's Theorem [5, 6]:

“If a given macroscopic surface of a crystal does not coincide in orientation with some portion of the boundary of the equilibrium shape, there will always exist a hill-and valley structure which has a lower free energy than a flat surface, while if the given surface does occur in the equilibrium shape, no hill-and valley structure can be more stable.”¹

1.3 Motivation

Surface free energy results from the bond energies among atoms and the entropy associated with their structures at a given temperature. According to Herring's analysis, we can tell for a surface with any orientation whether it is energetically favorable (or neutral) to either keep the original orientation or to form a hill-and-valley structure. The free energy of a faceted surface (hill-and valley structure) is given by

$$(1.1) \quad \gamma_h = \gamma_1 f_1 + \gamma_2 f_2 + \gamma_3 f_3$$

where $\gamma_1, \gamma_2, \gamma_3$ are the surface free energy of the three boundary planes, and f_1, f_2, f_3 are determined by the following

$$(1.2) \quad \hat{\mathbf{n}} = f_1 \hat{\mathbf{n}}_1 + f_2 \hat{\mathbf{n}}_2 + f_3 \hat{\mathbf{n}}_3$$

¹There are special (degenerate) γ -plots for which such a faceted surface has a surface free energy that is equal to that of the original planar surface, as illustrated below.

where $\hat{\mathbf{n}}$ is the unit vector in the direction investigated and $\hat{\mathbf{n}}_1, \hat{\mathbf{n}}_2, \hat{\mathbf{n}}_3$ are the unit normal vectors of the facets.²

Let τ_1, τ_2, τ_3 be the reciprocal vectors to $\sigma_1, \sigma_2, \sigma_3$ respectively, and let $\mathbf{c} = \gamma_1 \tau_1 + \gamma_2 \tau_2 + \gamma_3 \tau_3$. Then Eq(1.1) can be re-written as

$$(1.3) \quad \gamma_h = \mathbf{c} \cdot \hat{\mathbf{n}}.$$

If $\gamma_h < \gamma(\hat{\mathbf{n}})$, the faceted hill-and-valley structure will be energetically favorable; whereas, if $\gamma_h = \gamma(\hat{\mathbf{n}})$, there will be no driving forces for faceting (neutral case).

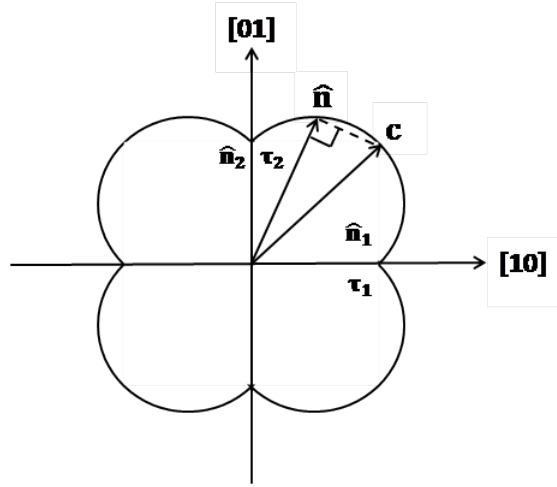


Figure 1.1: Gamma plot of the simple square lattice with additive nearest neighbor forces.

Kossel crystals [8] are simple squares (two dimensional crystals) or cubes (three dimensional crystals) that interact through nearest-neighbor additive forces having central symmetry (bond energies). The γ -plot for a two dimensional Kossel crystal is illustrated in Fig. 1.1. It is composed of segments of four circles that pass through the origin; for a three dimensional Kossel crystal, it is composed of segments of eight spheres that pass through the origin. For this γ -plot, we can examine the possibility of a surface breaking up into a hill-and-valley structure with orientations [10] and [01]. In this simple case, $\mathbf{c}$ is a vector that lies at 45° with respect to these axes and a length such that it touches the γ -plot. Then, because an angle inscribed in a semicircle is a right angle, we see that $\gamma_h = \mathbf{c} \cdot \hat{\mathbf{n}} = \gamma(\hat{\mathbf{n}})$ for this model. This is a special case for which the free energy of the hill-and-valley structure is exactly equal to the free energy of any faceted surfaces. In other words, there is no driving force for faceting, even though a hill-and-valley structure can exist for any orientations tilted with respect to [01] or [10].

However, there are some important considerations that are missing from the preceding analysis. One missing thing is the entropy that results from various surface configu-

²It turns out that it is to use only three orientations; for a proof, see [7]

rations, e.g. a mixture of small facets and large facets, as shown in Fig. 1.2. When the system size gets large, the variation of surface configurations will increase significantly. There will be a lot of possible surface configurations corresponding to the same minimal surface free energy, but the classical surface energy does not include this configurational entropy per unit area, S_{conf} . (See Chapter 4, Figure 4.1 for actual results from simulations.) If Herring's analysis is generalized to include the configurational entropy due to these colonies, the free energy for a faceted surface will be lower by an amount TS_{conf} . Therefore, the role of this configurational entropy should be investigated.

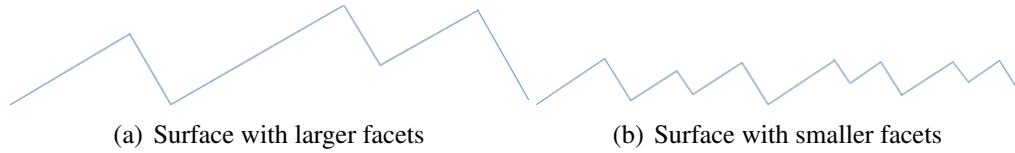


Figure 1.2: Surface composed of a mixture of facets with various sizes.

Another missing thing is the energy associated with corners and edges of a surface due to facets. When a surface is large, a hill-and-valley structure most likely results in a lot of corners and edges. The excess energies of these would have a significant effect on morphology. Edge and corner energies also give rise to the sizes of facets that compose a hill-and-valley structure. In other words, a change of scale of any surface topology would result in new corners and edges. The contributions of corners and edges to crystal faceting should also be investigated.

Furthermore, although Herring's theorem pointed out the existence of the hill-and-valley structure and their orientations, it does not give the sizes of the structures. As mentioned above, size can be influenced by including the effects of corners, edges, and the configurational entropy.

Therefore, this simple model is a good test case for the role of configurational entropy, edge and corner energies in crystal faceting.

Chapter 2

Solid-on-Solid Model

2.1 Growth Models

Growth processes are phenomena of considerable scientific interest with a broad range of practical applications. Almost all forms in nature are products of some kind of growth. An understanding of growth has relevance in various fields: materials science, chemical physics, medicine, and even sociology.

Mechanisms of growth are usually quite complicated; however, one can often use a more-or-less simplified model to describe some its most important features. The large variety of materials and the various mechanisms of growth lead to a large number of growth models, and many have been developed and investigated.

Interest in growth models is motivated, in part, by connection with practically important processes in which the material is either added (e.g. crystal growth, biological growth) or removed (e.g. corrosion, erosion). On the other hand, much of this interest arises from the fact that these growth models exhibit new features that are interesting from the point of view of non-equilibrium statistical physics.

One of the most challenging problems is understanding the dynamics of growth and morphology of rough surfaces. One measure of the morphology of a surface can be characterized by roughness. At equilibrium, the idea of a thermal roughening transition between a flat interface and a rough high-temperature interface was suggested long ago by Burton and Cabrera [9]; later it was confirmed experimentally and the equilibrium roughening transition was studied extensively. Today, the roughening transition is well understood. Since growth is a non-equilibrium process, the roughening for growing surfaces is more difficult. An example would be diffusion limited aggregation [10].

Growth models can be divided crudely into two classes according to the character of the growth mechanism: models with mechanisms based on energy considerations, for

which the temperature is usually the most important parameter, are able to describe the kinetics of crystal growth; and models based on random events and random numbers.

Growth models can be divided roughly into continuous models and discrete models. The former are governed by a stochastic differential equation in the variables that describe the surface. The latter are given by defining a space of configurations and by giving rules of growth that govern the possible processes and their probabilities.

In the case of discrete models, the surface configuration can often be represented by a d -dimensional array of integers - heights of the columns of atoms relative to a flat reference surface. Discrete models can be defined for various kinds of lattices (the simple cubic lattice is often used). In numerical simulations, relatively small finite systems must be used; however, periodic boundary conditions can be employed to relate to large surfaces.

2.2 Solid-on-Solid Models

A special class of models, so-called solid-on-solid (SOS) models [11], have been used to study the equilibrium statistical mechanics of surfaces. These models fulfill a SOS-constraint that every occupied site is directly above another occupied site (thus there are no overhangs or holes). A particular variant is a restricted solid-on-solid model (RSOS) defined on a simple cubic lattice and having the additional constraint that the difference of heights of neighboring sites i, j is restricted by a condition $|h_i - h_j| < S$, where S is some integer. Even more restricted is a single step solid-on-solid model in which the difference can take only two values, 0 or 1. The surface configurations in the RSOS model can be mapped into the N -state vertex model [12, 13].

It turns out that the mathematics of the solid-on-solid model is similar to the mathematics of the Ising model [14]. An atom has one interaction energy with an occupied neighboring crystalline site and a different interaction energy with neighboring site which is not occupied. This is similar to the Ising model, where there is one interaction energy if the neighboring atom has the same spin and a different interaction energy if it does not.

The random deposition model, in which particles simply fall vertically down until they reach the top of the column in which they were dropped or they reach the substrate, with normal incidence (with or without diffusion) also fulfills the SOS-condition.

In the case of SOS-models, in addition to the SOS-constraint, the energy for each surface configuration is given by a monotonically increasing function V of the difference of heights $|h_i - h_j|$ of neighboring columns i, j :

$$(2.1) \quad H_{SOS} = \sum_{\langle i, j \rangle} V(|h_i - h_j|)$$

Various SOS models with different functions V can be considered. In a standard SOS model the function V is just the absolute value $|h_i - h_j|$. If the energy is taken of quadratic form $(h_i - h_j)^2$, one arrives at the so-called Discrete Gaussian model (DGSOS).

For a SOS model on some lattice where the space of possible configurations is given, one must complete the growth model by specifying the rules of growth. In addition, one can consider not only growth processes but also evaporation processes in which a particle is removed from the surface.

2.3 Roughening Transition

Some surfaces are smooth on the atomic scale and others are rough. The surfaces that are rough on an atomic scale usually have isotropic properties, and so are the rounded on a macroscopic scale. The surfaces that are smooth on an atomic scale have anisotropic properties and tend to form macroscopic facets. A surface can be in different states having different roughness, and by changing physical parameters it can undergo a phase transition, known as surface roughening transition. The idea that there could be a phase transition of this type in the equilibrium structure of crystal surfaces was first suggested by Burton and Cabrera [9, 15]. They conjectured that the low index crystal faces in equilibrium with vapor, melt or solution, would become rough above a certain temperature T_R , the so-called roughening temperature. This can have important consequences for the speed of growth (for small deviations from equilibrium) as well as the equilibrium shape of a crystal.

Typically, a two-dimensional surface in equilibrium undergoes a roughening transition at a temperature T_R : the surface is microscopically smooth below T_R but rough above. Growing surfaces are even rougher than at equilibrium; because, in addition to the thermal fluctuations there are stochastic fluctuations due to the growth process itself, even at temperatures below T_R .

The roughening transition is defined to occur when there is a logarithmic divergence of the height fluctuations for $T > T_R$ [12]. The roughening transition was first simulated for SOS-models. It has been shown that the SOS model gives rise to a roughening transition and that the height-height correlation function diverges logarithmically with distance along the surface [12]. The critical temperature for the roughening transition depends on the specific material system and the details of the interactions between the atoms. Furthermore, the numerical value of the roughening transition depends on both the crystal structure and the orientation of the surface.

2.4 Modified Solid-on-Solid Model

We consider a growth model of the form

$$H = \sum_{(i,j),(i',j') \text{ are } NN's} |h_{ij} - h_{i'j'}|^p$$

where (i, j) and (i', j') are nearest neighbors and h_{ij} is the height of the surface at site (i, j) .

The well-known solid-on-solid model corresponds to the case $p = 1$, and the discrete Gaussian model corresponds to $p = 2$. The roughening transition has been simulated for these models [16]. But one problem with these models is the lack of explicit or implicit inclusion of the energies from corners and edges of the surface. On a crystal surface, these energies from corners and edges, especially on a tilted surface, have a significant impact on the behavior of the surface. In order to investigate these effects, we employed various values of p .

For $p < 1$, h^p is a convex function, such that $h_1^p + h_2^p > (h_1 + h_2)^p$. This means that a big step has lower energy than two smaller steps, which is equivalent to saying that this model gives positive energies to corners and edges. Therefore this model disfavors corners and edges and results in big steps and facets. For $p > 1$, h^p is a concave function, such that $h_1^p + h_2^p < (h_1 + h_2)^p$. This means that a big step has higher energy than two smaller steps, which is equivalent saying that this model gives negative energies to corners and edges. Therefore this model favors corners and edges at the expense of big steps. However, corner and edge energies are small compared to bulk bond energies, so we allow p to take the values 0.9, 1, 1.1 to simulate various cases.

Although the changes in p values from 1 are not very large, we will later see how these small changes affect the surface configuration and result in interesting and significant morphologies.

Chapter 3

Monte-Carlo Simulation

3.1 History, Background and Application

Experimental physics has been carried out by experiments for centuries. Gradually, ideas about why certain natural phenomena occur were formulated by many people. Eventually these ideas were made more logical by the use of mathematics and gave rise to the what we call “theory” today. However, some experiments are too complicated to explain by traditional theoretical methods or are limited by many conditions and sometimes impossible to implement. With the development of fast computers, computer simulation becomes easier and more and more powerful, especially for solving some intractable problems. In many fields, computer simulation first enables the possibility for deep investigation, new models and techniques. Computer simulation becomes a brand new way to carry out research, providing a theoretical model for the experimental data, or providing results that can be compared directly with data from experiments.

Monte Carlo (MC) simulations are often used in computer simulations of physical systems [17]. Rather than following the time evolution of a system, Monte Carlo simulations use stochastic methods to sample configurations. In particular, Monte Carlo simulations are based on a sequence of random numbers representing a random process. As a result, different sequences of random numbers will not give identical results but will give the same results statistically, within sampling errors.

An early reference to the Monte Carlo method is that of Comte de Buffon [18] who proposed a Monte Carlo-like method to evaluate the probability of tossing a needle onto a ruled sheet. The modern Monte Carlo age was ushered in by von Neumann and Ulam [19] during the initial development of thermonuclear weapons. Ulam and von Neumann used the phrase “Monte Carlo” and were pioneers in the development of Monte Carlo techniques and their implementations on digital computers.

Monte Carlo methods [20–22] are especially useful for simulating systems with many coupled degrees of freedom, such as fluids, disordered materials, strongly coupled solids, and cellular structures. The range of different problems that can be explored by using Monte Carlo simulations is very broad. Models that can be naturally or approximately discretized can be treated. There are many examples of the use of the Monte Carlo method that can be drawn from many areas, e.g., social science, traffic flow, population growth, finance, genetics, quantum chemistry, radiation sciences, radiotherapy, and radiation dosimetry.

One important advantage of simulations is that various physical effects that are simultaneously present in real systems may be isolated by means of separate considerations. We can strive to understand physical properties and processes as completely as possible by varying “experimental conditions” of simulations.

On the other hand, because of limits on computer speed there are some complex problems that are inherently not suitable for computer simulations. Long computation times and insufficient computer memory that is a problem now may be alleviated in the future, but one can sometimes use novel algorithms to overcome them. Another problem is statistical and computational error. The storage of data and computation can generate and accumulate error, and inherent errors of algorithms can result in unavoidable statistical error due to a finite number of samples or ensembles.

3.2 Random Numbers

In computer simulation, the generation of random numbers is crucial. It may be conceptually impossible to generate true random numbers from a computer because computer output is entirely predictable. Fortunately, the random numbers in computer simulations can just be pseudo-random, which means that random sequences that are generated are statistically uncorrelated, and therefore different from each other in all measurable respects. In other words, it suffices if two different random number sequences give the same results statistically. It is worthy mentioning that randomness is also related to the problem to which it is applied. What is “random enough” for one problem may not be random enough for another. Therefore, a good random number generator should at least meet the requirements for a specific application.

In many cases, we want to generate random numbers which obey certain probability distributions, e.g., normal distributions, exponential distributions. One of the most fundamental distributions is the uniform distribution, which generates random numbers within a specified range, with any one number just as likely as any other. Many other random numbers from other distribution are basically also generated indirectly from uniform random numbers. So a reliable uniform random number generator is an essential part of

modeling by means of Monte Carlo simulations [23].

One of the oldest and most widely used methods of Pseudo Random Number Generation is the Linear Congruential Generator, which generates the sequence of integers $R_1, R_2, R_3, \dots$, each between 0 and $m - 1$ by the following recurrence relation:

$$(3.1) \quad R_{j+1} = aR_j + c \pmod{m}$$

The sequence generated using this equation would eventually repeat itself, with a period less than m . If the numbers m, a and c are chosen properly, the period will be of maximal length comparable to m . Though this sounds complicated, it really means is that we take a starting value (the seed) in the generating functions and the resulting number is then used as a random number, it becomes the new seed for generating the next random number.

The linear congruential method is really fast in implementation and of universal use, but it has the disadvantages of suffering from sequential correlation on successive numbers. If n sequential random numbers are used as coordinates in n dimensional space, the points will tend to lie on $(n - 1)$ dimensional hyperplanes. If we deal with a problem in which only a small fraction of the the n dimensional random number space is used, then the discreteness becomes a pronounced issue. Thus, good random number generators either maximize the number of planes that are constructed to give the illusion of randomness or practically eliminate this artifact entirely.

Selecting the right numbers to use in linear congruential generators is complex and easy to get wrong. Luckily the hard work has already been done for us. Back in 1969 Lewis, Goodman and Miller [24] suggested $n = n * 16807 \pmod{2147483647}$. This choice has been studied widely and tested and has been used extensively and successfully. In 1988 Stephen Park and Keith Miller [25] wrote an excellent paper called “Random Number Generators: Good Ones Are Hard To Find”. In it they look at some of the problems with commonly used random number generators and suggest that $a = 16807$, $m = 2147483647$ in $R_{j+1} = a * R_j \pmod{m}$ be adopted as a “minimum standard”.

Because of multiplication in the generation recursion, it is impossible to implement the recursion directly in a high-level language because the product of a and $m - 1$ will exceed the maximum value that a certain computer can handle. A trick due to Schrage [26] without using any intermediates is therefore extremely interesting. Schrage’s algorithm is based on an approximate factorization of m ,

$$(3.2) \quad m = aq + r, \text{ i.e., } q = \lfloor m/a \rfloor, r = m \pmod{a}$$

with square brackets denoting the integer part. In the case of small r , especially when $r < q$ and $0 < z < m - 1$, it can be shown that

$$az \pmod{m} = \begin{cases} a(z \pmod{q}) - r\lfloor z/q \rfloor & \text{if it is } \geq 0 \\ a(z \pmod{q}) - r\lfloor z/q \rfloor + m & \text{otherwise} \end{cases}$$

Schrage's algorithm uses the values $q = 127773$ and $r = 2836$.

This minimal standard satisfies the majority of applications. It has been shown that other multipliers a can also be used and substituted for the minimal standard. Low order correlations, the cross-correlation of data with itself as a function of time separation between, can be calculated. In Figure 3.1, 100 successive random numbers are used for calculating the auto correlations up to a maximal time separation, time-lag, of 10.

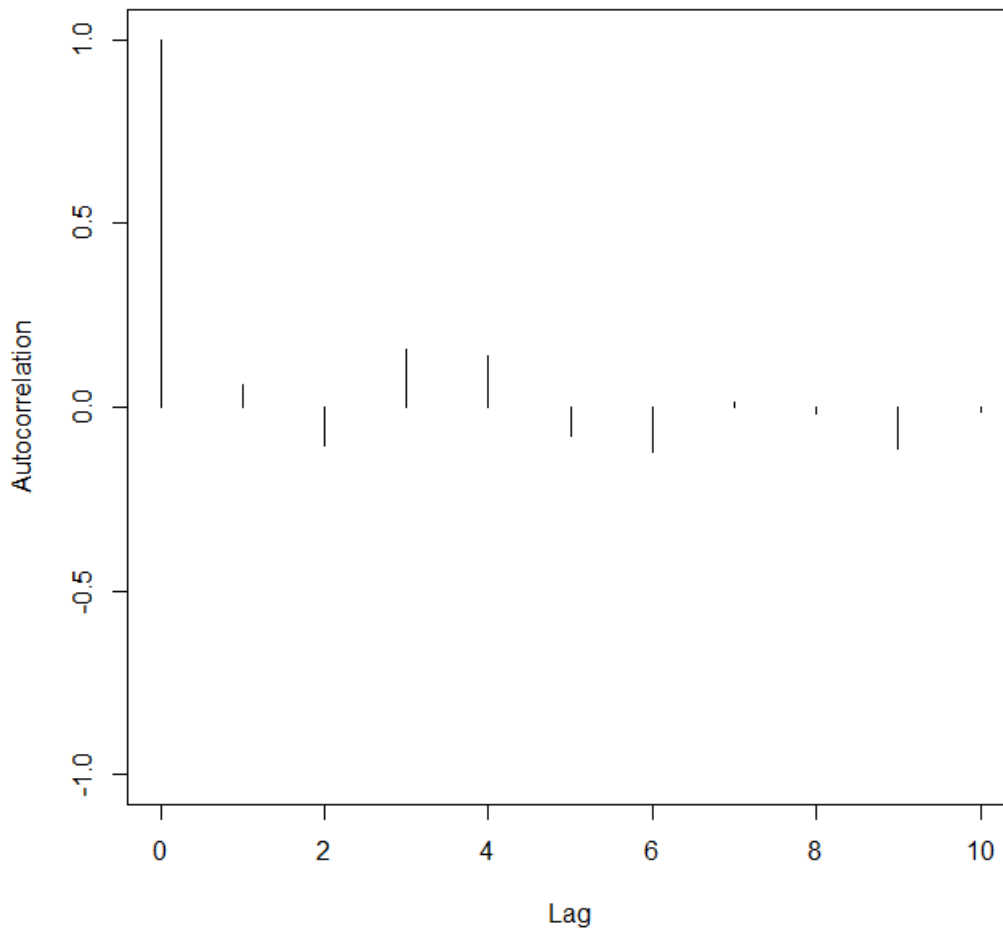


Figure 3.1: Auto correlation coefficients vs. Lag for 100 generated random numbers

In Figure 3.2, 10000 successive random numbers are used for calculating the auto correlations up to a maximal lag of 10. In both cases, the auto correlation is generally small for the low orders. When the sequence is short, the auto correlation is much larger

than that for a longer sequence. This indicates the shortcoming of this random generator for short sequences.

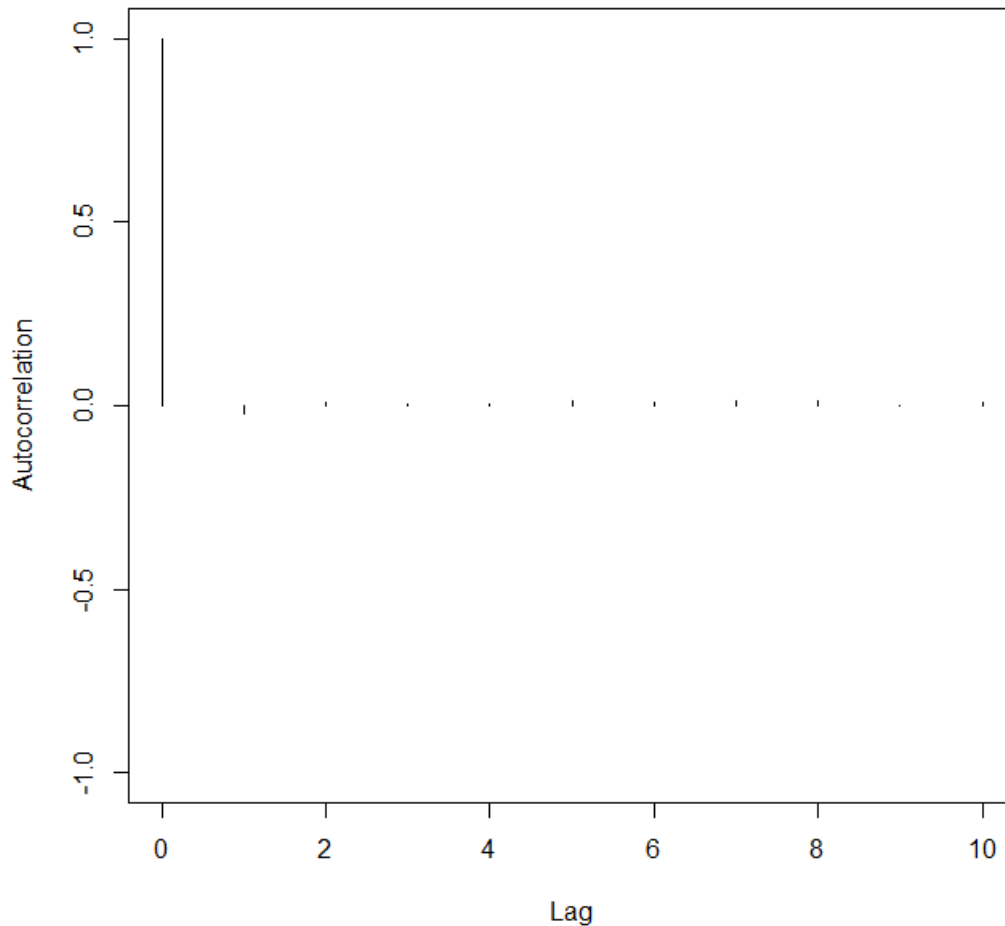


Figure 3.2: Auto correlation coefficients vs. Lag for 10000 generated random numbers

A very simple way to get rid of the low order serial correlation is to shuffle the output. Random numbers are stored and picked out later on a randomized basis. It has been shown that this generator passes almost all statistical tests. For even longer random sequences, a better way is simply to add two different random sequences. Combining the two sequences breaks up the serial correlations to a considerable extent.

3.3 Markov Chain and Metropolis Sampling

The concept of Markov chains is central and essential to Monte Carlo simulations. A Markov chain [27,29,31], named after Andrey Markov, is a stochastic process that undergoes transitions from one state to another, among a finite or countable number of possible states. A discrete-time random process involves a system which is in a certain state at each step, with the state changing randomly between steps. Since the system changes randomly, it is generally impossible to predict with certainty the state of a Markov chain at a given time in the future. However, the statistical properties of the system's future can be predicted. In many applications, it is these statistical properties that are important.

We define a stochastic process at discrete times labeled sequentially as $t_1, t_2, \dots$, for a system with a finite set of possible states $S_1, S_2, \dots$. The process starts in one of these states and moves successively from one state to another, and each such move is called a step. If the chain is currently in state S_i , then it moves to state S_j at the next step with a probability W_{ij} . If this probability does not depend upon which state the chain was in before the current state, then such a process is called a Markov process [30]. The corresponding sequence of states is called a Markov chain, and the above conditional probability W_{ij} can be interpreted as the transition probability to jump from state i to state j [31]. It is obvious and required to meet the following

$$(3.3) \quad W_{ij} \geq 0, \quad \sum_j W_{ij} = 1$$

The total probability that the system is in state S_j at time t is given by $P(S_j, t) = \sum_i W_{ij}P(S_i, t-1)$. The master equation describes the change of the probability with time t :

$$(3.4) \quad \frac{dP(S_j, t)}{dt} = - \sum_i W_{ji}P(S_j, t) + \sum_i W_{ij}P(S_i, t)$$

This equation indicates that the total probability is conserved, so the probability of a state S_j that is lost by transitions is gained in the probability of staying at that state, and it describes the balance of gain and loss processes. It is very important in “importance sampling” of Monte Carlo processes.

The Metropolis sampling algorithm [32,33] is a Markov chain Monte Carlo method to obtain a sequence of random samples from a probability distribution for which direct sampling is difficult. In classical physics, the configurations generated from Metropolis sampling are obtained from a previous state by using a transition probability that depends on the energy difference between the initial and final states. The resulting sequence of states forms a time ordered path which is referred to as a Monte Carlo time (steps). In equilibrium, the time behavior is steady and the differential term in the master equation becomes zero. Equilibrium is guaranteed by employing the additional condition known

as “detailed balance”:

$$(3.5) \quad W_{ji}P(S_j, t) = W_{ij}P(S_i, t),$$

which is used as a simple and reliable condition to provide the desirable equilibrium state. Therefore, it causes the RHS of equation 3.4 to be zero term by term. The probability of state S_i occurring in a classical system is given by

$$(3.6) \quad P(S_i, t) = e^{-E_i/k_B T} / Z$$

where Z is the partition function which contains all of the essential information about the system under consideration, T is the temperature, and k_B is the Boltzmann constant. The general form for the partition function for a classical system is

$$(3.7) \quad Z = \sum_{all\,states} e^{-H/k_B T}$$

where H is the Hamiltonian for the system. The summation is over all possible states of the system and thus depends upon the size of the system and the number of degrees of freedom. It is generally not easy to calculate the partition function for a complex system; however, one can avoid this by generating a Markov chain of states. Each new state is generated directly from the preceding state. In the generation of the Markov chain process, the denominator Z cancels and the relative probability is the ratio of the individual probabilities. Therefore, only the energy difference $\Delta E = E_i - E_j$ between the two successive states is needed.

Any transition rate that satisfies detailed balance is acceptable. The Metropolis sampling used in statistical physics is the following:

$$W_{ij} = \begin{cases} \exp(-\Delta E/k_B T) & \Delta E > 0 \\ 1 & \Delta E < 0 \end{cases}$$

The Metropolis algorithm is implemented as follows:

1. Start from an initial state
2. Randomly choose another state according to a symmetric jump function from the current state
3. Calculate the energy change ΔE
4. Generate a random number r such that $0 < r < 1$
5. if $r < \exp(-\Delta E/k_B T)$, jump to the new state; otherwise, stay in current state
6. Go back to (2) and continue until one reaches a desired number of iterations

Chapter 4

Surface Measurements

The following is a snapshot of a surface configuration from simulation on a one dimensional surface of slope 1 with projected length 100 at low temperatures.

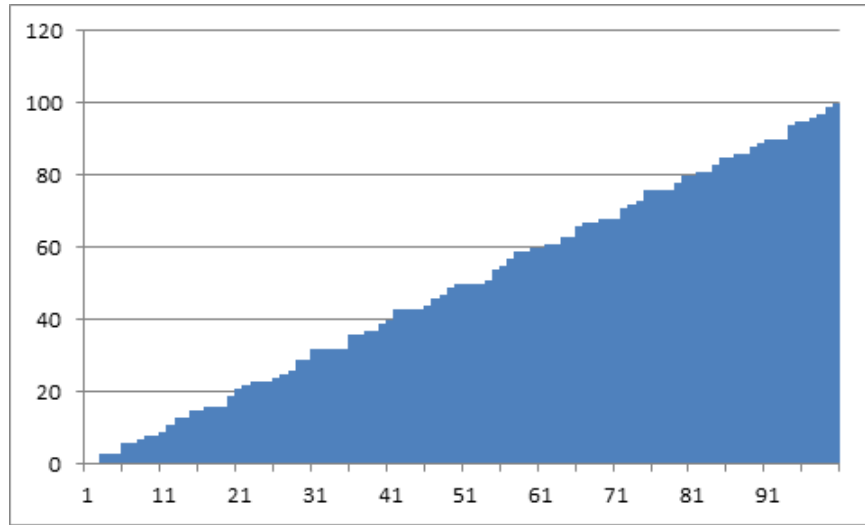


Figure 4.1: Surface configuration on a one dimensional surface of slope 1 with projected length 100 at low temperatures

From the plot, we can clearly observe colony structures consisting of larger and smaller facets on a small scale, as well as surface fluctuations on a large scale. To better understand the surface configurations, we can study the correlations and fluctuations in detail in the following [\[34\]](#).

4.1 Correlation Function and Correlation Time

Time-correlation functions are an effective and intuitive way of representing the dynamics of a system [35]. This is one of the most common tools of time-dependent thermal dynamics and provides a statistical description of the time-evolution of a variable for an ensemble at thermal equilibrium. Correlation functions are generally applicable to any time-dependent process for an ensemble, but are commonly used to describe random (or stochastic) and irreversible processes [37]. Their use is equivalent to autocorrelation in statistics, which measures the similarity between observations as a function of the time separation between them.

