Introduction to Fractals and Diffusion Limited Aggregation

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ABSTRACT

The goal of this report is to serve as an introduction to the concept of fractals and generation of fractal surfaces through computer simulations, with the main emphasis being on the study of Diffusion limited aggregates and to give a review of the work done by various researchers on the subject. The primary focus is on the methods employed to create these simulations and to report in brief their substantive findings. Methods of analysis and results of these simulations are not explained in detail.

Contents of the report include the introduction which gives a brief history and the fundamentals required to understand fractal geometry, examples of fractal constructs (or mathematical objects which have fractal properties) , the box counting method and some information about fractal and multifractal analysis, applications of fractals in different fields, explanation of Random walks, Brownian motion and percolation clusters and some other relevant concepts followed by the summary of all research papers describing their objectives, methods used in the simulations and their distinct features.

Table of Contents

- **INTRODUCTION**

The concept of fractals has existed since the 17th century. But most of the work on this subject remained obscured until recently due to its unfamiliarity, lack of a clear definition and disagreements with key features of Euclidean geometry. Fractal geometry is the study of sets with properties such as self-similarity or self-affinity, perhaps in an approximate sense. They also had property of being a function that is continuous but not differentiable.

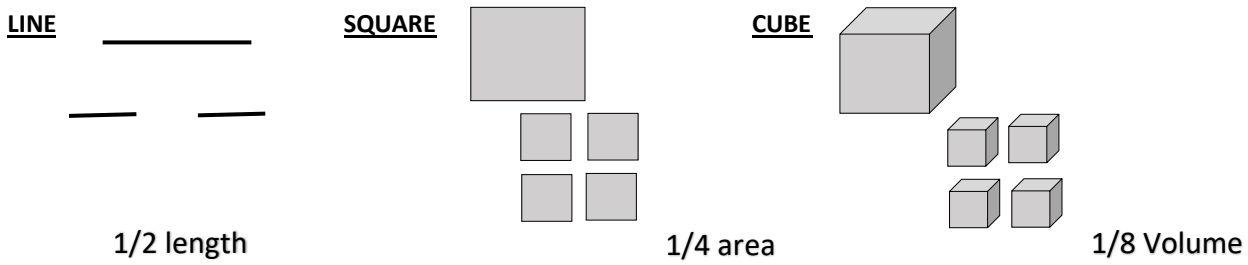
In 1883 Georg Cantor published subsets of the real line known as cantor sets, which had unusual properties that are now recognized as fractals. By the early 1900's Helge Von Koch and Waclaw Sierpinski who put forth a more geometric definition through hand drawn images of a similar function, the Koch snowflake and the Serpinski triangle respectively Later Felix Hausdroff expanded on the definition of what a "dimension" of an object is. But not until much later in the 1960's did the concept of fractals become mainstream. This was done by Benoit Mandelbrot, who coined the term "fractal" by giving it a mathematical definition through the aid of computer-generated images. His Mandelbrot set was a fractal constructed in the complex plane using the process of reiteration and this was done using just a simple equation. This eventually led him to put forth the theory of roughness and how natural objects which aren't perfectly geometrical (Euclidean geometry) could have dimensions that are not integers. This helped extend the concept of fractional dimensions to geometric patterns in nature.

Fractals have found applications in diverse fields. While to the common public the word fractal is most often only known as complex, abstract, beautiful computer-generated imagery, its applications extend to various subjects like Modelling natural structures: Geographical terrain, botanical plant structures, Image compression in Computer graphics, Analysis of medical diagnostic images, Applications in Engineering and architecture etc. Though the idea of fractals is generally attributed to repeating geometric patterns that are infinitely self-similar and iterated or mathematical objects that have fractal dimensions, they can also be used to describe complex processes in time. In recent times fractals have become much more relevant, especially fields of mathematics and the study of dynamical systems and chaotic phenomena.

What are fractals?

The geometry of Fractals is not easily explained in classical terms (i.e. fundamental geometrical shapes in Euclidean space). A fractal is not the locus of the points that satisfy some simple geometric condition, nor is it a set of solutions to a simple equation. Even though there is no rigid definition of a fractal, mathematically they can describe as sets that exhibit some form of self-similarity or scale invariance and contain an infinite amount of detail. Fractals differ from traditional geometrical figures in the way that they scale.

Scaling the length of a line simply increases its length by 2, which is 1(the ratio of the new to the old side length) raised to 1 (the dimension the line) i.e. the dimension of a line. Doubling the edge lengths of a square(polygon) multiplies its area by 4, which is 2 (the ratio of the new to the old side length) raised to the power of 2 (the dimension of the space the polygon resides in).Likewise, if the length of a cube is doubled, its volumes scales by 8, which is 2 (the ratio of the new to the old radius) to the power of 3(the dimension that the sphere resides in).



Doubling the edge lengths of a square(polygon) multiplies its area by 4, which is 2 (the ratio of the new to the old side length) raised to the power of 2 (the dimension of the space the polygon resides in).Likewise, if the length of a cube is doubled, its volumes scales by 8, which is 2 (the ratio of the new to the old radius) to the power of 3(the dimension that the sphere resides in).

However, if a fractal's one-dimensional lengths are all doubled, the spatial content of the fractal scales by a power that is not necessarily an integer.(e.g. Sierpinski gasket, cantor set, Koch curve) .This power is called the **fractal dimension** of the object, and it is always less than the topological dimension (the space with an integer dimension within which the fractal is embedded). But some mathematical fractals have integer dimensions that exceed their topological dimensions. The Sierpinski Gasket, Cantor set, and Koch curve are some of the simplest objects that have fractal characteristics that can be easily illustrated. These structures can be generated using simple iterative schemes and basic knowledge of geometry.

SERPINSKI GASKET:

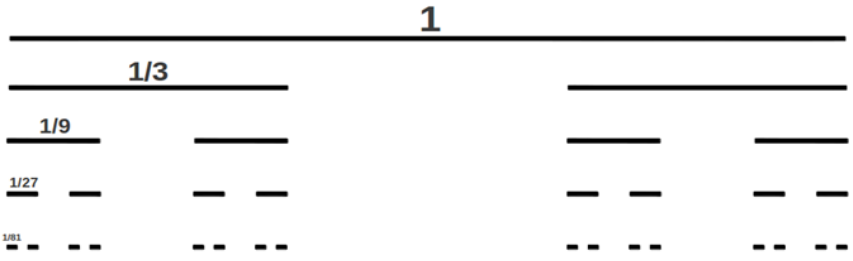
Consider an equilateral triangle. Using the midpoints of its sides and divide it into four congruent equilateral triangles (i.e. each new triangle will have a side of length 1/2 the original), each with half the scale of the original. Now remove the innermost triangle, leaving behind three such triangles. Now each triangle is a scaled down version of the initial triangle by 1/3 which means we need 3 copies of this to cover the original triangle. This is the Sierpinski gasket. Now repeat the construction with each of these triangles. And continue in this manner, indefinitely. The resulting configurations are depicted in the figure above.

What we have observed here as well as in the previous cases of the line, square and cube is that, when an object is scaled by factor of *k* (i.e., we shrink it to 1/*k*th of its original size), we need *N* copies of the new object to cover the original one.

If a line is split into two equal halves (k=2), then we will need 2 copies to recreate the original (*N*=2), hence ***N=k.*** For a square of side ½ the original (k=2), we will require 4 copies to cover the original (*N*=4), therefore here $\boldsymbol{N=k^2}$.And for a cube of side ½ the original (k=2) and we will need 8 copies to cover the original (*N*=8), hence $\boldsymbol{N=k^3}$In general $\boldsymbol{N=k^d}$ where *d* is referred to as the *dimension of the object.* This notion, when generalized suitably to apply to objects that do not have the property of self-similarity, gives the ***Hausdroff dimension*** or the ***fractal dimension*** of the object. In case of the Sierpinski gasket k=2 and N=3, so the Hausdroff dimension is:

$3=2^d$ ≈ log3 = *d* log2 ≈ *d* =$\frac{\log 3}{\log 2}$ ≈ d = 1.585

CANTOR SET:



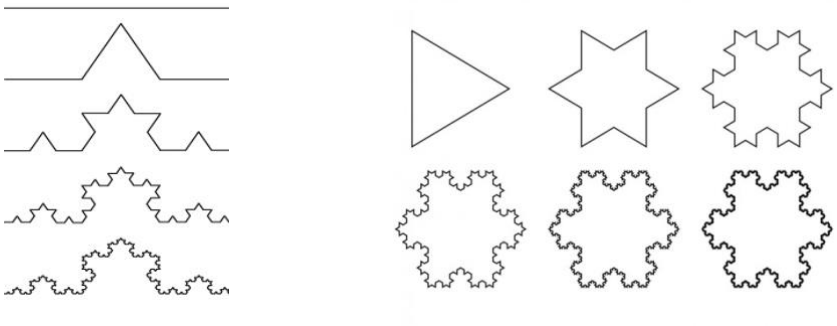
The Cantor set is one of the simplest fractals. The general process of generating this fractal requires a line to be be split into 3 equal parts then removing the middle 3rd and repeating the process with the remaining two parts , and keep iterating. Starting with a line of length L the middle third is removed to form two lines of length L/3 separated by a gap of length L/3. In the second stage the thiddle third of each of the remaining lines is removed leaving 4 lines each of length L/9. After n generations the system contains 2^n lines each of length $L/3^n$.As the number of iterations n incereases the number of line

segments goes on increasing but their total length goes on decreasing , eventually approaching 0 for the limit n→∞.Here k=3 and N=2.Hence

$2=3^d$ ≈ log2= *d* log3 ≈ *d* =$\frac{\log 2}{\log 3}$ ≈ <u>d = 0.631</u>

and we can see how the dimension of an object can be a non-integer number. A mathematical function said to be analogous to the cantor set is called the cantor function or the Devils staircase.

<u>Van Koch curve:</u>



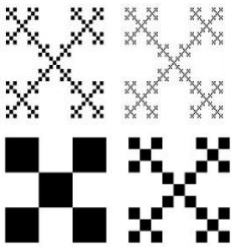
The Koch curve has the property of being continuous everywhere, but differentiable nowhere. It's Basically a curve on which no tangent can be drawn on any point. The construction basically entails dividing a line segment into 3 segments of equal length, then draw an equilateral triangle that has the middle segment as its base and points outward, then remove the line segment that is the base of this triangle. Repeat the process for all four sides.

With each iteration the total length of the curve increases by factor of 4/3 i.e. increasing 4 times as many line segments, each with a length 1/3 the length of the segments in the previous iteration. Here k=3 and N=4.Hence the fractal dimension of the curve is:

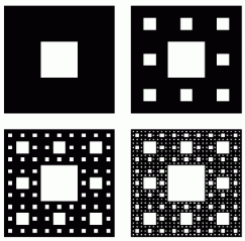
$4=3^d$ ≈ log4= *d* log3 ≈ *d* =$\frac{\log 4}{\log 3}$ ≈ d = 1.26186

which is greater than that of a line but less than that of a 2-D surface.

