University of Texas at Austin

Honors Thesis

Equilibrium and Non-Equilibrium Molecular Absorption

A study of the Ising model and the infinite parking limit problem

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1 Introduction

Randomness is present in so many everyday systems that we often forget its importance in both mathematical and chemical situations. Chemical reactions depend on random interactions and collisions, the movement of particles is often randomly determined, and randomness plays a role in the way in which diffusing particles interact with a solid surface. Looking specifically into this last situation, we know that there are many ways in which diffusing particles can interact with solids. Particles can diffuse through either water or air, and at low concentrations, this process is well-modeled by random processes. When looking at this situation, there are two distinct types of molecular absorption to consider: equilibrium or nonequilibrium absorption. That is, when the diffusing particle comes into contact with the surface, it can either stick exactly where it lands or move around a little to come to a more stable equilibrium arrangement. These processes might look very similar on the macroscopic level, but on the microscopic level, they are studied using very different mathematical techniques. Sometimes the process is modeled by a simpler problem in order to use more rigorous mathematics to address things which are very complicated. Other times, it is more beneficial to solve a problem computationally with programming. These different approaches each have benefits and are both used in comprehensive studies of natural processes.

To get a feel for these two different ways of studying this problem, we will examine two different models: an equilibrium model and a non-equilibrium model. One of the most common models used to study equilibrium systems is the Ising model. We start by thinking of the Ising model as a finite system with boundary conditions, and then we consider the limit as the size of the grid goes to infinity. The value of the spin at each lattice site depends on two different things-the values of the neighboring lattice sites and any applied external magnetic fields. The contributions of each of these pieces depends on the system and is controlled by constants. It was originally proposed by Ising to model the spontaneous magnetization in ferromagnetic substances. The restriction on the spin states and the ordered pattern of the grid points allow this model to be analyzed mathematically, while still giving interesting information about the behavior of many different chemical systems. As the number of points in the grid goes to infinity, we use this model to look at phase transitions, switches between one defined state and another.

In his PhD dissertation, Ising studied the model in the one dimensional case, which is a line of points, each with their own spin state[NM]. He concluded that there was no phase transition in this sytem, even in the infinite case. One explanation for the lack of phase transition is that as you move down the line, when you change states from up to down or vice versa, there is no memory of any pattern from before. Therefore, the spin states are not likely to remain in any particular ordering, since it only takes one place to lose a pattern completely. Ising also predicted that his model would not show phase transitions in any other dimension. He did not prove this rigorously, and as was seen decades later, there is a phase transition in all dimensions 2 and higher. The proof of the existence of a phase transition in two dimensions was shown by Peierl[P], and the exact point at which this transition occurs was later proven by Kramers and Wanniers[KW]. The complete proof was finally published in 1944 by Onsager[Ons].

To study non-equilibrium absorption, irreversible random sequential absorption (RSA) models are frequently used to approach problems. In these problems, particles adhere to a surface one at a time, and once they land, they are permanently stuck in that location. The models vary in how they treat the other variables in this problem, and these approaches range from simplified to sophisticated. For example, the particle shape and orientation can be varied in problems which consider more than one dimensional particles, the absorption surface can be considered to have discrete or continuous points for the particle to land on, and molecular interactions can be studied and varied as well. Since this is a category of models rather than a specific, well-defined model like the Ising model, study of this problem requires a much more careful description of the assumptions and simplifications which are being made. The value of the model is often determined by these simplifications, and the exact system being studied should be well-understood before employing a model to describe its behavior.

While models provide a large amount of insight into a problem, it is often beneficial and sometimes even necessary to use computational approaches to address a problem. If the situation is too complicated for a model to accurately represent, more extensive calculations can be made in computational approaches. Because computational methods are usually designed for a particular problem or situation, they do not require the same generality as models. When no model has been established and verified for a system, computational approaches which verify experimental findings provide a starting point for understanding what is happening in the system. In the two-dimensional RSA problem, an analytical solution has not been found, and code has been written to predict the answer to the problem. This code allows mathematicans to stop focusing on theorems which are most likely incorrect. For example, there was a conjecture that the shape of the object did not effect the jamming limit, and another which said that the jamming limit in the case of a square was the one dimensional result squared[Pen]. Both of these have been discarded because of computational estimates. In these and other ways, computational methods are a necessary part of exploring how mathematics relates to physical systems.

2 Equilibrium Problems

A study of equilibrium systems begins with entropy. Entropy is the measure of the amount of disorder in a system. Mathematically, this is represented as $S = k \ln \Omega$, where S is the entropy, k is Boltzmann's constant, and Ω is the number of different microstates a system can take. A microstate is a specific arrangement of particles in the system where each particle's state is specified. In a system with a fixed energy and volume, each configuration occurs with equal likelihood. A macrostate is a collection of microstates which appear the same from a macroscopic level, for example the collection of microstates which all have the same entropy associated with them. Consider the distribution for the position of gas molecules around a room. The distribution of particles is random, and each potential configuration occurs with equal likelihood. However, there are many more configurations in which the particles are distributed randomly about the room than there are configurations in which

all the gas molecules occupy a single corner. Therefore, the macrostate in which all the gas molecules are scattered around the room is more likely to occur and has a higher entropy.

2.1 The Partition Function

One of the most important equations in statistical mechanics is the partition function,

$$Z = \sum_{\sigma} e^{-\beta H(\sigma)} \tag{1}$$

where $H(\sigma)$ is the Hamilitonian (the energy associated with the configuration σ) and $\beta = \frac{1}{kT}$. It turns out that many different thermodynamical variables can be derived from this. For example, the probability of finding a system in a particular state σ is

$$P(\sigma) = \frac{e^{-\beta H(\sigma)}}{Z} \tag{2}$$

Some other thermodynamic variables which come from the partition function are

$$\text{Free energy } = -kT \ln Z = E - TS$$

$$\text{Internal Energy } = kT^2 \frac{\partial \ln Z}{\partial T}\bigg|_V$$

$$S = kT \frac{\partial \ln Z}{\partial T}\bigg|_V + k \ln Z$$

From this short list, we begin to get the idea that it is not the partition function itself that we care about, but rather the natural log of the partition function.

2.2 Phase Transitions and how to find them

A phase transition is a point where the partition function or one of the properties derived from it is no longer analytic. In order to prove that a system has a phase transition, we look at two different regions of a graph and an analytic function on each of the domains. Then, we check to see if the function on one of the regions is the analytic continuation of the other. If this is not true, then we know that there is at least one point between the two regions where the function is non-analytic. It could be the case that there are multiple phase transitions in the system, so this method only proves the presence of a phase transition, not the location or total number of phases. Often one region has a constant value function, and in a different region, it is a varying function. The point at which the constant function and the variable function meet is a non-analytic point. Common examples of phase transitions are the state changes associated with different substances, the switch between an ordered and disordered system, or as discussed in this model, spontaneous magnetization, the switch to an ordered collection of spin states. It is important to note here that a phase transition does not exist in finite grid systems because in a finite system, the partition function is a

finite sum of analytic functions. The sum of a finite number of analytic functions is itself analytic. Therefore, while the Ising model is initially considered in the finite case, phase transitions appear as the size of the grid goes to infinity[Cip].