It is interesting and important to study the correlation function to determine the correlation time of the simulated system. This enables us to get an idea how fast the system will achieve a statistically independent equilibrium configuration following a previous one. The correlation function also describes the fluctuations of the system and is essential to calculate error terms of other important quantities. Roughly speaking, the statistical error in a property calculated as an average over a simulation run is proportional to square root of the correlation time [36].

The correlation function describes the similarity or the correlation at various time lags in the system. It takes the form

$$(4.1) \quad f(t) = [\langle h(t') \cdot h(t' + t) \rangle - \langle h(t')^2 \rangle] / [\langle h(t')^2 \rangle - \langle h(t') \rangle^2]$$

where $h(t)$ is a characteristic function of concern and $\langle \cdot \rangle$ represents the expectation value. In our case, $h(t)$ is the surface height used to describe surface configurations. $f(t)$ is therefore a correlation of height for a time lag t .

By using the correlation function given above, the correlation time t_C of the system is

$$(4.2) \quad t_C = \sum_{t=1}^{\infty} f(t)$$

The RHS of Equation 4.2 sums the correlations with various simulation time lags. In practice, the summation cuts off at some point where the correlation is small and the sum of the rest terms is in the desired error range; the summation also stops when negative correlation occurs.

In calculating the correlation function by using equation 4.2, the unit time lag can be any meaningful time length compared with the correlation time. Here, the correlation function and correlation time t_C are calculated by using two different time units, one is a time unit of every simulation step and the other is a simulation sweep (one simulation

sweep equals to the number of steps needed to sample each member of the system). The results using simulation steps are then converted back to simulation sweeps and compared with the results using simulation sweeps, as shown in Figure 4.2. Here $f(t)$ is the number of steps of height 1 on a one dimensional surface since this is a significant and easy function to investigate the surface configurations.

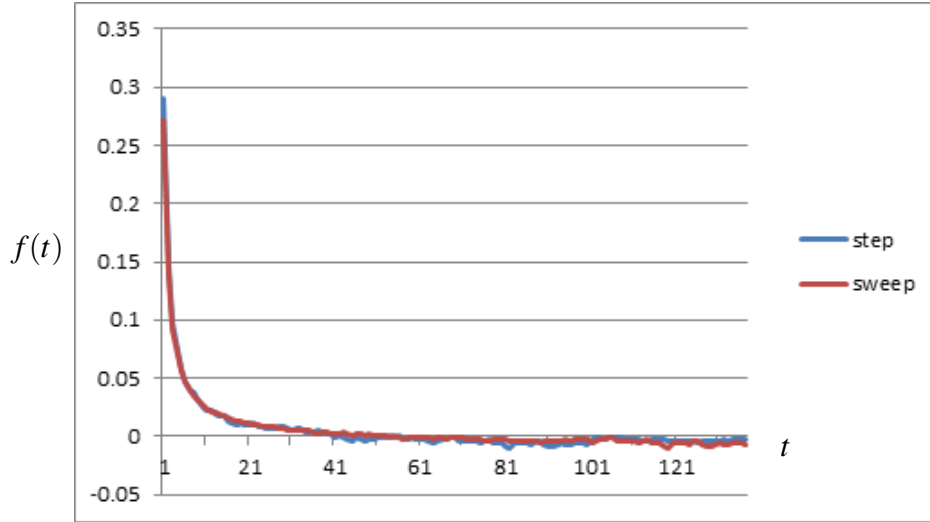
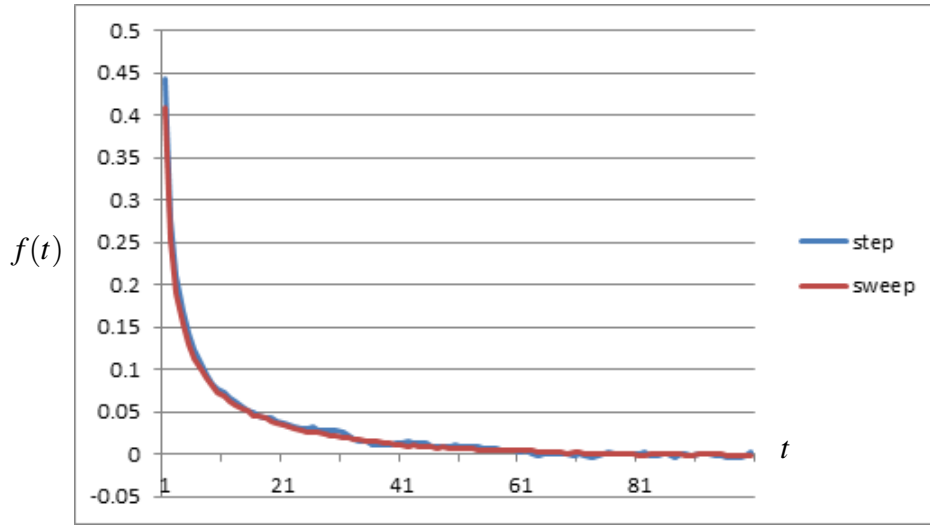
(a) $f(t)$ on slope=1 surface(b) $f(t)$ on slope=1/2 surface

Figure 4.2: Correlation function calculated by using (a) time lag unit in simulation step and (b) simulation sweep for a one dimensional surface with length 20

We see that the correlation function calculated in both ways are highly similar in values and almost identical for surface of both slope = 1 and slope = 1/2. The corre-

sponding correlation time for slope = 1 is equivalently 1.126 sweeps when calculated in step units and 1.123 sweeps when calculated in sweep units. The corresponding correlation time for slope = 1/2 is equivalently 2.915 sweeps when calculated in step units and 2.708 sweeps when calculated in sweep units. The correlation time calculated in both ways are very close compared with the sweep scale. The values are slightly higher using step intervals as expected since a smaller grid is used to sum the correlation functions. Since in practice the simulation is generally carried out using the time scale of simulation sweeps, this comparison tells us that using simulation sweeps as the time lag in calculating the correlation time is much more efficient compared to the case using simulation steps and that the errors are small compared to the units of simulation sweeps. Therefore, we should use the simulation sweep as the time scale for calculating correlation functions.

Correlation functions are calculated for various system sizes L from 8 to 256 for a one dimension surface of slope 1. The results are shown in Figure 4.3. From the plots, we can see that the correlations behave similarly in all cases. A correlation curve consists of two segments, a relatively steep curve at early times and a relative shallow curve at later times. The inverse of the slope from the semi-log plot corresponds to the correlation time as well. Therefore, the observation tells us there is a relatively fast relaxation at early times and followed by a relatively slow relaxation.

We can also see the difference between various system sizes. The correlation time is then plotted as a function of system sizes for the above results in Figure 4.4. From the plot, a power law is observed. As the system size gets larger, the correlation time gets longer and the relaxation gets slower. The exponent of the power law is significantly greater than 1, which would give rise to quite long computation time for much larger systems.

In order to understand the correlation more deeply, calculations of the correlation function are carried for various system sizes and plotted in 4.5. The three curves overlap in the first part of the fast relaxation region and then separate in the slow relaxation regions. The larger the system size, the slower the relaxation.

Fig. 4.6 shows relation between the correlation time and the inverse surface slope. We see that there are more available sites to add and remove atoms on a steep slope than on a shallow slope, which results in a shorter correlation time for a steep slope.

4.2 Surface Fluctuations

From the plots of the correlation functions above, we infer that the slow relaxation corresponds to long-wave surface fluctuations, which will also affect other quantities pertaining to the surface. In order to study surface fluctuation, we employ a discrete Fourier transformation (DFT) [38].

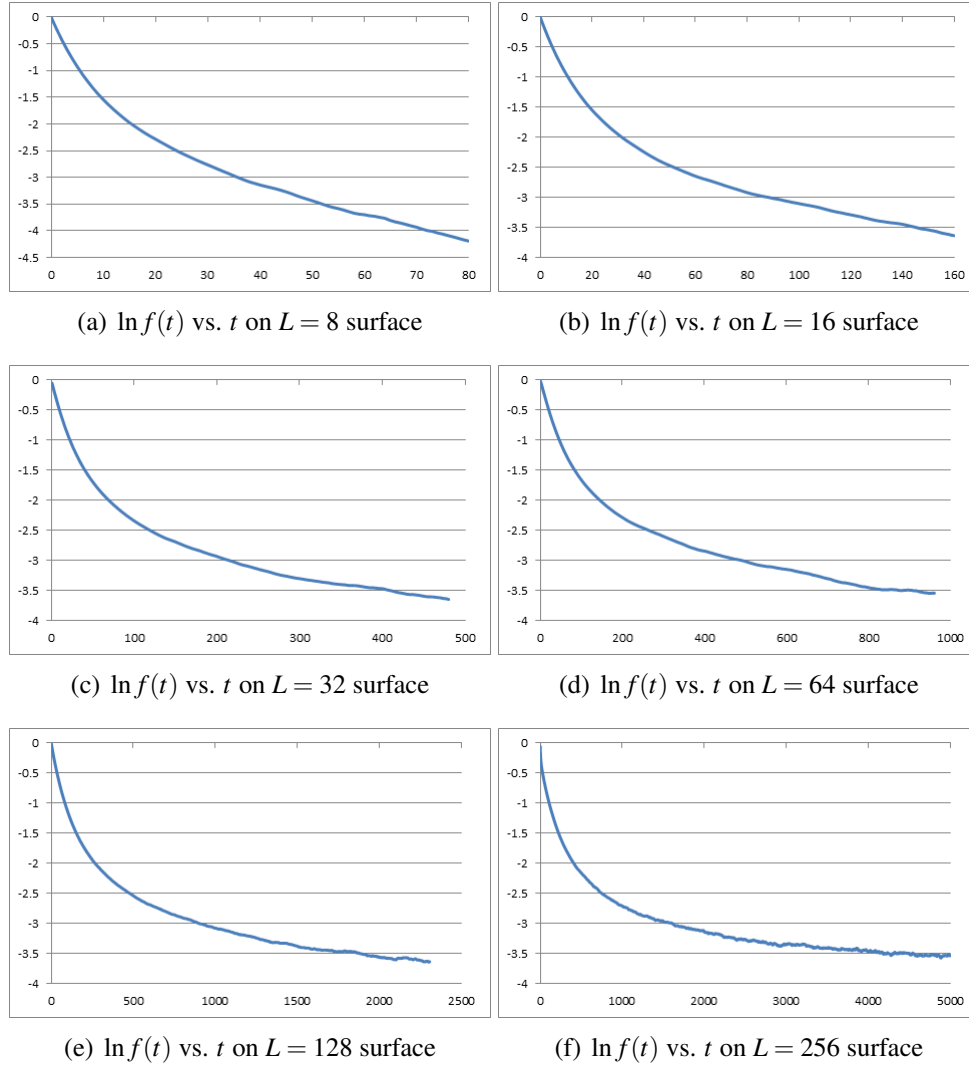


Figure 4.3: Semi-log plot of correlation function ($\ln f(t)$) of a one dimensional surface of slope 1 for various system sizes L from 8 to 256

In mathematics, DFT is a specific kind of discrete transform, used in Fourier analysis [39]. It transforms one function into another, which is called the frequency domain representation, or simply the DFT, of the original function (which is often a function in the time domain). The DFT is a discrete variant of the continuous Fourier transform and requires an input function that is discrete. The input to the DFT is a finite sequence of real or complex numbers, making the DFT ideal for processing information stored in computers.

We can use DFT to analyze the surface configurations generated by our simulation

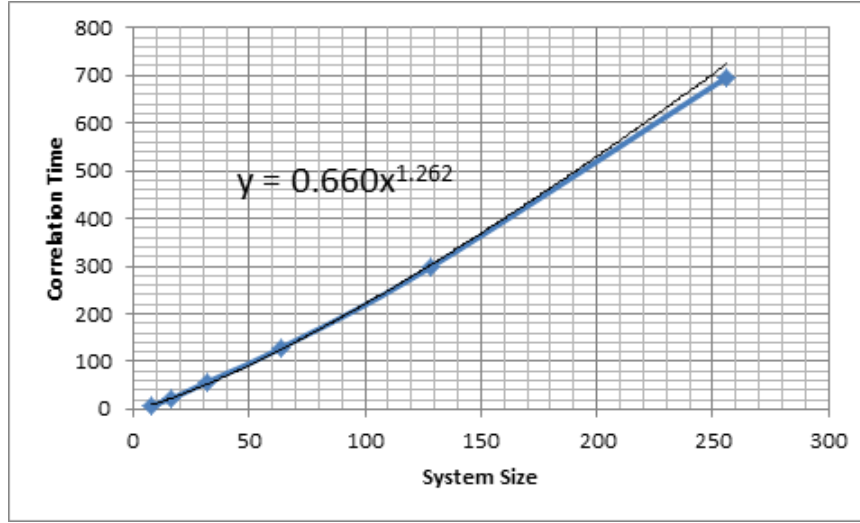


Figure 4.4: Correlation time vs. System size on a one dimensional surface of slope 1

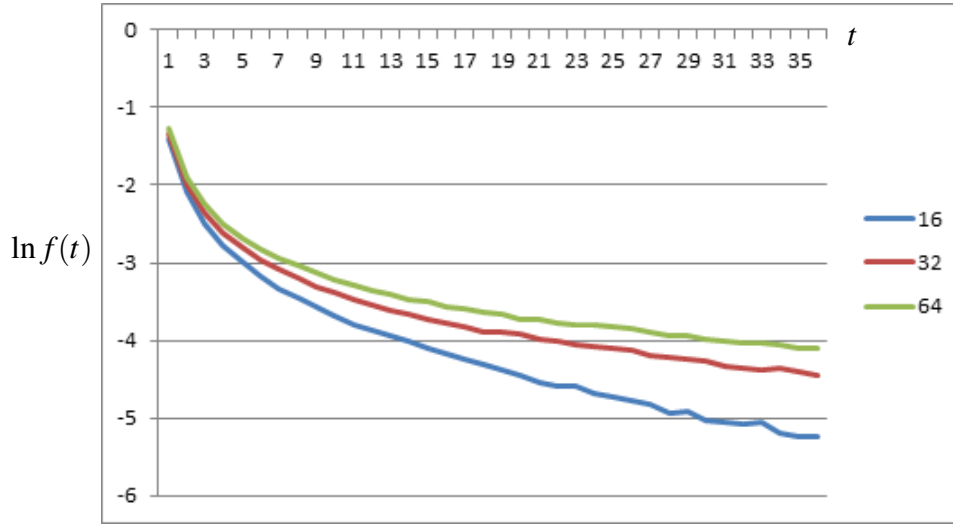


Figure 4.5: Correlation function for a one dimensional surface of slope = $1/2$ with length $L = 16, 32, 64$

data. At various simulation time steps, the current surface configurations are subtracted from their initial configuration to form a discrete data series. The DFT is then carried out on this data to explore the surface fluctuations. Figure 4.7 shows the subtracted surface configurations and their DFT at time tick 1000 sweeps, 2000 sweeps and 3000 sweeps for a one dimensional surface of slope 1 and size $L = 128$. From the surface configuration plots, it is shown clearly that the surface is still evolving, even when the surface is near to an equilibrium configuration. We also see, at each time tick, that the DFT has

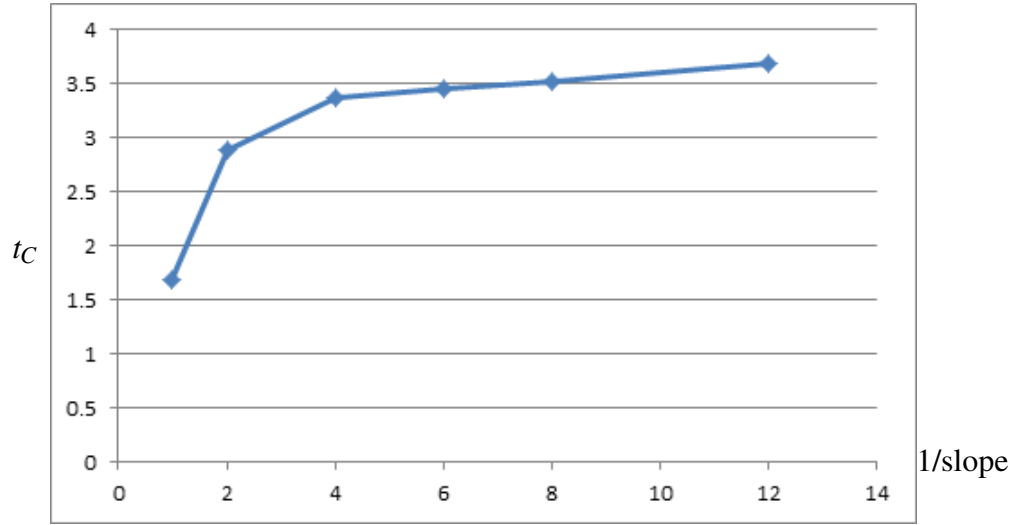


Figure 4.6: Correlation time vs. $1/\text{slope}$ on a one dimensional surface with length $L = 20$

similar characteristics. The amplitudes of the long waves (especially the first a few) are much larger than for the short waves because there are ever present long-wave fluctuations resulting in slow relaxation of the surface.

Having observed long-wave fluctuations of the surface, we can now generate some simple, but yet meaningful, quantities to study the surface. At a certain time tick, we can subtract the initial configuration from the current configuration to form a so-called excess configuration. We then generate an quantity called excess difference, which is the difference between the total number of excess atoms on the first and second half of the excess configuration. By using the quantity excess difference, we can again study the surface correlations.

For the simulation, we use two different models. One is the conserved model (CM), where the total number of surface atoms are fixed, so an atom can only be removed from a site and then added to another site on the surface. For the other model, called the non-conserved model (NCM), the total number of surface atoms is not fixed. Removing an atom from the surface is independent of adding an atom to the surface. The CM model requires a pair of added and removed atoms at the same time while the NCM model has equal probability of adding and removing atoms. Eventually, the two models will give the same results statistically.

We can use our new quantity excess difference to study the correlation time for these two models to check whether any significant difference occurs. In Figure 4.8, we show semi-log plots of the correlation function on a one dimensional surface of slope 1 for system sizes $L = 8, 16, 24, 32, 40, 48$. Here we observe very nice correlation functions having a long linear region for both the conserved and non-conserved model.

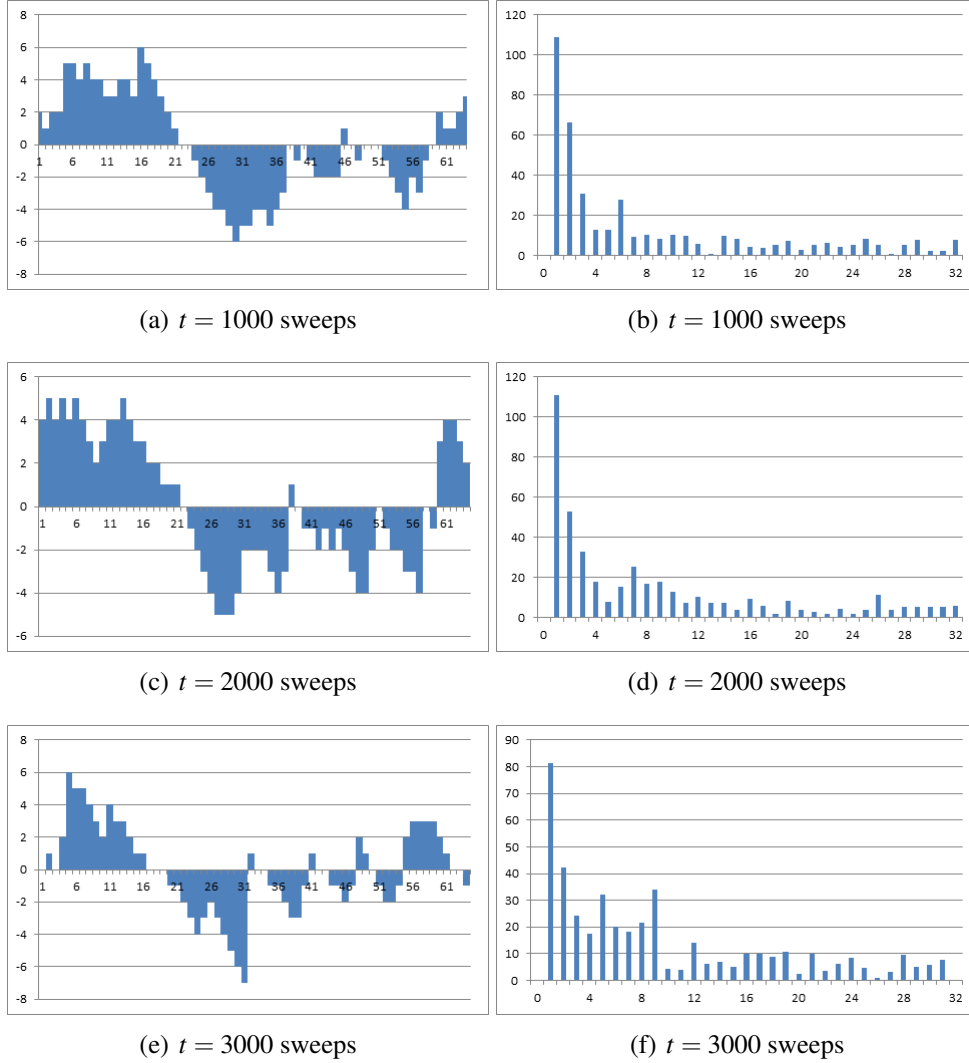


Figure 4.7: Subtracted surface configurations (left) and their DFT (right) at time ticks 1000 sweeps, 2000 sweeps and 3000 sweeps for a one dimensional surface of slope 1 and size $L = 128$

The correlation functions for the two models are very similar, and the only difference being the tail. It is expected that the correlation time of these two models should be close from a statistical point of view, and this is verified by our calculation.

Figure 4.9 shows the log-log plot of the the excess difference of the correlation time calculated for both models against system size. A power law is clearly shown with an exponent around two. This means that the larger the system size, the longer the correlation time, and the longer the system takes a long time to relax from previous configurations. In order to compare the new quantity excess difference with the previous quantity of the

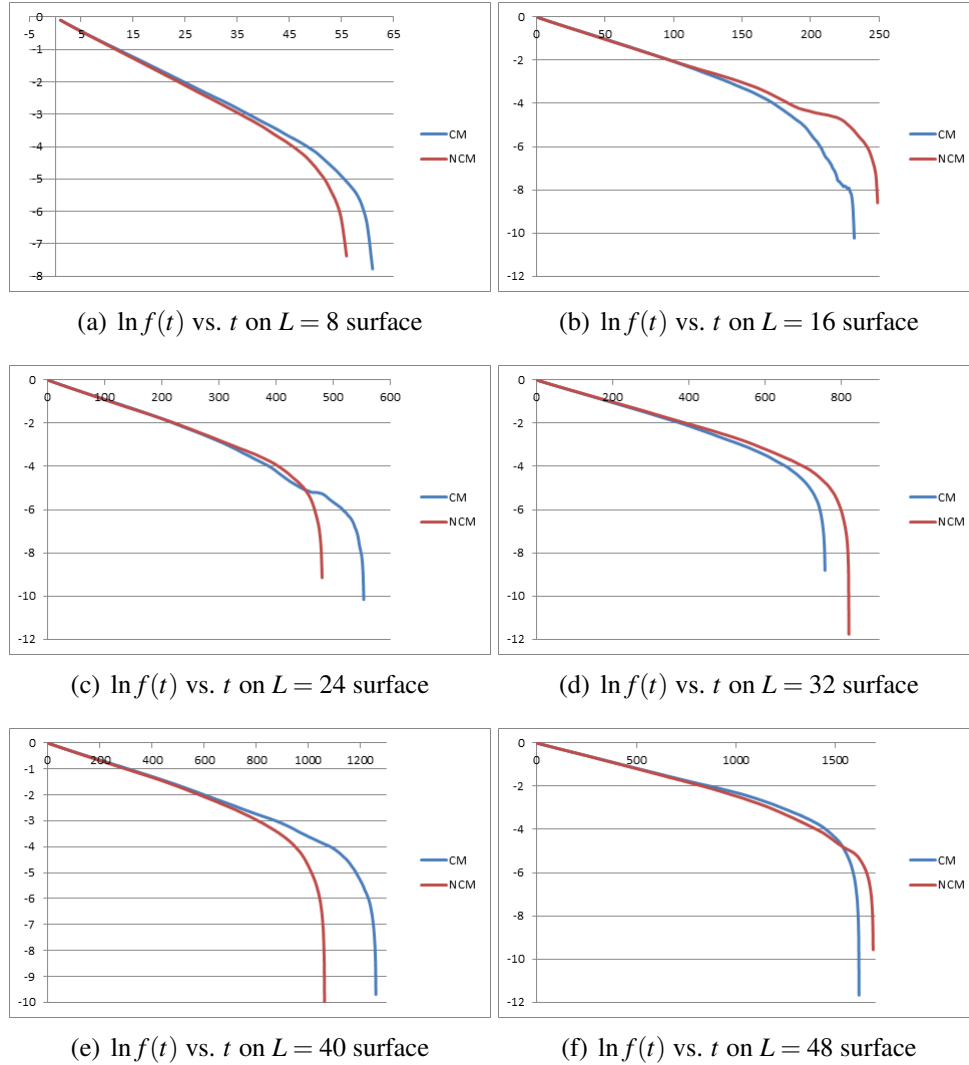


Figure 4.8: Semi-log plots of the excess difference of the correlation function on a one dimensional surface of slope 1 for system sizes $L = 8, 16, 24, 32, 40, 48$

number of steps of height 1, we also present the correlation function calculated by using step height for both the two models. In Figure 4.10, the semi-log plot of the correlation function on a slope=1 one dimensional surface with system sizes $L = 8, 16, 32, 64$ using height 1 steps is shown.

Again, the correlation function are very close for both the conserved and non-conserved model, apart from the tail parts. We still observe a fast relaxation region and slow relaxation region in the plots. In Figure 4.11, the log-log plot of the correlation time calculated for both models with system size is present. Aside from calculational error,

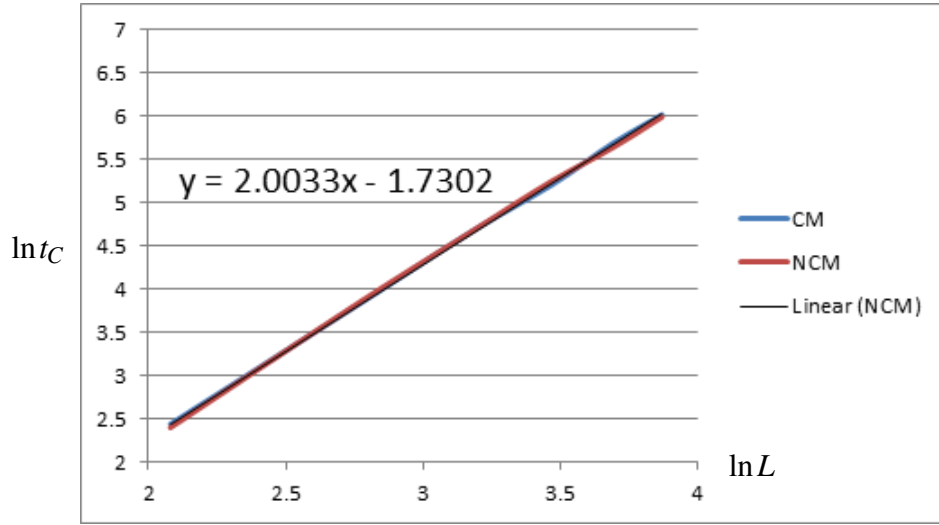


Figure 4.9: Log-log plot of the excess difference of the correlation time against system size on a one dimensional surface of slope 1 for system sizes $L = 8, 16, 24, 32, 40, 48$

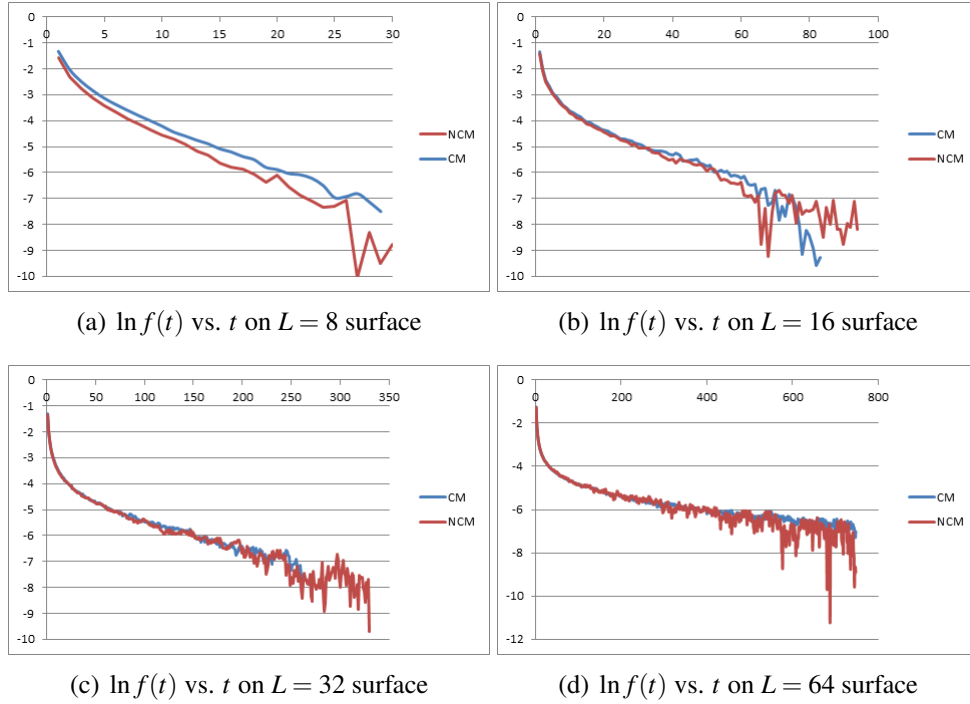


Figure 4.10: semi-log plot of the correlation function on a slope=1 one dimensional surface with system sizes $L = 8, 16, 32, 64$ using height 1 steps

a power law with system size is exhibited. The results are better for the non-conserved model, since the first point for the conserved model is far from the fitted line.

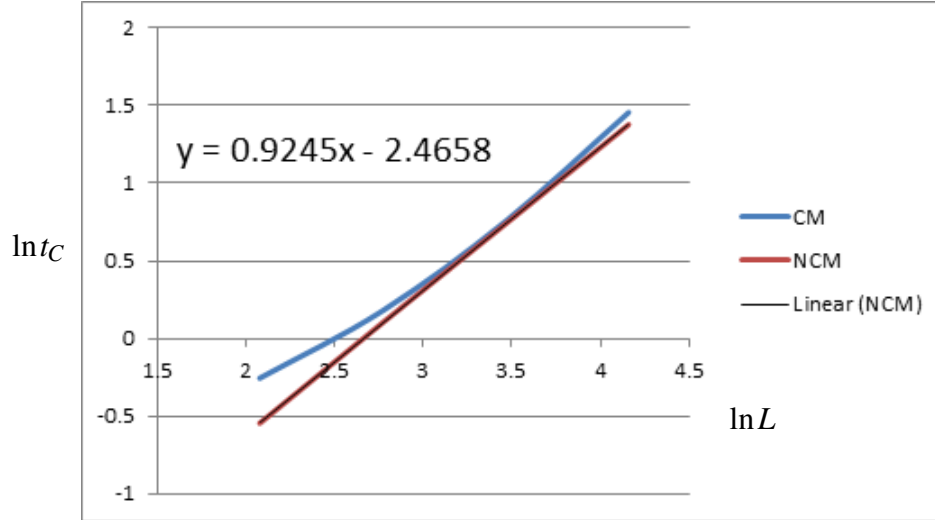


Figure 4.11: Log-log plot of the excess difference of the correlation time against system size on a one dimensional surface of slope 1 for system sizes $L = 16, 24, 32, 40, 48$

In summary, by investigating the surface correlation time of the CM and NCM by using various quantities, the two models behave similarly in regard to relaxation. These two models are statistically the same and in addition, the non-conserved model is more efficient for simulation and calculation. Therefore, the non-conserved model is chosen for our later simulations.