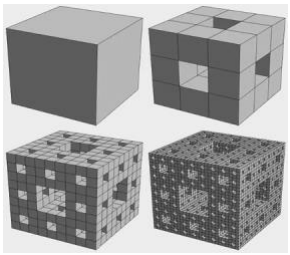
Some other examples of such geometrical fractals would be Cantor dust fractal, Menger sponge, Serpinski carpet, Vicsek fractal, Hilbert & Peano space filling curves, Apollonian gasket etc.



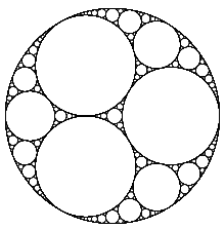
Vicsek fractal



Sierpinski carpet



Menger sponge



Apollonian gasket

Some fractals might show self-similar properties over an extended but finite range of scales. fractal surfaces can be thought of as having the properties of a self-similar fractal on short length scales and the properties of smooth surfaces on long

length scales. These structures are not themselves fractals but have associated with them some structure that is fractal. Some examples of this would be the Devils staircase, Mandelbrot set and Julia sets, Lorentz attractor etc. Unless the construction of the fractal set is especially simple, the Hausdroff dimension is a difficult number to get hold of, requiring more advanced analytical techniques like box counting methods, fractal and multifractal analysis.

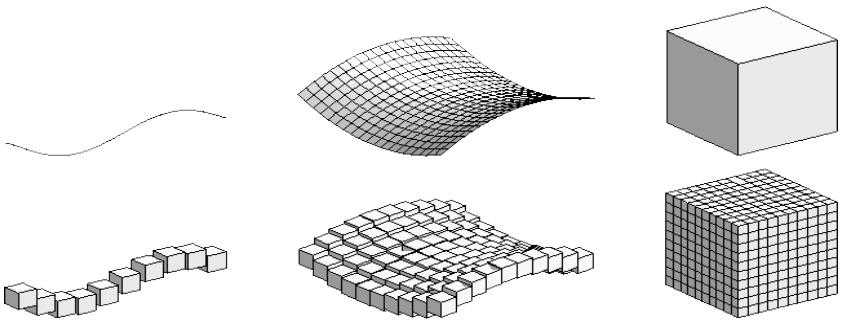
- **Box counting method:**

It was one of the earliest ways to numerically estimate fractal dimension. In certain aspects its similar to how we obtain the dimension for simpler fractals like the Sierpinski gasket and cantor set.

To compute the box-counting dimension, break up the embedding space into a grid of boxes (squares in case of 2-D space) of length *r*. Count the number of boxes *n(r)* inside which at least one point of the object lies, and this gives the fractal dimension *d*. The scaling relation is given by

$$n(r) = r^{-d}$$

Better defined as $d = \frac{lim}{r \to 0} \frac{log\,[\,n(r)]}{log\,r}$



The problem with this definition is that boxes cannot have 0 length. The box counting method only has finite resolution, so the limit $r \to 0$ cannot be taken and must be some finite value. The smaller the length scale, more the number of boxes required hence higher the resolution. Another variation off this method would be taking balls of radius *r* with centers at F, and if any point x from the fractal set falls within the radius of a ball, that ball is counted.

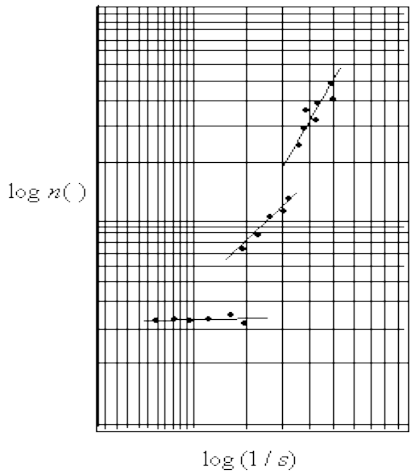
- **Multifractals**

Multifractals look at the varying dimensions of a complicated structures different parts. A Multifractal system is one which cannot be described using just one exponent, these systems exhibit varying dimensions over different regions. Multifractal analysis has proven to be useful in the study of processes in environments of complex geometry e.g. the scaling analysis of the aggregation probability distribution of the fractal objects. The properties of multi-fractals can also be seen in Systems where the probability distribution of a region varies for different locations. Multifractals are often observed to be systems that exhibit clustering and hence have uneven distributions. This type of analysis has been applied to scaling properties of molecular spectra, characterization of wavefunctions in the Anderson localization model and, diffusion limited reactions over fractal surfaces, analyzing financial markets, distortions in signals etc.

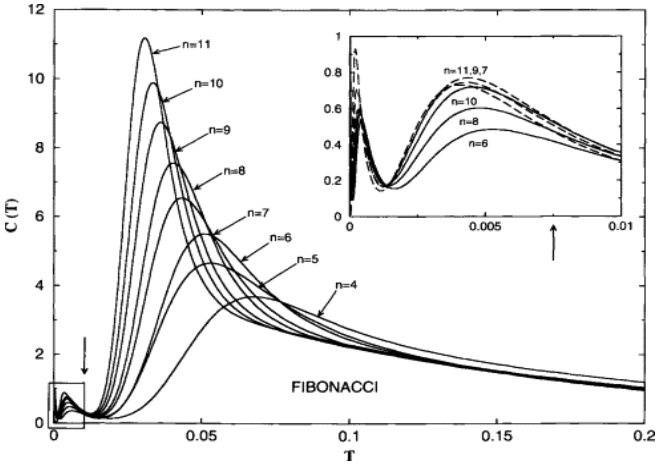
Fractals by nature have the property of scale invariance, which implies the need for a proportional scaling of the function itself when the input is varied by a factor. Consider the equation:

$$f(\lambda x) = a(\lambda x)^{-k} = \lambda^{-k} f(x) \sim f(x)$$

The equation is a power law relation. A power law states the proportional change of one quantity relative to change in another. This often indicates that the systems scale invariant and fractal nature. In the above equation, scaling by a constant λ multiplies the original relation by the constant λ^{-k}. Hence all power laws with a scaling exponent are equivalent up to constant factors. Each one is a scaled version of the others. The curve of log f(x) vs log x gives a linear relationship E.g. the fractal dimension is the slope of a log-log graph. Percolating clusters, Diffusion limited aggregates, the Ising model and certain thermodynamic systems exhibit phase transitions, such systems often have power law distributions associated with certain quantities whose exponents are referred to **as critical exponents**. These critical exponents though not the same for every system often denote similar quantities like the correlation function, correlation length,order parameter, the number of spatial dimensions, spatial distance etc.



Different dimensional slope values for different ranges found in a multifractal.



Plot of specific heat vs temperature for pore like structures at different levels of magnification.

Consider a system characterized by such an exponent α which can take on a set of values corresponding to different regions of the systems distribution Its probability distribution function is $f(\alpha)$ varies with α. $f(\alpha)$ needs to be related to some observable quantity, usually the fractal dimension. α is called the singularity exponent. The curve $f(\alpha)$ *versus* α for a set of points that share the same exponent is called the multifractal spectrum, which fully describes the statistical distribution of the system.

While the $f(\alpha)$ alone doesn't characterize the system under investigation, further analysis gives access to higher order moments of the distribution and other *multi-scaling exponents* which might be useful. Moments of a distribution are quantities that essentially help quantify the shape of the function. For a probability distribution function, lower moments are usually the total probability, mean and variance whereas the higher order moments give quantities such as skewness and kurtosis. Essentially the multifractal spectra allow viewing a distribution through a distorting lens.

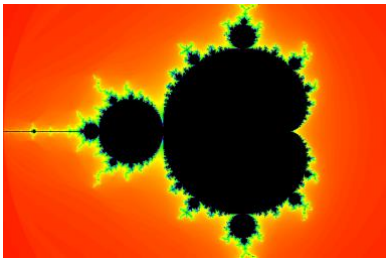
Mandelbrot and Julia sets:

The Mandelbrot set is probably the most recognizable and popular fractal. It's a fractal in the complex plane where the fundamental set contains all complex numbers ***c*** such that the iterative equation:

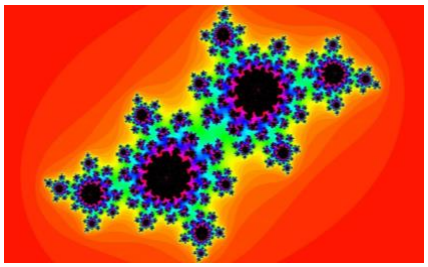
$$Zn_{+1} = Zn^2 + c$$

stays finite for all ***n*** starting with $Z_0 = 0$. As shown in the figure of the Mandelbrot set, the set of points that remain finite through all iterations is black, with warm colors (orange, shades of red) showing how quickly other values diverge to infinity.

The boundary between points that remain finite and those that diverge to infinity is extremely complicated, with self-repeating features that reveal progressively finer recursive details at increasing magnifications.



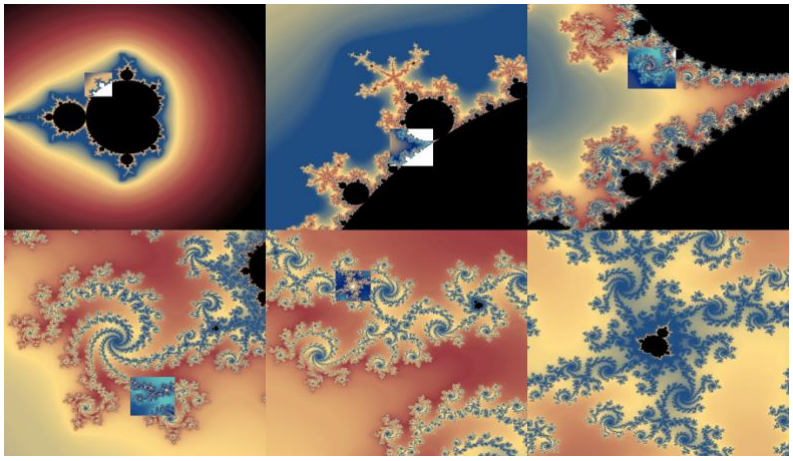
The Mandelbrot set



The Julia set for c= -0.7269+0.1889i

Julia Gaston pointed out the crucial difference between points that tend to a limiting position as the iteration proceeds, and those that never settle down. A is the set of points in the complex number plane that diverge to infinity. The ones that settle down are known as the Fatou set. In general the Julia set is infinite and is related to the periodic points of the iteration (those that return to themselves after a certain number of iterations).

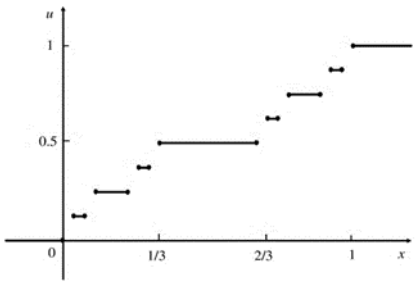
The Mandelbrot set is the set of Points on the complex plane which under *n* number of iterations for a fixed *c* go to an attractor (attracting point or periodic orbit). It is defined as the set of all ***c*** such that the Julia set is connected. The Julia set is its complement. The Julia set is the boundary between colored and black regions on the left image. Based on the study of bifurcations in dynamic systems, the Hausdroff dimension of the Mandelbrot set has been proven to be equal to 2***(M.Shishikura (1998)[4])***



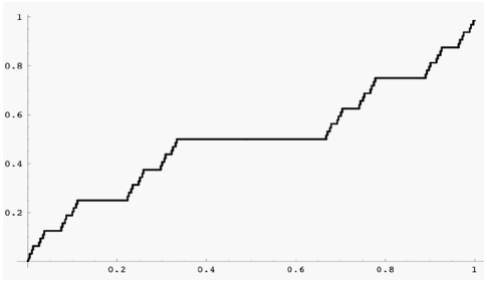
Zoomed in images of the Mandelbrot set at different levels.