2.3 Terminology used with the Ising Model

Before discussing how the Ising model can be used to study these phase transitions, we must introduce some of the terminology which will be used in this paper. The first is the idea of a lattice. A lattice is a regular arrangement of points in n dimensions with a predictable pattern. The type of lattice can vary, but in this paper, a square lattice in 2D is used because of its simplicity. The conclusions discussed can be applied to models with different shapes, though the proof of this often involves making topological equivalences beyond the scope of the topic addressed here. Another important concept is the idea of a dual lattice. A dual lattice is a lattice associated with the original lattice structure, formed by replacing each face with a vertex and every vertex with a face. In two dimensions, the dual lattice of a square lattice is also square, but for a triangular lattice, the dual lattice is hexagonal and vice versa (see Figure 1). The property that a square lattice and its dual lattice have the same structure simplifies some of the arguments made in two dimensions.

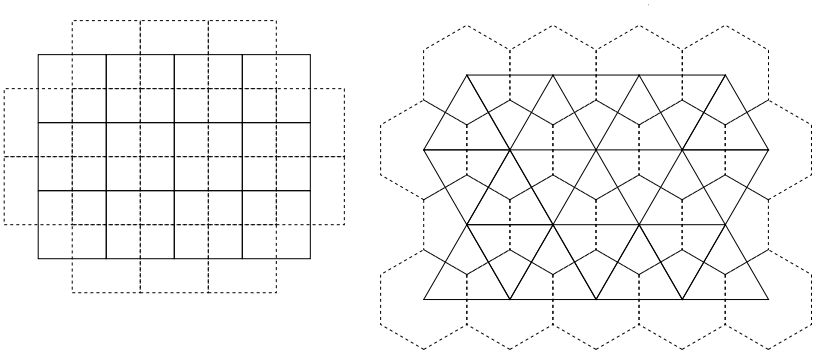

Figure 1: Dual Lattice for a Square Lattice and a Triangular Lattice

Another term used is the idea of nearest neighbors, denoted $< i, j >$. For any point i, the set of nearest neighbors is the set of grid points which are directly connected to point i. When looking at interactions between surrounding spin states, the effect of a state will be limited to its nearest neighbors. An example of a finite grid is shown in Figure 2 below (where solid squares represent the +1 state and empty squares represent the -1 state).

Now that we have the terminology, we look at arguments that a phase transition exists in the two dimensional square lattice Ising model[Cip].

2.4 Finding the Phase Transition

We know that differing spins in nearest neighbor spots have a higher conformational energy than the same spin neighbors. If the nearest neighbor interactions are strong enough, it is

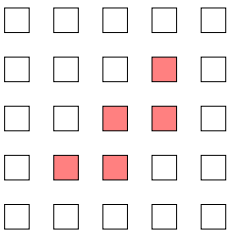

Figure 2: Possible Configuration of 5 x 5 grid

possible for the effect of one point to propagate a long distance, even an infinite distance. When we look for phase transitions in the Ising model, we begin by looking for evidence that the spin at spot x_0 is dependent upon the spin of a site x_1 far away.

The way to prove the existence of a phase transition is to find the temperature at which the partition function is non-analytic. In order to find this point for the Ising model, we need to first know the Hamilitonian for the system. The Hamiltonian has two contributions: the interactions between nearest neighbors and a particle's interaction with an external field. The amount of each of these two contributions is controlled with two parameters: J, the strength of the interaction between neighboring sites, and U, the strength of the external magnetic field. In this paper, we will consider an external magnetic field of 0, though U is left in as a parameter in the basic descriptions of the Hamiltonian. Therefore, $H(\sigma) = \sum_{<i,j>} J\sigma_i\sigma_j + \sum_i U\sigma_i$. Let us consider a grid of side length $\sqrt{N}$, with a total number of N vertices. Plugging into our formula for Z, we obtain a partition function:

$$Z = \sum_{\pm 1} e^{\sum_{<i,j>} -\beta J\sigma_i\sigma_j + \sum_i -\beta U\sigma_i} = \sum_{\pm 1} \left(\prod_{<i,j>} e^{-\beta J\sigma_i\sigma_j} \right) \left(\prod_i e^{-\beta U\sigma_i} \right) \tag{3}$$

Using the expansion $e^{\pm x} = \cosh x(1 \pm \tanh x)$ and taking U = 0, we can simplify this to

$$Z = \sum_{\pm 1} \prod_{<i,j>} \cosh(\beta J\sigma_i\sigma_j)(1 + \tanh(\beta J\sigma_i\sigma_j)) \tag{4}$$

Since cosh is an even function and tanh is an odd function, this is equivalent to

$$Z = \sum_{\pm 1} \prod_{<i,j>} \cosh(\beta J)(1 \pm \tanh(\beta J)) \tag{5}$$

The first piece does not depend on i, j, so it can be taken out to give

$$Z = \cosh(\beta J)^{2N} \sum_{\pm 1} \prod_{<i,j>} (1 \pm \tanh(\beta J)) \tag{6}$$

where the power of the cosh term is determined by the number of distinct nearest neighbors in the grid. This is the same as counting the sides of the squares which make up the grid, so this equals 2N for a grid of size N. The function which will become non-analytic is actually

the log of this value, so we can see this by looking at the free energy, F.

$$F(T) = \lim_{n\to\infty} \frac{1}{N} \log Z = \lim_{n\to\infty} 2\log\cosh(\beta J) + \frac{1}{N}\log\left(\sum_{\pm 1}\prod_{<i,j>}(1+\sigma_i\sigma_j T)\right) \tag{7}$$

where $T = \tanh(\beta J)$. We can see that the first term on the right hand side will always be analytic, but the second piece will not always be. Therefore, we will focus specifically on the second piece. Let $Z' = \sum_{\pm 1}\prod_{<i,j>}(1+\sigma_i\sigma_j T)$. Call this the modified partition function. This will be used later to prove the existence and location of the phase transition.

Up to this point, the problem has been defined by the different possible configurations and their relative likelihood of occurring. However, it is possible to consider the same system from a different perspective, which is often easier to deal with mathematically. Considering a particular configuration σ, we can relate σ to a path S_σ by treating the dual lattice as a graph, where an edge is present separating each pair of nearest neigbors with opposite spins. This idea is more easily described by a picture, as shown in Figure 3.