4.3 Histogram Methods

Results from Monte Carlo simulations exhibit a statistical distribution. The histogram method [40, 42] then can be used to extract information from Monte Carlo simulations, for example, to study transformation.

Suppose that a simulation is carried out at a temperature T_0 corresponding to $\beta_0 = 1/(kT_0)$. Since the surface configurations follow the Boltzmann distribution, the generated configurations have a frequency proportional to $\exp(-\beta_0 E)$, where E is the total energy for the system. Therefore, a histogram $H(E)$ of the simulated surface configurations provides an estimate for the equilibrium probability distribution. According to the Law of Large Numbers, histogram estimates tend to the exact values in the limit of an infinite number of runs. Though the histogram will suffer from statistical error in practice, $H(E)/N$ still provides a good estimate for the probability distribution $P(E; \beta_0)$ of having

energy E at temperature β_0 . Thus,

$$(4.3) \quad H(E) = \frac{N}{Z(\beta_0)} W'(E) e^{-\beta_0 E}$$

where $W'(E)$ is an estimate for the true density $W(E)$ of states and $Z(\beta_0)$ is the partition function of the system.

As we know, the density of states does not change with temperature. Therefore we can extract the approximate density of states

$$(4.4) \quad W'(E) = \frac{Z(\beta_0)}{N} H(E) e^{\beta_0 E}$$

By using $W'(E)$ to approximate the true density of states $W(E)$, we can relate the histogram measured at β_0 to estimate the probability distribution $P(E; \beta)$ for other arbitrary β , namely

$$(4.5) \quad P(E; \beta) = \frac{H(E) e^{\Delta\beta E}}{\sum H(E) e^{\Delta\beta E}}$$

where $\Delta\beta = (\beta_0 - \beta)$.

From a knowledge of the probability distribution at β , the average value of other quantities are easy to calculate. Thus, the heat capacity, entropy and free energy can be obtained at β .

In our p -value models, the range of the energy is undetermined and the number of possible energy values are not known. In this case, instead of keeping a simple list of all energies, we can take a bin-count of the energy to accumulate the histogram. The finer the bins, the better the result, but the slower the calculation, and more importantly, many bins may become empty which results in high variance of the estimation. Therefore, there exists a trade-off between the bin width and the calculation efficiency and computer memory.

Figure 4.12 shows the estimated energies and the heat capacity per site around $kT = 1.05$ for a initially tilted (111) surface with $p = 0.9$. We observe smooth curves for both quantities, which can be used for studying a transition.

Because of statistical errors, the estimation for other temperatures works well only for small temperature differences. The errors become significant for large temperature differences, especially for high temperatures.

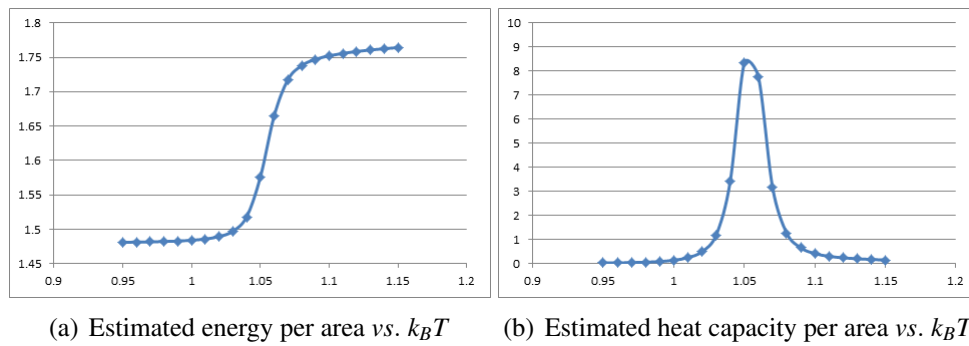


Figure 4.12: Estimated energy and heat capacity per projected site around $k_B T = 1.05$ for a initially tilted (111) surface for $p = 0.9$

Chapter 5

Configurational Entropy

5.1 Configurational Entropy

In statistical mechanics, configurational entropy is the portion of a system's entropy that is related to the position of its constituent particles rather than to their velocity, momentum and internal structure. It is physically related to the number of ways of arranging all the particles of the system while maintaining some overall set of specified rules and system properties. Configurational entropy is also known as macroscopic entropy or conformational entropy in the study of macromolecules. In general, configurational entropy is a fundamental aspect of statistical thermodynamics.

Configurational entropy is related to the number of possible configurations by Boltzmann's entropy formula

$$(5.1) \quad S = k_B \ln W,$$

where k_B is the Boltzmann constant and W is the number of possible configurations.

The mathematical field of combinatorics, and in particular the mathematics of combinations and permutations, is important in the calculation of configurational entropy. In particular, this field of mathematics offers formalized approaches for calculating the number of ways of choosing or arranging discrete objects, in our case of interest, atoms or molecules. However, it is important to note that the positions of molecules are not, strictly speaking, discrete (classical, not quantum). Thus a variety of approximations may be used in discretizing a system to allow for a purely combinatorial approach. Alternatively, integral methods may be used in some cases to work directly with continuous position functions.

5.2 Theoretical Derivation for Two Dimensional Simple Lattice

For a system in equilibrium at temperature T , we propose an associated configurational entropy for a 1-D surface.

For a particular simulation, denote by h_i the number of steps of height i and by l_j the number of facets of length j . Then the two dimensional configurational entropy is given empirically by

$$(5.2) \quad S_e/k_B \equiv \mathcal{S}_e = \ln \Omega_e$$

where

$$(5.3) \quad \Omega_e = \frac{(h_1 + \dots + h_i + \dots + h_h)!}{h_1! \dots h_i! \dots h_h!} \cdot \frac{(l_1 + \dots + l_j + \dots + l_l)!}{l_1! \dots l_j! \dots l_l!}$$

Theoretically, for a system of height H and length L , to reach the right side of a staircase structure from the left requires L horizontal moves and H vertical moves, each of one unit. All staircase structures are obtained by making all $(H + L)!$ permutations of $H + L$ moves and dividing by the number $H!L!$ of indistinguished moves. Thus the number of possible configurations is:

$$(5.4) \quad \Omega = \frac{(H + L)!}{H!L!}$$

By using the first two terms of Stirling's approximation, we obtain the theoretical entropy

$$(5.5) \quad \mathcal{S} = (H + L) \ln(H + L) - H \ln H - L \ln L$$

If equation 5.5 is used, the entropy per unit length can be written

$$(5.6) \quad \frac{\mathcal{S}}{L} = -\frac{H}{L} \ln\left(\frac{H}{H + L}\right) - \ln\left(\frac{L}{H + L}\right),$$

and depends only on the ratio H/L , which is the average slope of the surface. Therefore, Eq. 5.6 gives the theoretical entropy per unit length for a infinite system.

If we use a more accurate approximation, we obtain the theoretical entropy of a arbitrary large system

$$(5.7) \quad \mathcal{S} = (H + L) \ln(H + L) - H \ln H - L \ln L + \frac{1}{2} \ln(H + L) - \frac{1}{2} \ln H - \frac{1}{2} \ln L - \ln \sqrt{2\pi}$$

Therefore, the entropy per unit length $\frac{\mathcal{S}}{L}$ depends explicitly on L and not just the ratio H/L , as shown in the Eq. 5.8.

$$(5.8) \quad \frac{\mathcal{S}}{L} = -\frac{H}{L} \ln\left(\frac{H}{H+L}\right) - \ln\left(\frac{L}{H+L}\right) + \frac{1}{2L} \ln\left(\frac{H+L}{H}\right) - \frac{1}{2L} \ln 2\pi L$$

5.3 Comparison with Entropy from Simulation Results

In order to investigate the consistency of the above empirical entropy $\mathcal{S}_e$ with the entropy $\mathcal{S}$, a comparison is needed for various surface configurations. A consistent measurement is the entropy per unit system length for various configurations, so the comparison is meaningful for different system sizes.

Simulations are carried out for various system sizes and slopes. The average empirical entropy per unit length over 10000 runs each for each slope and length are compared to the theoretical results for a infinitely large system and illustrated in Figure 5.1. Meanwhile, the theoretical entropy for the same systems are also compared to the infinitely large system and illustrated in Figure 5.2. The theoretical entropy per unit length are much closer to the one for the infinitely large system. As the system sizes get larger, the empirical entropies get closer to theoretical entropy introduced above. This is strong evidencace that supports the correctness of our theoretical interpretation of the configurational entropy. As the slope of the surface gets steeper, the entropy gets larger as well. This is because a surface with a steeper slope has more possible configurations. We further check to see if the use of Eq5.8 make any significant change in the theoretical entropy. Results are present in Figure 5.2 and make very little difference compared to the spread of empirical entropy per unit length.

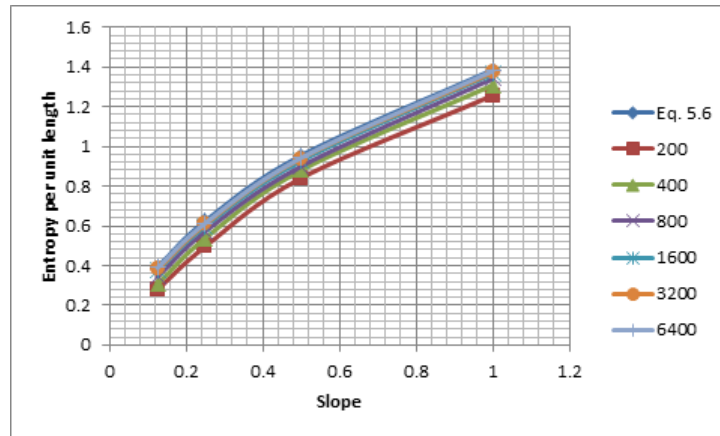


Figure 5.1: Theoretical entropy per unit length based on Eq. 5.6 and empirical entropy per unit length vs. surface slopes for different system sizes

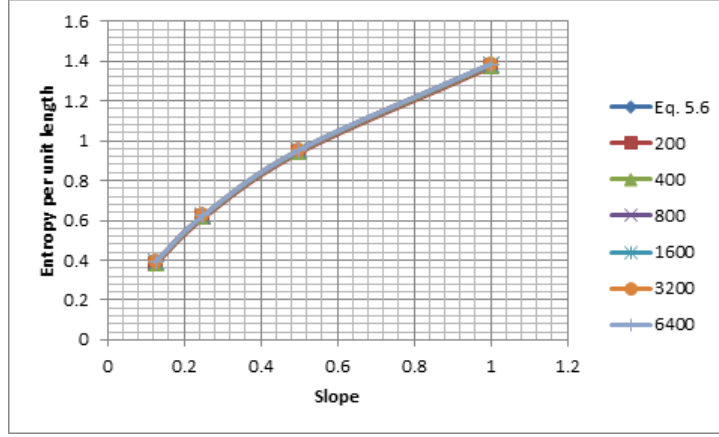


Figure 5.2: Theoretical entropy per unit length based on Eq. 5.6 and theoretical entropy per unit length based on Eq. 5.8 vs. surface slopes for different system sizes

It is worth mentioning that this consistency of the theoretical and empirical entropy is true at low temperatures. In this case, our theoretical formula describes the same situation as the simulation. At high temperatures, the surface would have holes and adatoms, not just a staircase structure.

The above analysis is based on a one dimensional surface but it can be extended to a three dimensional dimensional surface. The result is similar and the comparison with simulation is still good for low temperatures. For higher temperatures where the surface gets rough, the corresponding formula would not be suitable.

5.4 Height and Length Distribution

To get the distribution of height and length, we must maximize the entropy with the constraint of constant total height and length. By using Stirling's approximation, we obtain

$$(5.9) \quad \mathcal{S} = \left(\sum_i h_i \right) \ln \left(\sum_i h_i \right) - \sum_i (h_i \ln h_i) + \left(\sum_j l_j \right) \ln \left(\sum_j l_j \right) - \sum_j (l_j \ln l_j)$$

We must maximize $\mathcal{S}$ with constraints $\sum_i h_i \cdot i = H$, $\sum_j l_j \cdot j = L$.

By using Lagrange multipliers λ_1 and λ_2 , we obtain

$$\begin{aligned}
& \frac{\partial}{\partial h_i} \left[S - \lambda_1 \left(\sum_i h_i \cdot i \right) - \lambda_2 \left(\sum_j l_j \cdot j \right) \right] = 0 \\
& \Rightarrow \ln \left(\sum_i h_i \right) - \ln h_i - \lambda_1 \cdot i = 0 \\
(5.10) \quad & \Rightarrow h_i = \left(\sum_i h_i \right) e^{-\lambda_1 \cdot i}
\end{aligned}$$

$$\begin{aligned}
& \frac{\partial}{\partial l_j} \left[S - \lambda_1 \left(\sum_i h_i \cdot i \right) - \lambda_2 \left(\sum_j l_j \cdot j \right) \right] = 0 \\
& \Rightarrow \ln \left(\sum_j l_j \right) - \ln l_j - \lambda_2 \cdot j = 0 \\
(5.11) \quad & \Rightarrow l_j = \left(\sum_j l_j \right) e^{-\lambda_2 \cdot j}
\end{aligned}$$

We see that both the height and length obey exponential distributions. To verify these results, we get the height and length distributions solely from the geometry of the system by means of a technique illustrated in Figure 5.3.

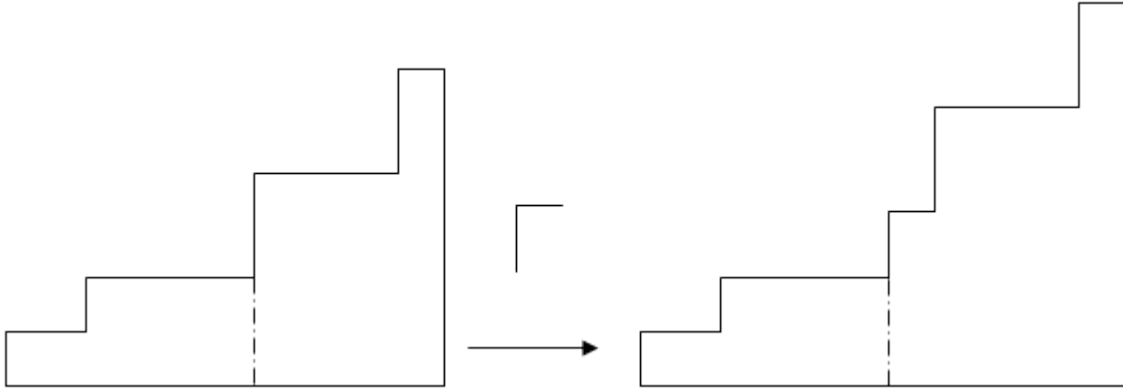


Figure 5.3: Inserting a step into a smaller system to form a larger system

For a system of length L and height H , we could have a step with $L + 1$ edges, but we also have a periodic boundary condition. Therefore, we do not allow a step at the last edge. The number of possible configurations will be $C_{L-1+H}^{L-1} = (L - 1 + H)! / (L - 1)! H!$

We proceed to calculate the probability of a step of height n at a given site, namely, (possible configurations with step of height n at a given site) / (all possible configurations) [45].

A configuration with step of height n at a given site is equivalent to inserting a $1 \times n$ step into a $(L-1) \times (H-n)$ configuration. We denote possible configurations with step of height n at a given site by $C_{L-2+H-n}^{L-2}$.

The probability of a step of height n at a given site: $P(n) = C_{L-2+H-n}^{L-2} / C_{L-1+H}^{L-1}$.

We also know that:

$$\begin{aligned}
 C_r^r + C_{r+1}^r + \cdots + C_n^r &= C_{n+1}^{r+1} \\
 \sum_{n=0}^H C_{L-2+H-n}^{L-2} &= C_{L-2}^{L-2} + C_{L-1}^{L-2} + \cdots + C_{L-2+H}^{L-2} = C_{L-1+H}^{L-1} \\
 (5.12) \quad \sum_{n=0}^H P(n) &= C_{L-2}^{L-2} / C_{L-1+H}^{L-1} + C_{L-1}^{L-2} / C_{L-1+H}^{L-1} + \cdots + C_{L-2+H}^{L-2} / C_{L-1+H}^{L-1} = 1
 \end{aligned}$$

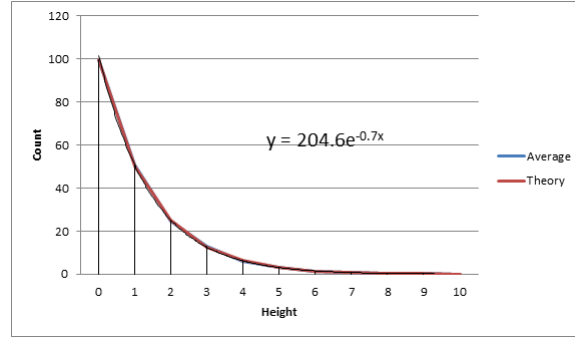
The expected number of height n is $L \cdot P(n)$. Thus we can also verify that $\sum_{n=0}^H L \cdot P(n) \cdot n = H$, specifically $C_{L-2+H-n}^{L-2} \cdot n = C_{L-1+H}^{L-1} \cdot H / L = C_{L-1+H}^L$.

5.5 Comparison of Theoretical and Simulation Distributions

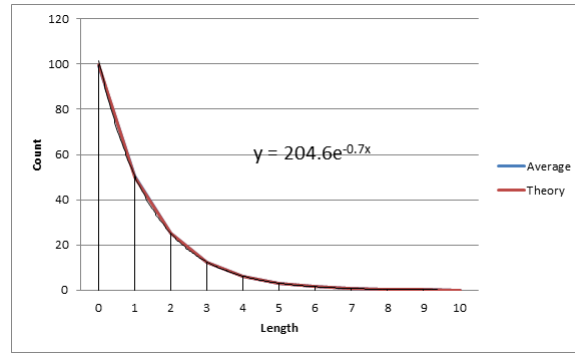
To test the theoretical distribution of heights and lengths, simulations are carried out for various slopes for relatively large system sizes. The system size chosen here is 200, which gives us a significant range of distribution and minimizes the size effect due to periodic boundary conditions. The empirical distribution is fitted to an exponential distribution to verify the our results of exponential distributed height and length distributions.

Figure 5.4 shows results for simulation of a one dimensional surface with system size 200 and slope 1, averaged over 100 runs. We see that the average value from the simulation is in good agreement with the expected value from the theoretical prediction. More important, the fitted exponential distribution is in good agreement with the simulation. Since the slope is 1, the height and length distribution should be equivalent. This has been verified from the simulation as well. The fitted parameters in height and length distribution are almost identical.

Figure 5.5 shows results for simulation of a one dimensional surface with system size 200 and slope $1/2$, averaged over 100 runs. Again, we see that the average count from the simulation is in good agreement with the expected count from the theoretical predictions. The fitted exponential distribution is consistent with the simulation. Since the slope is $1/2$, the height and length distributions should be different. This is verified from the simulation as well. There are more larger lengths than higher heights and the distribution for length distribution covers a broader range.



(a) Heights Count



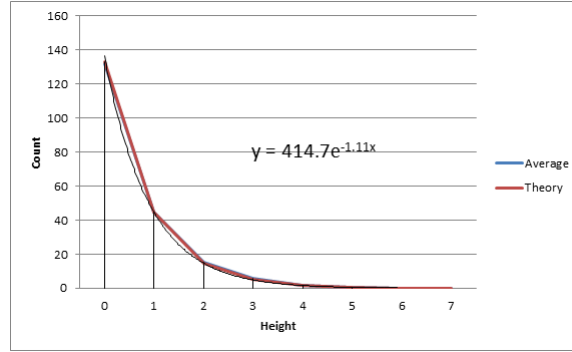
(b) Lengths Count

Figure 5.4: Average height and length count on a one dimensional surface with system size 200 and slope 1, averaged over 100 runs

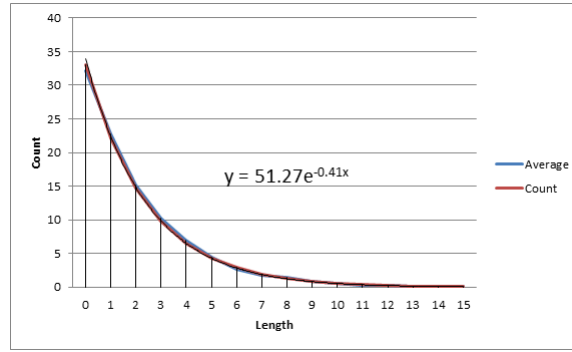
Figure 5.6 shows the simulation of a one dimensional surface with system size 200 and slope $1/4$, averaged 100 runs. Again, we can see that the average count from the simulation is in good agreement with the expected count from the theoretical predictions. The fitted exponential distribution is in good agreement with the simulation. Since the slope is $1/2$, the height and length distribution should be different. This is verified from the simulation as well. There are even larger lengths than higher heights and the distribution for length distribution covers an even larger range.

There is a trade-off between the height and length distribution for different slopes. If the height distribution is confined by the configuration, then the length distribution can cover a broader range. If the height distribution covers a broader range, the length distribution will be confined to a narrow range.

Note again that the height and length distributions are only valid at low temperatures where the surface configuration has a staircase structure.



(a) Heights Count



(b) Lengths Count

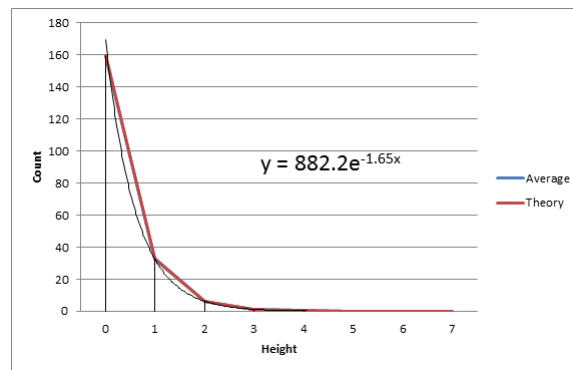
Figure 5.5: Average height and length count on a one dimensional surface with length size 200 and slope $1/2$, averaged over 100 runs

5.6 Size effect of height and length distributions

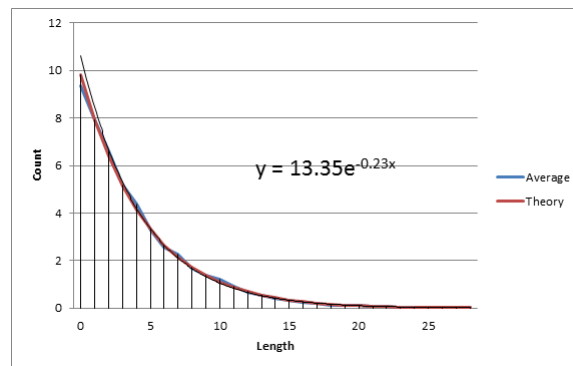
As shown above, the theoretical and simulated height and length distributions are consistent. What is what happens to the distribution when the system size changes?

We approach this problem by just tracking the probability of the height 0 steps $P(0)$ and height 1 steps $P(1)$ and varying the system sizes and the slopes of one dimensional surfaces.

In Figure 5.7, $P(0)$ and $P(1)$ obtained from simulation results are shown as a function of system sizes on various slopes. The behavior for $P(0)$ and $P(1)$ for various slopes are similar. The values for $P(0)$ increase very fast for small system sizes and then grow very slowly. The values for $P(1)$ decrease very fast for small system sizes and then change very slowly again. For small system sizes, the distribution is confined by the size; when the size increases to a certain value, the size effect is limited and the distribution converges to values for infinite system sizes.



(a) Heights Count



(b) Lengths Count

Figure 5.6: Average height and length count on a one dimensional surface with length 200 and slope 1/4 averaged over 100 runs

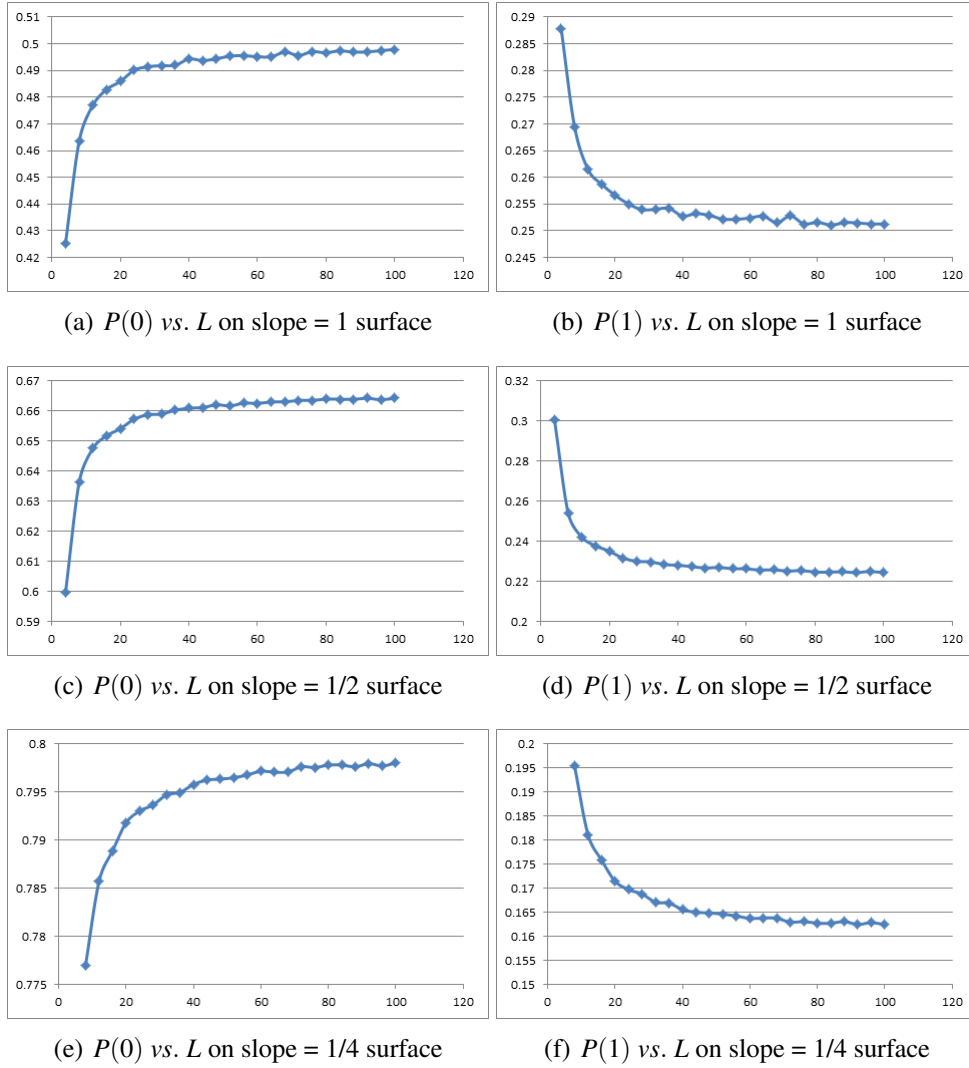


Figure 5.7: The probability of height 0 steps $P(0)$ and height 1 steps $P(1)$ for various system sizes and for various slopes.

Chapter 6

Simulation of Two Dimensional Surfaces

In order to characterize quantitatively a crystal surface, one natural measurement could be the variance of the surface height, which is the deviation of the surface from the initial surface,

$$\text{var}(h) = \left\langle \frac{\sum_{i,j}^N (h_{ij} - h_{ij}^{\text{init}})^2}{N^2} \right\rangle \cdot \cos \alpha$$

where N is the edge length of a square system, $\langle \cdot \rangle$ denotes the average value calculated from simulation data, and α denotes the angle between the tilted surface with respect to the corresponding (100) surface. Therefore, N^2 is the projected area size on the (100) surface, and $N^2 / \cos \alpha$ is the area of the original tilted surface.

Average energy $\langle E \rangle$ per area and heat capacity c_v per area (here, averaged on a N by N matrix) are also calculated:

$$c_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2 \cdot N^2} \cdot \cos \alpha.$$

Here, E is the total system energy calculated for the Hamiltonian H given by

$$H = \sum_{(i,j), (i',j') \text{ are } NN's} |h_{ij} - h_{i'j'}|^p$$

where (i, j) and (i', j') are nearest neighbors and h_{ij} is the height of the surface at site (i, j) .

The simulations are carried out from high temperatures to low temperatures. From a physical point of view, this corresponds to an annealing process, typical of experiments. From the point of view of simulation, this process helps the simulation to reach an equilibrium state [43].

6.1 Initially Flat (100) Surface

It is usual in the statistical mechanics literature to indicate critical roughening temperatures as calculated for the Ising model. This is a good starting point for our simulations with a flat surface and enables comparison with SOS results [44].

The first crystal surface studied is a simple cubic (100) surface. Monte Carlo simulations are carried out for $p = 0.9, 1$, and 1.1 at temperature ranges between $k_B T = 0.8$ to $k_B T = 1.5$ for system length sizes $N = 4, 8, 16, 32$. A total of 5000 simulation sweeps were done for each case.

6.1.1 $p = 1$

For $p = 1$, the variance of height is plotted as a function of temperature in Figure 6.1a. At low temperatures, the variance of height is small and the values for various system sizes are close because, at those temperatures, the surface does not vary a lot from the initial (100) surface. At high temperatures, the surface roughens and the variance of height is different for various system sizes. In order to better understand this size effect, the variance of height is plotted as a function of $\ln N$ in Figure 6.1b. From the plot, there is a clear linear relation between the variance of height and $\ln N$, which represents the existence of a power law for the size effect.

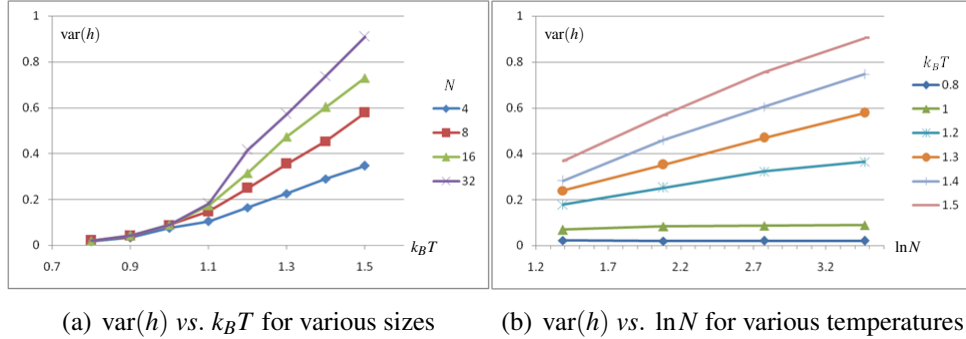


Figure 6.1: Variance of height for $p = 1$ for an initially flat (100) surface (a) as a function of temperature for various system sizes $N = 4, 8, 16, 32$, (b) as a function of $\ln N$ for various $k_B T$

The heat capacity per area is plotted in Figure 6.2. The heat capacities for all system sizes have peaks around $k_B T = 1.1$, which suggests that a roughening transition [45–47] occurs at that temperature. The plots of surface morphology below and above this temperature also give evidence of this transition. Figure 6.2 also shows that the peak gets higher when system size gets larger.

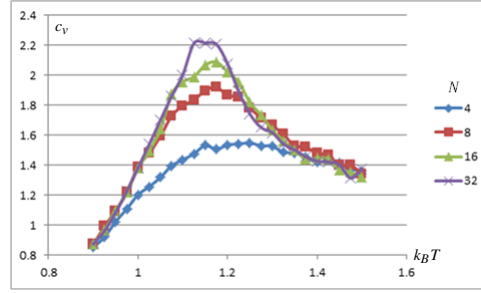


Figure 6.2: c_v vs. $k_B T$ for various system sizes N : heat capacity per area as a function of temperature for $p = 1$ for an initially flat (1 0 0) surface

6.1.2 $p = 0.9$

For $p = 0.9$, the variance of height is plotted as a function of temperature in Figure 6.3a. The variance of height is qualitatively similar to the $p = 1$ case, except the values are larger for $p = 0.9$. The variance of height is plotted as a function of $\ln N$ in Figure 6.3b and the slopes are also larger than that for $p = 1$.