<u>Devils staircase:</u>

Also known as the cantor function or thee infinite staircase. This staircase has steps with continually finer steps in-between, so no matter how small of a step is needed to be taken there will always be one to accommodate and an infinite number of steps in-between. It represents the integral of the mass of a "Cantor bar" as a function of distance. The process of construction is the same as that of the cantor set. However, each time a line segment of length L is replaced by two segments of length 1/3 (with the middle third missing) the mass density in the two remaining thirds is increased by a factor of 3/2 so that the total mass is conserved.



Cantor bars

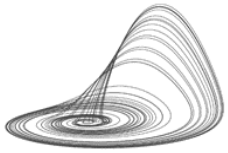


The Devils staircase

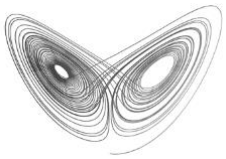
While this gives a power law relationship between the length segments L and its mass M it doesn't define the fractal dimension. This will require using the box counting method. The cantor function acts as a good example of why fractals do not have a fixed definition.

Strange attractors:

When a dynamical system tends to evolve towards to a specific set of numerical points, such points are called attractors. In most cases attractors with chaotic dynamics associated with them have fractal structure, these are known as strange attractors. Strange Attractors are extremely sensitive to initial conditions (also known as the "butterfly effect") of the system. Unlike most deterministic fractals who have no well-defined slope, some strange attractors might be differentiable in certain directions. Hausdroff dimensions of attractors can be obtained using the box counting and extrapolation methods but it serves as a crude estimate, often requiring knowledge of other quantities such as the correlation dimension (another type of fractal dimension) and Lyapunov exponents (gives rate of divergence of infinitesimally close trajectories in chaotic systems).



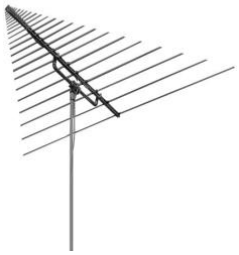
Rössler attractor



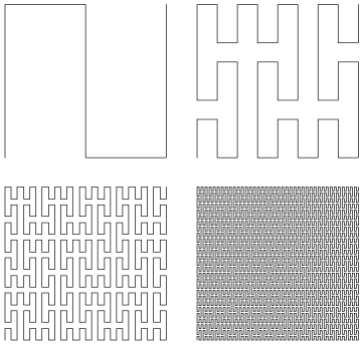
Lorentz attractor

- **Applications of Fractals**

1. While Sierpinski gasket and carpet, Hilbert, Peano and Koch curves might seem like trivial examples, their one very specific application is in designs of antennas. The first utilization of fractal antennas was done even without prior knowledge of the concept, in the form of log periodic antennas. They common form used in TV antennas and are arrowhead like in shape.



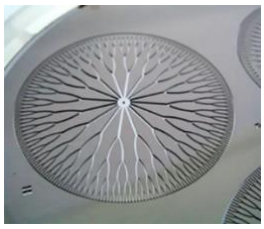
Log-periodic antenna



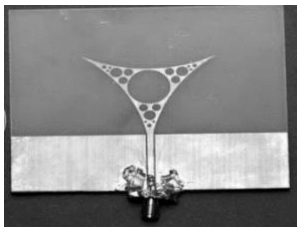
Peano curve. For large enough iterations covers the entire 2-D unit square i.e. its limit is a space filling curve

These antennas have broad band properties whereas in general normal antennas are built to work only at certain frequencies. And this was found to be due to its self-similar nature. Its structure consists of multiple pairs of metal rods of gradually increasing length. Fractal antennas are designed to maximize the effective length that could be fit inside a finite volume to optimize reception and transmission of electromagnetic radiation. They are often having the structure of space filing curves. The Peano and Hilbert curves are good examples of this. It has been experimentally proven that certain fractal antennas can be very efficient radiators despite their small size in terms of the wavelength. Antennas have certain fundamental theoretical limits that fractal antennas can often approach this limit whereas Euclidean-shaped antennas don't come very close to this limit.

2. According to researchers at Oregon State University, fractal figures can be etched into silicon chips, allowing for a cooling fluid (such as liquid nitrogen) to uniformly flow across the surface of the chip, keeping it cool. Researchers say this fractal pattern was derived from human blood vessels and provides a simple low-pressure system to easily cool sensitive computer chips.

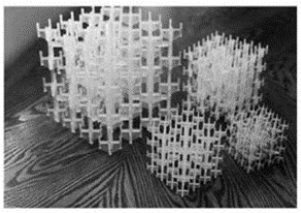


Fractal heat exchanger etched in silicon and designed by Deb Pence at Oregon State University

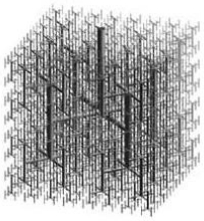


Apollonian Gasket CPW monopole Fractal Antenna

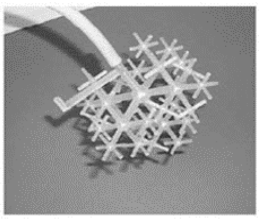
3. The eye exploits the fractal geometry that is ubiquitous throughout nature. This has led to research that predict advantages for fractal-based bionic implants. These implants include an increase in visual acuity by over an order of magnitude, potentially allowing people to read text and facial expressions – essential capabilities for performing everyday tasks. Furthermore, unlike current implant designs, fractal implants will trigger the physiological mechanism used by the human visual system to prevent our stress-levels from soaring.
4. Fractal analysis of CT scans can also quantify the health of lungs suffering from emphysema or other pulmonary illnesses to assess the health of blood vessels in cancerous tumors. Measurements show that cancerous cells feature a consistent fractal geometry, while healthy cells show some fractal properties but in an ambiguous way.
5. Amalgamated Research Inc (ARI) has created space filling fractal devices for the high precision fluid mixing. These devices allow fluids to be carefully and precisely blended without the need for turbulent stirring.
6. The mathematical basis of fractal geometry makes it a potentially useful tool to describe the heterogeneity of soil structure quantitatively. A quantitative description of soil structure would ideally be able to be directly related to the processes occurring within the soil.
7. Phenomena like earthquakes that show fractal distribution of frequency of occurrence this relationship can be used to infer the recurrence interval of a given size earthquake in an area. It may also give insight into the dynamics of earthquakes and is extremely useful in hazard mitigation, engineering and seismic hazard assessment.



A variety of structures with variable space filling density and channel sizing.



Example of a volume processing structure constructed with a non-integer pattern (a fractal dimension of 2.32)



Fractals used to distribute and/or collect fluids from a volume.

8. The results of the new study show that fractal patterns offer a promising approach to hard-soft materials integration and suggest that fractal patterns can influence the mechanical properties of 2D materials. In the new devices, the hard metal wires are engineered into fractal designs and then bonded to soft elastomers. Peano pattern, for example, the researchers showed that modifying the orientation of the pattern enhances the material's elastic strain in one or more selected directions and allows the pattern to support different types of deformations.

9. Control provided by fractal patterns could allow researchers to tailor stretchable electronics devices for different applications, depending on the type of stretching required. One potential application is "epidermal electronics," or skin-mounted sensors and actuators. A common example is electrodes, which measure electrophysiological processes in the brain, heart and muscle.

So far, we have seen fractals that are deterministic, modeled using mathematical equations and geometry. While these objects are complex, they are easier to understand, compared to natural fractals. Fractals in nature occur through processes that are often defined as random or chaotic. To understand these random processes, models are created that could be considered as close approximations. The methods of simulation and analysis for these models are complex often requiring at least a basic understanding of certain statistical and probabilistic concepts. An introduction to these concepts would prove useful when trying to comprehend the research done in these areas.

Correlation function:

Random models often consist of systems with a large number of interacting particles. The correlation function gives the measure of the effects of the particles on a particle at a distance *r*, denoted by *C(r). C(r)* measures how a quantity *X* varies over the entire system compared to X at points that are a distance *r* away. It is defined by:

$$C(r)=\frac{\int X(r+r')X(r')dr'}{\int X(r')dr'}$$

Usually the quantity *X (r)* is defined as density $\rho(r)$, having value 1 for occupied state and 0 for unoccupied ones.

$$C(r)=N^{-1}\,\Sigma\langle\rho(r')\,/\rho(r+r')\rangle$$

where N is the total number of particles for a Diffusion limited aggregate and *r* must be much smaller than the aggregate size. In general, the correlation function behaves as a power law i.e. ***C(r)*** is proportional to r^{η} for some real number η. A high correlation function means that different parts of the system tend to vary together, implying order. A low value of the correlation function means the system is disordered. The correlation function generally describes the radial distribution function i.e. describes how in a system density varies as a function of distance.
Experimentally one can indirectly measure the radial distribution (or the pair-correlation function) through scattering techniques like x-ray or neutron scattering. Systems such as the state of matter in fluid phase or the 2-D molecular gas can be characterized by interaction between particles, specifically the pair-correlation function (PCF). A full visualization of the PCF can be done using scanning tunneling microscopy (STM).

Universality:

Universality is a statistical property that implies same principles and behaviors for one system will be applicable also to a completely different system. This is because their correlation functions behave in the same way i.e. they have the same exponents in their expressions for C(r). Multiple such exponents (critical exponents) may be needed to explain the behavior of a system. Different physical systems can be divided into universality classes which have the same values of these exponents. This is often observed in a large class of systems in a scaling limit. This term might be applied to the behavior of a lattice model in the limit of the lattice spacing going to zero i.e. the number of lattice sites or bonds in the model is so high that it basically acts as a continuous medium instead of a discrete set of points. Universality is closely related to concepts of statistical mechanics such as phase transitions, scaling theory, renormalization groups, critical phenomena, multi-fractals etc.