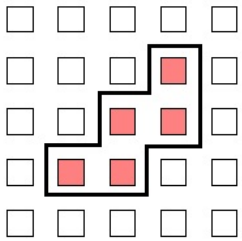

Figure 3: Figure 2 with path separating nearest neighbors

Note that while this particular path is connected, a "path" can be a collection of disjoint components, which may not even be made of entirely closed loops (as the system goes to infinity).

2.5 Peierl's Proof of Existance of Phase Transition in 2 Dimensions

Peierl proved, in 1936, that a phase transition does in fact exist for the two dimensional Ising model. The proof of the actual value would not come for another 5 years. Peierl's argument starts by considering a 2 dimensional lattice with boundary conditions, chosen to be a boundary of spin up (+1) lattice sites. From there, he asks the question "What is the likelihood that a point in the interior of the lattice is spin down ($\sigma = -1$)?". The overall goal is to show that at high temperatures, the probability of this happening is 1/2, and at sufficiently low temperatures, the probability is something less than 1/2. The high temperature value is simply the probability of having spin down when a spot does not feel the influence of its neighbors as opposed to the low temperature, where neighbor effects produce visible results. Pierl's argument focuses on bounding the probability at low temperatures to something less than 1/2.

2.5.1 High Temperature Argument

To show the high temperature probability, we think about which paths contribute to the partition function. Long paths indicate that the effect of spins on the boundary have a long range effect on things on the inside. However, as the size of the grid increases, these paths begin to contribute less and less to the partition function. Therefore, at high temperatures, the contributions come almost entirely from short paths, which indicates that there are only small islands of same spin sites before the pattern is lost. This means that the configuration is not dominated by interactions between neighbors, and so as the lattice size increases, the sites become less sensitive to the spin of their neighbors. As expected, this means that as $N \to \infty$, the sites become equally likely to be ± 1. So the probability that a site x_0 is $+1$ given a $+1$ spin far away is $1/2$ because the far away spins have no effect on the spin at x_0. Note that this is not a rigorous proof of the high temperature value. This discussion is included here to give an idea of the high temperature behavior. A more rigorous approach will be taken after the low temperature argument is discussed.

2.5.2 Low Temperature Argument

As we recall, the modified partition function is

$$Z = \sum_{\sigma \in \Omega} e^{-\beta H(\sigma)} \tag{8}$$

where Ω is the set of all configurations of spins.

In order to calculate the probability of $\sigma = -1$ at point x_0 in the lattice interior at low temperature, we will find an expression for $P(\sigma_{x_0} = -1)$. The probability of any configuration, σ, is written as

$$P(\sigma) = \frac{e^{-\beta H(\sigma)}}{Z} \tag{9}$$

where Z is the partition function.

We showed above that each different configuration results in a path, separating unlike nearest neighbors, drawn on the dual lattice. In order to count the number of different configurations which have $\sigma_{x_0} = -1$, we can instead count pathways which enclose x_0. Consider all sets of pathways which enclose x_0. Call this set Ω_S. Now, it is possible that $S \in \Omega_S$ and $x_0 = 1$. This could occur if there is a path, S', completely inside of S, which also encloses x_0. Therefore, we can only bound P(x_0 = -1) by $P(\Omega_S)$, but this is okay because we are only looking for an upper bound for our probability. We can say that

$$P(\sigma_{x_0} = -1) < P(\Omega_S) = \frac{1}{Z} \sum_{\sigma \in \Omega_S} e^{-\beta H(\sigma)} \tag{10}$$

Letting the length of the pathway S be defined as $\mathrm{n_S}$, we can see that for $\mathrm{n_S}$ nearest neighbor

pairs, $\sigma_i\sigma_j = -1$, and we can split this up as

$$P(\sigma_{x_0} = -1) < P(\Omega_S) = \frac{1}{Z}\sum_{\sigma\in\Omega_S} e^{-\beta E n_S} e^{-\beta E\sum_{<i,j>\notin S}\sigma_i\sigma_j} \quad (11)$$

$$= e^{-\beta E n_S}\frac{1}{Z}\sum_{\sigma\in\Omega_S} e^{-\beta E\sum_{<i,j>\notin S}\sigma_i\sigma_j} \quad (12)$$

Here, we introduce a different configuration, σ', related to σ. This configuration is formed by reversing the spin of all sites contained within S. Therefore, the sum over the nearest neighbors in this configuration is the same as in σ, except that the boundary of S no longer $-n_S$. It now contributes $+\mathrm{n_S}$. Therefore,

$$\sum_{<i,j>\notin S}\sigma_i\sigma_j = \sum_{<i,j>}\sigma'_i\sigma'_j - n_S \quad (13)$$

And we can see that

$$\sum_{<i,j>\notin S}\sigma_i\sigma_j < \sum_{<i,j>}\sigma'_i\sigma'_j \quad (14)$$

This puts an upper bound on the function, because when we plug this back in, we find that

$$P(\sigma_{x_0} = -1) < e^{-\beta E n_S}\frac{1}{Z}\sum_{\sigma\in\Omega_S} e^{-\beta E\sum_{<i,j>}\sigma'_i\sigma'_j} \quad (15)$$

Notice that there is a one-to-one correspondence between σ and σ'. Therefore, we can replace $\sigma \in \Omega_S$ with $\sigma' \in \Omega'_S$, where Ω'_S is the set of configurations derived by switching the signs within S.

$$P(\sigma_{x_0} = -1) < e^{-\beta E n_S}\frac{1}{Z}\sum_{\sigma'\in\Omega'_S} e^{-\beta E\sum_{<i,j>}\sigma'_i\sigma'_j} \quad (16)$$

We know that $e^{-\beta H(\sigma)} > 0$ for all σ, and we can again bound this function by

$$P(\sigma_{x_0} = -1) < e^{-\beta E n_S}\frac{1}{Z}\sum_{\sigma'\in\Omega'} e^{-\beta E\sum_{<i,j>}\sigma'_i\sigma'_j} \quad (17)$$

But since this is now the sum over all configurations, $\sum_{\sigma'\in\Omega'} e^{-\beta E\sum_{<i,j>}\sigma'_i\sigma'_j} = Z$. Plugging this in, we get

$$P(\sigma_{x_0} = -1) < e^{-\beta E n_S}\frac{1}{Z}Z = e^{-\beta E n_S} \quad (18)$$

This means that we can bound the probability of x_0 being enclosed in a path of length $\mathrm{n_S}$. To completely bound the probability that $\sigma_{x_0} = -1$, we need to look at the different path lengths which could enclose x_0. Obviously, the smallest path is of length 4, and we can sum the contributions from each path length according to

$$Prob(\sigma_{x_0} = -1) < \sum_{S\in\mathcal{S}} Prob(\Omega_S) < \sum_{S\in\mathcal{S}} e^{-\beta E n_S} \quad (19)$$

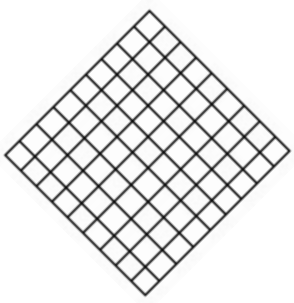

Figure 4: Grid which must contain any paths of length n_S enclosing x_0

where $\mathcal{S}$ is the collection of all paths S of varying lengths. If we let $N(n_S)$ be the number of paths of length n_S, this can be rewritten as

$$Prob(\sigma_{x_0} = -1) < \sum_{n_S=4}^{\infty} N(n_S) e^{-\beta E n_S} \tag{20}$$

So consider the number of paths of length n_S. Intuition tells us that this should be bounded because each path must be within a square of side length $n_S/\sqrt{2}$ around x_0, as shown in Figure 4.