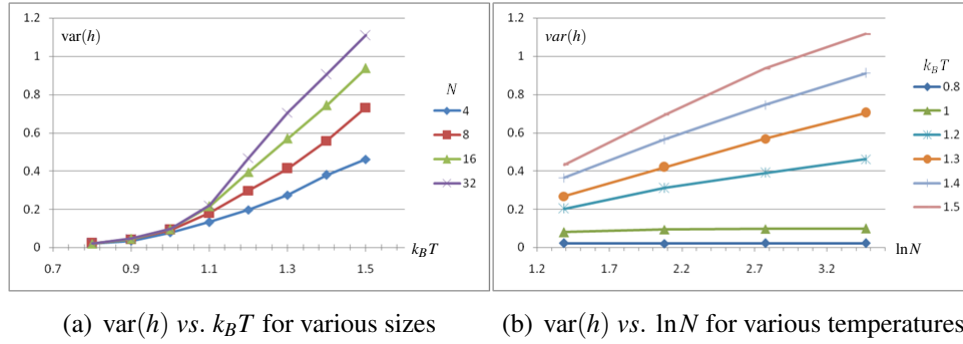


Figure 6.3: Variance of height for $p = 0.9$ for an initially flat (100) surface (a) as a function of temperature for various system sizes $N = 4, 8, 16, 32$, (b) as a function of $\ln N$ for various $k_B T$

The heat capacity per area is plotted in Figure 6.4. The heat capacities for all system sizes again have peaks around $k_B T = 1.1$ which indicates that a roughening transition occurs at that temperature [48]. The peak gets higher and sharper as the system size increases. Plots of surface morphology below and above this transition temperature also gives evidence of this transition. Figure 6.4 also shows that the peak for each system size is larger than for $p = 1$.

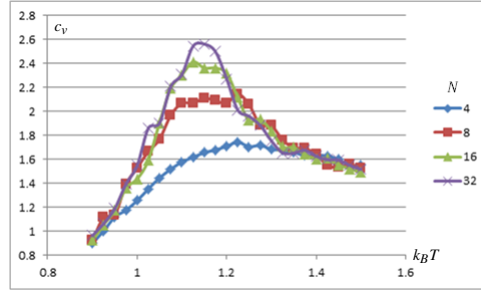
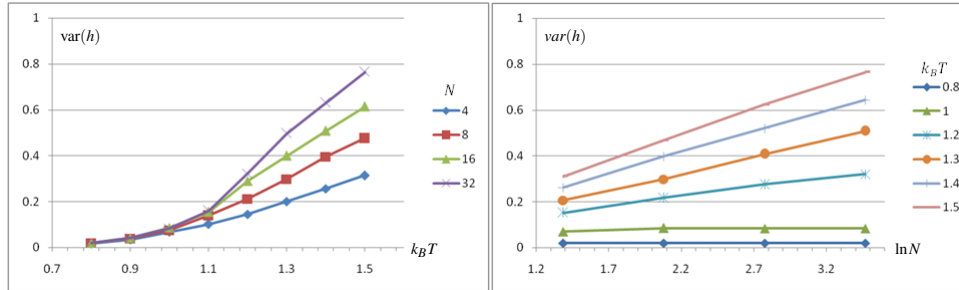


Figure 6.4: c_v vs. $k_B T$ for various sizes: heat capacity per area as a function of temperature for $p = 0.9$ for an initially flat (1 0 0) surface for systems of various length sizes

6.1.3 $p = 1.1$

For $p = 1.1$, the variance of height is plotted as a function of temperature in Figure 6.5a. The variance of height is similar to the that for $p = 0.9$ and $p = 1$, but is the smallest among all three cases. The variance of height is plotted as a function of $\ln N$ in Figure 6.5b; the slopes are also the smallest of the three cases.



(a) $\text{var}(h)$ vs. $k_B T$ for various length sizes (b) $\text{var}(h)$ vs. $\ln N$ for various temperatures

Figure 6.5: Variance of height for $p = 1.1$ for an initially flat (100) surface (a) as a function of temperature for various system sizes $N = 4, 8, 16, 32$, (b) as a function of $\ln N$ for various $k_B T$

The heat capacity per area is also plotted in Figure 6.6. The heat capacity for all system sizes have peaks around $k_B T = 1.1$, which indicates that a roughening transition occurs at that temperature. Plots of surface morphology below and above this transition temperature also give evidence of this transition. The peak for each system size is the smaller than for $p = 0.9$ and $p = 1$.

All three models behave similarly with respect to the variance of height, and the heat capacity per area. The variance of height increases as temperature increases, and the larger the system size, the faster it increases with T . The variance of height increases

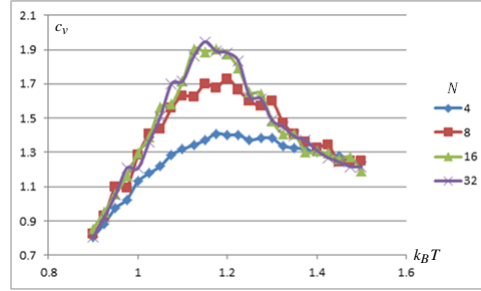


Figure 6.6: c_v vs. $k_B T$ for various sizes: Heat capacity per area as a function of temperature for $p = 1.1$ for an initially flat (1 0 0) surface for various length sizes

linearly with the logarithm of the system size.

The effect of p -value can also be seen by comparing the variance of height and the peak in the heat capacity [49]. The larger the p -value, the smaller the variance of height, and the lower the peak in the heat capacity. For p values smaller than 1, the model favors corners, which gives a higher value in variance of height; for p values bigger than 1, the model disfavors corners, which gives a lower value in variance of height.

6.1.4 High Temperature Behavior of Heat Capacity

At high temperatures, the effect of various p -values is not dominating. All three models behave similarly and only differ slightly in values. The heat capacity at high temperatures is proportional to $1/p$, as shown below.

The Hamiltonian is:

$$H = \sum_{(i,j), (i',j') \text{ are NN's}} |h_{ij} - h_{i'j'}|^p$$

At high temperature, the summation in the partition function can be converted to integral:

$$Z = \int_{\{h_{ij}\}} e^{-\beta \sum |h_{ij} - h_{i'j'}|^p} dh^A$$

where $A = N^2$ is the total number of sites over the surface.

Let $x_{ij} = \beta^{1/p} \cdot h_{ij}$

Then,

$$Z = \int_{\{h_{ij}\}} \beta^{-A/p} e^{\sum |x_{ij} - x_{i'j'}|^p} dx^A = \beta^{-A/p} \cdot \text{const}$$

The average energy is:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = A/p \cdot k_B T$$

Therefore

$$\Rightarrow c_v/Ak_B = 1/p; \text{ high temperatures.}$$

In order to test this high temperature behavior, simulations are carried out for various p values at high temperatures. The heat capacity at various p values at $k_B T = 3$ and $k_B T = 5$ are plotted in Figure 6.7. By fitting the data at various p values, a $1/p$ behavior is clearly evident at high temperatures.

According to the derivation above, this general behavior does not depend on p or the initial surface configurations. Later, we showed that the results from other surface configurations indicate such a behavior at high temperatures.

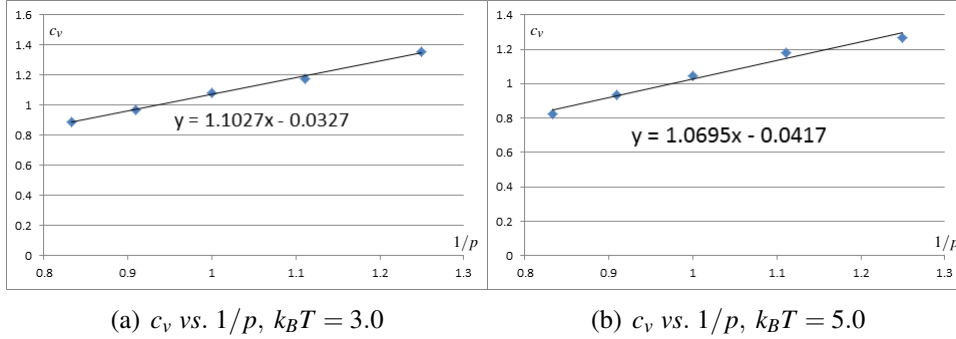


Figure 6.7: Heat capacity c_v vs. $1/p$ values at high temperatures for an initially flat surface

6.2 Initially Tilted (111)Surface

For an initially flat (1 0 0) surface, various p values do not effect the properties significantly. Here, the same model as above is extended to an initially tilted surface with respect to the close-packed (100) surface, to see the effect of various p values. The initial (111) surface is plotted in Figure 6.8.

The simulations are the same as above, same p values (1, 0.9, 1.1) and same system length sizes (4, 8, 16, 32). The simulations are carried out in two temperature regions, one is the low temperature region where potential transition may occur, and the other is at

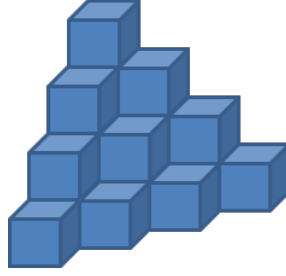


Figure 6.8: Initial configuration of a small (111) surface

high temperatures. In both regions, the variance of height, energy per area, heat capacity per area and the acceptance ratio of the simulation are calculated.

The first tilted surface studied is the (111) surface. The initial condition is a surface parallel to (111) and contains only of monotonic steps. It can also be thought of as a plane consists of kink sites. This tilted surface is important and interesting in both theoretical and experimental studies. This is also a high-symmetry surface that might give general and meaningful results for other tilted surfaces.

6.2.1 $p = 1$

The case $p = 1$ corresponds to the common solid-on-solid model and the results are plotted in Figure 6.9. From these plots, we see at temperatures lower than $k_B T = 0.5$ that the variance of height is almost constant but has different values due to the size effect. The larger the system size, the higher are the values. The energy is also constant so the heat capacity is zero. The acceptance ratios of the process at lower temperatures are also constant because, for the $p = 1$ model, atoms at the surface can rearrange at the many kink sites where there is no energy cost. This rearrangement is based on the initial (111) configuration and only the system size can change the values correspondingly. At higher temperatures, the surface atoms would have enough energy to go beyond the limitation of the surface configuration to form hill-and-valley structures, so the surface gets rougher and rougher. Even at higher temperatures, the energy, the heat capacity and the acceptance ratio have similar values for various system sizes.

Figure 6.10 shows the snapshots of surface at $k_B T = 0.1$ and $k_B T = 1.0$. From the figure, we see that there is no qualitative changes in the surface configuration, but the surface gets somewhat rougher at the higher temperature.

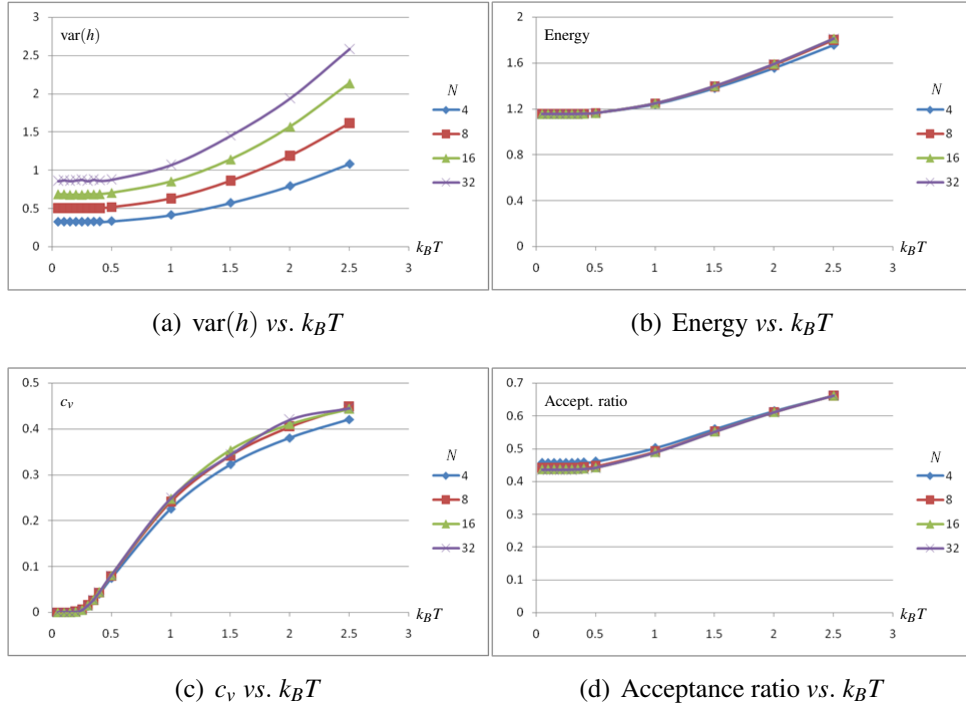


Figure 6.9: Variance of height, energy per area, heat capacity per area and the acceptance ratio at low temperatures for $p = 1$ on an initial (111) surface

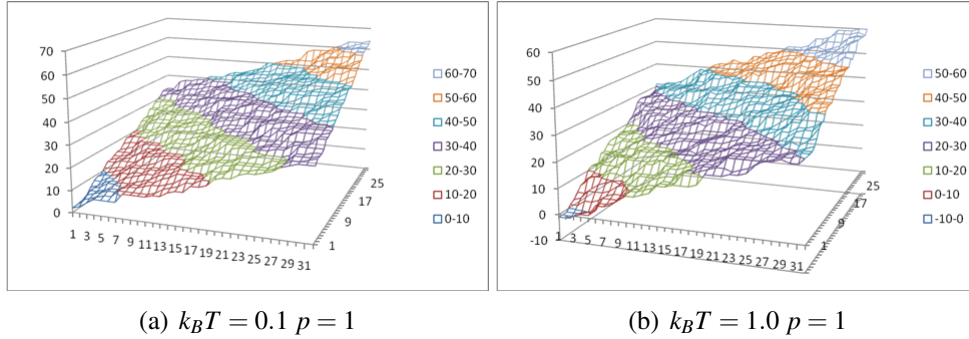


Figure 6.10: Snapshots of an initial (111) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 1$. The numbers on the right denote height above the (100) surface.

6.2.2 $p = 0.9$

Results for $p = 0.9$ are plotted in Figure 6.11. This model favors large steps and big facets, but for the initially tilted surface, it is much easier to add atoms to or remove atoms from the many kink sites than for a flat surface. Therefore, at low temperatures,

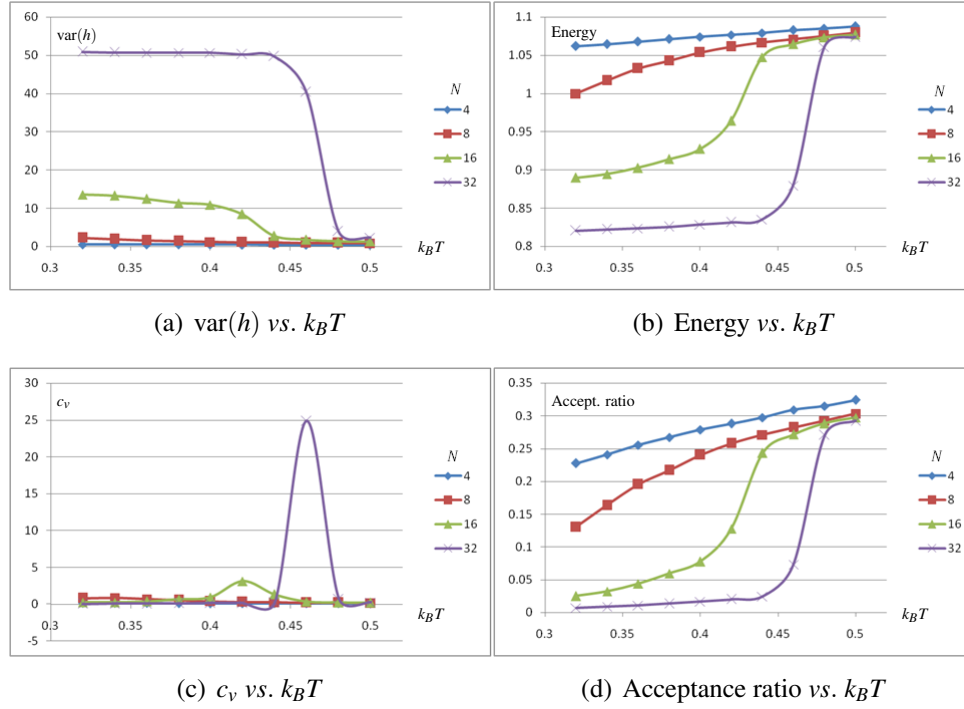


Figure 6.11: Variance of height, energy per area, heat capacity per area and the acceptance ratio at low temperatures for $p = 0.9$ on an initial (111) surface

surface contains big steps and has a very large variance of height. The variance of surface height in the plot is larger and flatter as the system size gets larger because, the system size gets larger, facets can get larger and steps can get higher; this results in higher variance of height and lower energy per area for larger system sizes. In the faceted state, the variance of height and surface energy stay relatively constant, the heat capacity is almost zero, and the acceptance ratio is very low. This means that there is not much happening on the surface once the surface is locked into the faceted state; this becomes more obvious for larger system sizes. As the temperature gets higher, the surface atoms get enough energy to rearrange to get rid of the faceted state. Therefore, a transition from the faceted surface to a macroscopically smooth surface occurs as the temperature gets higher. This phenomenon is quite different from the typical roughening transition, and we could call it a "smoothing transition", although microscopically the surface becomes rougher. The transition from faceted to non-faceted occurs at different temperatures for various system sizes; the transition temperature shifts to higher values as the system size gets larger, and the transition is more obvious for larger system sizes. Associated with this transition, there is also a transition in the energy and a peak in the heat capacity becomes apparent. Especially for larger system sizes, a sharp transition is observed in variance of height, energy per area and acceptance ratio, and a sharp peak is observed in the heat capacity.

Snapshots of surface at $k_B T = 1.0$ and $k_B T = 0.1$ are shown in Figure 6.12. From the figure, we can see that there are large facets and steps at lower temperatures and the faceted surface gets smooth and roughened as the temperature gets higher.

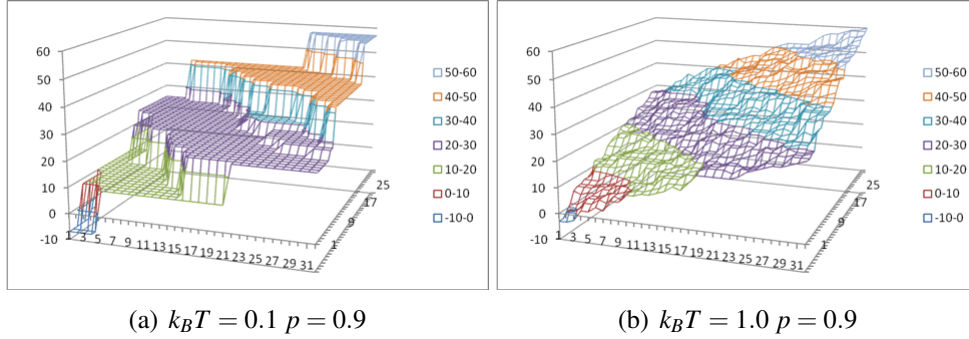


Figure 6.12: Snapshots of an initial (111) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 0.9$. The numbers on the right denote height above the (100) surface.

6.2.3 $p=1.1$

Results for $p = 1.1$ are plotted in Figure 6.13. The model disfavors large steps and big facets; therefore, the surface is smooth at low temperatures and roughens microscopically as the temperature increases. At temperatures lower than $k_B T = 0.05$, the variance of height is almost zero, the energy per area is close to 2 which is a indication of the staying at the initial surface, and the acceptance ratio is nearly zero. At these low temperatures, the surface is almost the initial (111) surface without any significant changes. As the temperature gets a little bit higher, the surface atoms begin to rearrange to form rougher surfaces. There seems to be a transition from a smooth tilted surface to a roughened surface around $k_B T = 0.1$, and the sharp peak in the heat capacity is a sign of such a transition. Above the transition temperature $k_B T = 0.1$, the variance of height increases fast and increases with system size. For the energy per area, heat capacity and acceptance ratio the values seem to be independent of system sizes. For $p = 1.1$, the variance of height and the energy per area is not increasing as fast as that in the $p = 1$ case.

Snapshots of the surface at $k_B T = 0.1$ and $k_B T = 1.0$ are shown in Figure 6.14. We see that the surface configurations are similar to the $p = 1$ case but smoother at low temperatures and not very rough at high temperatures.

For both the $p = 0.9$ and $p = 1.1$ cases, the existence of a peak in the c_v plot at low temperatures suggests a likely transition. The $p = 0.9$ case is likely to be a “smoothing transition”, while the $p = 1.1$ case is likely to be a microscopic “roughening transition”. The behavior of the $p = 1$ case is in between these two cases.

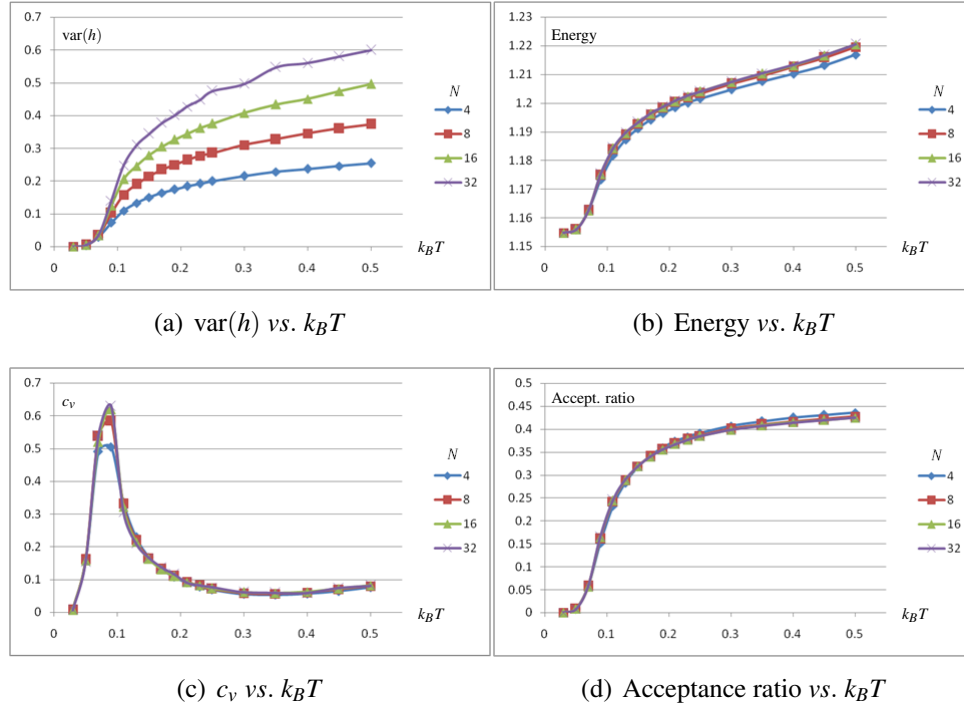


Figure 6.13: Variance of height, energy per area, heat capacity per area and the acceptance ratio at low temperatures for $p = 1.1$ on the (111) surface

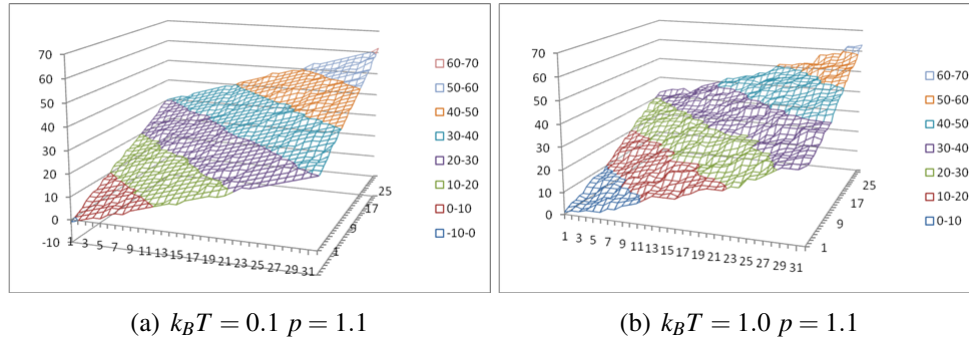


Figure 6.14: Snapshots of an initial (111) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 1.1$. The numbers on the right denote height above the (100) surface.

Size Effect

From the calculations above, we see that the variance of height shows a size effect for various system sizes [50].

For $p = 0.9$, $\text{var}(h)/N^2$ is plotted as function of temperature for each of the system

sizes in Figure 6.15, where N is the edge length of the system. As system size gets larger, $\text{var}(h)/N^2$ seems to saturate and the transition region from faceted to non-faceted seems to be narrower as system size increases.

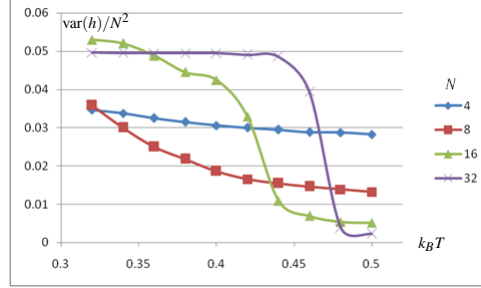


Figure 6.15: $\text{var}(h)/N^2$ vs. $k_B T$ for $p = 0.9$ on an initial (111) surface at various temperatures

For $p = 1$ and $p = 1.1$, $\text{var}(h)$ is plotted as a function of $\ln N$ at various temperatures in Figure 6.16, where N is the edge length of the system. In both cases, there is a linear relation between these two quantities. This linear relation has a unique slope at various temperatures in the $p = 1$ case, while the slope gets bigger as temperatures increases in the $p = 1.1$ case. From this size effect, we can predict the behavior for larger system sizes. As we discussed above, the faceted state at low temperatures in the $p = 1.1$ case is structure-related and temperature dependent and this results in different slopes for various temperatures.

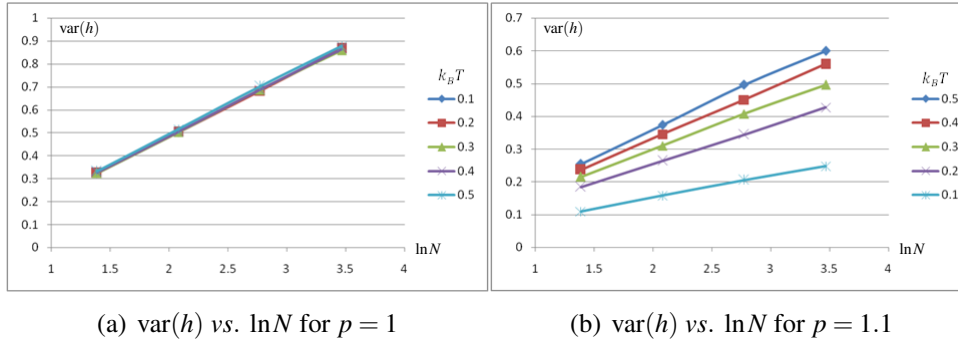


Figure 6.16: $\text{var}(h)$ vs. $\ln N$ for $p = 1$ and $p = 1.1$ on an initial (111) surface

6.2.4 High Temperatures

At high temperatures, the surface would be microscopically rough and no transition is expected for all three models. The effect of various p values is dominated by temperature

and all three models behave similarly.

For $p = 1$, the high temperature results are plotted in Figure 6.17. By fitting the data, one can see that the variance of height increases as a function of temperature for all system sizes. The larger the system size, the faster the variance increases. The energy per area increases linearly as a function of temperature and the values for various system sizes are close. The heat capacity per area seems to converge to $1/p$, which is 1 in this case, at high temperatures for all system sizes, as expected as in the discussion of the high temperature behavior on an initially flat surface earlier.

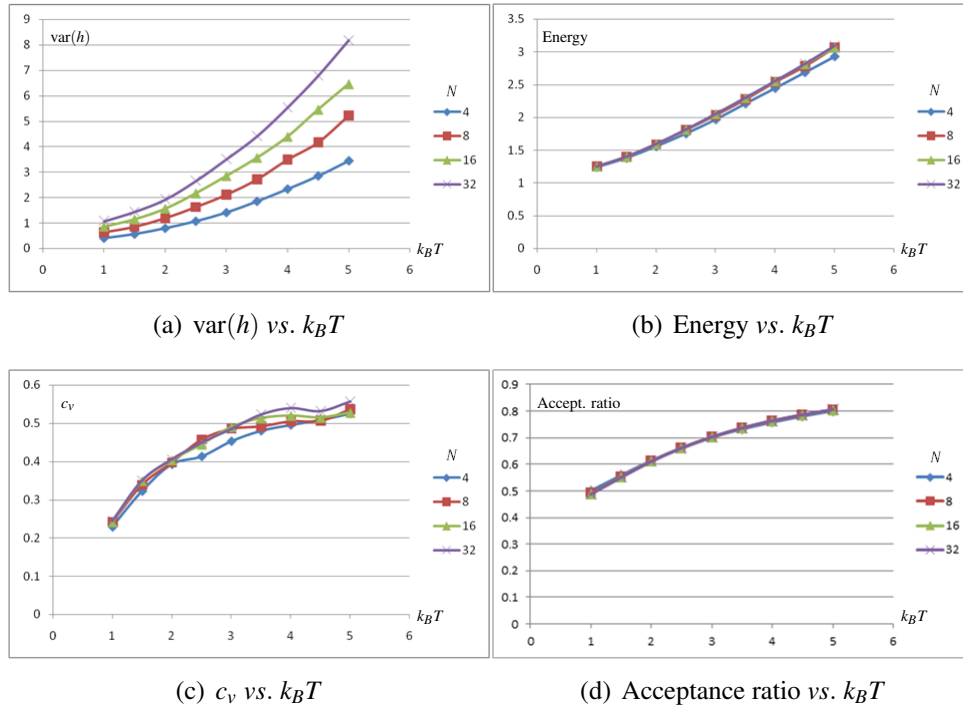


Figure 6.17: Variance of height, energy per area, heat capacity per area and the acceptance ratio at high temperatures for $p = 1$ on an initial (111) surface

For $p = 0.9$, the high temperature results are plotted in Figure 6.18 and resemble those for $p = 1$. The differences are: the variance of height and energy per area increases faster, the acceptance ratio is higher and the heat capacity seems to converge to $1/p = 1/0.9 = 1.1$.

For $p = 1.1$, the high temperature results are plotted in Figure 6.19. The results are similar to $p = 1$ and $p = 0.9$. The variance of height and energy site increases slowest of all three models and the acceptance ratios are the smallest as well. The heat capacity seems to converge to $1/p = 1/1.1 = 0.9$.

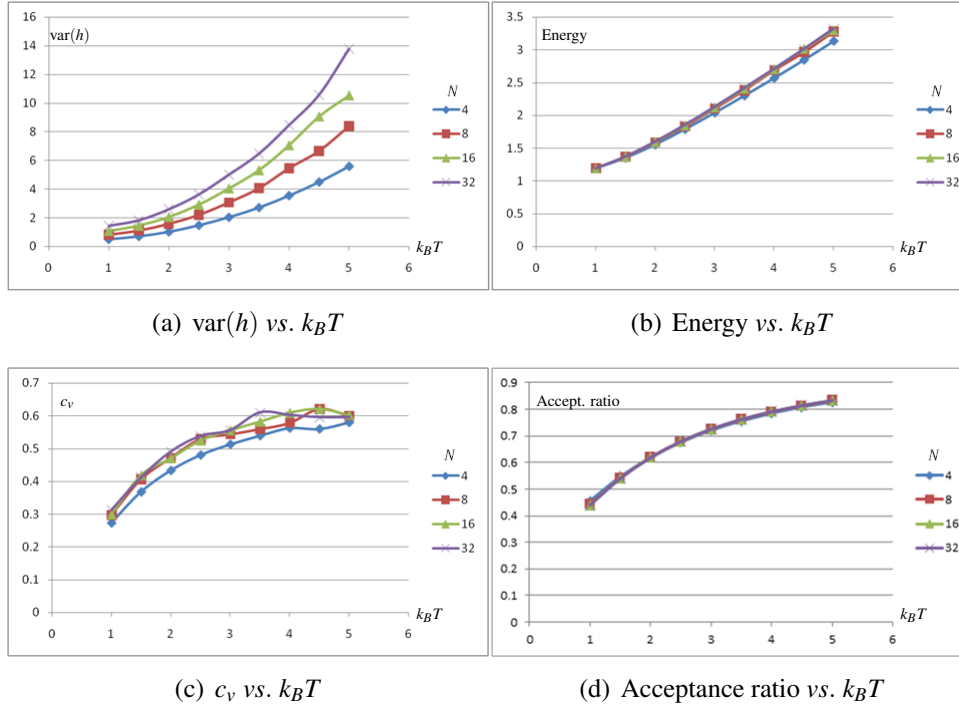


Figure 6.18: Variance of height, energy per area, heat capacity per area and the acceptance ratio at high temperatures for $p = 0.9$ on an initial (111) surface

6.3 Initially Tilted (112) Surface

The (112) surface is similar to the (111) surface but has shallower slopes in both directions. The same models are examined for an initial (112) surface to see whether something new or different happens. The initial (112) surface is plotted in Figure 6.20.