Dynamic scaling:

Dynamic scaling first introduced by Fereydoon Family and Tamas Vicsek, as an analysis tool to determine the self-similarity of a system changing with time**.** ***Vicsek and Fereydoon (1984) [5]*** proposed this with reference to 2-D DLA Clusters. They studied the size distribution of a clusters size ***s*** and time ***t*** in order to explain the temporal evolution, diverging from earlier studies that primarily focused on the morphology of aggregates. The distribution ***n(s,t)*** shows a power law decay, indicating some kind of critical behavior. They gave the scaling relation representing the cluster size distribution as

$$n(s,t) \sim t^{-w} s^{-\tau} f(s/t^{z})$$

where ***w*** and ***z*** are dynamic exponents while τ is a static exponent and the term t^{-w} describes the power-law decay of n(s,t) with time for every *s.*

Brownian motion:

Brownian motion was coined by Robert brown while investigating the motion of particles like dust and pollen on the surface of water, but it was later elaborated on by Einstein in one of his seminal papers in 1905. He described it in terms collisions of fluid molecules with microscopic particles suspended in the fluid due to random fluctuations leading to a random jittery motion. Due to the many body interactions Brownian motion had to be described using statistical mechanics and probabilistic models. Einstein's theory involved establishing a relationship between a diffusion coefficient and the **mean square displacement** of the particle and relating this diffusion coefficient to physical quantities that can be measured. In this case since the model is that of random motion over a surface the mean squared displacement can the thought of as the measure of the portion of the system a particle has explored. The density of Brownian motion satisfies Einstein's differential diffusion equation. $\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$

The solution to which is an expression having a normal distribution. Even though the process itself is random, some quantities could be predicted using statistical methods. Einstein's equation showed that diffusion and surface growth processes are very similar to Brownian motion, so the question arose: can Brownian motion explain other random phenomena? Most diffusion processes had some degree of randomness associated with then. So Brownian motion, being a random walk model, could explain various random and surface growth phenomena. Although Brownian motions are continuous everywhere, they are differentiable nowhere. Essentially this means that a Brownian motion has fractal geometry.

Weiner process:

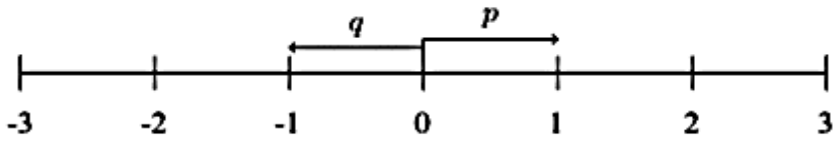
Mathematically Brownian motion is known as Weiner process which is a kind of stochastic process. In contrast to a deterministic process which has an exact value at any point in time, the value of a stochastic changes over time in an uncertain way. It can be described as a collection of random variables; thus, we only know the distribution of the possible values of the process at any time. The Wiener process W(t) is in essence a series of normally distributed random variables, and for later time points, the variances of these normally distributed random variables increase to reflect that it is more uncertain (thus more difficult) to predict the value of the process after a longer period of time.

- **Random Walks**

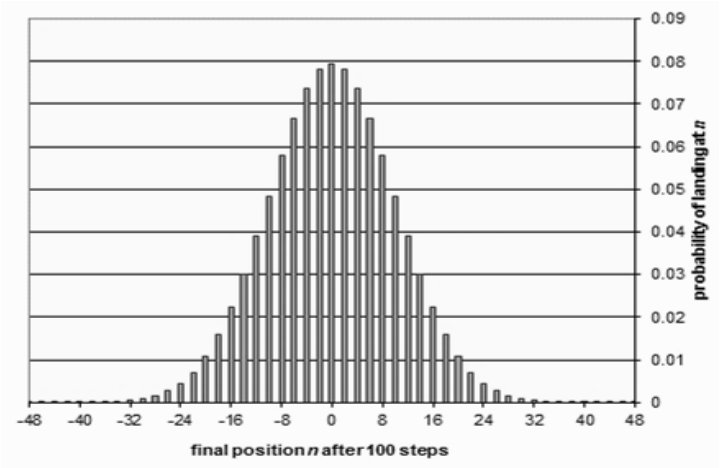
A random walk is a very general type of random process, it always involves taking a series of steps and the direction of the steps is determined probabilistically, but random walks take place in many different settings according to many different rules.

Simple random walk:

The most basic random walk is on the integer number line. let's say your random walker is a point on the number line. So, you start at the origin (0) and you can randomly move either to the left (-1) or the right (+1) by one number whose outcome is determined by a coin flip. If its heads you move to the right and left if its tails. let's say that the probability of moving to either side is equal (since our coin is unbiased). So, if the probability of moving to the right is ***p,*** where *p* is any number between 0 and 1*. T*hen that of moving to the left will be ***q= 1-p*** therefor*e* ***p + q= 1***. In our case **p= q= 1/2**. Now if we start our trials of flipping the coin, we can easily notice that the walker will mostly hover around 0 (which is the average value).



But for many trials the distribution will spread out and the probabilities of a walker being at a specific location begin to form a normal distribution (bell curve). And it has been observed that for such a random walk of N steps most of the time the walker will be in between $\sqrt{\mathbf{N}}$ and $-\sqrt{\mathbf{N}}$. This is known as a simple random walk and its results can be explained using concepts of probability theory such as the central limit theorem and the law of large numbers.



Now let's take the case of a biased coin where p and q are not equal. Say ***p= 1/4*** then ***q= 3/4***. Therefore, the smaller p is the more biased it is to the left and the bigger p is the more its biased to the right. This is a binomial process with probability *p*. Then the average distance gone in one step is

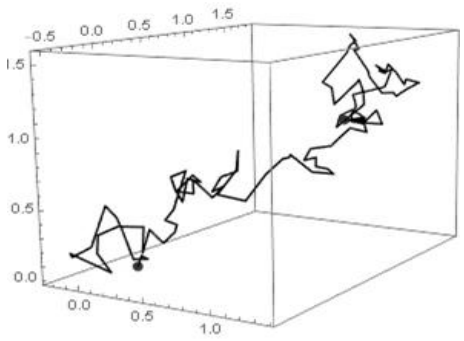
$$\boldsymbol{Avg= (p)(+1) + (1-p)(-1) = 2p-1}$$

So, for N flips the expected value would be ***Avg=N(2p-1)***. Now let's say *p=3/4* then *q=1/4* and hence the *Avg=1/2*. Then the resulting distribution is still a normal distribution but, skewed to the right since *p* has the higher probability, and has its mean value around (1/2) *N.* Hence certain characteristics of the walk can be obtained from the probability distribution.

A 1-D simple random walk random walk is an example of a Markov chain. A Markov chain is a mathematical system that experiences transitions from one state to another according to certain probabilistic rules. The defining characteristic of a Markov chain is that a sequence of possible events, the probability of each event occurring depends only on the state attained in the previous event, where the probability of moving from on state to another is called the transition probability.

A 2-dimensional integer random walk follows similar rules as the simple random walk. Where we the walker starts out at the origin and is equally likely to move up or down or left or right i.e. Four different directions. In general, for random walk along a d-dimensional integer lattice there are *2d* directions to move and the probability of moving in either direction is (½)d. The distribution here will also be a normal distribution around the bell curve, but in higher dimensions. Random walks can be broadly defined as recurrent or transient. A recurrent walk is guaranteed to return to its starting position while a transient walk has a positive probability of this never happening. 1-D and 2-D random walks are proved to be recurrent, in fact they return to their starting positions multiple times. But 3-D and walks in higher dimensional integer grids are transient. An intuitive understanding for this is that in higher dimensions there is more space to move and hence more options to move away from the origin.

2-D random walk



3-D random walk

While the 1-dimensional random walk is easy to understand it is too simple to describe anything in nature. Natural or random phenomena are usually described by higher dimensional random walks. Even 2-D and 3-D random walks can satisfactorily explain many random physical phenomena. Applications of random walks are used describe in a range of phenomena like population genetics, Brownian motion, population dynamics, polymers, image segmentation etc.

Self-avoiding Random Walk:

As its name suggests, it's a RD which does not allow visiting the same point more than once. Such RD cannot be called a truly random or even a Markov process. In one dimension the problem becomes trivial as the walker will only be able to move in one dimension. In two or more dimensions it becomes so difficult that it is almost impossible to solve.

Off-lattice Random Walk:

This type of random walk doesn't have a trajectory restricted to the lattice sites. Based on the imposed conditions it can randomly walk off the lattice sites e.g. Consider a random walk on a uniform square lattice where the random walker doesn't necessarily jump from one lattice site to another in the four directions, instead it moves with a certain step length in any direction. Where the step length will have to be a function of the angle as well as direction.

Monte-Carlo simulations:

A Monte Carlo method are essentially solving a problem using stochastic methods. A stochastic process is a mathematical object or system defined by multiple random variables. The terms *stochastic processes* and *random* processes can be used interchangeably. It's always involves generation of random numbers to access different configurations (distributions or microstates) of a system. MC simulations are widely used to solve problems in statistical physics especially that of phase transitions. They are useful for solving problems that can't be solved analytically. A widely known example is of the Ising model, where the MC method is used to study phase transitions in magnetic materials. MC methods can be described through the following steps:

1. Define a set of possible inputs within a certain range i.e. establish the variables which could be used to describe the system.
2. Generate input randomly from a probability distribution over the domain.
3. Perform a deterministic computation on the inputs.
4. Aggregate the results.

The inputs are supposed to be truly random (as its often difficult to generate completely random numbers) and the number of inputs should be large i.e. many trials should be carried out for a given simulation otherwise it would turn out to be a poor approximation. The **Ziff–Gulari–Barshad (ZGB) model** is a simple Monte Carlo method for catalytic reactions of oxidation of carbon monoxide to carbon dioxide on a surface. The model can be classified under the directed percolation model (percolation in a specific direction due to some force). The model consists of these three basic irreversible steps:

1. *Adsorption* of the reacting species CO and O_2

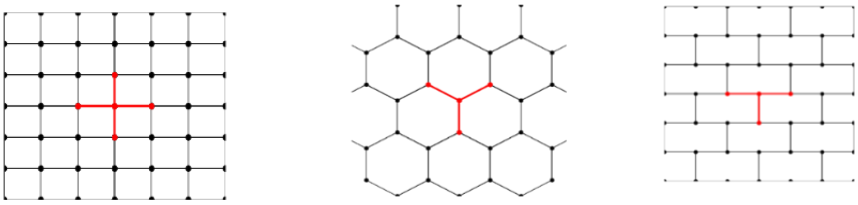
2. The actual *reaction step* on the surface: CO + O → CO_2
3. Desorption of the products.

The production of carbon dioxide from catalytic surfaces is of fundamental interest from both scientific and technological points of view.

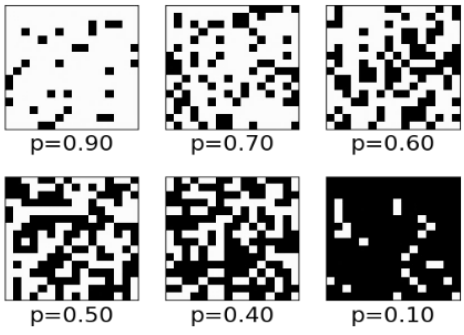
- **Percolation theory**

Percolation is the process by which a fluid or similar substance moves through a porous medium e.g. The process of making coffee, where the water (solvent) permeates through the coffee grounds and the chemical compounds (soluble constituents) seep through the filter paper or when rainwater seeps underground and travels through the tiny spaces between rocks and soil particles. But in a mathematical sense it refers to simplified model of a random system made up of a grid or lattice structure and the nature of connectivity in it. The mathematical study of percolation, known as percolation theory, brings new understanding to a variety of topics in various fields. Percolation processes typically exhibit universality (Here it applies to the behavior of a lattice models in the limit of the lattice spacing going to zero .i.e. the number of lattice sites or bonds in the model is so high that it basically acts as a continuous medium instead of a discrete set of points). Concepts of statistical mechanics such as universality, renormalization groups, phase transitions, scaling theory, critical phenomena and fractals which are used to characterize percolation clusters.