This is a bounding box because if any path gets more than $n_S/2$ away from x_0, it will not be able to get back to it in the last $n_S/2$ steps and therefore will not enclose it. The number of paths surrounding x_0 is obviously bounded by the number of random walks within this square. The number of random walks of length n_S is given by the $(n_S)^2/2$ possible starting points in the grid multiplied by the number of different paths which can begin at that point, 4^{n_S}. This is because at each point in the random walk, you can choose one of 4 directions to go in (allowing backtracking). This product is then divided by n_S because there are n_S possible starting points for each walk. Therefore,

$$N(n_S) < \frac{\frac{n^2}{2} 4^{n_S}}{n_S} = \frac{1}{2} n_S 4^{n_S} \tag{21}$$

Substituting this in, we obtain the final bound for our probability:

$$P(\sigma_{x_0} = -1) < \frac{1}{2} \sum_{n_S=4}^{\infty} n(4e^{-\beta E})^{n_S} < \frac{1}{2} \sum_{n_S=1}^{\infty} n(4e^{-\beta E})^{n_S} \tag{22}$$

Using the power representation of functions, we know that $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$ for $|x| < 1$, and taking the derivative, $\frac{x}{(1-x)^2} = \sum_{n=1}^{\infty} n x^n$. When we let $x = 4e^{-\beta E}$, we get

$$P(\sigma_{x_0} = -1) < \frac{1}{2} \left[\frac{4e^{-\beta E}}{(1 - 4e^{-\beta E})^2} \right] \tag{23}$$

Clearly, we can force the second piece of this equation to be less than 1 if we take β to be sufficiently large. Therefore, the probability for sufficiently low temperatures is less than

1/2. Since the high temperature gave a constant function of 1/2, we know there must be a point where the function is non-analytic. Therefore, at least one phase transition must exist in this system.

2.6 Locating the two-dimensional critical point

The point at which the phase transition occurs is called the critical point. In order to find it, we use a fact that is beyond the scope of this thesis: that phase transitions come in pairs[Cip]. This relies on the idea of a duality between the high and low temperatures. The high temperature model of a lattice can be related to the low temperature model on the dual lattice. Because the dual of a square lattice is a square, the critical temperature is the same in both systems, which helps us solve for the critical temperature using a simple argument. This proof was first published by Kramers and Wanniers[KW].

The argument begins by considering the expansion of the partition function. Recall that we have already determined that only one piece of the partition function can be non-analytic, and we called this Z' with

$$Z' = \sum_{\pm 1} \prod_{<i,j>} (1 + \sigma_i \sigma_j T) \tag{24}$$

with $T = \tanh(\beta J)$. When this function is expanded, it has the following form: $\sum_{\pm 1}(1 + T\sum_{<i,j>} \sigma_i\sigma_j + T^2 \sum_{<i,j>} \sigma_i\sigma_j \sum_{<k,l>} \sigma_k\sigma_l + \dots)$. Let c_n be the coefficient of T^n. Thus c_n must come from n different $\sigma_i\sigma_j$ pairs multiplied together. From this, we find a new way to think about this expansion, using the lattice as a graph. Each term corresponds to a subgraph of this lattice, such that if $\sigma_i\sigma_j$ is a term in the coefficient, then it is an edge in the subgraph. We know by the algebra of expanding polynomials that each pair will appear only once, so there are no repeated edges. Therefore, we can once again consider graphs on the grid instead of particular configurations. For example, Figure 5 shows a configuration associate with the term $(\sigma_1\sigma_2)(\sigma_1\sigma_5)(\sigma_3\sigma_4)(\sigma_4\sigma_8)(\sigma_2\sigma_6)(\sigma_5\sigma_6)(\sigma_6\sigma_7)(\sigma_6\sigma_{10})(\sigma_{10}\sigma_{11})(\sigma_7\sigma_{11})$.

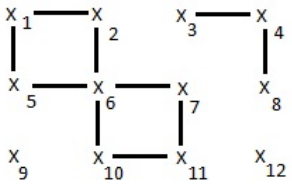

Figure 5: Subgraph of grid

One other key point about this new way of thinking about the expansion is that only vertices which have an even number of edges contribute to the modified partition function. This is because for each spot, x_i, we are summing over the configuration where $x_i = -1$ and when $x_i = +1$. Therefore, if sigma is raised to an odd power $\sum_{\sigma_i=\pm 1} \sigma_i^{2k+1} = \pm 1 \mp 1 = 0$, while $\sum_{\sigma_i=\pm 1} \sigma_i^{2k} = 1+1 = 2$. This means that a subgraph only contributes to the coefficient of T^n if every vertex in the subgraph has an even number of edges. Therefore, we are only

considering closed loops in the finite system (paths which are not loops must have a vertex with an odd number of edges unless they travel out to infinity). From this point on, when the term "path" is used, it will refer only to the path types which contribute to the coefficient; that is, paths where every vertex has an even degree. We know that a path of length m contributes 2^{N} to the coefficient of T^{m}. Therefore, $c_m = 2^N n_m$ where n_m is the number of different subgraphs with length n. Thus,

$$Z' = \sum_{m=0}^{\infty} 2^N c_m T^m \tag{25}$$

We now have the ability to find the critical point, assuming that one exists. First, consider a configuration σ. We now want to relate sigma to one of the paths along the lattice. We do this in a different way than in the low temperature argument, because we are trying to relate configurations to graphs on the lattice, rather than on the dual lattice, as in the previous argument. Therefore, we consider a configuration of shaded vs unshaded squares. A square is shaded if the bottom right corner has a spin state of +1 and unshaded if the bottom right corner is in the -1 state. This is a good method of relating a configuration of squares to a spin state configuration because it preserves nearest neighbors. That is, the squares which border a chosen square are the squares associated with the nearest neighbors of the vertex at the bottom right hand side of the center square. Therefore, in the configuration of squares, nearest neighbors are designed by squares which share an edge. To distinguish a configuration of squares from a spin state configuration, the Greek letter τ will be used to designate a configuration of squares, with the state of each square being represented by τ_i. Now, recalling our modified partition function expansion, we look for a different way to write $T^{m(\tau)}$. We can say that $m(\tau) = \sum_{<i,j>} \delta(i,j)$, where $\delta(i,j) = 1$ if $\tau_i \tau_j = -1$ and 0 otherwise. Defining δ this way is basically allowing it to be a function that counts the length of the path associated with the configuration τ when the path is drawn to split nearest neighbors with different states. This gives us a graph on the grid associated with τ.