6.3.1 $p = 1$

The results are plotted in Figure 6.21. The plots are qualitatively similar to the (111) case and only differ in values. The energy per projected site is exactly half of the previous values, which is true since the slopes in both directions are just half of that on the (111) surface. The values of other quantities are all smaller than for (111) surface. And at lower temperatures, the values of the variance of height and the acceptance ratios are approximately half of those for the (111) surface.

Snapshots of the surface at $k_B T = 0.1$ and $k_B T = 1.0$ are shown in Figure 6.22. From the figure we could see that there is no qualitative changes in the surface configurations, but the surface gets rougher as the temperature gets higher.

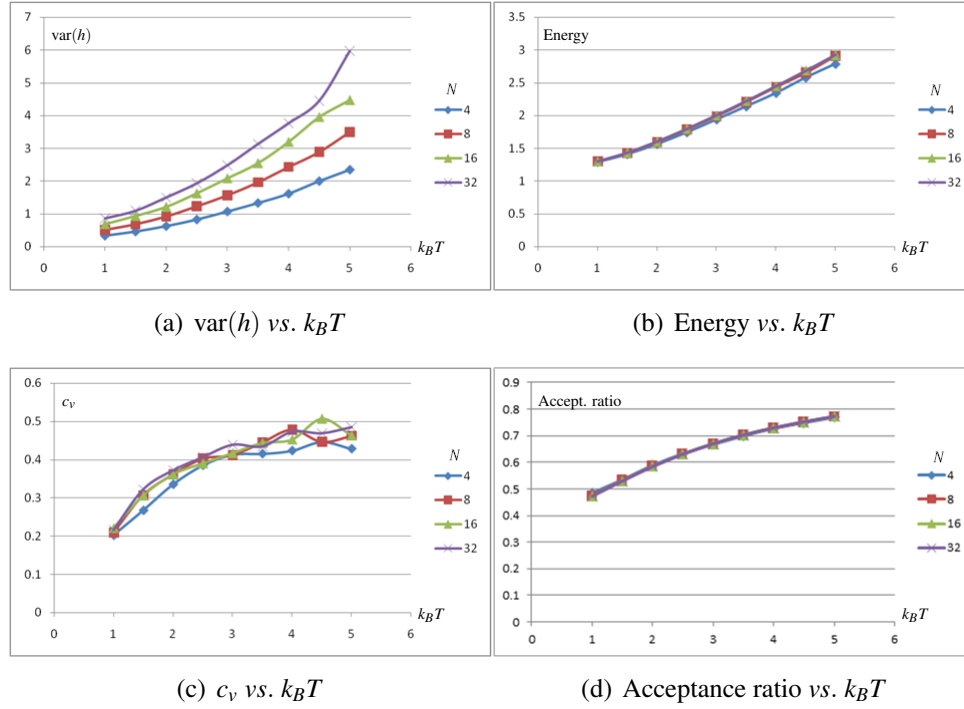


Figure 6.19: Variance of height, energy per area, heat capacity per area and the acceptance ratio at high temperatures for $p = 1.1$ on an initial (111) surface

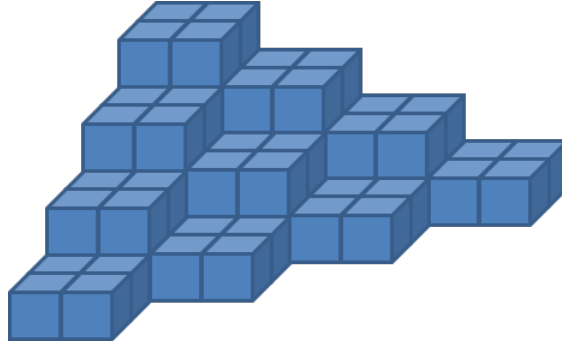


Figure 6.20: Initial configuration of a small (112) surface

6.3.2 $p = 0.9$

The results are plotted in Figure 6.23. A macroscopic “smoothing transition” is still observed, similar to the (111) surface. The variance of height at lower temperatures is approximately a quarter of that on the (111) surface, the energy per area at lower temperatures is approximately half of that on the (111) surface, and the peak in the heat capacity is also smaller.

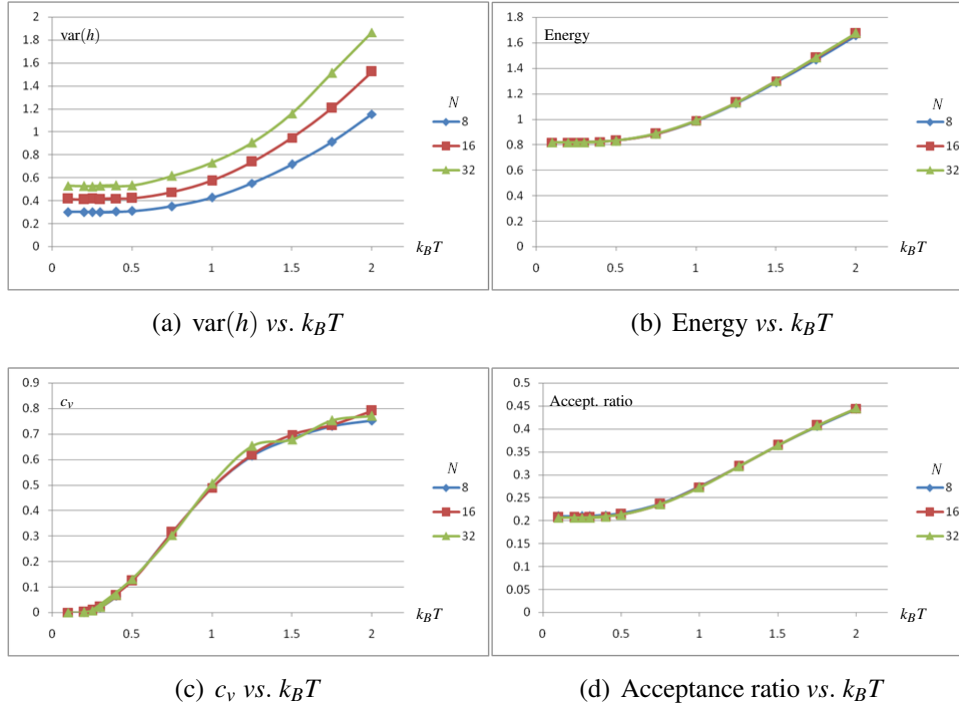


Figure 6.21: Variance of height, energy per area, heat capacity per area and the acceptance ratio for $p = 1$ on an initial (112) surface

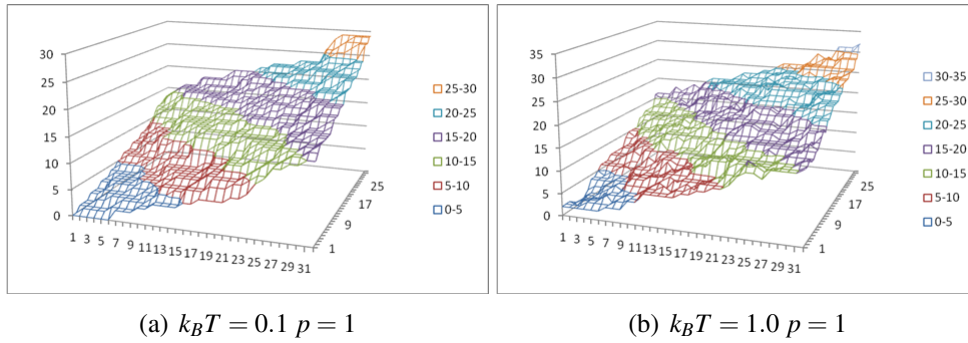


Figure 6.22: Snapshots of an initial (112) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 1$. The numbers on the right denote height above the (100) surface.

Snapshots of the surface at $k_B T = 0.1$ and $k_B T = 1.0$ are shown in Figure 6.24. We see that there are large facets and steps at lower temperatures and the faceted surface gets macroscopically smooth and microscopically roughened as the temperature gets higher.

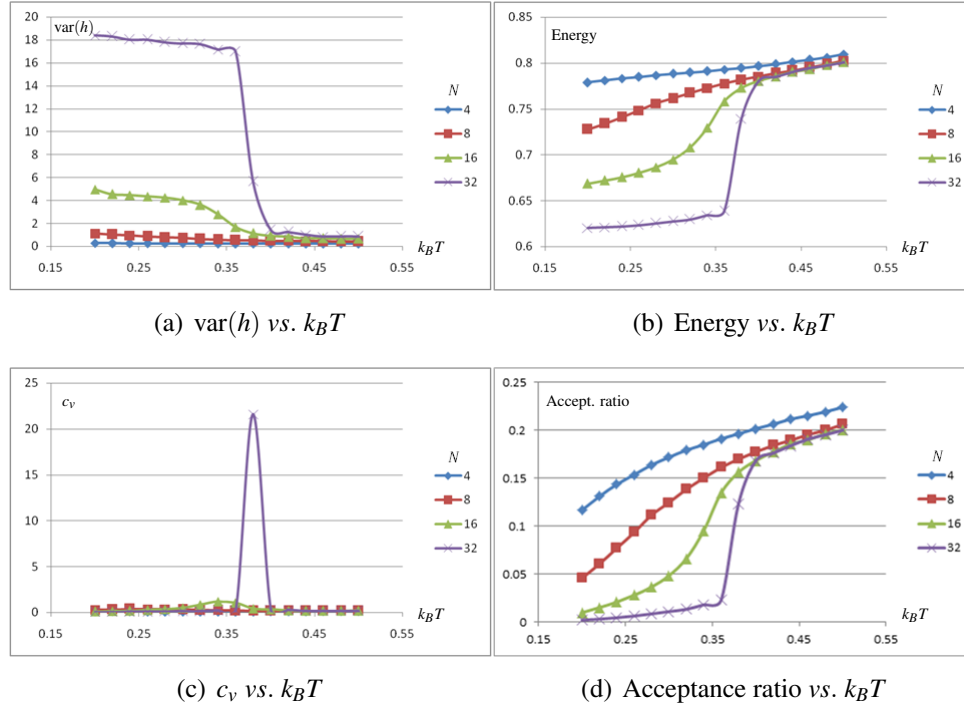


Figure 6.23: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 0.9$ on an initial (112) surface

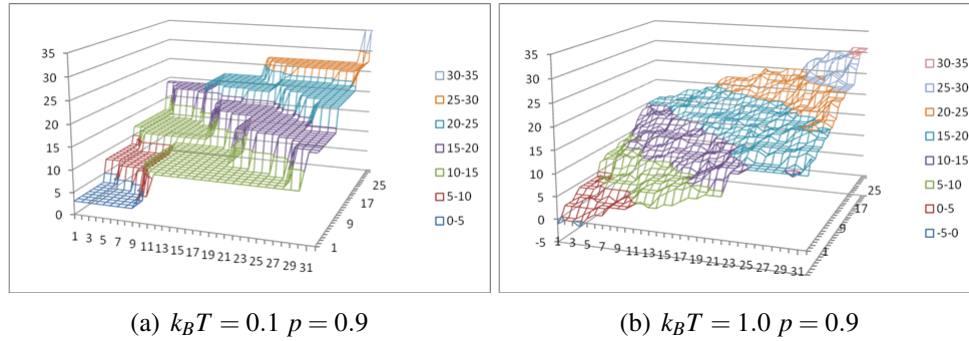


Figure 6.24: Snapshots of an initial (112) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 0.9$. The numbers on the right denote height above the (100) surface.

6.3.3 $p = 1.1$

Results are plotted in Figure 6.25. The plots still indicate similar characteristics as those for the (111) surface. At temperatures lower than $k_B T = 0.05$, the (111) surface does not change a lot from the initial configuration since adding atoms to or removing atoms from

this surface would increase the surface energy; however, the (112) surface does allow a few atoms to be added or removed without increasing the surface energy. Therefore, the variance of height at these low temperatures has different values for various system sizes. The transition from a smooth tilted surface to a roughened tilted surface is not as obvious as for the (111) surface. The peak in the heat capacity therefore is not as sharp. The values of variance of height, energy per area and acceptance ratio at higher temperatures are approximately half of the values for the (111) surface.

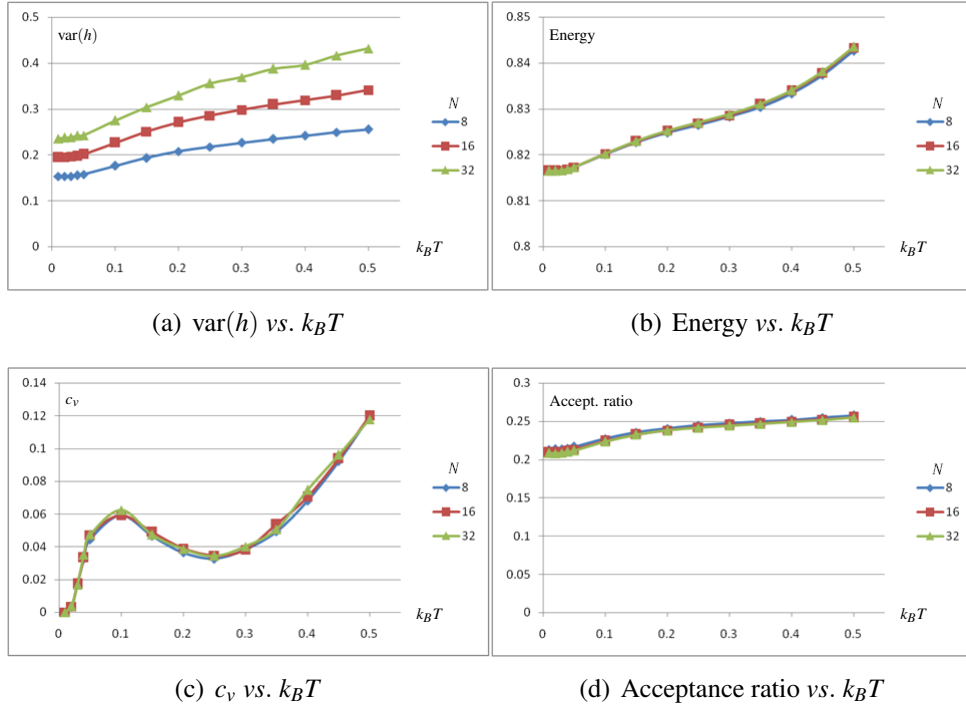


Figure 6.25: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 1.1$ on an initial (112) surface

Snapshots of the surface at $k_B T = 0.1$ and $k_B T = 1.0$ are shown in Figure 6.26. We see that the surface configuration is similar to the $p = 1$ case but smoother at low temperatures and not very rough at high temperatures.

6.4 Initially Tilted (110) Surface

The (110) surface is studied since it is tilted only in one direction and is studied for $p = 1, 0.9$ and 1.1 . The same model is applied to an initial (110) surface to see whether something new or different would happen. The initial (110) surface is plotted in Figure 6.27.

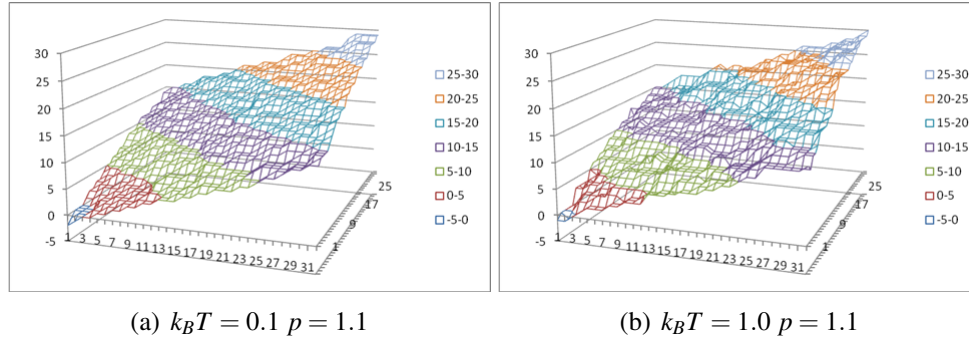


Figure 6.26: Snapshots of an initial (112) surface at $k_B T = 0.1$ and $k_B T = 1.0$ for $p = 1.1$. The numbers on the right denote height above the (100) surface.

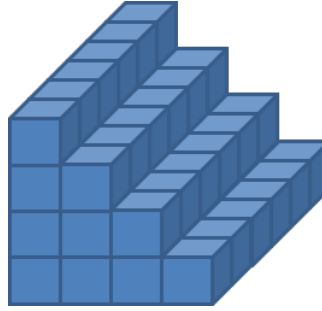


Figure 6.27: Initial configuration of a small (110) surface

6.4.1 $p = 1$

The results are plotted in Figure 6.28. For the $p = 1$ case, the fundamental trends in variance of height and heat capacity are more complicated than the other two surface configurations above. The variance of height in low temperatures behaves differently. We observed that the variance of height is larger compared to higher temperatures, which is not seen for the (111) and (112) surfaces. The underlying reason is that the initial (110) surface configuration consists of ledge sites but not kink sites, which are present on the initial (111) and (112) surfaces. For the (111) and (112) surfaces at low temperatures, there are enough kink sites to add or remove atoms; therefore, significant large steps are hard to form and the surface only fluctuates thermodynamically. For the (110) surface, the only possible way to nucleate a step in a ledge, which provides kinks and growth of that ledge, and then nucleates another step, etc. As a result, it is possible to form larger steps, so the variance of height also fluctuates accordingly, as seen in Figure 6.28. As the system sizes gets larger, the variance of height gets larger and the fluctuation also becomes more obvious.

In order to verify the fluctuation of the surface at low temperatures, we carried out

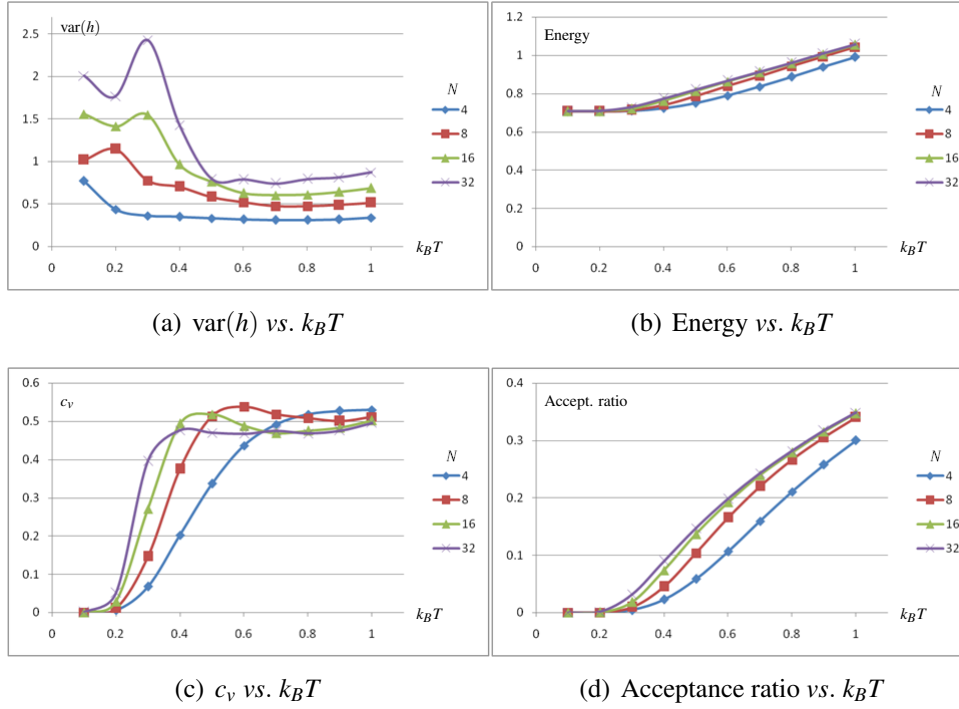


Figure 6.28: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 1$ on an initial (110) surface

simulation at $k_B = 0.3$ for a surface with system length size 32. The results are shown in Figure 6.29. We observed that the variance of height, the heat capacity per area and acceptance ratio all fluctuates as simulation proceeds and the energy keeps constant as expected.

Snapshots of the surface at $k_B T = 0.4$ and $k_B T = 1.0$ are shown in Figure 6.30. At low temperatures, the surface has a slight hill-and-valley structure on the surface. What is important is that the rows are roughened collectively. Although still seems smooth, this morphology results in big values of variance of height. At high temperatures, the surface is microscopically roughened overall and the hill-and-valley structure no longer exists.

6.4.2 $p = 0.9$

The results are plotted in Figure 6.31. For the $p = 0.9$ case, the characteristics are similar: there are big facets and large steps at low temperatures and the surface smooths out at high temperatures; the clear peak in the heat capacity and the jump in variance of height suggests a transition. Such transitions occur at higher temperatures ($k_B T \approx 0.7$) compared to the (111) surface ($k_B T \approx 0.45$) and the peak values are smaller.

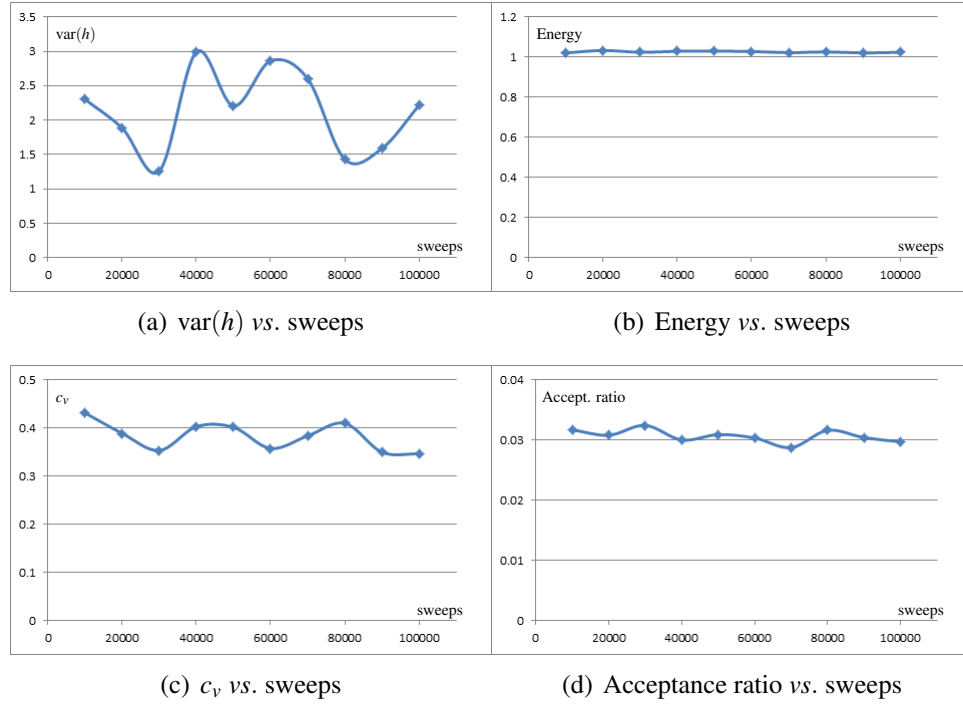


Figure 6.29: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 1$ on an initial (110) surface, as a function of simulation sweeps

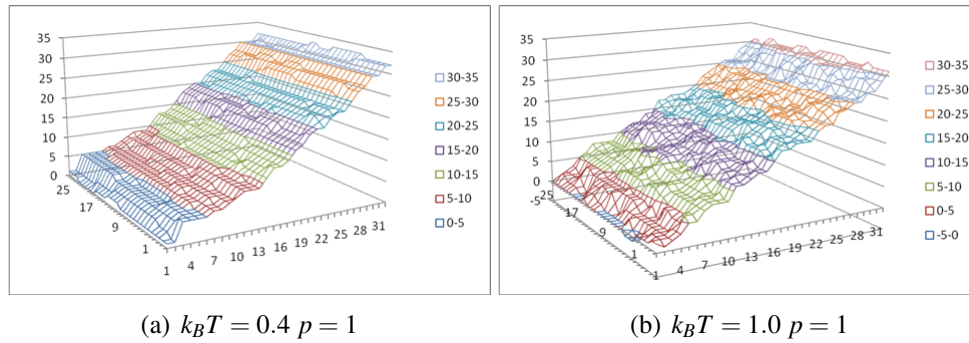


Figure 6.30: Snapshots of an initial (110) surface at $k_B T = 0.4$ and $k_B T = 1.0$ for $p = 1$. The numbers on the right denote height above the (100) surface.

Snapshots of the surface at $k_B T = 0.4$ and $k_B T = 1.0$ are shown in Figure 6.32. From the figure, we see that there are big facets and big steps at lower temperatures and the faceted surface becomes “macroscopically smooth” and “microscopically roughened” as the temperature gets higher.

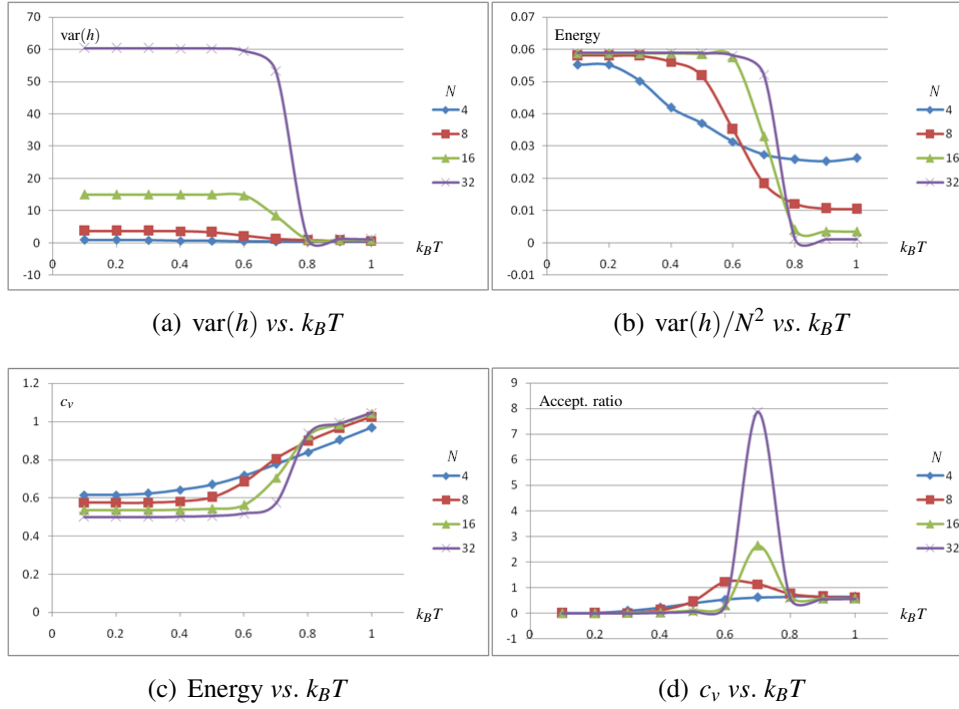


Figure 6.31: Variance of height, energy per area, heat capacity per area for $p = 0.9$ on an initial (110) surface

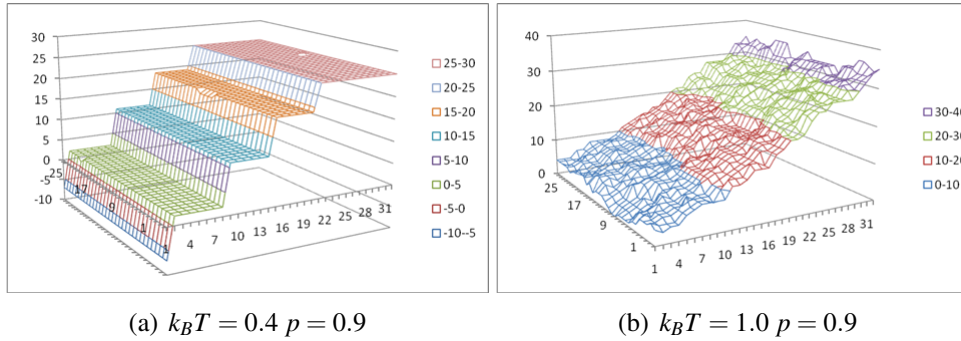


Figure 6.32: Snapshots of an initial (110) surface at $k_B T = 0.4$ and $k_B T = 1.0$ for $p = 0.9$. The numbers on the right denote height above the (100) surface.

6.4.3 $p=1.1$

The results are plotted in Figure 6.33. For $p = 1.1$ case, the overall trends are still the same as for (111) and (112) surfaces but the peak in heat is not as obvious as before; the transition region is not that sharp and is wider in range. And the variance of height seems

to show a fluctuation at low temperatures. The energy and acceptance ratios in (110) surface are really close to those for the (111) surface.

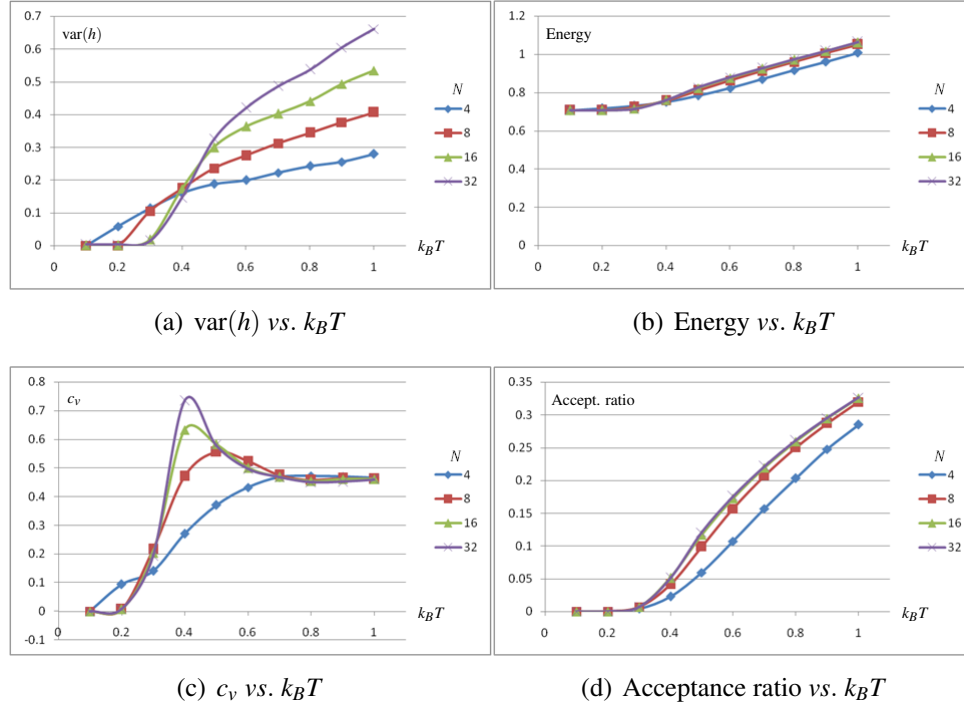


Figure 6.33: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 1.1$ on an initial (110) surface

Snapshots of the surface at $k_B T = 0.4$ and $k_B T = 1.0$ are shown in Figure 6.34. At low temperatures, the surface does not change a lot from the initial (110) surface and is very smooth. At high temperatures, the surface is roughened as before.

6.5 Finite Size Scaling Analysis

From the calculations above, we see that the variance of height shows a size effect for various system sizes.