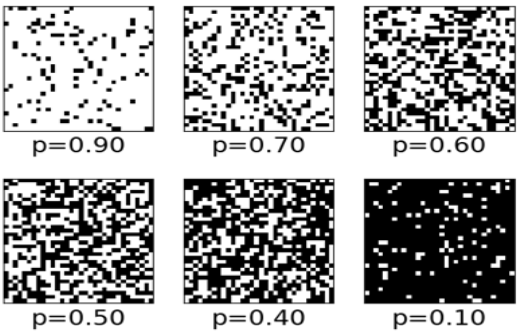
Consider a square lattice (array) of size N×N on which consists of lattice points usually called "sites" and the edge between two neighboring sites are called "bonds". The sites are filled with a probability ***p* (*0<p≤1*)**, or absent with a probability ***1-p.*** When *p* is small there is a small population of bonds (adjacent nearest-neighbor sites that are filled in either of the four directions). In this square lattice which is a 2-Dimensional array we have 4 nearest neighbors while in a 1-Dimensional array we would have only 2 nearest neighbors. So, for an *N*-Dimensional array we would have $\mathbf{2^n}$ **neighbors**. Universality asserts that the type of lattice doesn't have a significant effect on the mechanism so simulations can be done a triangular or even hexagonal lattice of the same size (given the lattice size is large). Now here the sites are either isolated from each other or form small groups with their nearest neighbors, these groups are called clusters.



The percolation cluster in the physical world is an example of a porous medium that allows a liquid to pass from one end of the medium to another depending on whether there is a path for the liquid to flow through. Now if we consider this example analogous to our model then the cluster formed due to occupation of sites acts as the porous medium and the occupation probability *p* signifies and open bond (allowing liquid through) and *1-p*, a closed one. Hence several adjacent occupied sites from one end of the lattice to another will signify a path for the flow.



16×16 square lattice



32×32 square lattice

64×64 square lattice

Three different figures for percolation on a 16×16, 32×32, 64×64 square lattice for p=0.1, 0.4, 0.5, 0.6, 0.7, 0.9. (a white square block signifies an Occupied site and black ones signify empty sites). If *p* is close to 0 most occupied sites will be either isolated or form only few clusters of very small sizes (p=0.1=10%). On the other hand, if p is close to 1 then nearly all occupied sites are connected to each other, forming a singular large cluster spanning the whole length of the lattice (p=0.9=90%) also called an" **infinite" cluster**.

While this isn't easily observed for smaller lattices these infinite clusters can be clearly observed above a certain value of p close to 0.6 for a large lattice. This clear distinction exists for large lattices. Such large lattices could be called as infinite lattices for which there exist a clear threshold value of p called as a critical point **" p_c"** where for the first time an infinite cluster network percolates throughout the lattice with finite probability. This clearly indicates a phase transition. The percolation threshold is not a universal quantity, its value is sensitive to the details of the model.

Percolation transition is characterrized by a set of critical exponentsThese exponents describe the fractal properties of the percolation medium at large scales and sufficiently close to transition. The study of percolation theory and the methods used to model a percolation cluster acts as a basis for better understanding the working of Diffusion limited aggregation.

- **<u>Diffusion Limited Aggregation (DLA):</u>**

Most physical, chemical and biological phenomena that give rise to natural or random patterns is due to some interaction between transport phenomena and thermodynamic properties. Convection, Conduction and diffusion are the dominant transport mechanisms out of which diffusion is prominently observed in various natural settings like formation of river networks, frost on glass, veins of minerals in geological formations and also in laboratory settings like ion deposition, electro deposition, solidification processes, thin film mechanisms etc. In the past decade a huge amount of research has been done to create algorithms for such kind of growth processes. In most of these algorithms a particle travels through a medium until it comes into contact with another particle or cluster of particles; then the roving particle sticks fast, becoming a member of the cluster. The process is repeated thousands of times, building up a connected aggregate whose geometry might be dense or fine, compact or ramified, directional and dendritic or almost compact sphere like-depending on the conditions imposed on the movement of the particles and surfaces on which they take place. This serves as a model for process like

A Lichtenberg figure

DLA cluster grown from a copper sulfate solution in an electrodeposition

crystallization, condensation of colloids and polymers, of ions and molecules on thin films, breakdown of dielectrics, cracking and fracturing in solids and the growth of tumors and bacterial colonies.

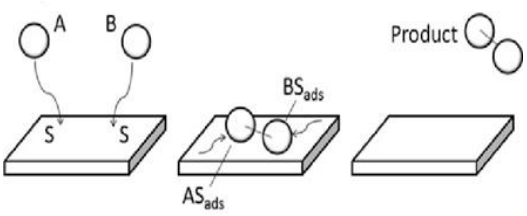
One of the models created to study these phenomena is the DLA model. As its name suggests DLA is a simulation of a type of controlled reaction where the reaction mechanism is primarily an effect of diffusion of particles. Diffusion limited growth processes have been subject of considerable theoretical interest in recent times with most of the research focused on establishing the relationship between the geometry of clusters and their growth mechanisms. Diffusion limited reactions (DLR) are commonly used studied kinetics of catalytic surface reactions. In order to do this, we need surfaces on which the reaction can take place These surfaces used in real life aren't always uniform and isotropic, hence we need to generate rough surfaces E.g. DLA surface.

Reactions on surfaces:

Heterogenous catalysts has immense importance in chemical technology. Heterogenous catalysts are types of catalysts that are in a different phase from the reactants or products. These types of catalysts are especially useful since they themselves do not get consumed during the reactions. The atomic and electronic structure of the catalytic surfaces, as well as the adsorption and reactions on them, are examined by surface spectroscopy and surface microscopy. Often these catalytic surfaces are not perfectly fractal or perfectly uniform, being somewhere in between. For many industrial chemical reactions, noble metals like Pt, Pd or Rh are used as catalytically active materials. But these are highly expensive so they cannot be used in their pure form. Usually a thin layer of noble metals is coated over some other inert support. Hence the random deposition and other similar models are used to generate such surfaces. Also, in such surface reactions at least one of the steps is adsorption of reactants. The general form of the reaction is A+ S ⇌ AS → products where A is the reactant and S is the adsorption site on the surface. Factors affecting the reaction are the rate constants for adsorption, desorption and reaction, concentration of adsorbate, number of occupied sites and unoccupied surface sites and surface coverage (the fraction of sites occupied). Two such common reaction mechanisms are: Langmuir–Hinshelwood and Eley Rideal mechanisms. As shown by ***Chaudhari et al. (2004) [7a]*** for monomer dimer reactions:

Langmuir–Hinshelwood (LH) mechanism: The distinguishing feature of an LH reaction is that both the reactants (A & B) are adsorbed on the surface prior to reacting to for the product (AB). The product may stay on the surface or desorb. Following are the steps of the mechanism:

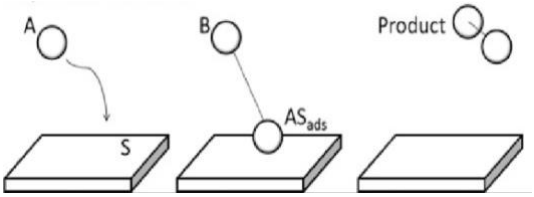
a) $\mathbf{A_g + * \rightarrow A_s}$
b) $\mathbf{B_{2g} + 2_* \rightarrow 2B_s}$
c) $\mathbf{A_s + B_s \rightarrow AB_g + *}$



Where the subscripts g, s and * denote gas phase molecule, adsorbed molecule and vacant surface site.

Eley-Rideal (ER) mechanism: The only difference here is that at least one of the reacting species is not adsorbed locally prior to the reaction, hence not in equilibrium with surface temperature. ER mechanism can be simply represented by the following reaction equation:

a) $\mathbf{A_g + B_s \rightarrow AB_g + *}$

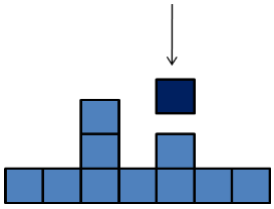


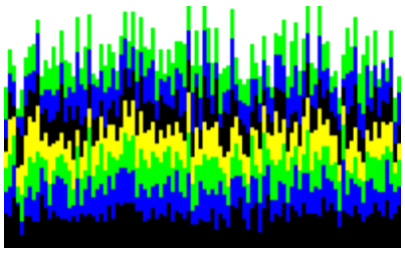
The common surface models used to simulate such DLRs are:

1. Random deposition (RD)
2. Random deposition with diffusion (RDWSD)
3. Eden model
4. Ballistic deposition (BD)
5. Witten-Sander model (DLA)

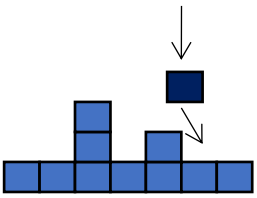
Although the literature has covered a variety of topics, this review will focus on the simulations done using these five major models that will repeatedly studied by researchers. The following part of this section will be about the description of these models, methods of simulations, specific parameters introduced to modify the models, minor details of the analysis and results.

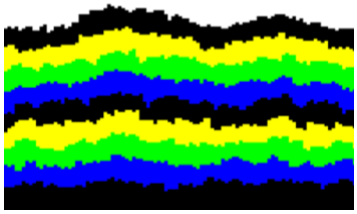
The **random deposition** model also known as the rain model, is the simplest way to generate rough surfaces. It involves picking a column on random from the length of a flat surface. Then particles are dropped from above and fall in a straight-line trajectory until they stick to the cluster. There is no guarantee of the surface being porous like BD.



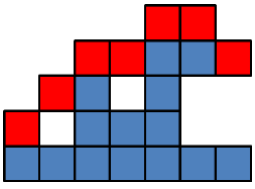


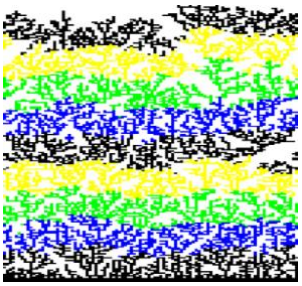
In **random deposition with surface diffusion** a particle can move a short distance to find a more stable configuration. The particles can diffuse on the surface on its nearest neighbors from the column in which they were dropped, until they find the position with the minimum height (or maximum, depending on the conditions specified). Commonly the randomly launched particle reaches the top of the column (i) having neighbors on its left (i-1) and right (i+1). It can then move to the column with the minimum height, this process continues till it finds the column with the minimum possible height.This model is used in chemical vapor deposition methods which are widely used for the preparation of supported catalytic materials. In both RD an RDWSD it was found that the bulk and the surface mass do not have fractal properties while the width of the surface is a self-affine fractal exhibiting non-trivial scaling with the surface height and the system size.