So now we have $T^m(\tau) = \prod_{<i,j>} T^{\delta(i,j)}$. This can be rewritten to show that

$$\begin{aligned} T^{\delta(i,j)} &= \frac{1}{4}[(\tau_i + \tau_j)^2 + (\tau_i - \tau_j)^2 T] \\ &= \frac{1}{4}[\tau_i^2 + 2\tau_i\tau_j + \tau_j^2 + \tau_i^2 T - 2\tau_i\tau_j T + \tau_j^2 T] \\ &= \frac{1}{2}[(1+T) + \tau_i\tau_j(1-T)] \\ &= \frac{(1+T)}{2}[1 + \tau_i\tau_j\frac{1-T}{1+T}] \end{aligned}$$

From this, we know that $T^{m(\tau)} = \prod_{<i,j>} \frac{(1+T)}{2}[1 + \tau_i\tau_j\frac{1-T}{1+T}]$. We know that there are 2N nearest neighbor pairs, so this can be simplified to $T^{m(\tau)} = (\frac{(1+T)}{2})^{2N} \prod_{<i,j>}[1 + \tau_i\tau_j\frac{1-T}{1+T}]$. Since $Z' = \sum_{m=0}^{\infty} c_m T^m$ and path of length m corresponds to two different configurations

(as before, we have one configuration and then the flipped configuration), we get that

$$Z' = \sum_{m=0}^{\infty} c_m T^m = \frac{1}{2} \sum_{\pm 1} T^{m(\tau)} \tag{26}$$

summing over all configurations. Plugging in our expansion for $T^{m(\tau)}$, we get that

$$Z' = \frac{1}{2}(\frac{(1+T)}{2})^{2N} \sum_{\pm 1} \prod_{<i,j>} [1 + \tau_i \tau_j \frac{1-T}{1+T}] \tag{27}$$

Here, we see that the second piece of this equation is exactly the modified partition function, with $\frac{1-T}{1+T}$ in place of T. So this can be written as

$$Z'(T) = \frac{1}{2}(\frac{(1+T)}{2})^{2N} Z'(\frac{1-T}{1+T}) \tag{28}$$

At this point, we recall the high temperature argument we sketched previously. By looking at the equation above, we notice that when T is high, $\frac{1-T}{1+T}$ is low, and vice versa. Because $T = \tanh(\beta J)$, this means that there is a pairing between high temperatures and low temperatures. With a few modifications, the low temperature argument above can be used to bound the high temperature from below. As we bounded the low temperature by 1/2 above, we can bound the temperature to greater than or equal to 1/2, so in accordance with the argument, we know that the high temperature probability must be 1/2.

Because the free energy was the function in which non-analyticity could occur, consider what this relationship means for F(T). The non-analytic part of F(T) was

$$F'(T) = \lim_{N \to \infty} \frac{1}{N} \log(Z') = \log(\frac{(1+T)}{2})^2 + F'(\frac{1-T}{1+T}) \tag{29}$$

Since we are dealing with the square lattice, which is self-dual, we know that if F' is non-analytic at T, it must also be non-analytic at $\frac{1-T}{1+T}$, and that these two points must be equal. Therefore, solving

$$T_C = \frac{1 - T_C}{1 + T_C} \tag{30}$$

will find the T corresponding to the phase transition. The solution to this equation is $T_C = \sqrt{2} - 1$.

2.7 Conclusions

This proves the existence and location of a phase transition in the two dimensional problem with a square lattice. Using higher level mathematics, this solution has been extended to show that there is in fact just one phase transition in this system, and the argument was generalized to include other types of grids as well. However, very little has been rigorously proven for dimensions 3 or higher, as complexity increases significantly in these dimensions.

The arguments outlined above use many simplifications, but it is a powerful model which can be used as a starting point to describe many different systems. When applying the Ising model to absorption of molecules, it is assumed that the absorbing surface can only accept molecules at lattice points, and in this application of the model, the ± 1 states no longer represent spin states. Instead, the site is given a +1 if the site is occupied and a -1 if it is free. This provides a starting point to consider equilibrium absorption systems, though other modifications are typically needed as well.

3 Irreversible Absorption

3.1 The Random Parking Limit Problem

The one dimensional model for RSA is called the random parking limit (RPL) problem. This problem was originally proposed by Rényi in 1958[R]. In the problem, cars of a fixed, finite length are placed randomly and sequentially along a curb. The cars are not allowed to overlap, and so if a car is going to be put in a place where it will hit previous cars, it is removed. There is a uniform distribution for the placement of the car along the curb, and the cars are placed until they reach a jamming limit. This is the point where there is no more space for cars to be added. Rényi proved that at the jamming limit, the percentage of the curb occupied by cars is always the same. He proved that the fraction of the curb covered was

$$\int_0^\infty \exp(-2\int_0^t \frac{1-e^{-u}}{u}\,dx)\,dt \approx 0.7476 \tag{31}$$

In 1960, Palásti extended this problem to the RSA, two dimensional case, which filled a plane with translations of a fixed, bounded, and open set, D, in the plane. Copies of D are translated to a place in the plane randomly, keeping their orientation, again without overlapping previous objects in the plane. He made the conjecture that the jamming limit did exist and that in the case when D was a square, that the jamming limit was the square of the limit in one dimension[Pal]. This conjecture was quickly disproven with computations which suggested this guess was too low. When computational results varied, an experiment was designed by IBM to accurately model the situation and find an experimental value for the jamming limit. They used latex spheres as the particle because it was rigid enough to hold its structure once it had bound,and it would bind irreversibly. Great care was taken to ensure that diffusion of molecules after absorption was minimized by the techniques used to dry the slide and pictures were taken to see that this wasn't occurring. The value calculated by this method was a coverage of $(55 \pm 1)\%$. This matched some of the computational results of the time and helped direct the study of the subject in the future [OL].

Since the original work in the 60's, there have been a lot of variations introduced into this problem. The one dimensional case has been solved analytically, though the two dimensional case is not. However, many things have been proven about the two dimensional case, in specific and general scenarios. The most prominent of these is the proof in 2002 by Penrose that the jamming limit in two dimensions did exist and that there was an applicable law

of large numbers for a large class of variations to this model. In order to do this, Penrose employed the techniques of Markov processes and also a geometric approach. That argument is beyond the scope of this paper. For a detailed proof of these statements, see [Pen].