For $p = 0.9$, $\text{var}(h)/N^2$ is plotted as function of temperature for each of the system size in Figure 6.35. As the system size gets larger, $\text{var}(h)/N^2$ seems to saturates at lower temperatures and the transition region from a faceted to a non-faceted surface seems to be narrower as the system size increases.

For $p = 1$ and $p = 1.1$, $\text{var}(h)$ is plotted as a function of $\ln N$ in Figure 6.36, where N is the edge length of the system. In both cases, there is a linear relation between these

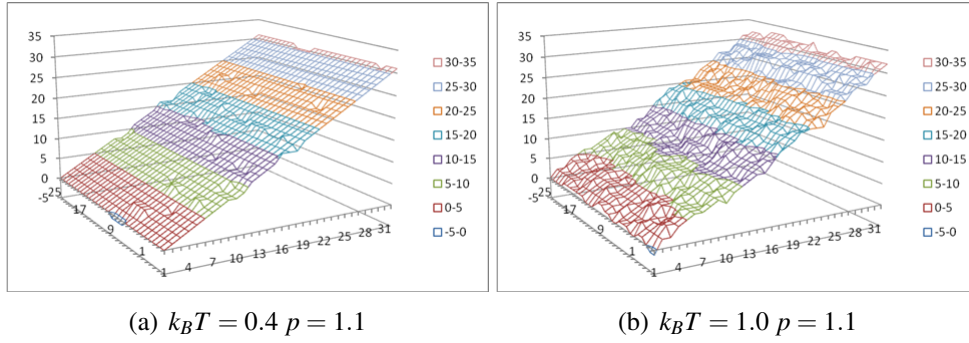


Figure 6.34: Snapshots of an initial (110) surface at $k_B T = 0.4$ and $k_B T = 1.0$ for $p = 1.1$. The numbers on the right denote height above the (100) surface.

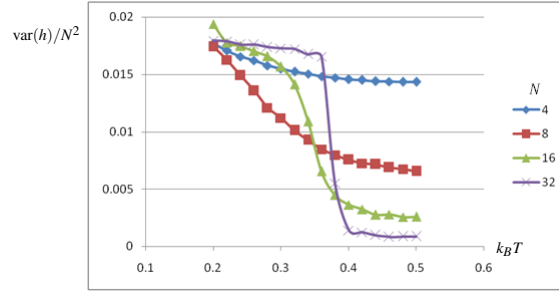


Figure 6.35: $\text{var}(h)/N^2$ vs. $k_B T$ for $p = 0.9$ on an initial (112) surface

two parameters; the slope gets larger as temperatures increases.

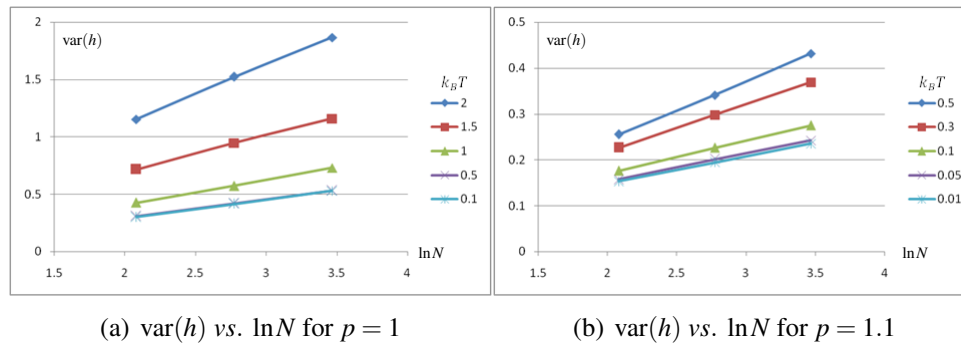


Figure 6.36: $\text{var}(h)$ vs. $\ln N$ for $p = 1$ and $p = 1.1$ on an initial (112) surface

6.6 Other p Values

As we saw above, small changes in p values result in significant changes in the behavior of the surface configurations. Besides the three values we investigated above, some other values are also studied.

In Figure 6.37, the variance of height, energy per area, specific heat capacity and the acceptance ratio for $p = 1.5$ is plotted. The behavior is very similar to the results in $p = 1.1$ model. The difference is that the peak at low temperature is more obvious and the peak temperature moves to a higher value.

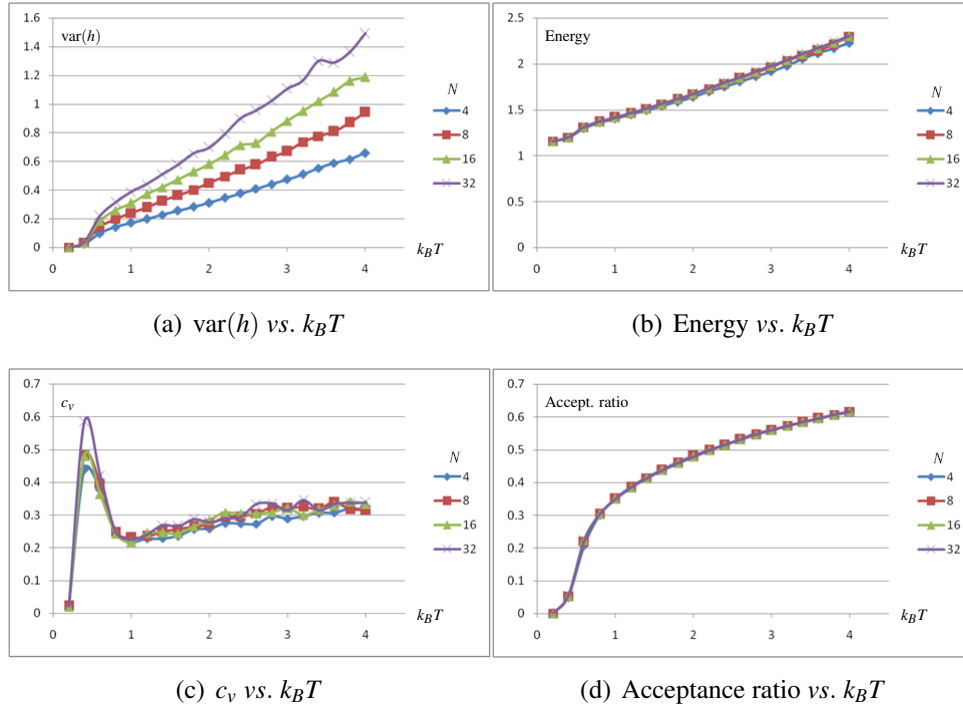


Figure 6.37: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 1.5$ on an initial (111) surface

In Figure 6.38, the variance of height, the energy per area, the heat capacity and the acceptance ratio for $p = 2$ is plotted. The biggest difference is that the peak is even more obvious and the peak moves to the higher end. The reason is that the model with p values larger than one disfavors high steps; the bigger the p values, the more difficult to have high steps. As discussed previously, there is a trade-off between the p values and the temperature. Large p values will avoid having high steps, but high temperature will enhance the probability of having high steps. Therefore, large p values will result in a higher-end peak position in heat capacity.

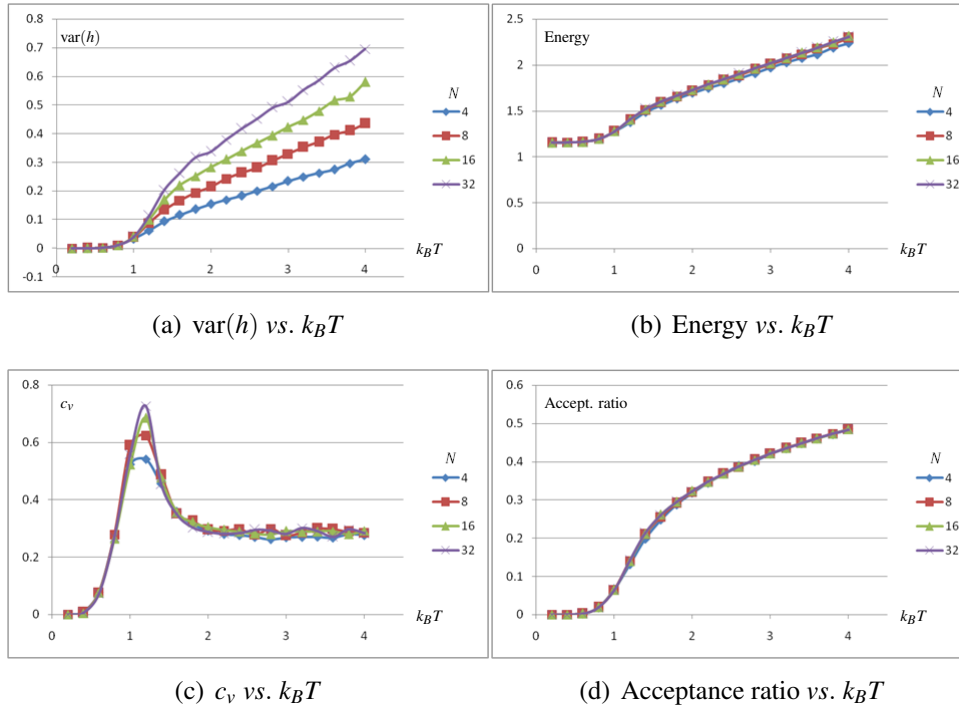


Figure 6.38: Variance of height, energy per area, heat capacity per area and acceptance ratio for $p = 2$ on an initial (111) surface

If the p value is much larger, the peak in heat capacity will move to a even higher value. If the p value equals infinity, the surface will stay at the initial smooth surface and nothing much will occur.

6.7 Facet Area Distributions

In the previous sections, one key measurement used to study the property of the crystal surface is the variance of height. This quantity indicates the surface morphology by measuring the variance from the initial configuration, but it is not necessarily linked to the surface roughness directly. For example, a surface configuration with large steps and large facets at low temperatures would have similar variance of height to a rough surface configuration formed at high temperatures, but these two surface configurations are quite different from one another. Therefore, the variance of height alone is not a convincing indication of the morphology of the crystal surface, so we need other measurements.

What we are interested in is whether large facets would form on a crystal surface. An intrinsic measurement would be a histogram of facet areas on a given surface. For a

faceted surface at low temperatures, there would be a few large facets, while for a microscopically roughened surface at high temperatures, there would be many small facets of various heights.

Another related measurement would be the the area decomposition of the total crystal surface. Although the histogram of the facet areas provides meaningful information about the surface morphology, it does not weight various facets with their sizes. The surface may contain very few large facets but this will not be apparent in a histogram of the facet area, because the histogram is still dominated by many smaller facets. One possible improvement is to count the total area for a given facet size, so the large facets will be accentuated.

We denote by n_i the number of facets of size i and by $A_i = n_i \cdot i$ the total area for facets of size i . So n_i provides the histogram for facets of size i over the surface, and A_i provides the total area for facet of size i over the surface. Such measurements are used to investigate the surface morphology at various temperatures and surface configurations.

The high symmetry (111) surface is studied by using the two measurements mentioned above at various temperatures for all three p -values. Low temperatures and high temperatures are studied to see whether there are different features and whether there are different patterns. For the $p = 0.9$ and $p = 1.1$ cases, more attention is payed to the measurements near the transition region to see whether something significant is happening. The area of the surface studied is 32 by 32.

6.7.1 $p = 1$

For the $p = 1$ case, the crystal surface gets rougher as the temperature gets higher. It is not expected to have special transitions in the surface morphology, and this is verified by using the two measures for various temperatures. The histograms of the facet area (n_i vs. i) and the area decomposition (A_i vs. i) are measured at $k_B T = 0.1, 1.0, 5.0$. The histogram of the facet area and the area decomposition are decreasing functions of the area size, and appear to be exponential distributions. Therefore, log plots of the results are presented below to get a better understanding.

For $k_B T = 0.1$, Figure 6.39(a) shows that the histogram of facet area obeys an exponential distribution aside from the first a few small sizes. Figure 6.39(b) shows an exponential distribution in the area decomposition. There is a very small probability of getting facets larger than 60. The average number of facets for the 32 by 32 surface is 331.

For $k_B T = 1.0$, Figure 6.40 shows behavior similar to $k_B T = 1.0$. The slopes of the log plots get larger in negative values, and the largest facet obtained is smaller than the one for $k_B T = 0.1$. The average number of facets for the 32 by 32 surface is 365. As the

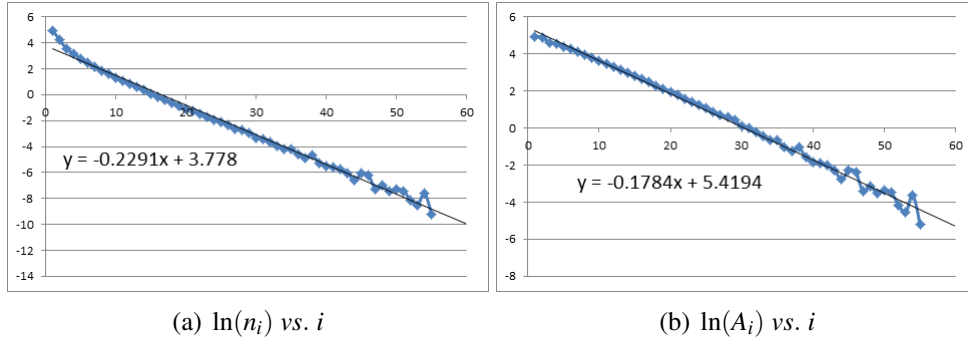


Figure 6.39: Log plot of the histogram of facet area and the area decomposition at $k_B T = 0.1$ for a 32 by 32 (111) surface, $p = 1$. n_i is the number of facets with area size i , A_i is the total area for facets with area size i

temperature gets higher, the surface gets rougher and there are more smaller facets and fewer larger ones.

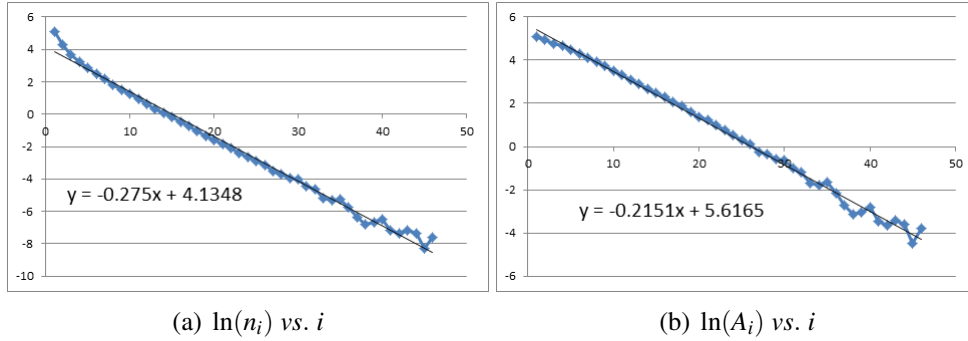


Figure 6.40: Log plot of the histogram of facet area and the area decomposition at $k_B T = 1.0$ for a 32 by 32 (111) surface, $p = 1$. n_i is the number of facets with area size i , A_i is the total area for facets with area size i

For $k_B T = 5.0$, Figure 6.41 shows the same trend as indicated in Figure 6.40. As the temperature gets higher, the surface gets even rougher and there are no facets larger than 25.

6.7.2 $p = 0.9$

For the $p = 0.9$ case, there is a faceted surface at low temperatures and a roughened surface at high temperatures. A transition occurs between $k_B T = 0.45$ and $k_B T = 0.5$ as shown by the variance of height for a 32 by 32 surface. The measurements are taken for low and high temperatures and temperatures around the transition.

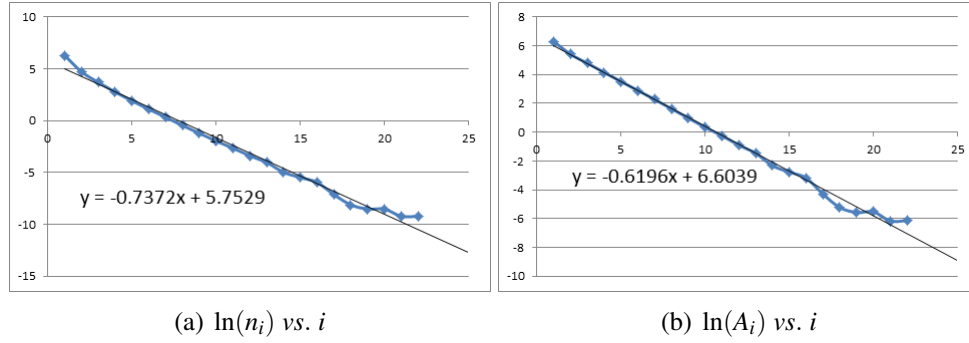


Figure 6.41: Log plot of the histogram of facet area and the area decomposition at $k_B T = 5.0$ for a 32 by 32 (111) surface, $p = 1$. n_i is the number of facets with area size i , A_i is the total area for facets with area size i

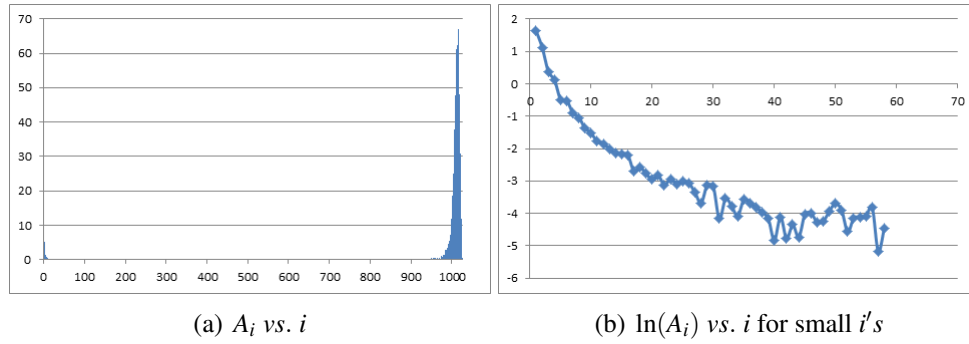


Figure 6.42: Plot of the area decomposition for all facets and log plot of the area decomposition for small facets at $k_B T = 0.3$ for a 32 by 32 (111) surface, $p = 0.9$. A_i is the total area for facets with area size i

At the low temperature $k_B T = 0.3$, the faceted surface has one large facet which is about 1000 in size. There are a few very small facets near the steps between facets. The log plot of the area distribution for these small facets is shown in Figure 6.42(b). There are only a few small facets and their area decomposition is close to an exponential distribution.

Beginning at the low temperature $k_B T = 0.45$, as the temperature gets slightly higher, there are more small facets and larger small facets. The largest small facet is increased from 20 to 60 in size and the one big facet has a broader variation in size. The log plot of area decomposition for the small facets also shows an exponential distribution aside from the first few small facets, as shown in Figure 6.43.

At temperature $k_B T = 0.5$, the transition from the faceted surface to a roughened surface occurs and there are no large facets and steps. The largest facet decreases from

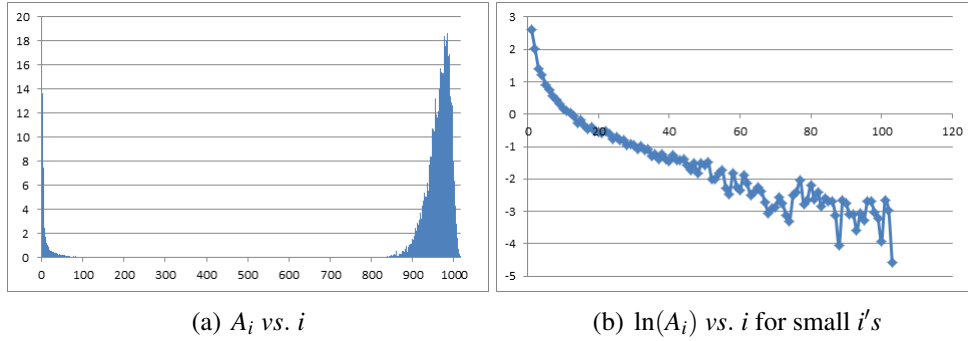


Figure 6.43: Plot of the area decomposition for all facets and log plot of the area decomposition for small facets at $k_B T = 0.45$ for a 32 by 32 (111) surface, $p = 0.9$. A_i is the total area for facets with area size i

about 1000 to about 100 in size. Log plots of the histograms of facet area and area decomposition are shown in Figure 6.44. The log plot of the area decomposition shows an exponential distribution while the log plot of the histogram of facet area shows an exponential distribution in the tail part. The properties are similar to the ones shown for the the $p = 1$ case. The average number of facets is 242.

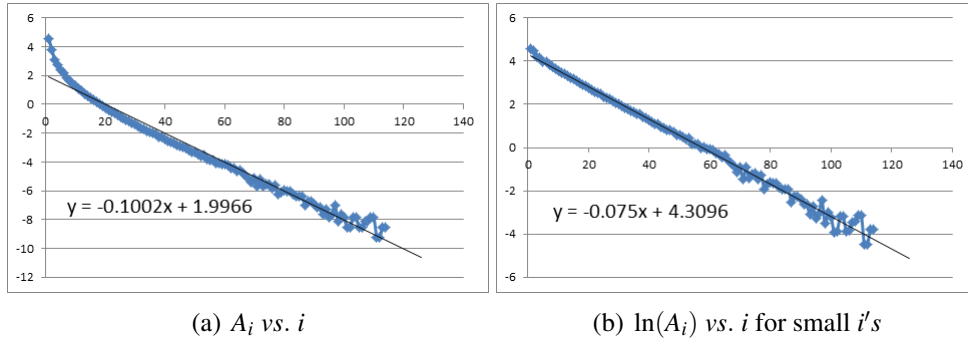


Figure 6.44: Log plot of the histogram of facet area and the area decomposition at $k_B T = 0.5$ for a 32 by 32 (111) surface, $p = 0.9$. A_i is the total area for facets with area size i

At the high temperature $k_B T = 5.0$, the surface gets very rough and the effect from the p value is nearly eliminated. Log plots of the histogram of facet area and the area decomposition are plotted in Figure 6.45. Now, there are no big facets, and the largest one is no larger than 20. The average number of facets is 770.

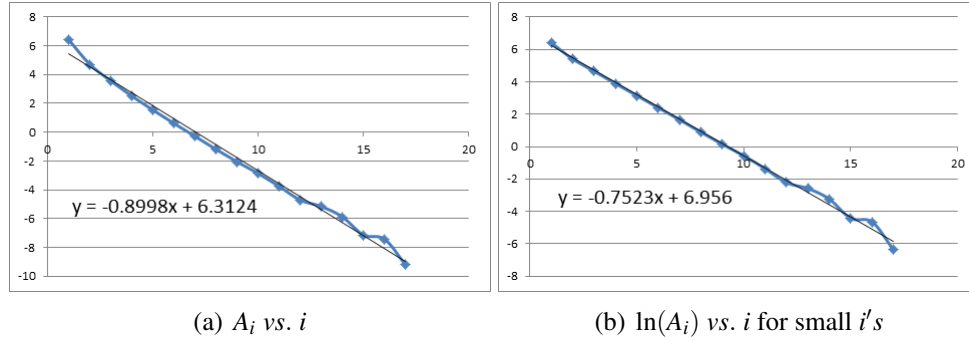


Figure 6.45: Log plot of the histogram of facet area and the area decomposition at $k_B T = 5.0$ for a 32 by 32 (111) surface, $p = 0.9$. A_i is the total area for facets with area size i

6.7.3 $p = 1.1$

In the $p = 1.1$ case, there is a peak in the heat capacity around $k_B T = 0.1$. Therefore, temperatures around $k_B T = 0.1$ are studied together with high temperature cases.

At the very low temperature $k_B T = 0.08$, the model does not allow the crystal surface to change a lot from the initial configuration since it does not favor big steps. As shown in Figure 6.46, the overall distributions are similar to previous cases with an exponential distribution, but an odd-and-even effect is also clearly present in both the plots. One reason for this is related to the initial (111) configuration and the model with $p = 1.1$. This model does not favor big steps, so adding or removing an atom from the initial configuration is non-favorable. In the initial configuration, the facets are all of size one. If one atom is added to or removed from the surface, a facet of size three would be formed. One would need to add or remove another atom nearby to form a facet of size two. Therefore it is more likely to have facets of odd rather than even sizes. The average number of facets is 855.

At slightly higher temperature $k_B T = 0.1$, the effect of the initial configuration is mitigated by the higher temperature and the odd-and-even effect is largely reduced. Log plots of the histograms of facet area and the area decomposition are plotted in Figure 6.47. Both log plots show nice exponential distributions as expected. The average number of facets is 518, which is greatly reduced compared to $k_B T = 0.08$, which again shows that the odd-and-even effect is reduced and larger facets get easier to create.

From low temperature $k_B T = 0.1$ to high temperature $k_B T = 5.0$, the surface gets rougher and the variance of height gets larger. The facets area and number of facets does not change significantly. The average number of facets is 682 compared to 518 at $k_B T = 0.1$. Only the facet heights change a lot and result in higher variance of height. Log plots of the histograms of facet area and the area decomposition are plotted in Figure

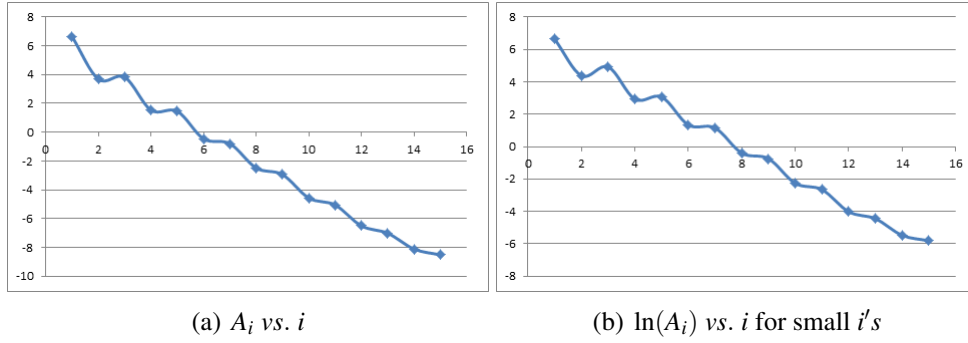


Figure 6.46: Log plot of the histogram of facet area and the area decomposition at $k_B T = 0.08$ for a 32 by 32 (111) surface, $p = 1.1$. A_i is the total area for facets with area size i

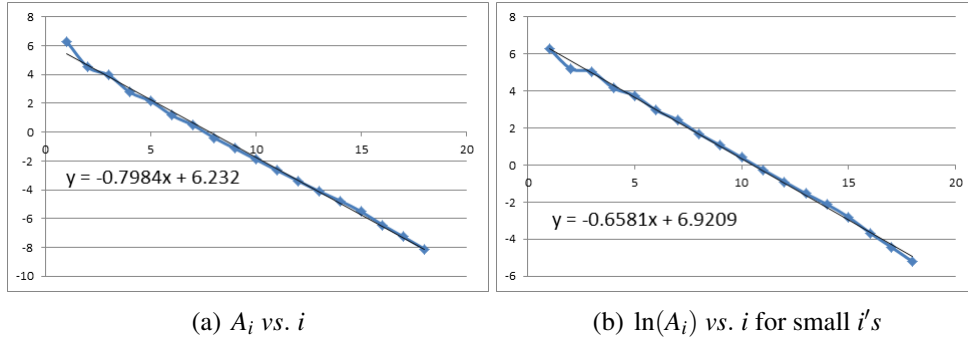


Figure 6.47: Log plot of the histogram of facet area and the area decomposition at $k_B T = 0.1$ for a 32 by 32 (111) surface, $p = 1.1$. A_i is the total area for facets with area size i

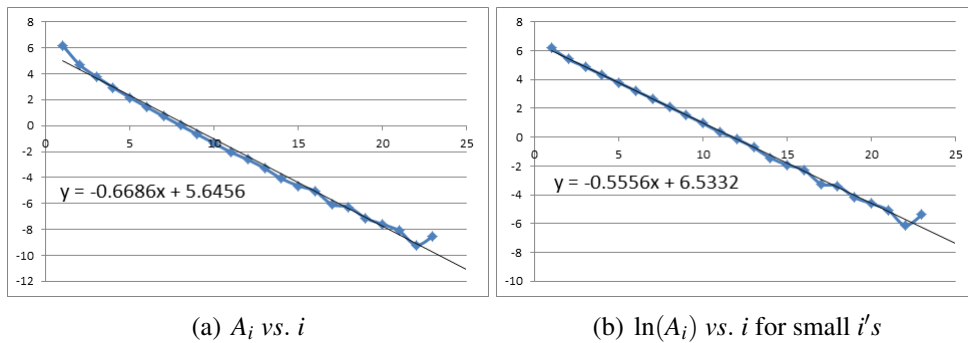


Figure 6.48: Log plot of the histogram of facet area and the area decomposition at $k_B T = 5.0$ for a 32 by 32 (111) surface, $p = 1.1$. n_i is the number of facets with area size i , A_i is the total area for facets with area size i

6.48. The area decomposition has an exponential distribution and the histogram of facet

area has an exponential distribution.

For various p values, the properties at high temperature are similar, both the log plots has exponential or nearly exponential distributions. For $p = 0.9$, the slopes in the plots have the largest absolute values and have the largest number of facets; the $p = 1.1$ slopes have the smallest absolute values and have the smallest number of facets. This is because the $p = 0.9$ model favors big steps and it is easier to roughen. It is harder to form larger facets, which results in larger slope and a larger number of facets. The same arguments apply to other cases.

6.8 Facet Height Distribution

From the previous section, the histograms of facet area and area decomposition both have exponential distributions at various temperatures for all three p values. The area decomposition has a very nice exponential distribution at both low and high temperatures. Therefore, it is worthwhile to investigate the underlying mechanism of this exponential distribution.

One approach is to check the height distribution over all surface steps. The intuition is that if there is high probability of having a step, there would be lower probability of having a large facet. If we could find a link between the height distribution over the surface steps, we may also find an explanation of the exponential distribution for the area decomposition.

6.8.1 $p = 0.9$ for (111) surface

For the (111) surface, the $p = 0.9$ model shows exponential distribution in the area decomposition above the transition temperature. At low temperatures, most of the steps are positive. As the temperature gets higher, the surface gets rougher and there are more negative steps. Thus both the positive step heights and negative step heights measured at $k_B T = 0.5$, which is just above the transition, and $k_B T = 5.0$. The total step height, which is a combination of the positive and negative heights are also calculated.

Denote pos_i to be the number of positive steps with height i , neg_i to be the number of negative steps with height i , and tot_i to be the total steps of height i .

At temperature $k_B T = 0.5$, there are a lot of positive steps and just a few negative steps. The log plot of number of positive and negative steps are plotted in Figure 6.49. The number of total steps and the log plot are plotted in Figure 6.50. For the positive steps, there are steps of relatively large heights and the log plot shows that the distribution of positive steps has a parabolic behavior, which indicates that the positive steps have a

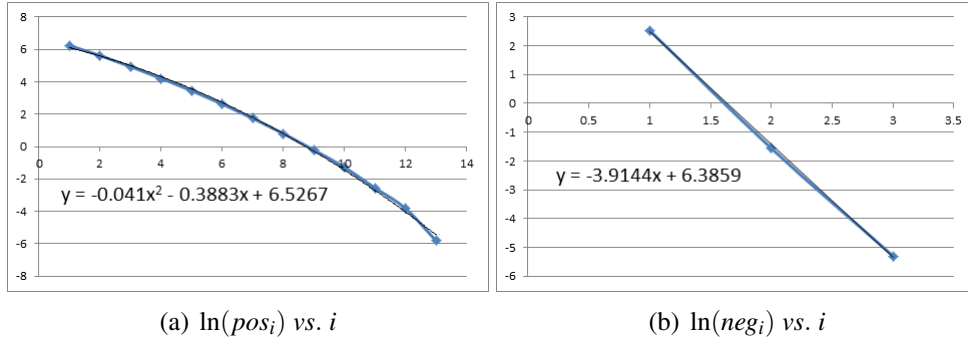


Figure 6.49: Log plot of the histogram of positive and negative steps at $k_B T = 0.5$ for a 32 by 32 (111) surface. pos_i is the number of positive steps of height i , neg_i is the number of negative steps of height i

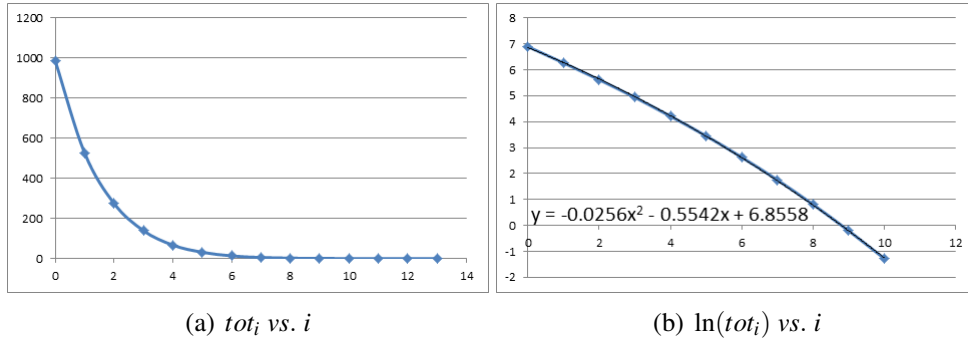


Figure 6.50: Histogram of total steps and the log plot of it at $k_B T = 0.5$ for a 32 by 32 (111) surface. tot_i is the number of steps of height i

Gaussian distribution. For the negative steps, there are only shallow negative steps and the log plot shows that they obey a exponential distribution. For total steps, there is a Gaussian distribution mainly contributed by positive steps.