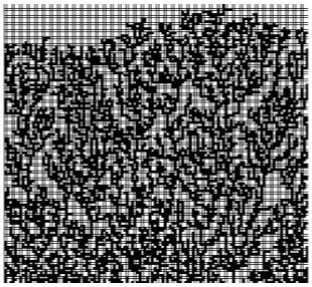




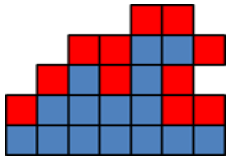
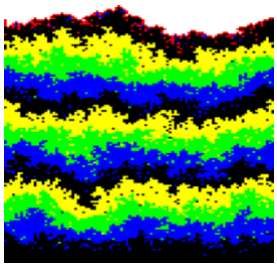
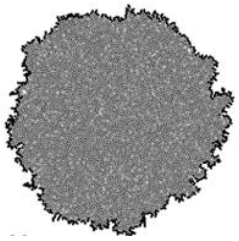
In **ballistic Deposition**, Particles when dropped vertically from above stick to a particle below or its neighbour on either side. The surface generated by BD is a porous structure. Despite of the sizes of the empty regions being widely scattered, the structure can be considered homogeneous on a large length scale. BD and RDWSD show correlations between different columns while random deposition doesn't.



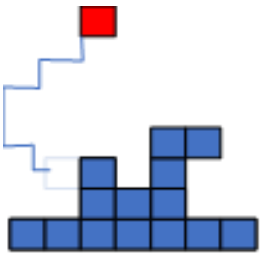
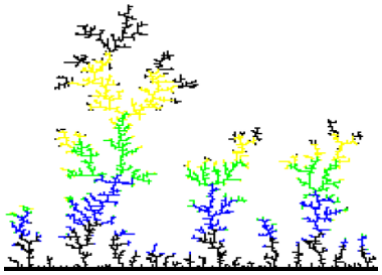
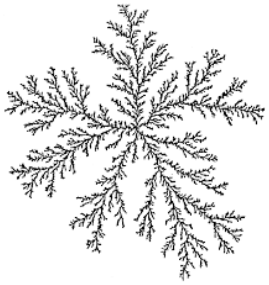




The **Eden growth model**, first described in 1961, was one of the earliest to describe something close to the DLA model. IT describes the growth of specific types of clusters such as tumor growth and deposition of materials. It is a space filling growth process. These clusters grow by random accumulation of material on their boundary. It worked as a way of studying biological growth and was simulated on a computer for clusters up to about 32,000 cells. By the mid-1980s, clusters with a billion cells had been grown, and a slight anisotropy had been observed. One simple model for this is as follows: Pick a random point and consider it the seed particle. Choose one of the nearest neighbors to the seed at random, and that's the next particle added to the cluster. Since all the sites have equal probability of getting selected this kind of growth gives almost completely dense clusters imitating bacterial colonies and epidemic spread. It's easier to generate large clusters due to its relatively simple algorithm.

Earliest account of the diffusion-limited aggregation (DLA) model was proposed by ***Witten and Sander(1981)[11]*** which was a slight variation on the Eden model, introduction of the random walk. The particle undergoes a random walk before attaching itself the cluster. These random walk trajectories are added to the aggregate one by one. If the particle went outside the lattice boundary, it was terminated. They ran the simulation for 3600 particles.

***Chaudhari et.al. (2002a)[6a], (2002b)[6b] and (2004a)[7a*]** have utilized the RD and RDWSD models to perform Eley-Rideal DLR's over rough surfaces while comparing the results to reactions performed over DLA's such as the cantor set, devil's staircase and the Sierpinski Gasket. The procedure followed for both models is the same as discussed before. Every particle is guaranteed to stick to the surface. Every time a particle is added to a column the reaction count of that surface site is increased by one. The number of particles used ranges from the order of 10^4 to 10^8 and the substrate length L ranging from 200 to 1600 lattice units. The surface thickness can be expressed as:

$$\mathbf{t} = \left[\frac{\sum_i (\mathbf{h_i} - \mathbf{H})^2}{\mathbf{N_s}}\right]^{1/2}$$

Where $\mathrm{h_i}$ is the height of the ith column, $\boldsymbol{H} = \frac{\sum_i \boldsymbol{h_i}}{\boldsymbol{N_s}}$ is the mean height and $\mathbf{N_s}$ is the number of surface sites. In most cases $\mathrm{N_s} = \mathrm{L}$. The overall surface h roughness was defined as:

$$\boldsymbol{S_r} = \boldsymbol{h_{max}} - \boldsymbol{h_{min}}$$

Where $\boldsymbol{h_{max}}$ & $\boldsymbol{h_{min}}$ are maximum and minimum heights of columns. After depositing enough particles to generate the surface, the particles are turned into the reacting species. Different cases were also studied such as keeping the lattice size same while varying the number of particles launched and vice versa. Empty sites available for the particle to occupy are called active sites, and they increase as the substrate length is increased. RD generally shows a homogenous probability distribution while RDWSD has a spike shaped distribution with a greater number of non-active sites.

Chaudhari et.al. (2003)[9] and (2005a)[8a] also adopted the same model for RD except for the addition of a factor called the initial sticking probability P_{ini}. If P_{ini} in taken to be 1 then every particle is guaranteed to stick to the surface, which is of course not realistic as the rate of sticking may vary throughout the physical reaction and all sites would have non-zero activation energy. The sticking probability for individual sites was defined for each site using decay and enhancing function. These functions help replicate an auto-poisoning reaction. The decay function is defined as:

$$P(n_i) = P_{ini} \exp(-n_i/m)$$

Where n_i is the reaction count of a site ***i*** and ***m*** is used to adjust the rate of decay. A lower value of *m* causes faster decay while a higher value leads to faster decay. The reaction probability distribution for different values of P_{ini} and ***m*** were studied. A random number is generated whenever a particle reaches a site, and is compared with ***P*** which lead to one of the two cases:

- **Case 1:** ***Random number*** $\leq$ ***P,*** then $n_i = n_i + 1$**, otherwise new particle is launched.**
- **Case 2:** ***Random number*** $\leq$ ***P,*** then $n_i = n_i + 1$**.** But if ***Random number*** $>$ ***P,*** then the particle can randomly move in either direction but only onto columns with heights less that its current column, if an adjacent column is larger, new particle is launched.

Similarly, **Chaudhari et.al. (2005b)[8b]** have expressed the sticking probability of adsorption as:

$$P = f \exp(-\Delta E/kT)$$

where ***(-*** ΔE is the binding energy, ***T*** is the surface temperature, ***f*** is a pre exponential factor and ***k*** is the Boltzmann constant. Also, the rate of reaction ≈ ***kΘ*** was used as parameter in the Monte-Carlo algorithm, where Θ is the coverage of the absorbate.

Monomer-Dimer reactions are a type of heterogeneous catalytic reaction. They can be studied using ER as well as LH mechanisms. ***Chaudhari and Lee (2008) [10]*** *and* ***Chaudhari et.al. (2004b) [7b]*** have studied ZGB square lattice models. While both have studied mono-dimer reaction based on LH mechanism and its effects on production rates and coverage of the species for varying sticking probabilities, the former also includes its effect on phase transitions. The latter has performed both ER and LH reactions on surfaces generated by RD and RDWSD and gives details of the steps involved in the simulation. The simulation is performed over a 2-D surface with the column are broken into unit cells with co-ordinates (i, j). Also, a larger than usual number of 10^8 particles is used on lattice of length L=75 lattice units. Following are the steps for the LH mechanism simulation:

a) Particle is randomly dropped on a column, if site is already occupied then trial ends and new particle is launched.
b) The particle is chosen to be a monomer (A) or dimer (B) with probability (y_A) and (1-y_A) $respectively$.
c) A can adsorb onto a single empty site while B, once incident on an unoccupied site checks for one more empty site with same height in the nearest neighborhood. If this condition is met, then B_2 is adsorbed into two sites as B.
d) After adsorption if A and B_2 happen to be nearest neighbors at the same height, reaction occurs, and they desorb leaving behind two empty sites. If the heights do not match, reaction does not take place.

In case of ER mechanism if in step a) the incident molecule is A and the site is also occupied by A, then the molecule is backscattered i.e. trial ends. If the site molecule is B then both desorb leaving one empty site, completing the ER process.

Chaudhary et. Al (2004c)[7c] have again studied the ER mechanism over a surface created using RD but the difference being the usage of dynamic scaling theory for analysis instead of multifractal scaling. The process remains the same as previously mentioned. The Following equations are used for analysis:

$$P(x, y, h; t) = \frac{r(x,y,h;t)}{r_{\Sigma}(t)} \qquad (1)$$

$$P_a(t) = \frac{\Sigma P(x,y,h;t)}{N_f} = \frac{1}{N_f} \qquad (2)$$

$$\sigma(t) = \left[\frac{\Sigma (P(x,y,h;t) - P_a)^2}{N_f}\right]^{1/2} \qquad (3)$$

P is the count of the number of particles visited at individual sites at time t, where *r* (*x, y, h*; *t*) is the reaction event occurring at (*x, y, h*) at time t. r_{Σ} is the total number of reaction events. The tern t essentially indicates the occurrence of an event. $\boldsymbol{N_f}$ is the number of free sites (only sites that are accessible to the particles) P_a is the average probability of each site. The resultant RPD is heterogeneous due to higher probability of reaction at the top surface sites. This is measured by standard deviation of ***P*** denoted by ***σ(t***). An analysis of this type basically requires us to obtain scaling relations for certain quantities. In this simulation the relations obtained are:

for σ with t:	$\boldsymbol{\sigma = t^{\beta}}$	***(4)***
& as σ becomes independent of t at $\boldsymbol{t \to \infty}$:	$\boldsymbol{\sigma = L^{\alpha}}$	***(5)***
With the combined expression	$\boldsymbol{\sigma\ (t, L) = L^{\alpha}\ f\ (t/\ L^{\gamma})}$	***(6)***

where $\boldsymbol{\gamma = \frac{\alpha}{\beta}}$**.** ER reactions performed over different rough surfaces with different as well as same surface densities to calculate $values\ of\ \alpha$ and β to find the dependence of the scaling exponents on surface heterogeneity. It was concluded that these exponents are independent of surface roughness.

Witten and Sander (1981) observed that their DLA model acted like a "critical" object i.e. having scale independent correlations over a large length scales similar to percolating clusters or self-avoiding random walks and percolating clusters. They also noticed that critical correlations arise due to the irreversible growth process. Investigations of the properties of the model have shown to produce branched fractal clusters that strongly resemble adsorption patterns in in variety of physical situations.