One interesting advance in this field was the proof of the one dimensional jamming limit. It was originally proven using Markov processes, but in 1989, Hemmer presented an interesting proof which used a discretized version of the problem to prove the limit for the continuous case[H].

3.2 Hemmer's Discrete Proof of RPL

The actual proof can be found in [H]. Consider a lattice in one dimension with car length l and lattice spacing $a = \frac{l}{1+r}$ for some integer r. We say that a spot is occupied if it is the location of the center of a car. Because of this, there will be $r/2$ spaces on either side of an occupied spot which are unoccupied, but which are not a valid spot for a car to be added. These $r/2$ spaces are the spaces taken up by half the car. Another consequence of this naming system is that there be r spaces between any two occupied spaces ($r/2$ for each of the cars). We want to find $\rho(t)$, which is defined as the average fraction of occupied sites at a given point in time, t. From there we can solve for the coverage

$$R(t) = \frac{\rho(t)}{a\rho_{max}} = (r+1)\rho(t) \tag{32}$$

$\rho_{max} = \frac{1}{l}$ because one spot out of every car length is occupied (since only the center point is considered "occupied"). The final jamming limit will be evaluated according to

$$R = \lim_{r\to\infty} \lim_{t\to\infty} R(t) \tag{33}$$

Since this is a time-dependent function, we can simplify the problem by saying that at time t = 0, the lattice is empty and there is a constant probablity of a available site becoming occupied during a time interval dt. Call this probability $k\,dt$ for some constant k. Available implies that placing a car at the site would not overlap with another car. Note that k is dependent upon the lattice spacing (since a car covers r+1 sites). Therefore, we can write $k = c/r$, where c is a constant which no longer depends upon r.

Since $\rho(t)$ is a time dependent function, it can change in a time interval dt. Therefore we want to find $\frac{d}{dt}\rho(t)$. If the probability of any point i being open at time t is $p_0 = e^{-kt}$ where k is defined as above and $P_r(t)$ is the probability that the r sites are unoccupied, then the probability of i being an available point is $P_r(t)p_0(t)P_r(t) = p_0[P_r(t)]^2$. The reason we can multiply these probablities is that they are independent of one another. The influence of an occupied site is only r places because that is the required number of spots between each occupied site. Therefore, once you have r unoccupied sites, the sites to the left have the same chance of being occupied as before. Therefore,

$$\frac{d}{dt}\rho(t) = kp_0(t)[P_r(t)]^2 \tag{34}$$

because this is probability that a spot is available times the probability that the available spot is filled (k). Integrating both sides and using a dummy variable t', we see that this is the same as saying that

$$\rho(t) = k \int_0^t dt' p_0(t')[P_r(t)]^2 \tag{35}$$

In order to figure out how $P_r(t)$ can change in the dt time interval, we remember that we are considering a semi-infinite lattice. This means that we are considering an infinite line of points which starts at a finite point on one side and extends infinitely in the other. We can say this because we know that the point i and the next r lattice points on one side are all unoccupied. Therefore, we must only worry about the other side. This means that we can consider the points to the left of i as being unaffected by points on one side. The starting point in this semi-infinite lattice of points can only become occupied during dt if the first r+1 points are unoccupied, which we will call $P_{r+1}(t)$. Similarly, the second point in the lattice can only become occupied if the first $r + 2$ points are unoccupied, $P_{r+1}(t)$. We can continue this pattern, adding the values to get the total value for $\frac{d}{dt}P_r(t)$:

$$\frac{d}{dt}P_r(t) = -k\left[P_{r+1}(t) + P_{r+2}(t) + \cdots + P_{2r}(t)\right] \tag{36}$$

The k term must be multiplied in to the equation because it is the probability that one of the unoccupied spaces gets filled, and the probability is negative because during a time interval dt, we would expect the probability of r sites being unoccupied to decrease, not increase. Again using the fact that unoccupied sites which are greater than r length away from each other do not influence each other, we can see that

$$P_{r+m}(t) = P_r(t)[p_0(t)]^m \tag{37}$$

Taking this result, we plug in to Equation 36 to get the summation

$$\frac{d}{dt}P_r(t) = -kP_r(t)\sum_{m=1}^{r}[p_0(t)]^m \tag{38}$$

Since this is a finite geometric series, we know $\sum_{n=a}^{r} x^n$ converges to $\frac{a-ax^r}{1-x}$, so this series converges to

$$\sum_{m=1}^{r}[p_0(t)]^m = \frac{p_0(t) - p_0(t)^{r+1}}{1 - p_0(t)} \tag{39}$$

Therefore, we can plug this in to Equation 38 to obtain

$$\frac{d}{dt}P_r(t) = -kP_r(t)\left[\frac{p_0(t)\left(1 - p_0(t)^r\right)}{1 - p_0(t)}\right] \tag{40}$$

When we integrate this, we get the following equation:

$$P_r(t) = \exp\left\{-k\int_0^t \frac{1-[p_0(t')]^r}{1-p_0(t')}p_0(t')\,dt'\right\} \tag{41}$$

Note that the k can go in the limit of integration by the fundamental theorem of calculus. Therefore, using Equation 35,

$$\rho(t) = k\int_0^t dt' p_0(t')\left(\exp\left\{-2k\int_0^{t'} \frac{1-[p_0(t'')]^r}{1-p_0(t'')}p_0(t'')\,dt''\right\}\right) \tag{42}$$

and plugging Equation 42 back in to the formula for coverage (Equation 32)

$$R(t) = (r+1)k\int_0^t dt' p_0(t')\left(\exp\left\{-2k\int_0^{t'} \frac{1-[p_0(t'')]^r}{1-p_0(t'')}p_0(t'')\,dt''\right\}\right) \tag{43}$$

Here, we make a few substitutions to simplify the expression. Recall that $p_0(t) = e^{-kt}$ and $k = c/r$. Let $y = r[1-p_0(t'')] = r(1-e^{-kt''})$ and $x = r[1-p_0(t')] = r(1-e^{-kt'})$. With this substitution, we obtain the new expression

$$R(t) = \frac{r+1}{r}\int_0^{r(1-\exp(ct/r))} dx\left(\exp\left\{-2\int_0^x dy\frac{1-(1-y/r)^r}{y}\right\}\right) \tag{44}$$

In theory, we think of the system as taking the limit as t goes to infinity and then make this continuous by taking r goes to infinity. However, in practice, it is easier to take $r \to \infty$ and then $t \to \infty$, so we obtain

$$lim_{t\to\infty}\int_0^{ct} dx\exp\left\{-2\int_0^x dy\frac{(1-e^{-y})}{y}\right\} \tag{45}$$

This limit is equal to Equation 31, which completes the proof.