At temperature $k_B T = 5$, the surface is rough with a comparable number of positive and negative steps. Log plots of number of positive and negative steps are plotted in Figure 6.51. The plot of number of total steps and the log plot are plotted in Figure 6.52. From these plots, both the positive and negative steps have similar Gaussian distributions and the total steps also has a Gaussian distribution.

6.8.2 $p = 1$ for (111) surface

For the (111) surface, the $p = 1$ model shows exponential distribution in the area decomposition at both low and high temperatures. The height distribution is similar to the

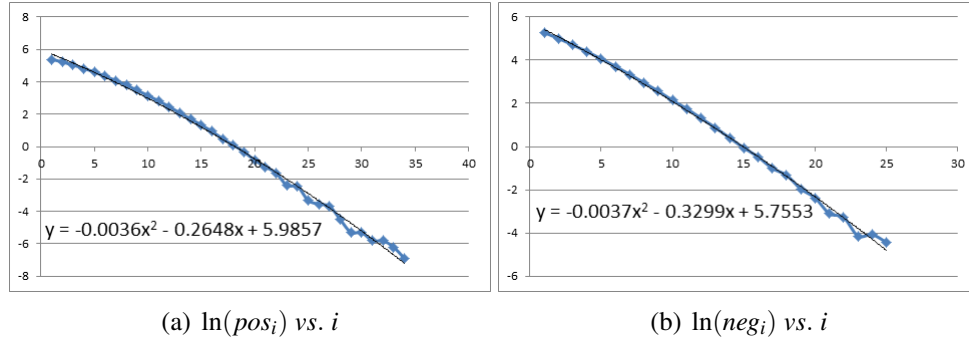


Figure 6.51: Log plot of the histogram of positive and negative steps at $k_B T = 5$ for a 32 by 32 (111) surface. pos_i is the number of positive steps of height i , neg_i is the number of negative steps of height i

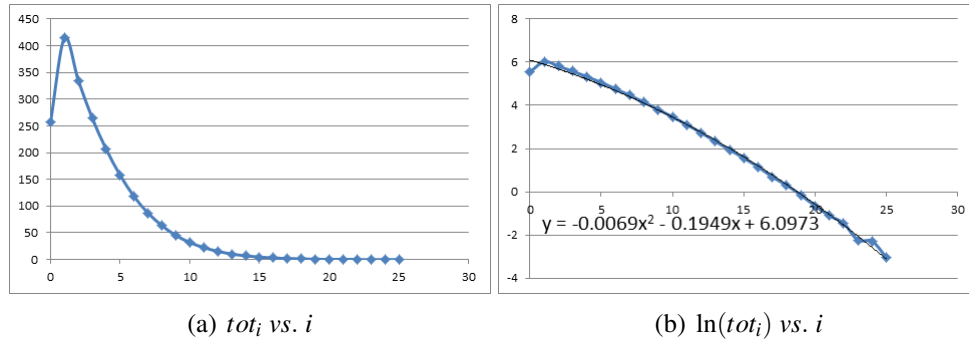


Figure 6.52: Histogram of total steps and the log plot of it at $k_B T = 5$ for a 32 by 32 (111) surface. tot_i is the number of steps of height i

$p = 0.9$ case. Log plots of number of steps at $k_B T = 0.5$ and $k_B T = 5$ are plotted in Figure 6.53. At both temperatures, the steps obey a Gaussian distribution. At low temperatures, there is a mainly small steps and at higher temperatures, there are higher probability of having higher steps as the surface gets rougher.

6.8.3 $p = 1.1$ for (111) surface

For the (111) surface, the $p = 1.1$ model also shows exponential distribution in the area decomposition at both low and high temperatures. The height distribution should also be similar to the other cases. The log plot of number of steps at $k_B T = 0.5$ and $k_B T = 5$ are plotted in Figure 6.54. At both temperatures, the steps obey a Gaussian distribution as before. At low temperatures, there are mainly small steps and at higher temperatures, there are higher probability to have higher steps as the surface gets rougher.

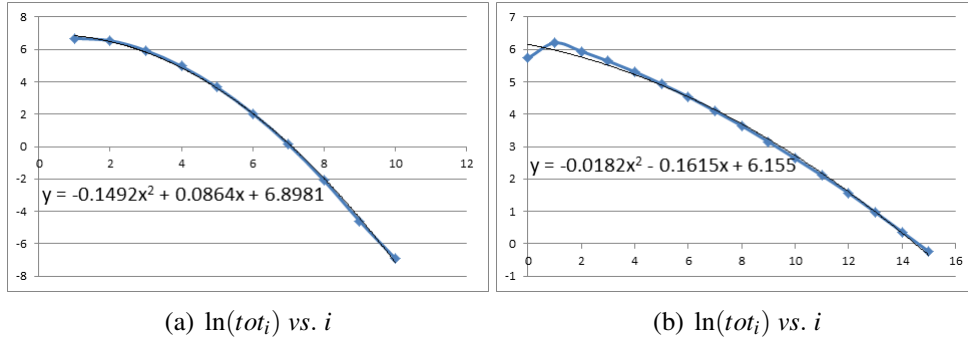


Figure 6.53: Log plot of the histogram of total steps at $k_B T = 0.5$ and $k_B T = 5$ for a 32 by 32 (111) surface. tot_i is the number of steps of height i

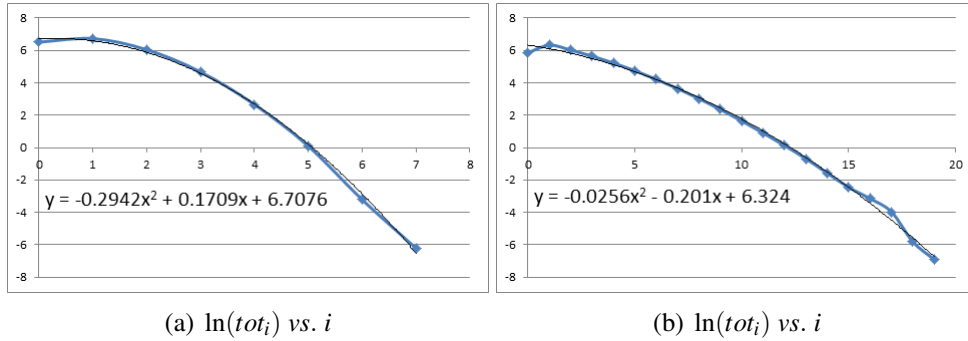


Figure 6.54: Log plot of the histogram of total steps at $k_B T = 0.5$ and $k_B T = 5$ for a 32 by 32 (111) surface. tot_i is the number of steps of height i

6.8.4 Connection with Facet Area

The height distribution for various p values all obey a Gaussian distribution and we want to connect this to the exponentially distributed area decomposition. Assume the probability of facet with area a is $\frac{1}{\lambda} e^{-\lambda a} da$. Then the probability of having a facet with area a or larger is $\int_a^\infty \frac{1}{\lambda} e^{-\lambda a} da = e^{-\lambda a}$.

On the other hand, since the heights obey a truncated Gaussian distribution, the probability of not having a step is approximately $\propto e^{-\text{const}}$, where the *const* involves the fitting parameters in each individual case. Therefore, in order to have a facet with size at least a requires a neighboring atoms having no steps between them, which is $\propto \prod_1^a e^{-\text{const}} = e^{-\text{const} \cdot a}$.

This approximation may give a hint to the reason one observes exponential distribution for the area decomposition, but no explicit form is given.

6.9 Hysteresis Effect

Hysteresis is widely present in the condensed matter, both as an adverse effect and a phenomenon useful in technological applications. Hysteresis occurs in several phenomena. In physics we encounter it in plasticity, friction, ferro magnetism, ferro electricity, superconductivity, adsorption and desorption. More generally, hysteresis arises in phase transitions. Hysteresis also appears in chemistry, biology, economics, even in experimental psychology, and so on. In natural systems hysteresis is often associated with irreversible thermodynamic change.

Hysteresis effects are often caused by phase transitions [51] which are accompanied by abrupt changes of some of the involved physical quantities, as well as by the absorption or release of energy in the form of the latent heat. The area of the hysteresis loop itself gives a measure of the amount of energy that has been lost or absorbed during the phase transformation.

In our previous $p = 0.9$ models, the smoothing transition is observed when the simulation is carried out from high temperatures to low temperatures. When the simulation is continued to raise the temperatures again, the hysteresis effect is also observed.

The simulation is started from a initially tilted surface from temperatures higher than the transition temperature. The temperature is lowered gradually and at each temperature, various length of simulation is carried out for comparison. When the temperature is significantly below the transition temperature, the temperature is then raised gradually at the same temperatures as before at various simulation lengths. By implementing the simulation, we can investigate whether there is a hysteresis effect and how it depends on the rate of temperature changes.

In Figure 6.55, the various of surface height and energy per area is plotted for various simulation lengths, from 5120 to 81920 sweeps at each temperature. The simulation is carried out from $k_B T = 0.6$ to $k_B T = 0.2$ and then back to $k_B T = 0.8$. We can easily and obviously see the hysteresis effect and different size of the hysteresis loops for various rates of temperature changes.

The "jumps" of physical properties in phase transitions are never instant. Upon heating or cooling they always spread over a temperature range, narrow or wide. The width of a transition range is not a fixed value. As we saw in the above figure, the transition covers a different area for different temperature rates. This suggests that the smoothing transition we have here has a rate-dependent hysteresis effect, which is due to a dynamic lag between the temperature rate and the surface configurations. It is expected that the hysteresis effect will disappear when the temperature changes really slow.

To further verify this rate-dependent hysteresis effect, more simulation is carried out for fast rate changes. In Figure 6.56(a), the simulation is started from an initially

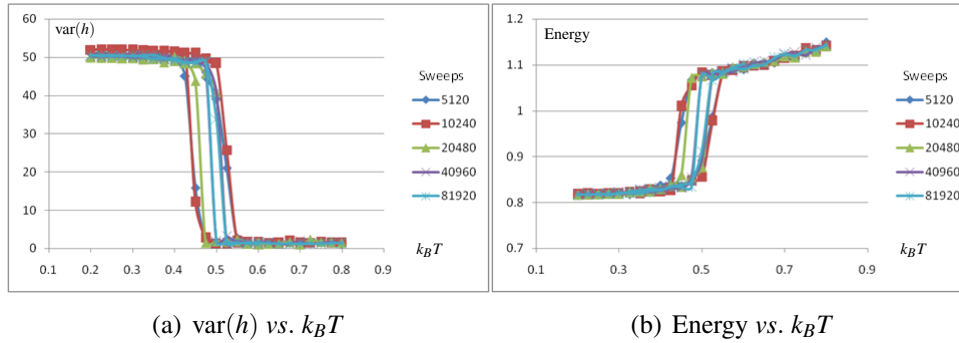


Figure 6.55: Variance of height, energy per area for a initially tilted (111) surface with $p = 0.9$. The temperature is from $k_B T = 0.6$ to $k_B T = 0.2$ and back to $k_B T = 0.8$. At each temperature, various simulation sweeps are carried out for comparison, from 5120 sweeps to 81920 sweeps

tilted surface and the temperature is lowered at various fast rates, from 10 to 5120 sweeps at each temperature. We can see that the transition is more diffuse for faster rates and the transition occurs at a lower temperature. What is more important, for the faster-rate changes, the variance of the faceted surface below the transition region is smaller, compared to the steady faceted surface after a long simulation run. The reason is that the simulation rate is fast and the system just does not have time to fully respond to the temperature change. If given longer simulation, the surface will eventually go to the equilibrium configuration. In Figure 6.56(b), the simulation is started from a equilibrium faceted surface below the transition. The temperature is raised at various rates same as in (a) for comparison. The transition region covers different sizes of area and the transition temperature is different as well, but the surface will all eventually go to a smooth surface.

The above comparison is carried out for two directions of temperature change. One natural question is what will happen if we carry out the simulation continuously from high temperatures to low temperatures and then back to high temperatures at fast rates. In Figure 6.57, the simulation is started from $k_B T = 0.5$ to $k_B T = 0.2$ and then back to $k_B T = 0.8$ at various rates, from 640 sweeps to 5120 sweeps at each temperature. For the fastest rate, 512 sweeps, the variance of surface height below the transition temperature is much lower than others. When the temperature is raised, the variance does not increase again and just follows an ordinary hysteresis loop. For the slowest rate, 5120 sweeps, the surface below the transition temperature is already in equilibrium and it also follows an ordinary hysteresis loop. For the the mid-rate cases, when raising the temperature, the variance of surface height increases as well, and then decreases when the temperature is even higher.

As above, we saw that for fast rates, the surface does not come to the equilibrium configuration immediately. One may ask, how long will it take to come to the equilibrium.

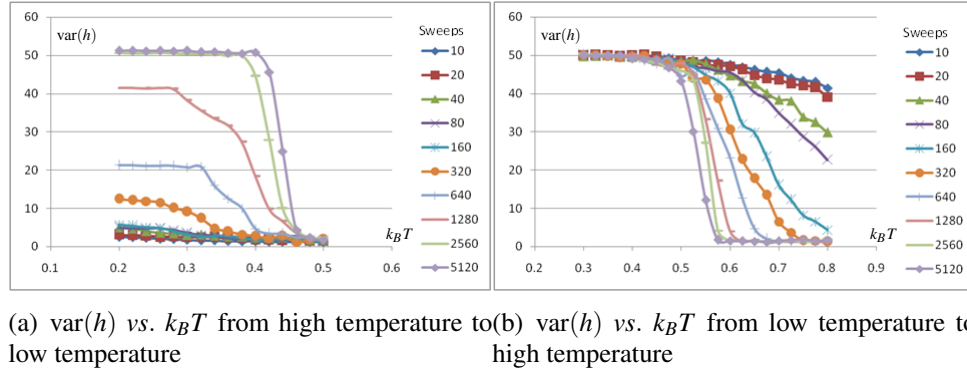


Figure 6.56: Variance of height for a initially tilted (111) surface with $p = 0.9$. The temperature is from $k_B T = 0.5$ to $k_B T = 0.2$ in (a) and from $k_B T = 0.3$ to $k_B T = 0.8$ in (b). At each temperature, various simulation sweeps are carried out for comparison, from 10 sweeps to 5120 sweeps

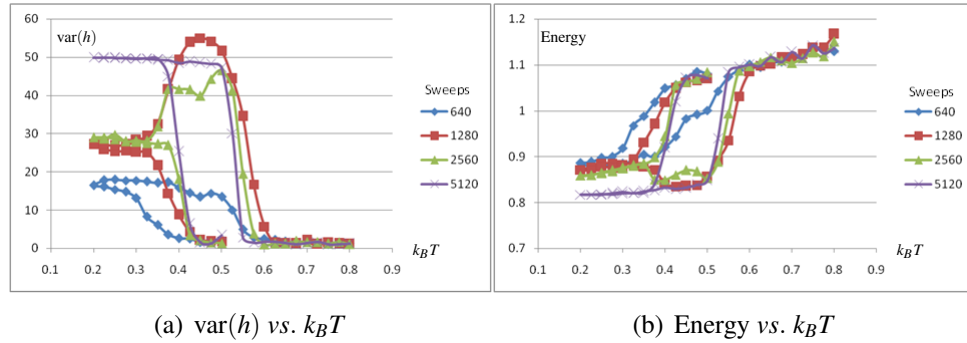
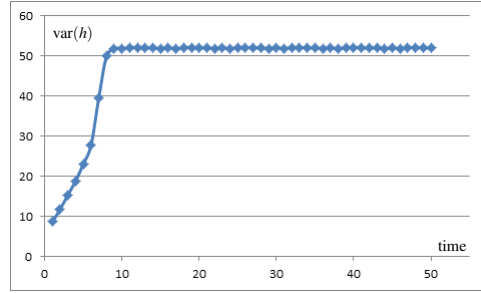


Figure 6.57: Variance of height, energy per area for a initially tilted (111) surface with $p = 0.9$. The temperature ranges from $k_B T = 0.5$ to $k_B T = 0.2$ and back to $k_B T = 0.8$. At each temperature, various simulation sweeps are carried out for comparison, from 640 to 5120 sweeps

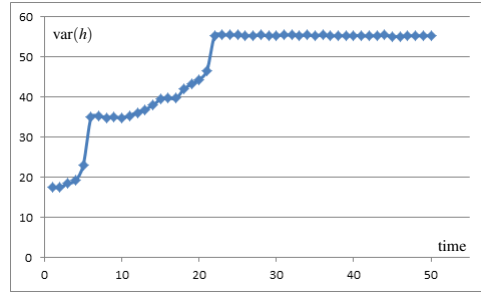
So we can investigate this problem by starting the simulation from a initially tilted smooth surface at temperature below the transition, to see how the variance of surface height changes.

In Figure 6.58, the simulation is carried on a (111) surface at $k_B T = 0.3$ for the $p = 0.9$ model. The variance of surface height is calculated after every 10000 sweeps. Three different characteristic cases are plotted.

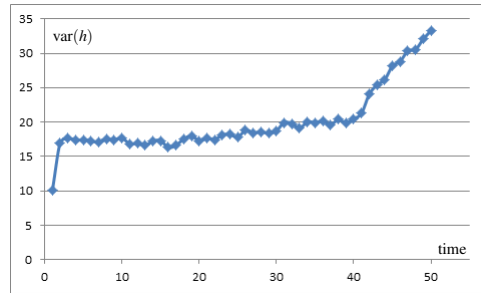
We can see that the variance takes different paths in these three cases. In (a), the variance rapidly goes to the equilibrium value and the jump is very sharp. In (b), the variance increases gradually and has several intermediate steps. In (c), the variance locks



(a) 1



(b) 2



(c) 3

Figure 6.58: Variance of height for a initially tilted (111) surface with $p = 0.9$ at $k_B T = 0.3$. The simulation is calculated after every 10000 sweeps and the time unit is also in 10000 sweeps.

in a intermediate phase for a relatively long time and then goes into the equilibrium. Some other simulation shows that it may take even longer time at these phases.

Chapter 7

Symmetric Model

7.1 Symmetric Extension

The SOS model treated in former chapters is used mainly to focus on the effect of various p values on the surface morphology, but does not take into account the symmetry of surface configurations that would pertain to an actual crystal. This problem arises because the SOS model favors a specific direction, say the z direction, but we know for a cubic crystal that the x and y directions are equivalent. Therefore, facets are observed corresponding to the z direction; facets are not observed for x and y directions. Especially for a initially tilted highly symmetric surface, say (111), a SOS simulation does not result in a highly symmetric faceted surface that would be expected on the basis of crystal symmetry.

In order to address this symmetry issue, the previous SOS model can be extended to include the generic symmetry. One simple and natural extension is to include similar terms for the other two directions which are not considered in the previous model. Therefore, the symmetric solid-on-solid (SSOS) model is based on a Hamiltonian of the form:

$$H = \sum_{(i,j),(i',j') \text{ are NN's}} \left| h_{x_{ij}} - h_{x_{i'j'}} \right|^p + \sum_{(i,j),(i',j') \text{ are NN's}} \left| h_{y_{ij}} - h_{y_{i'j'}} \right|^p + \sum_{(i,j),(i',j') \text{ are NN's}} \left| h_{z_{ij}} - h_{z_{i'j'}} \right|^p$$

where (i, j) and (i', j') are nearest neighbors, $h_{x_{ij}}$ is the height of the surface in the x direction at site (i, j) , $h_{y_{ij}}$ is the height of the surface in the y direction at site (i, j) , and $h_{z_{ij}}$ is the height of the surface in the z direction at site (i, j) .

The SSOS model is symmetric in the x , y and z directions but still follows a solid-on-solid constraint. The extra terms give extra solid-on-solid constraints for the surface. Many previous surface morphologies are prohibited since they violate the solid-on-solid

requirements in other directions. The result is that only kink sites on the surface are possible sites for adding and removing atoms. Such a model is quite similar to that originally proposed by Kossel and Stranski, except that model had no SOS constraint at all.

Since the Hamiltonian in the SSOS model has more terms than the one for the SOS model, simulations are even more expensive and require more computational time. Thus, this model is mainly used to investigate initially highly symmetric surfaces to see what differences occur.

Monte Carlo simulations are carried out for $p = 0.9, 1, 1.1$ in both high and low temperature ranges for system sizes $N = 16$ and 32 . A total of 2000 sweeps of simulation are done for each case. As for the SOS model, the variance of height, energy per area, heat capacity per area and the acceptance ratio of the simulation are calculated.

7.2 Simulations on the (111) Surface

The (111) surface is a highly symmetric surface and symmetry plays an important role in crystal equilibrium facets and growth facets. The SSOS model is applied to an initially tilted (111) surface for all three p values particularly investigated for the SOS model.

7.2.1 (111), $p = 1$

$p = 1$ is used for the conventional SOS model. For the SSOS model, the corresponding simulation results are shown in Figure 7.1. The effect of the extra constraints are obvious. The variance of the surface height is nearly constant for a broad temperature range and the energy per area is nearly constant as well. As discussed above, adding and removing atoms only occurs at kink sites for the SSOS model. In the $p = 1$ case, morphological change does not result in energy changes. Therefore, the energy is fixed at the same value as for the initial configuration and the simulation result is not dependent on temperature. As a result, the heat capacity is always zero and the acceptance ratio of the simulation is always one. Even as the temperature gets higher, this model would not generate a rougher surface configuration as observed in the SOS model for $p = 1$ and would not result in larger variance of the surface height.

Snapshots of surface are taken at (a) $k_B T = 0.5$ and (b) $k_B T = 5$ respectively in Figure 7.2. The surface is smooth at both low and high temperatures. The morphologies are not significantly different.

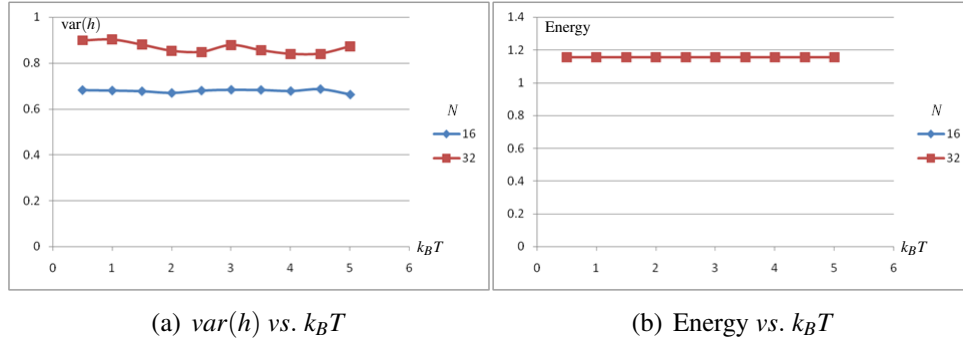


Figure 7.1: (a) Variance of height, (b) energy per area for $p = 1$ on an initially titled (111) surface

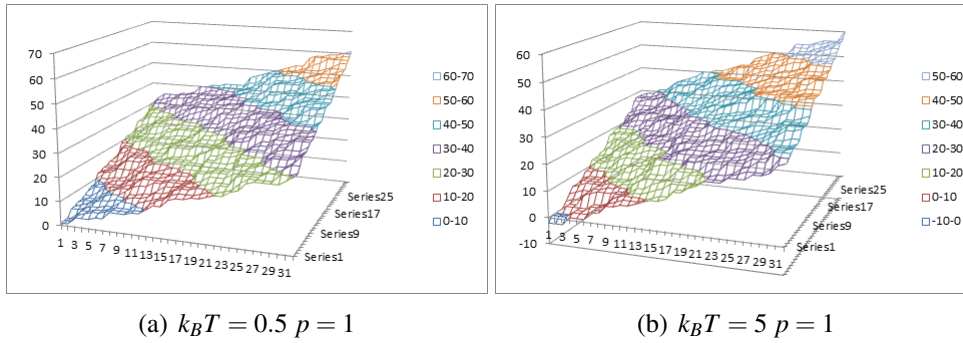


Figure 7.2: Snapshots for an initial (111) surface at $k_B T = 0.5$ and $k_B T = 5$ for $p = 1$

7.2.2 (111), $p = 0.9$

The simulation results are plotted in Figure 7.3. The most important finding is that the SSOS model still preserves some of the same qualitative characteristics of the SOS model. As seen in Figure 7.3, facets are observed at low temperatures and the variance of the surface height is still dependent on the system size. Once the facets are formed at lower temperatures, the variance of surface height and the energy per area are almost constant, the heat capacity is almost zero, and the acceptance ratio decreases as the temperature decreases. This suggests that the surface is in a faceted state only, and equilibrium is reached by adding and removing atoms at kink sites. As the temperature increases, a transition from a faceted surface to a smooth surface occurs around $k_B T = 1$. The variance of height decreases, the energy per area increases in the transition region, and a peak exists in the heat capacity. In the SOS model, $p = 1$ case results in different transition temperatures for various system sizes, the energy per area also differs for different system sizes for the faceted surface, and the acceptance ratio is also different. For the SSOS model, the transition occurs in the same temperature region with almost same energy and

acceptance ratio for various system sizes. The transition temperatures are higher than for the SOS model due to the introduction of the extra terms in the Hamiltonian.

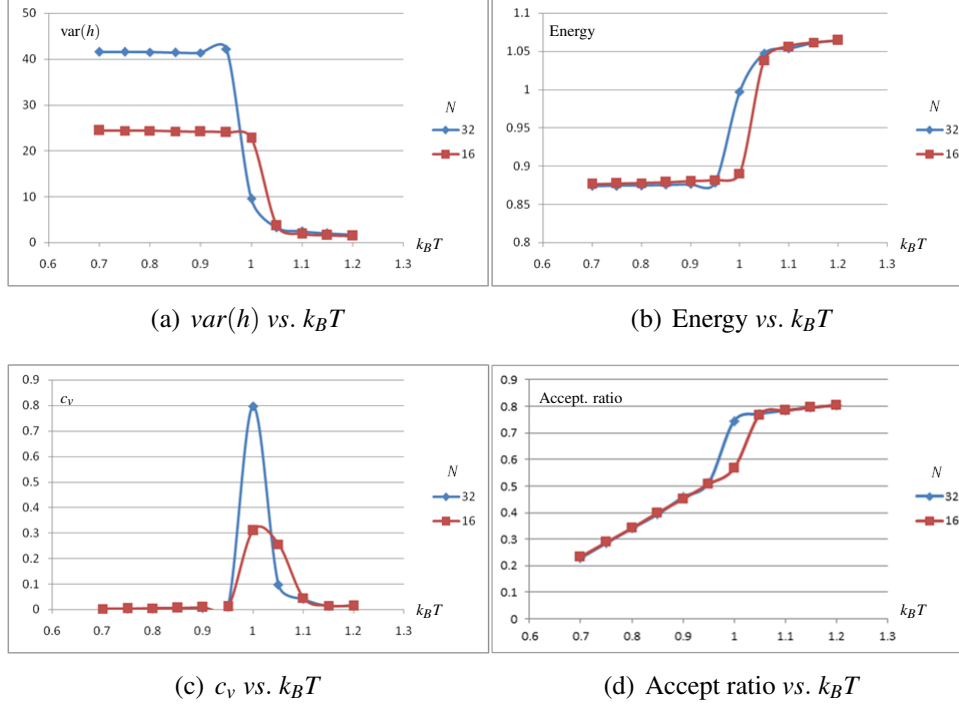


Figure 7.3: Variance of height, energy per area, heat capacity per area and the acceptance ratio for $p = 0.9$ on an initial (111) surface

Snapshots of the surface are taken at temperatures in the transition region, $k_B T = 0.95, 1, 1.05$ and 1.1 , as shown in Figure 7.5. The transition from the faceted surface to the smooth surface is clearly evident. At higher temperatures, the surface would be even smoother and get close to the case $p = 1$.

Snapshots of the simulated surfaces clearly demonstrate true crystal symmetry. Compared to the SOS model, these facets are now in all (x, y, z) directions. Compare Figure 7.5(b) from SSOS model with Figure 6.12(a) from the SOS model to observe the difference.

7.2.3 (111), $p = 1.1$

The results are plotted in Figure 7.6 and somewhat resemble the results for the SOS model. For the case when $p = 1.1$, the model disfavors large steps and big facets; therefore, the variance of height and energy per area is relatively smaller than for $p = 1$ and $p = 0.9$ and gets larger as the temperature increases. At very low temperatures, the variance of height

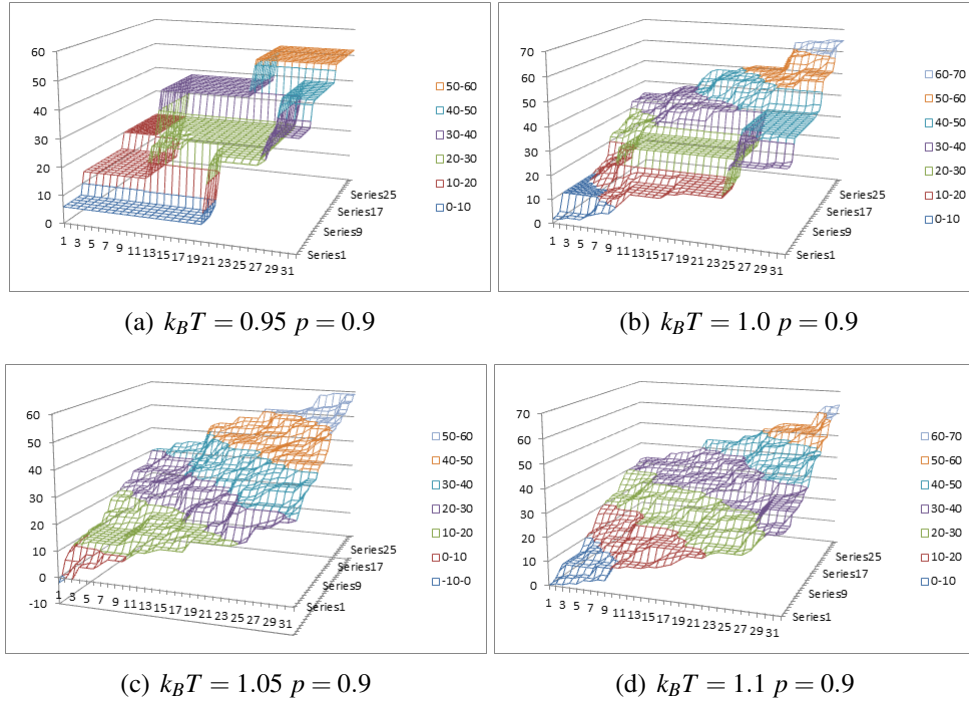


Figure 7.4: Snapshots on an initial (111) surface at (a) $k_B T = 0.95$, (b) $k_B T = 1.0$ for $p = 1$, (c) $k_B T = 1.05$ and (d) $k_B T = 1.1$ for $p = 0.9$. Note especially that there are facets in all (x, y, z) directions

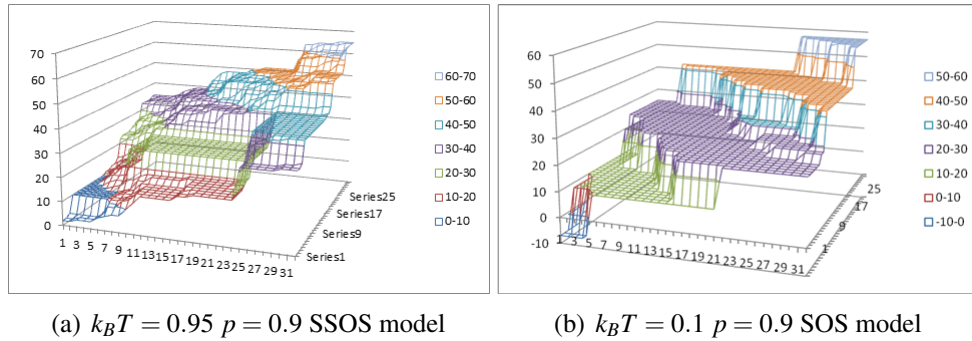


Figure 7.5: Snapshots on an initial (111) surface (a) at $k_B T = 0.95$ from SSOS model (b) at $k_B T = 0.1$ from SOS model for $p = 0.9$

is almost zero, the energy per area is closed to 2, and the acceptance ratio is nearly zero. At these low temperatures, the surface is again almost the initial (111) surface without any significant changes. As the temperature gets a little bit higher, the surface atoms begin to be added and removed at the kink sites. There seems to be a transition from a smooth

tilted surface to a relatively roughened surface at low temperatures, and the sharp peak in the heat capacity shows evidence of this. Above the transition temperature, the variance of height increases faster and has larger values for larger system sizes. The energy per area, heat capacity and acceptance ratio have similar values for various system sizes. Due to the effect of p values and the constraint of the model, the variance of height and energy per area saturates to values smaller than for the $p = 1$ case at high temperatures.