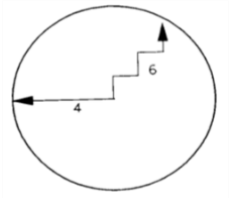
Certain features of such geometries can be explained by the fractal dimensionality. It is often useful to think of the fractal dimension of fractal objects as the exponent that describes the scaling relationship between mass (or measure, μ) (M) and length (L) denoted by **M~** $\boldsymbol{L^{D}}$. Here mass could be interpreted as the space the object occupies.
Where D in case of a Euclidean object would be its dimension. E.g. 2 for a square. This could be considered analogous to the density of an object. Density is irrelevant to classical geometry, but fractals have the unique feature of decreasing density with increasing length scale. Therefore, as the length scale is μ times bigger, the mass obeys the following relation:

$$\mathbf{M(\mu L) = \mu^{D_f}\ M(L)}$$

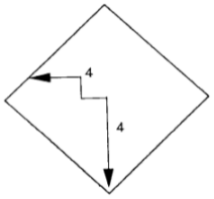
Where D_f is the fractal dimensionality giving us a kind of **power law** relation. This relationship shows how mass scales as function of linear size .The average ratio of nearest-neighboring number for a DLA cluster should remain constant if the fractal dimensionality is constant during the aggregation process, though this is not always the case (as these clusters are not perfectly self-similar but instead self-affine). In a two-dimensional lattice there are four nearest neighbors at maximum and six in three-dimension space. If the fractal is compact, the proportion of particles having higher neighboring number will be elevated and vice-versa. The process produces a relatively compact cluster whose density correlations are independent of distance in the limit of large size.

Luo et.al. (1991) [12], *and* ***Lee & Luo (1992)[13]*** have given detailed explanations for simulations of 2-D and 3-D DLAs studied the effects of different launching boundaries by essentially creating two models, each giving different results by introducing minor changes. Their DLA model was a modification on the Witten-Sander model. Efforts are made to create a model that is easy to reproduce and wouldn't have too many changing variables, reduce simulation time. The random walk imposed is self-avoiding in nature. Basic procedure is a combination of the percolation cluster and random walks as stated earlier. One of the most important features of the model is the launching boundary or perimeter which consists of one the points on which the particle begins the random walk. Launching perimeters can be square or circular in shape and spherical or cube like for 3-D models. The particles launched, undergo a RD on the lattice until they reach the seed. Particles launched from square boundary are equi-stepped (only dependent on lattice constant i.e. step length) while ones launched from a circular perimeter are equidistant from the seed. Considering a 2-D model, a square launching perimeter means all neighbors are at equal distances and has an equal probability of moving in either direction, but the circular fence means each step is a function of the angle, given by the express

S= R (sin | mod (Θ /90º) | + cos | mod (Θ/90°) |)



Circular equi-distant boundary



Square equi-stepped boundary

Where S is the least steps to the seed particle, R is the radius of the circle with launching perimeter as the circumference and the seed as the center, ***Θ*** is the rotating angle from x-coordinate and have values equal to 45° + 90° x (x =0,1,2,3 corresponding to each quadrant of a circle). And it was observed that a circular launch perimeter leads to more random walk time due to the resulting irregularity in walk directions, (since we considering a uniform square lattice, results might differ in case of an off-lattice walk) hence affecting the overall results of the simulation. The launching perimeter is at a distance $\mathbf{R_{max} + 5}$ units of lattice constants from the center seed. The DLA overall has three different boundaries, inner (R_{in}), outer (R_{out}) and Maximal cluster radius (R_{max}) . The inner and outer radii are modeled to expand equivalently to save run time. The relation between the three radii is given as

$$\mathbf{R_{max} : R_{max} + R_{in} : R_{max} + R_{out}}$$

$\mathbf{R_{in}/R_{out}}$ usually has ratio of about 0.5**.** A particle is allowed to walk only up to a certain distance, in this case its $\mathbf{3R_{max}}$. If the particle moves out of this radius its terminated and a new particle is launched. Aside from these common features following are the differences in the two models:

The first model has a fixed center meaning the seed particle remains in the same place. For this model a simulation of 2000 to 16000 particles with a square launching boundary gives an isotropic cluster whereas a circular one gives slightly diamond shaped cluster. Results obtained from this simulation are in good agreement with the experimental results. The second model has moving seed particles. Hence the center of the growing cluster is randomly chosen after every time a particle is launched. The inner and outer perimeter are changed along with the launching boundary, centered at the randomly chosen seed particle. Some points of the launch radius on each turn may fall on one of the occupied sites of the growing cluster, in that case another point on the radius is chosen until all points on the circle are occupied. Then the center is changed hence choosing a new launch circle. This method helps create a cluster with constantly varying fractal dimension.

The sites on the lattice were designated values based their status and number of surrounding neighbors. Vacant sites, occupied sites and any vacant nearest neighbor site were denoted by 0,1 and 2 respectively. Particles on the vacant sites (0) are free to move and allowed to settle on any nearest neighbor site (2), and on settling are fixed to the site (1).It was clear that a square launching boundary is much more effective than a circular perimeter. Limiting cases for cluster in both directions was also significant. When extrapolated to a large cluster size was like the Eden cluster i.e. Dense interior, and when extrapolated to zero cluster size behaved like the Witten sander model i.e.no chance of particles attaching to the interior core.

In addition to using the same procedure ***Lee et.al (1993) [14]*** also performed Eley-Rideal reactions on the DLA surface. Here a large number of particles is deposited to form the DLA surface. On reaching the required limit the launched particles are turned into reacting species. Once one of these particles reaches a surface site, the reaction count is increased by one. Then the Reaction probability distribution (RPD) is obtained once large enough particles are launched. Results of the simulation of different surfaces such as DLA Cantor set, and Devils staircase were comparatively studied. It was noted that even for a basic reaction mechanism like E-R, catalysis shows high sensitivity to the structure of the surface. **Lee and Lee*(1994) [15]** introduced the sticking probability and also decay and enhancement functions to study the RPD profiles.

L.Niemeyer et. al (1984) [16] discussed how dielectric breakdown results in a discharge patterns that are fractal in nature. At, above the materials dielectric strength a material that is normally an electrical insulator may begin to conduct electricity – i.e. it ceases to act as a dielectric. This is known as dielectric breakdown. They did a comparative study of the theoretical model with satisfyingly designed experiments. The experiment was designed to produce, to a good approximation, an equipotential channel system growing in a plane with a radial electrode from a central point, analogous to cluster created by DLA processes. Analysis of the Lichtenberg figure (branching dendritic structure associated with electrical discharges) showed a power law relation between the fractal dimension and the number of branches within a radius r from the center of the circle at D=1.7. $\mathbf{n(r) \sim \frac{dN(r)}{dr} \sim r^{(D-1)}}$ While the number of points inside given *r* itself is a power law with *D:* $\boldsymbol{N(r) \sim r^{(D)}}$

Paul Meakin (1985) [17] described a more complex algorithm to quantitatively explain the diamond shaped distortion in DLAs by introducing a new parameter (R). Unlike the usual Witten-Sander model Meakin adopted an off-lattice random walk for the simulation. The parameter R is the ratio of the sum of projections of co-ordinates along the lattice axes to that of the diagonal axes: $R = \frac{\Sigma\ projections\ onto\ lattice\ axes}{\Sigma\ projections\ onto\ diagonal\ axes}$

The Ordinary density-density correlation function is expressed as:

$$\mathbf{C(r) = \frac{1}{2\Pi r N \delta r}\ \Sigma\ \rho(r')\ \rho\ (r'')}$$

ρ(r) is 1 for occupied states and 0 for unoccupied ones. Meakin also defined correlation functions w.r.t bond vectors b(r) which define the bonds associated with pairs of particles by a distance δ. The bond correlation function is given by:

$$\mathbf{C'(r) = \frac{1}{2\Pi r N \delta r}\ \Sigma\ |\ b(r') \cdot b(r'')\ |}$$

&

$$\mathbf{C''(r) = \frac{1}{2\Pi r N \delta r}\ \Sigma\ b(r') \cdot b\ (r'')}$$

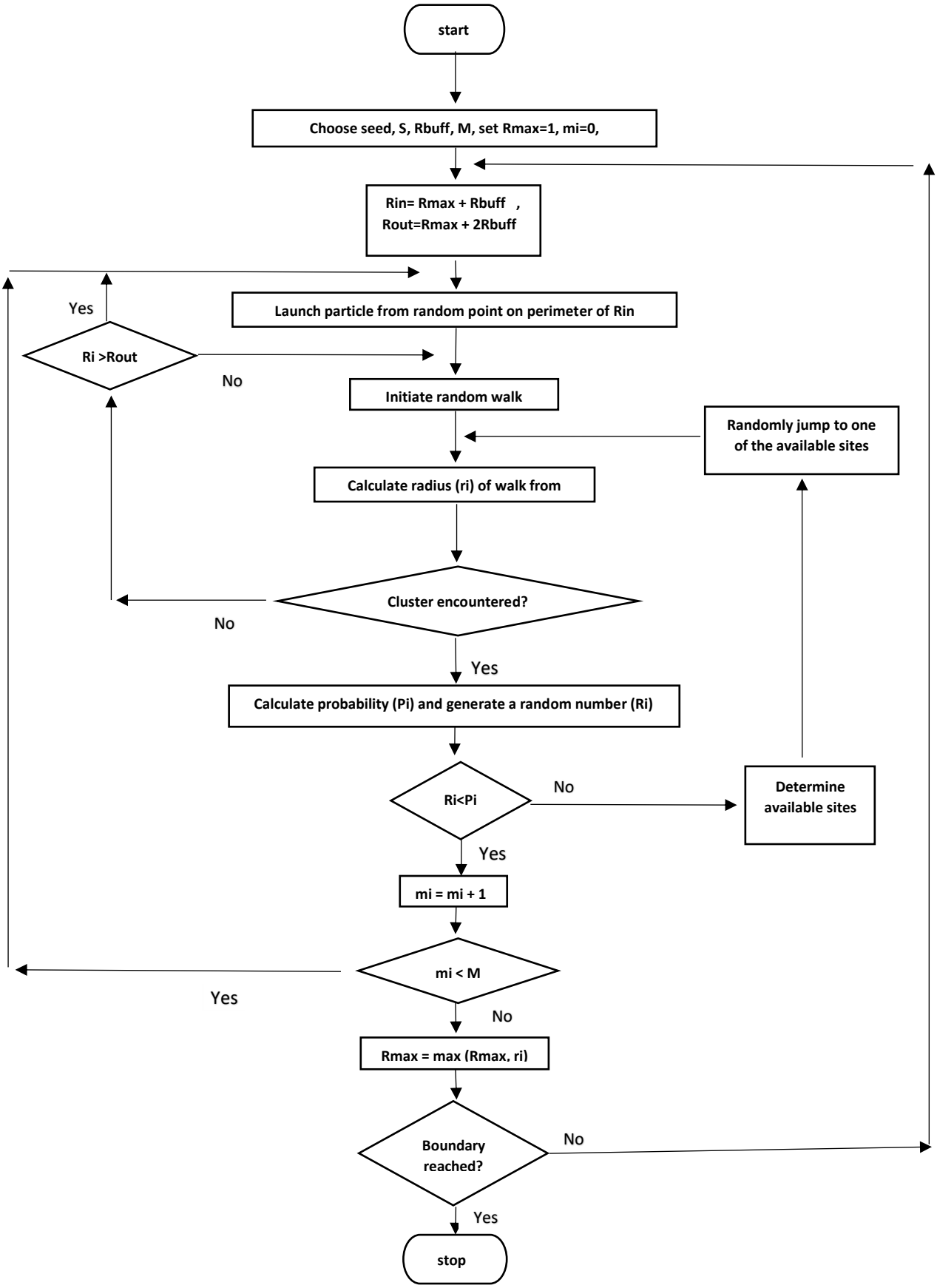
While C(r) and C'(r) scale similarly, C"(r) is shown to have a different scaling exponent. Measurements of these bond correlation function lead to the conclusion that growth in DLAs is highly directional.