3.3 Computational work on the RPL problem

As part of my research into this method of problem solving, I programmed the RPL problem in one and two dimensions to obtain an estimate for the coverage at the jamming limit. The programs were written in Fortran90, and were based off an idea similar to the discrete model which was presented above. The discretized version was originally presented to me by Dr. Stanton as the drunken painter problem. Imagine you have a sidewalk, with many sidewalk squares, and you need to get them all painted. You hire a drunken man to paint the squares for you, but he can only paint a certain number of squares at a time and is not consistent about where he paints. For example, if he begins with one square at a time, he may paint the first square, skip the next two, paint two more in a row, skip one, and continue down the row in this random fashion. When he gets to the end of the sidewalk, he goes back to the beginning to try to get what he missed, again filling in the available squares one at a time and randomly (with uniform distribution). It is fairly intuitive that as long as he keeps

going back, he will eventually paint the entire sidewalk this way. However, if he has the restriction that he must paint two squares at a time, this is no longer the case. For example, he may paint the first two, skip one, and then paint the next two. Now there is no way for him go back and paint that empty square because he can only paint two squares at a time. In this case, the saturated/jamming limit is obviously going to be something less than 1. The claim is that if you were to take the length of the sidewalk, L, to approach infinity and $N \to \infty$, where N is the number of squares painted at the same time, this will approach the true Rènyi limit (J. Stanton, personal communication). Figure 6 demonstrates how this could work for the N = 2 case .

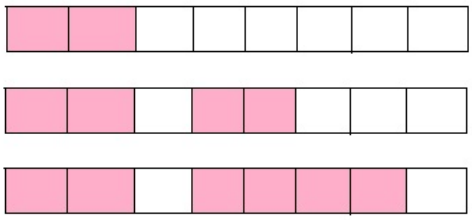

Figure 6: N = 2 Drunken Painter Problem Visualization

The drunken painter problem is an easier problem to approach computationally, because it allows for arrays to be used (which have discrete locations). However, after studying the problem, it turned out to be easier to code this using a summation. The summation is derived by looking at a particular N value and what happens as L increases. For example, let us consider again the N = 2 case. When L = 1, the coverage is obviously 0. For L = 1, there is only one possible outcome, which has a coverage P = 1. When you get to L = 3, there are two different outcomes, as shown in Figure 7 below.

Looking at this, it is possible to derive a recursive formula for the coverage which is dependent upon N and L. The summation is

$$f_{i+1} = \sum_{i=0}^{L-N} \frac{1}{L-N+1} \left[\frac{i}{L} f_i + \frac{L-N-i}{L} f_{L-N-i} \right] + \frac{N}{L} \tag{46}$$

This summation was used to try to calculate terms in the sequence which sums to the coverage for the N = 2 and N = 3 cases to look for patterns which would explain the closed form for N = 2 or give an expression for N = 3. To this effect, the first 10 values for L when N = 2 are shown in Table 1 below. No reasoning behind the closed form could be found,

Figure 7: N = 2, L = 3 combinations

though it seems to link to the appearance of the exponetial in the discrete proof shown above.

L	**f**	Δf
1	0	-
2	1	1
3	$\frac{2}{3}$	$-\frac{1}{3}$
4	$\frac{5}{6}$	$\frac{1}{6}$
5	$\frac{4}{5}$	$-\frac{1}{30}$
6	$\frac{37}{45}$	$\frac{1}{45}$
7	$\frac{52}{63}$	$\frac{1}{315}$
8	$\frac{349}{420}$	$\frac{1}{180}$
9	$\frac{338}{405}$	$\frac{41}{11340}$
10	$\frac{11873}{14175}$	$\frac{43}{14175}$

Table 1: Coverage values for N = 2 with varying L

This summation is also a much easier expression to code than to actually require the random process to occur. This improved the efficiency of the program and allowed more accurate answers to be found than the original problem which duplicated the random process described in the problem statement. The code for this problem is attached in the appendix.

For the two dimensional problem, the drunken painter problem is no longer a valid way to look at the discretized version of the problem. This is because there is no clear way to progress through the squares anymore in a way which will not affect the randomness of the answer. Therefore, when programming the two dimensional case, the random process had to be used. This decreased the accuracy in this answer. For this problem, squares of a set amount are put down on a grid of large size, randomly. A counter kept track of how many squares were put down and how many squares were thrown away because they tried to go in a spot which was already occupied by another square. Once this counter got to $s^2/4$, where s is the length of the grid size, the grid was scanned and a list of a all possible remaining locations was compiled. This list was then used to generate further placements for the squares. Whenever a spot was taken off of this list, the list was updated to take away

that location. This increased the efficiency because instead of having to rescan the whole grid each time, a much smaller list was scanned to determine how many spots remained. Once this list had no more valid spaces, the process was complete. Again, the grid size (side length s) and the square car size (side length h) were sent to infinity to make the continuous approximation. The following data was collected for the two dimensional problem.

h	s	Coverage	Time (s)
20	100	0.48000	0.006
20	1000	0.56720	0.41100001
10	500	0.5752	.068
30	800	0.545625	0.308
300	1000	0.63	37.60599
30	1000	0.56070	0.63500
200	10000	–	greater than 1000

Table 2: Two dimensional program data

One problem with this program is that it is difficult to get large values of s and h because of the amount of space and run time required. When working with s squared, the program efficiency becomes much more important, and this can be improved as an extension to the work done for this thesis. Again, there is the problem of working with the limit of two variable, because you have to take the limit as both h and s approach infinity. These results give an average value of 0.560, which we can compare to the reported estimate of 0.562 for the unit square[Pen].

3.3.1 Results of Continuous Case

After taking N and L sufficiently large, an approximation for the jamming limit in one dimension was found. The results are shown in Table 3 below.

N	L	P	Run Time (s)
10^3	10^5	0.74529227846365198	119.9520
10^2	10^4	0.74726098402662600	1.189
3×10^2	10^4	0.74076849275107626	1.162
3×10^2	10^5	0.74756388177479466	120.86700
10^3	10^6	–	greater than 600

Table 3: Drunken Painter Problem Limit - 1D

The actual answer to this problem is 0.7475979202[W]. Some of the computational results are closer than others, but this does not seem to correlate with run time or with the size of N and L. This is because two different variables are going to infinty making it more difficult to take a computational limit. This leads to an interesting extension of this thesis, which would be to look at the ratio of N/L and how that relates to the accuracy of the result produced

and to the run time of the program. From the small number of cases shown above and others which were done less formally during troubleshooting stages, there does not seem to be an identifiable relationship between the accuracy of the result and these variables. While it is obvious that N and L must both get large to model the continuous case, there may be an ideal ratio between the rates at which these two variables go to infinity, or a relationship between the amount of time it takes for a computation to run and the accuracy of the value. This requires a more sophisticated approach to program optimization and evaluation than was done for this paper.