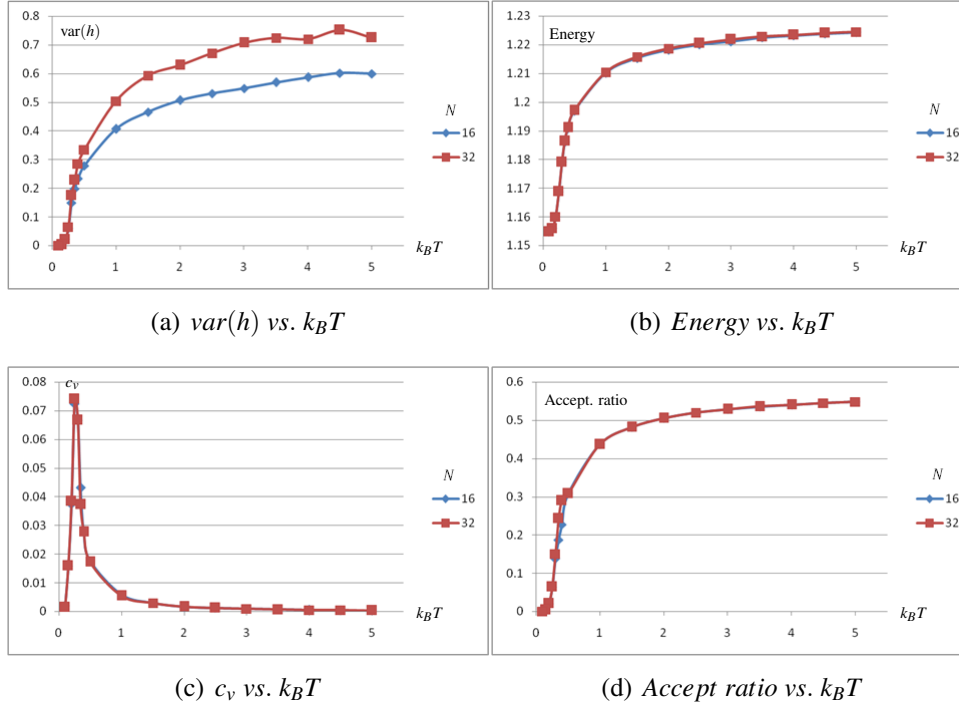


Figure 7.6: Variance of height, energy per area, heat capacity per area and the acceptance ratio for $p = 1.1$ on an initial (111) surface

Snapshots of surface morphology are shown at $k_B T = 0.5$ and $k_B T = 5$ respectively in Figure 7.7. No significant difference in morphology is observed. The surface is smoother at low temperature and it gets a little bit rough at higher temperatures, resulting in a higher variance of surface height and energy per area.

7.3 Simulations on the (112) Surface

The (112) surface has shallower slopes in two directions as compared to (111). The SSOS model is applied to an initial (112) surface and the Monte Carlo simulations are carried out as before.

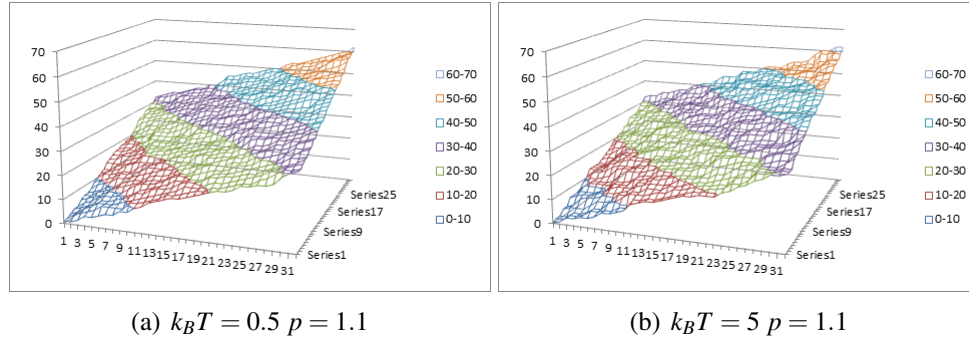


Figure 7.7: Snapshots on an initial (111) surface at (a) $k_B T = 0.5$ and (b) $k_B T = 5$ for $p = 1.1$

7.3.1 (112), $p = 1$

The results are plotted in Figure 7.8. The plots are similar to the (111) case and only differ in values. The energy per area is quantitatively half of the previous values, which is true since the slopes in both directions are just half of that on (111) surface. The variance of surface height is also close to half of values of the (111) surface.

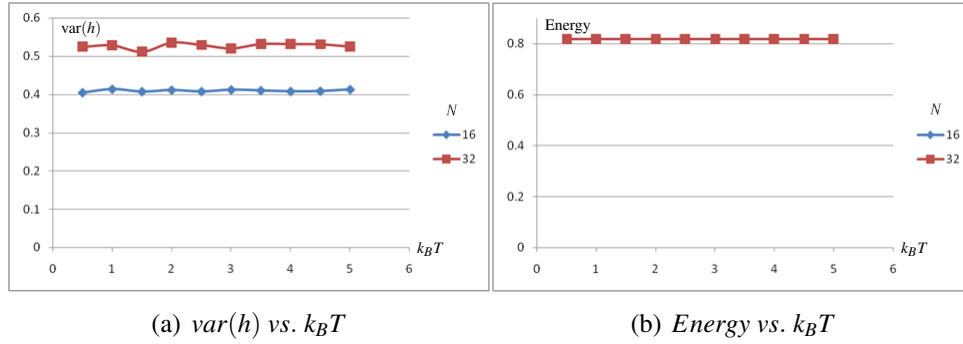


Figure 7.8: Variance of height, energy per area for $p = 1$ on an initially tilted (112) surface

7.3.2 (112), $p = 0.9$

The results are plotted in Figure 7.9. A transition is still observed, similar to the (111) surface, but covers a broader range of temperature. The variance of height at lower temperatures is smaller than that on the (111) surface, the energy per area at lower temperatures are approximately a half of that on the (111) surface, and the peak in the heat capacity is also close to the value for the (111) surface.

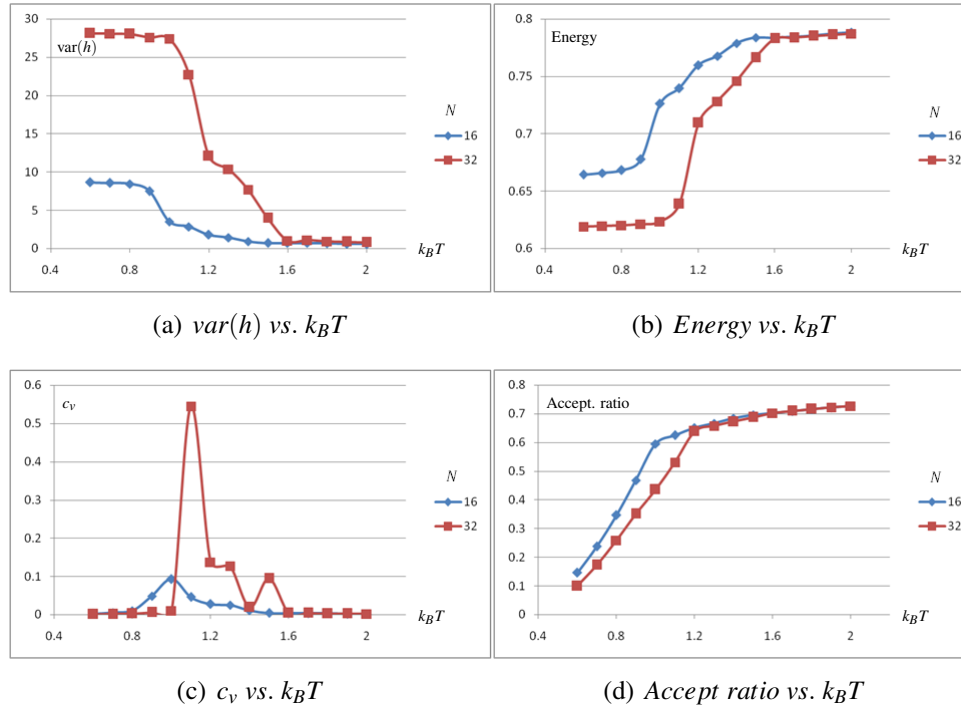


Figure 7.9: Variance of height, energy per area, heat capacity per area and the acceptance ratio for $p = 0.9$ on an initial (112) surface

Snapshots of surface are taken at $k_B T = 0.5$ in Figure 7.10 to show the faceted surface, together with Figure 6.24(a), for a initially tilted (112) surface.

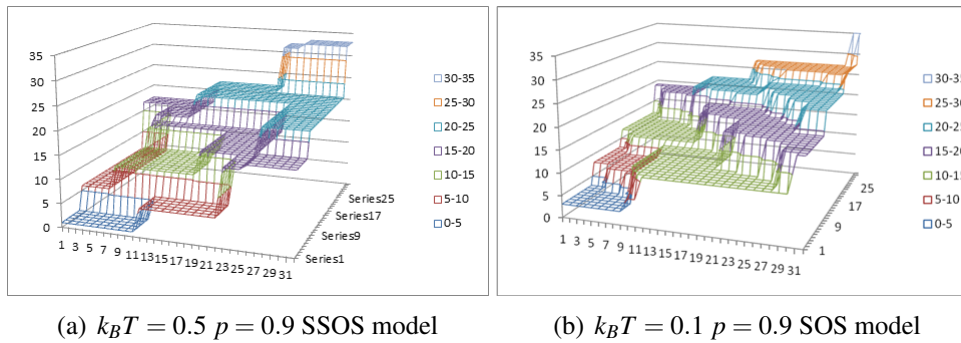


Figure 7.10: Snapshots on an initial (112) surface (a) at $k_B T = 0.5$ from SSOS model (b) at $k_B T = 0.1$ from SOS model for $p = 0.9$

7.3.3 (112), $p = 1.1$

The results are plotted in Figure 7.11. The characteristics are similar to the results from (111) surface, but the values of the energy per area is approximately half. The peak in the heat capacity is close to the one from (111) surface but with a smaller value due to fact that (112) surface is flatter surface than the (111) surface and thus the transition is not that obvious.

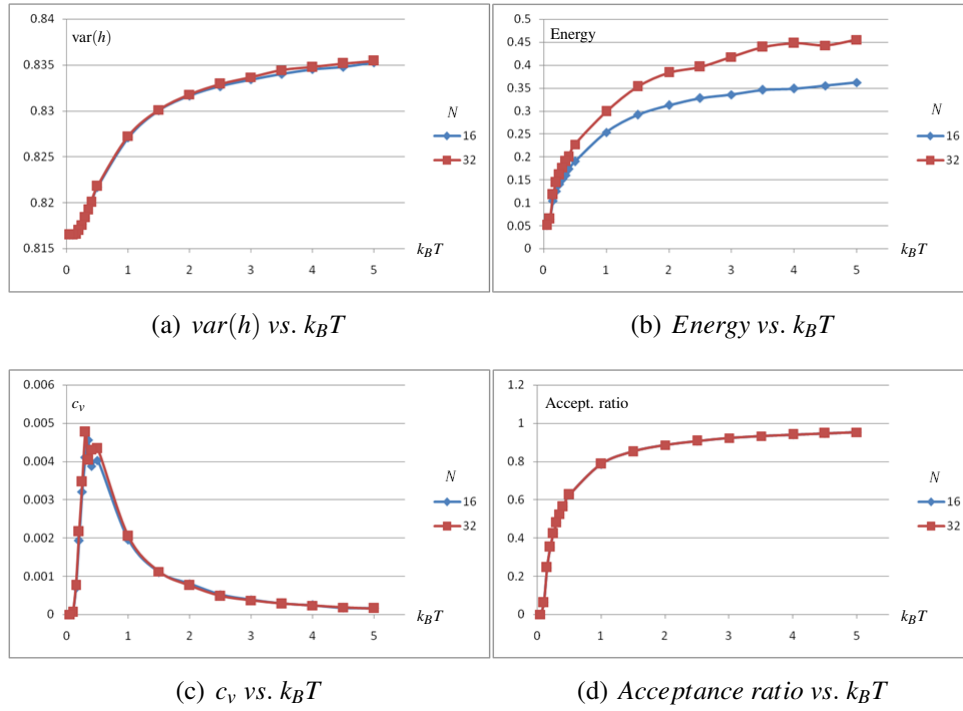


Figure 7.11: Variance of height, energy per area, heat capacity per area and the acceptance ratio for $p = 1.1$ on an initial (112) surface

7.4 Scaling Analysis for Finite Size

From the calculations above, we also see that the variance of height shows a size effect for various system sizes. The calculations and comparisons are carried out on an initial (111) surface.

For $p = 1$, the variance of the height is plotted as a function of temperature in Figure 7.12. The variance of height is kept at a relative fixed level for various system sizes and the semi-log plot shows almost the same slopes of lines for various temperatures.

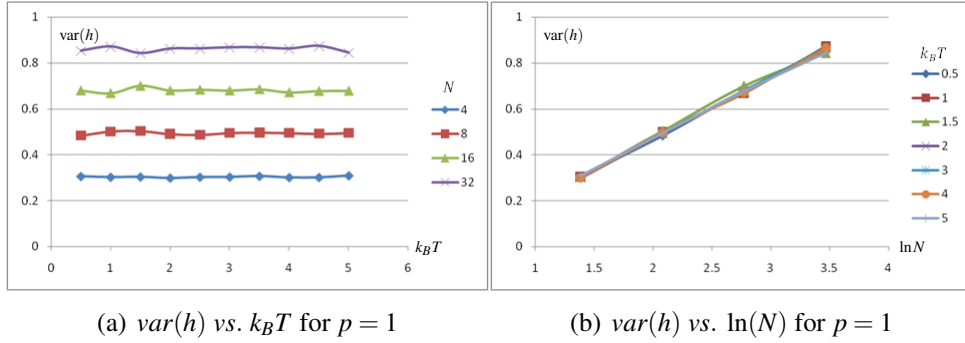


Figure 7.12: $\text{var}(h)$ vs. $k_B T$ and $\text{var}(h)$ vs. $\ln(N)$ on an initial (111) surface for $p = 1$

For $p = 0.9$, the variance of the height is plotted as a function of temperature in Figure 7.13. The variance of height falls from high values for the faceted surface and then stays at a relatively fixed level for various system sizes. The semi-log plot shows different slopes of lines for various temperatures. As the temperature gets higher, the slopes get closer to each other.

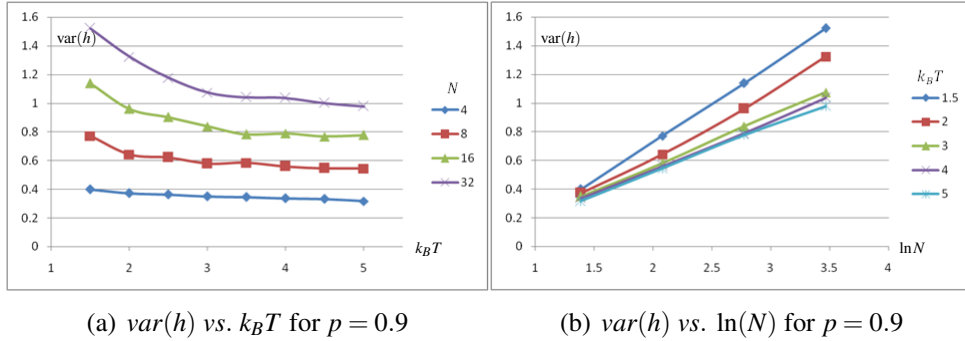
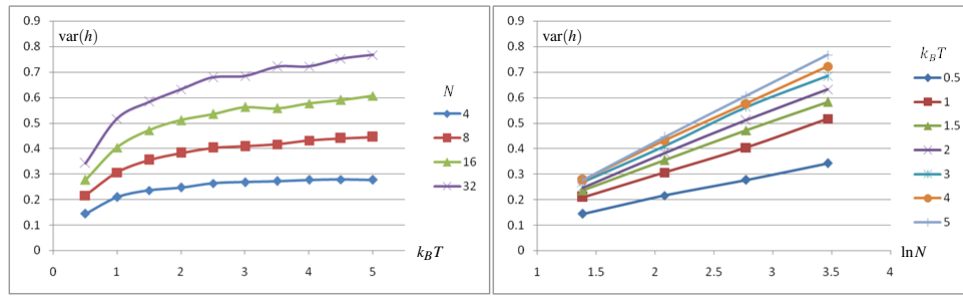


Figure 7.13: $\text{var}(h)$ vs. $k_B T$ and $\text{var}(h)$ vs. $\ln(N)$ on an initial (111) surface for $p = 0.9$

For $p = 1.1$, the variance of the height is plotted as a function of temperature in Figure 7.14. The variance of height is increasing gradually for various system sizes as the temperature gets higher. The semi-log plot shows different slopes of lines for various temperatures.

From the simulations and comparisons carried out above, we could see that the symmetry of the initial configuration is preserved in the SSOS model and verified by the snapshots of the surface topologies. What is more important is that the transition properties are also preserved for the $p = 0.9$ case.

(a) $\text{var}(h)$ vs. $k_B T$ for $p = 1.1$ (b) $\text{var}(h)$ vs. $\ln(N)$ for $p = 1.1$ Figure 7.14: $\text{var}(h)$ vs. $k_B T$ and $\text{var}(h)$ vs. $\ln(N)$ on an initial (111) surface for $p = 1.1$

Chapter 8

Summary and Conclusions

Following Gibbs, surface free energy is defined as the surface excess per unit area of the grand potential energy of a material compared to its bulk. It quantifies the disruption, relaxation and rearrangement of intermolecular bonds that occur when a surface is created. Surfaces must be intrinsically less energetically favorable than the bulk of a material for stability. Surface free energies of crystals are anisotropic and provide a driving force for morphological changes, such as the formation of facets. The Wulff Construction is an important method to determine the ultimate equilibrium shape of a crystal by minimizing its surface free energy. Equilibrium shape is of practical interest only for very small crystals because of the mass transport needed to change shape. For a large crystal, the free energy of a large planar surface can sometimes be lowered by rearranging the atoms into a hill-and-valley structure of a size large compared with atomic dimensions but still small compared to the size of the crystal. According to Herring's Theorem: "If a given macroscopic surface of a crystal does not coincide in orientation with some portion of the boundary of the equilibrium shape, there will always exist such a hill-and-valley structure that has a lower free energy than a flat surface."

The above result was based only on the surface free energy of a single large surface, which includes some entropy but does not take into account the free energy associated with surface structure, such as the entropy associated with the morphology of faceting (colonies of facets having different sizes). Variations in the configurations that occupy the crystal surface lead to positive entropy that would further lower the effect of surface free energy. Moreover, Herring's result only pointed out the orientations that the hill-and-valley structure can have but did not show the sizes of facets, which are influenced by corner and edge energies as well as the entropy associated with the surface configurations. Therefore, the effect and role of configurational entropy and corner energies in crystal surface structure was studied by using Monte Carlo simulation. Our model consists of simple squares (two dimensional crystals) or cubes (three dimensional crystals) that interact through nearest-neighbor additive forces having central symmetry (bond en-

ergies). These are known as “Kossel crystals”.

For a two-dimensional Kossel crystal, the empirical configurational entropy can be measured from a knowledge of the various heights and lengths of the facets that result from the simulation. The theoretical configurational entropy can also be calculated by using statistical mechanics. As the size of simulated systems gets larger, the empirical entropy gets closer to the theoretical entropy. Furthermore, by maximizing the surface entropy for a surface composed of only positive steps, one can determine that the heights and lengths should follow an exponential distribution and this is verified by simulation. One can also obtain from statistical mechanics the size distributions of facet heights and lengths, which agrees well with simulation. These results are only valid at low temperatures because at high temperatures steps of alternating signs will occur.

Another important factor that can influence the surface configurations is the effect of corner and edge energies on a faceted crystal surface. We study such effects for a three dimensional Kossel crystal (two dimensional surface) by means of a modified solid-on-solid model. This is done by means of a Hamiltonian which accounts for nearest-neighbor height differences raised to a power p . For $p = 1$, the model becomes the usual solid-on-solid (SOS) model with no specific energies assigned to corners and edges. For p slightly smaller than 1 (for example $p = 0.9$), the model gives positive energies to corners and edges; therefore, this model disfavors corners and edges. For p slightly greater than 1 (for example $p = 1.1$), the model gives negative energies to corners and edges; therefore, this model favors corners and edges. On an initially flat (100) surface, different p values do not have a significant effect on surface configurations, which only differ quantitatively. There is a roughening transition for all three p values, and at high temperatures the heat capacity is proportional to $1/p$. However, on an initially tilted surface, such as (111), (112) and (110), an interesting “macroscopic smoothing” transition is observed for $p = 0.9$. Unlike the traditional roughening transition, the surface is faceted at low temperatures and is smooth at high temperatures. For this “macroscopic smoothing” transition, a hysteresis effect is observed but becomes less pronounced as the simulation gets longer at each temperature.

To further investigate these surface configurations, more analysis is carried out. At high temperatures, the area of small facets follows an exponential distribution for all three p -values. Facet height follows a Gaussian distribution for all three p -values. Based on these results, a theoretical connection between facet areas and facet height distributions is made. In order to identify precisely the location of the smoothing transition in the $p = 0.9$ case, a histogram method is implemented to calculate physical quantities at other temperatures, based on simulation results at a certain temperature. In particular, we study the variation of surface height per unit area, the energy per unit area, the heat capacity per unit area, and the acceptance ratio. To investigate the relaxation of the system, the correlation time is calculated by using several different measures. A fast relaxation is observed, followed by a very slow relaxation. A discrete Fourier analysis of the surface

was implemented and we verified that there exists a long-wavelength fluctuation of the surface, which may account for the slow relaxations.

The modified SOS model discussed above is biased by reference to a specific growth direction. Therefore, it does not represent the true symmetry of a crystal. We introduce a symmetric solid-on-solid (SSOS) model that takes the symmetry of surface configurations into account. For the SSOS model, the qualitative smoothing transition is still observed for $p = 0.9$, but values of surface variance are more restricted and bounded by certain limits at high temperature for all three p -values. Snapshots of the simulated surfaces clearly demonstrate true crystal symmetry. Compare, for example, Figure 6.12(a) with Figure 7.5(a) and 7.10(a) with 6.24(a).

In the future, we hope to extend our theoretical analysis of one-dimensional surfaces, for example to determine a formulae for the facet height and length distributions for two-dimensional surfaces and compare with simulation results. Moreover, a similar modified SOS model can be applied to other lattices, for example, an hexagonal lattice, to investigate possible transitions. Finally, we might be able to treat a variety of crystals by using realistic interaction potentials, and hence provide a link to experiments.

Bibliography

- [1] A. Bravais, *Mémoire sur les systèmes formés par les points distribués régulièrement sur un plan ou dans l'espace*, J. Ecole Polytech, Vol. 19, Pages 1128, 1850.
- [2] J.W. Gibbs, *The collected works of J. Willard Gibbs*, Yale University Press, New Haven, 1957.
- [3] J.W. Gibbs, *A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces*, Transactions of the Connecticut Academy of Arts and Sciences, Vol. 2, Page 382, 1873.
- [4] G. Wulff, *Zeitschrift für Krystallographie und Mineralogie*, Vol. 34, Pages 449-530, 1901.
- [5] C. Herring, *Surface Tension as a Motivation for Sintering*, Physics of powder metallurgy, Pages 143-179, 1951.
- [6] C. Herring, *The Use of Classical Macroscopic Concepts in Surface-energy Problems*, Structure and Properties of Solid Surfaces, University of Chicago Press, Chicago, Page 5, 1953.
- [7] W.W Mullins, R.F Sekerka, *Application of linear programming theory to crystal faceting*, J. Phys. Chem. Sol., Vol. 23, Issue 6, Pages 801-803, 1962.
- [8] R.F.P. Grimbergen, P. Bennema, H. Meekes *On the prediction of crystal morphology. III. Equilibrium and growth behaviour of crystal faces containing multiple connected nets*, Acta Cryst. A, Vol. 55, Issue 1, Pages 84-94, 1999.
- [9] W.K. Burton and N. Cabrera, *Crystal Growth and Surface Structure*, Disc. Faraday Soc., Vol. 5, Pages 33-40, 1949.
- [10] T. A. Witten and L. M. Sander, *Diffusion-Limited Aggregation, a Kinetic Critical Phenomenon*, Phys. Rev. Lett., Vol. 47, No. 19, Page 1400, 1981.
- [11] D.B. Abraham, *Surface Structures and Phase Transitions Exact Results*, Phase Transitions and Critical Phenomena, Vol. 10, Pages 1-74, 1986.

- [12] S. T. Chui and J. D. Weeks, *Phase Transition in the Two-dimensional Coulomb Gas, and the Interfacial Roughening Transition*, Phys. Rev. B, Vol. 14, Pages 4978-1982, 1976.
- [13] H. J. F. Knops, *Exact Relation between the Solid-on-Solid Model and the XY Model*, Phys. Rev. Lett., Vol. 39, Pages 766769, 1977.
- [14] G. H. Gilmer and P. Bennema, *Simulation of Crystal Growth with Surface Diffusion*, J. Appl. Phys., Vol. 43, Page 1347, 1972.
- [15] W.K. Burton, N. Cabrera and F.C. Frank, *The Growth of Crystals and the Equilibrium Structure of their Surfaces*, Phil. Trans. R. Soc., A243, Pages 299-358, 1951.
- [16] R.H. Swendsen, *Monte Carlo studies of the interface roughening transition*, Phys. Rev. B. Vol. 15, Page 5421, 1977.
- [17] K. Binder and D. Stauffer, *Applications of the Monte Carlo Method in Statistical Physics*, Springer-Verlag, Berlin, 1984.
- [18] G. Comte de Buffon, *Essai d'arithmétique morale*, Supplément à l'Histoire Naturelle, Vol. 4, 1777.
- [19] J. von Neumann and S. Ulam, *Bulletin of the American Mathematical Society*, Abstract 51-9-165, 1945.
- [20] R. H. Landau and M. J. Páez, *Computational Physics*, Wiley, 1997.
- [21] N. Giordano, *Computational Physics*, Prentice-Hall Press, 1997.
- [22] J. Yeomans, *Statistical Mechanics*, Oxford Univ. Press, 1992.
- [23] A. M. Ferrenberg and D. P. Landau, *Monte Carlo simulations: Hidden errors from "good" random number generators*, Phys. Rev. Lett., Vol. 69, Pages 33823384, 1992.
- [24] P. Lewis, A. Goodman, and J. Miller, *A Pseudorandom Number Generator for the System 360*, IBM Systems Journal, Vol. 8, Pages 135-146, 1969.
- [25] S. Park and K. Miller, *Random Number Generators: Good Ones are Hard to Find*, Commun. ACM, Vol. 31, Pages 11921201, 1988.
- [26] L. Schrage, *A More Portable Fortran Random Number Generator*, ACM Transactions on Mathematical Software, Vol. 5, Pages 132-138, 1979.
- [27] M. Iosifescu, *Finite Markov Processes and Their Applications*, Wiley, Chichester, 1980.

- [28] K. L. Chung, *Markov Chains with Stationary Transition Probabilities*, Springer, New York, 1967.
- [29] E. Nummelin, *General Irreducible Markov Chains and Non-Negative Operators*, Cambridge Univ. Press, Cambridge, 1984.
- [30] J. G. Kemeny and J. L. Snell, *Finite Markov Chains*, Springer, New York, 1976.
- [31] K. L. Chung, *Markov Chains with Stationary Transition Probabilities*, 2nd edition, Springer, New York, 1967.
- [32] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *Equation of State Calculations by Fast Computing Machines*, J. Chem. Phys., Vol. 21, Pages 1087-1092, 1953.
- [33] W. K. Hastings, *Monte Carlo Sampling Methods Using Markov Chains and Their Applications*, Biometrika, Vol. 57, Pages 97-109, 1970.
- [34] A. M. Ferrenberg and R. H. Swendsen, *Optimized Monte Carlo Data Analysis*, Phys. Rev. Lett., Vol. 63, Pages 1195-1198, 1989.
- [35] D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford Univ. Press, 1987.
- [36] H. Müller-Krumbhaar and K. Binder, *Dynamic properties of the Monte Carlo method in statistical mechanics*, Journal of Statistical Physics, Vol. 8, Pages 1-24, 1973.
- [37] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd edition, Academic Press, 2002.
- [38] T. J. Deeming, *Fourier Analysis with Unequally-spaced Data*, Astrophysics and Space Science, Vol. 36, Page 137, 1975.
- [39] M. B. Priestley, *Spectral Analysis and Time Series*, Vol. 2, Academic, London, 1981.
- [40] A. M. Ferrenberg and R. H. Swendsen, *New Monte Carlo Technique for Studying Phase Transitions*, Phys. Rev. Lett., Vol. 61, Pages 2635-2638, 1988.
- [41] A. M. Ferrenberg and R. H. Swendsen, *Optimized Monte Carlo Data Analysis*, Phys. Rev. Lett., Vol. 63, Pages 1195-1198, 1989.
- [42] A. M. Ferrenberg and R. H. Swendsen, *Phase Transitions and Critical Phenomena*, Phys. Rev. Lett., Vol. 63, Pages 1195-1198, 1989.

- [43] W. Janke, *Computer Simulations in Condensed Matter Physics VII*, Springer-Verlag, Berlin, 1994.
- [44] A. D. Sokal, *Computer Simulation Studies in Condensed Matter Physics: Recent Developments*, Springer-Verlag, Berlin, 1988.
- [45] K. Krickeberg, *Probability Theory*, Addison-Wesley, 1965.
- [46] U. Wolff, *Collective Monte Carlo Updating for Spin Systems*, Phys. Rev. Lett., Vol. 62, Pages 361-364, 1989.
- [47] U. Wolff, *Nonuniversal Critical Dynamics in Monte Carlo Simulations*, Phys. Rev. Lett., Vol. 58, Pages 86-88, 1987.
- [48] Carlos. E. Fiore and M. G. E. da Luz, *Exploiting a semi-analytic approach to study first order phase transitions*, J. Chem. Phys., Vol. 138, 014105, 2013.
- [49] K. Kawasaki, *Phase Transitions and Critical Phenomena*, Academic, New York, 1972.
- [50] P. G. DeGennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca NY, 1979.
- [51] R. V. N. Melnik, *Coupled Thermomechanical Dynamics of Phase Transitions in Shape Memory Alloys and Related Hysteresis Phenomena*, Mechanics Research Communications, Vol. 28, Pages 637-651, 2001.