Chiu et.al. (1992) [18] gives a detailed account of the usage of the Monte-Carlo algorithm in DLA simulations with emphasis on the effect of sticking probability (S) and mean field parameter (M). The aim of introducing these parameters was to emulate physical processes and pattern formation due to some kind of local field intensity or concentration gradient. In addition to S, M acts as a factor contributing to diffusion. M serves as a tuning factor to simulate different degrees of non-equilibrium during the growth process. The significant distinction of this model is that, a particle on encountering a cluster site neighbor, isn't allowed to attach itself immediately, instead the encounter on the site is registered(mi). That site remains unoccupied until the number of times it is visited exceeds the mean field parameter. For M=1 corresponds to the normal DLA model gradually growing from isotropic to anisotropic. As $M \rightarrow \infty$ the model corresponds to the solution of a diffusion equation.

The simulation also included a buffering annulus (Rbuff) for diffusion to take place, which increased in width with respect to the growing cluster. It was observed that the center of mass (CM) of the cluster may shift as the cluster grows, hence it needs to be recalculated at every step and accordingly choose the new launching radius. The fractal dimension can be expressed in either of the two ways:

1. $\boldsymbol{N\ (r_g) \sim\ r_g^{\ D}}$ where r_g is the radius of gyration for the cluster and N (r_g) is the total number of particles within the cluster.
2. $\boldsymbol{N\ (R) \sim\ R^D}$ Where R is the distance from CM and N(R) is the number of particles within a circle of radius R.

Following is the algorithm used in the simulation:



While most of this section has been dedicated to explaining process of simulation, very little has been mentioned about the analytical techniques used to characterize these clusters. This is because most of the

papers mentioned apply multifractal analysis to their simulations and all have cited ***Halsey et al. (1986)*** for reference. The last section gives a brief description of this method.

Multifractals in DLA:

Multifractal analysis has been used as an effective analysis tool for investigating diffusion limited aggregates. Specifically, the method of moments (powers of scaling variables) is used here. As mentioned earlier multifractal scaling relates to the analysis of a distribution of an object over a finite volume, which in case of a DLA is the reaction probability over the size of the DLA cluster. P_i denotes the reaction probability of a site i, ***n(P)*** is the number of sites with reaction probability P and, L is the linear size of the fractal object (Length in case of BD, RD and RDWSD and average radius or DLA). Certain assumptions were made for the limiting case of L:

$$P(q) \propto L^{-\alpha(q)} \quad (1)$$

$$n[P(q)] \propto L^{f(\alpha)} \quad (2)$$

also $$M_q = \Sigma_i P_i^q = \Sigma_P n(P) P^q \propto L^{-\tau(q)} \quad (3)$$

M_q is the qth-order moment taken into consideration for a given reaction probability distribution, with scaling exponents denoted by α(q), τ (q) and f(α). P(q) denotes the value of P that has the highest weightage in the sum for the ***qth*** order moment and dominating value of α denoted by α(q). Substituting eqs. (1) & (2) into eq. (3) gives

$$\tau(q) = \alpha q - f(\alpha) \quad (4)$$

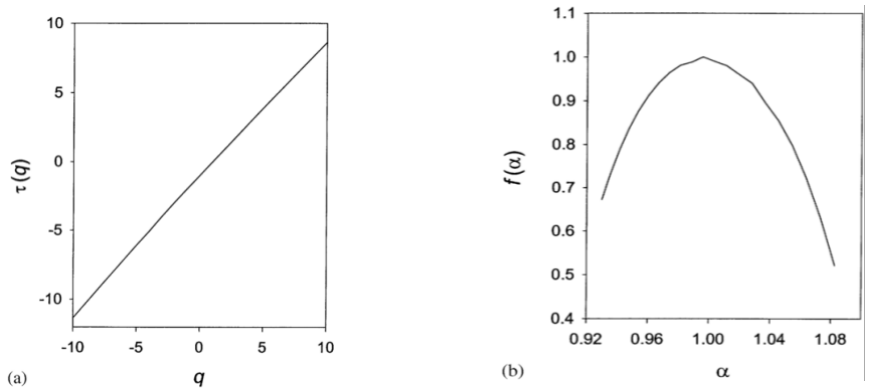
i.e. f (α(q)) = α(q)q − τ (q) which is the dispersion of the fractal dimension.

α(q) can be calculated by $$\alpha(q) = \frac{d\tau(q)}{dq} \quad (5)$$

which can be explicitly written as $$\alpha(q) = \frac{d\tau(q)}{dq} = \frac{\Sigma_i P_i^q \ln P_i}{\Sigma_i P_i^q \ln(1/L)} \quad (6)$$

Multifractality of the object can be analyzed using the two curves: (1) ***τ (q) versus q***
(2) ***f (α) versus α***

values of ***q*** need to be chosen in a way that they satisfy certain conditions. q should be selected such that f (α) > 0 and $D_q = \frac{\tau(q)}{(q-1)}$ where D_q (generalized dimension) can be defined as the distortion of the mean of the probability distribution. Equations (3), (4) and (5) are the three fundamental equations required in multifractal analysis. τ (q) can be calculated for each L from eq (3), α(q) from eq (5) and f (α) from eq (4). The distribution is called multifractal if all the moments in eqn. (3) scale as power laws with an infinite set of independent exponents τ (q) i.e. τ (q) vs q plots are linear.



Typical curves showing multifractal characteristics

- **Conclusion**

The purpose of this review was to help the reader become familiar with the concept of fractals and understand the different aspects of fractal surface generation. This review is supposed to provide a comprehensive view of the work done by all the researchers mentioned. While the individual aims of the papers might have different goals, they have much in common when it comes to the procedures and analysis techniques. With most of the focus on studying growth phenomena of diffusion limited clusters through multifractal analysis, though this review does not go into the details of multifractal analysis. Some of the significant results obtained by researchers have been reported in brief. It is clear that a significant amount of research has been done in this field in the last few decades, with advancements in computing technology making simulations much easier than before.

References

1) Paul Meakin, FRACTAL STRUCTURES (1990) Prog. Solid St. Chem. eel. 20. pp. 135--233.
2) Shailesh. A. Shirali, Fractal Dimension and the Cantor Set (2014), https://www.ias.ac.in/article/fulltext/reso/019/11/1000-1004
3) G Ambika, Ed Lorenz: Father of the 'Butterfly Effect'(2015), https://www.ias.ac.in/article/fulltext/reso/020/03/0198-0205
4) M.Shishikura, THE HAUSDORFF DIMENSION OF THE BOUNDARY OF THE MANDELBROT SET AND JULIA SETS, Ann. of Math. (2) 147(1998), no.2,225-267
5) Tamas Vicsek and Fereydoon Family, Dynamic Scaling for Aggregation of Clusters (1984), PHYSICAL REVIEW LETTERS VOLUME 52, NUMBER 19
6)
   a) Ajay Chaudhari, Ching-Cher Sanders Yan, Shyi-Long Lee*, Effect of surface roughness on diffusion limited reactions, a multifractal scaling analysis, Chemical Physics Letters 351 (2002) 341–348
   b) Ajay Chaudhari, Ching-Cher Sanders Yan, Shyi-Long Lee*, Eley–Rideal diffusion limited reactions over rough surface, Phys. Chem. Chem. Phys., 2002, 4, 5330–5334
7)
   a) Ajay Chaudhari, Ching-Cher Sanders Yan, Shyi-Long Lee*, 2A+ B2 →2AB catalytic reaction over rough surface: the effect of Eley-Rideal mechanism, Catalysis Today 97 (2004) 89–92
   b) Ajay Chaudhari, Ching-Cher Sanders Yan, Shyi-Long Lee*(2004), Dynamic Scaling for Eley-Rideal Reactions Over Rough Surface, DOI 10.1002/kin.20001
   c) Ajay Chaudhari, Ching-Cher Sanders Yan, Shyi-Long Lee*, Multifractal analysis of growing surfaces, Applied Surface Science 238 (2004) 513–517
8)
   a) Ajay Chaudhari *, Ching-Cher Sanders Yan, Shyi-Long Lee *(2005), Auto-poisoning Reactions Over Rough Surface: A Multifractal Scaling Analysis, DOI 10.1002/kin.20062
   b) Ajay Chaudhari *, Ching-Cher Sanders Yan, Shyi-Long Lee *, Eley–Rideal reactions over rough surface: effect of sticking probability, Chemical Physics 309 (2005) 103–107
9) Ajay Chaudhari, Ching-Cher Sanders Yan and Shyi-Long Lee, Multifractal scaling analysis of auto-poisoning reactions over a rough surface, J. Phys. A: Math. Gen. 36 (2003) 3757–3772
10) Ajay Chaudhari* and Shyi-Long Lee, Effect of sticking probability on monomer-dimer reaction, Bulletin of the Catalysis Society of India, 7 (2008)90-95

11) T. A. Witten, Jr and I. M. Sander, Diffusion-Limited Aggregation, a Kinetic Critical Phenomenon, VOLUME 47, NUMBER 19 PHYSICAL REVIEW LETTERS 9 November 1981.
12) Yeung-Long Luo, Wen -Li Yang and Shyi-Long Lee*(1991), Computer simulation of 2-D and 3-D Diffusion limited Aggregation.
13) Shyi-LONG Lee and YEUNG-Long Luo(1993), Simulation of DLA: effects of launching boundary shape and non-fixed center.
14) Shyi-Long Lee, Chih-Hung Chu, Yeung-Long Luo and Jia-Jen Ho (1993), Multi-fractal analysis of DL reactions over surfaces of Diffusion limited aggregates.
15) Chung-Kung Lee and Shyi-Long Lee (1994), Multifractal scaling analysis of autocatalytic and auto-poisoning reactions over DLA surfaces.
16) L.Niemeyer, L.Pietronero, and H.J.Wiesmann (1984), Fractal Dimension of Dielectric Breakdown, VOLUME 52, NUMBER 12 PHYSICAL REVIEW LETTERS 19 MARCH 1984.
17) Paul Meakin, The structure of two-dimensional Witten-Sander aggregates. J. Phys. A: Math. Gen. 18 (1985) L661-L666.
18) K. -C. Chiu, F. -S. Lee, S. -J. Tu, S. -M. Young, W. -Y. Hsu, C. -F. Chen, C. -S. Ro (1992) A Study in Monte Carlo Simulation of Modified DLA, CIIINESE JOURNAL OF PHYSICS VOL. 30, NO. 1
19) Thomas C. Halsey, Mogens H. Jensen, Leo P. Kadanoff, Itamar Procaccia, and Boris I. Shraiman, Fractal measures and their singularities: The characterization of strange sets, PHYSICAL REVIEW A VOLUME 33, NUMBER 2 FEBRUARY 1986