When looking at the drunken painter problem, it is possible to find a closed form for the value of the coverage in the N = 2 case. That is, as $L \to \infty$ with N = 2, the coverage goes to 1-e^{-2}. This limit was determined simply by looking at the values generated a program, not derived from the information in the problem. Knowning this, another goal of the project was to look into finding a closed form expression of the N = 3 case. If an analytic form could be found which was dependent upon N, then solving the continuous problem would simply become the evaluation of a limit. To this effect, a summation program was run for many values of L for both N = 2 and N = 3. The results are shown in Table 4 and 5 below. Note that in the N = 2 table, there is a value which isn't listed. This implies that the calculation exceeded allotted amount of time to calculate a coverage and had to be terminated.

L	**Coverage Limit**
2×10^3	0.8645179
2×10^4	0.8645370
10^5	0.86466201
10^6	–

Table 4: N = 2 Coverage

L	**Coverage Limit**
10	0.77249999999999996
10^2	0.81836255207265873
10^3	0.82312392206685980
10^4	0.82360005906626854
10^5	0.82364767276702722

Table 5: N = 3 Coverage

One question that this data raises is about the convergence of the N = 2 case in comparison to the N = 3 case. Since we know the value for the N = 2 case should be 0.864663716763 = 1 - e^{-2}, we can tell to what decimal point the calculated values converge. For example, the N = 2 case has converged to 5 decimal places by L = 10^5. Does this imply that the N = 3 case is converged up to 5 decimal places at this same point? Knowing this would make it easier to find closed form for the N = 3 case because it would automatically rule out things

which were close, but not close enough. However, there is no guarantee that the convergence works this way and this would need to be proven before it could be used.

3.4 Conclusion

The RPL problem in one dimension and RSA in two dimensions are helpful models to study irreversible absorption of molecules because of their ability to predict saturation levels which differ from a traditional equilibrium system. While a program was written to calculate the value of the jamming limit in the one and two dimensional cases, a closed form for N = 3 was never found, nor was the reason for the closed form for N = 2 discovered. The connection between the closed form for N = 2 and the discrete proof of the RPL given by Hemmer indicates that the drunken painter version of the problem is comparable to the actual continuous problem once the appropriate limits are taken.

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Appendix

```
!-----------------------------------------------------------------------
!
!  PROGRAM oneD
!
!     purpose: to write the one dimensional painter problem
!
!-----------------------------------------------------------------------

PROGRAM oneD

IMPLICIT NONE

DOUBLE PRECISION n, l, i, j, total
DOUBLE PRECISION, dimension(:), allocatable :: tarray
INTEGER t1,t2,count_rate,count_max

count_rate = 1
count_max = 1000

n = 1000
l = 1000000
i = 0
j = 0
total = 0
i = 0

Allocate(tarray(0:INT(l)))

DO WHILE(i <  n)
   tarray(INT(i)) = 0
   i = i+1
ENDDO

call system_clock (t1, count_rate, count_max)
j = 0
DO WHILE(i < (l+1))
   DO WHILE (j < (i - n + 1))
   total = total + (1/(i-n+1))*(j/i * tarray(int(j)) + &
           (i-n-j)/i * tarray(int(i-n-j)))
   j = j + 1
   ENDDO
   tarray(int(i)) = total + n/i
   i = i + 1
   total = 0
   j = 0
ENDDO
call system_clock(t2, count_rate, count_max)
PRINT*, 'N = ', n, ' l = ', l
PRINT*, 'P = ', tarray(int(l))
PRINT*, 'Elapsed Real Time = ', real(t2-t1)/real(count_rate)
DEALLOCATE(tarray)


END PROGRAM one
```

```
!-----------------------------------------------------------------------
!
!    PROGRAM twoD
!
!    PURPOSE:
!       To determine the solution to the two dimensional problem
!       using squares
!
!-----------------------------------------------------------------------

PROGRAM twoD

IMPLICIT NONE

DOUBLE PRECISION :: h, s, fail, total
DOUBLE PRECISION, dimension(:,:), allocatable :: grid,remain
INTEGER x,y,row,t1,t2,count_rate,count_max
DOUBLE PRECISION, dimension(0:1) :: random
INTEGER :: i,j,top

count_rate = 1
count_max = 1000
h = 200
s = 1000

Allocate(grid(0:INT(s)-1,0:INT(s)-1))

grid = 0    !!allocates the entire array to initial values of 0

call random_seed
call system_clock(t1,count_rate,count_max)
DO WHILE (fail < (s*s)/4 )
   call random_number(random)
   random = random * (s-h)
   random = nint(random)
   x = INT(random(0))
   y = INT(random(1))
   IF(check(x,y).EQ.0) THEN
     grid(x:x+INT(h)-1,y:y+INT(h)-1) = 1
     total = total + 1
   ELSE
     fail = fail+1
   ENDIF
ENDDO

PRINT*,'total = ', total, 'fail = ', fail

Allocate(remain(0:INT(s*s-(h*total)),0:2))
remain = -1
i = 0
j = 0
row = 0
DO WHILE (j < s)
   DO WHILE(i < s)
```

```
      IF(check(i,j).EQ.0) THEN
         remain(row,0) = i
         remain(row,1) = j
         row = row + 1
      ENDIF
      i = i + 1
   ENDDO
   j = j + 1
ENDDO  !!this fills a list with all the remaining possibilities
PRINT*, 'the size of remain is ', row
top = 0
call random_seed
DO WHILE(MAXVAL(remain).GE.0)
   call random_number(random)
   random = random * (row-1)
   random = nint(random)
   PRINT*, INT(random(0))
   i = INT(remain(INT(random(0)),0))
   j = INT(remain(INT(random(0)),1))
   IF(check(i,j).EQ.0) THEN
      CALL place(i,j)
      total = total + 1
   ENDIF
   remain(INT(random(0)),0) = -1
   remain(INT(random(0)),1) = -1
   !!either you put something there and now its not free
   !!or you didn't put anything and it already wasn't free
   !!eiher way, not free
ENDDO
call system_clock(t2,count_rate,count_max)
PRINT*, 'total = ', total
PRINT*, 'coverage = ', total/(s*s/(h*h))
PRINT*, 'Elapsed Real Time = ', real(t2-t1)/real(count_rate)
PRINT*, 'h, s ', h, ' and ', s

CONTAINS
   INTEGER FUNCTION check(x1,y1)
     IMPLICIT NONE
     INTEGER, INTENT(IN) :: x1,y1
     check = SUM(grid(x1:x1+INT(h)-1,y1:y1+INT(h)-1))
   END FUNCTION check

   SUBROUTINE place(x2,y2)
     IMPLICIT NONE
     INTEGER, INTENT(IN) :: x2,y2
     grid(x2:x2+INT(h)-1,y2:y2+INT(h)-1) = 1
   END SUBROUTINE place

END PROGRAM twoD
```