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Experiment 3

Diffusion limited aggregation: generation of a fractal

Key concepts: fractal, fractal dimension, Sierpiński triangle, diffusion limited aggregation (DLA), electrolysis

Introduction

The aim of this experiment is to generate a fractal in an electrochemical process and compare its fractal dimension with that of a fractal generated in a computer simulation. The fractal is generated by electrolysis of an aqueous $ZnSO_4$ solution on a plane surface [1]. Computer simulations use a model introduced in [2].

Theory

Simple linear objects such as e.g. section of a line, an arc of a circle have dimension 1, which means that the mass M of this object is proportional to its linear size L, $M(L) \propto L^1$. Planar objects such as e.g. a triangle, circle, rectangle have dimension 2; $M(L) \propto L^2$, while the spatial figures such as a cube or a ball have dimension 3; $M(L) \propto L^3$. *Fractals* are geometric objects of complex shape for which the relation between its mass and size cannot be described by an integer value 1, 2 or 3. The number describing the dimension of fractals can take fractional values. The fractal dimension d_f is a generalisation of the concept of dimensions of linear, planar and spatial objects. If the mass M of a geometric object depends on its linear size in the following way

$$M(L) \propto L^{d_f}, \tag{1}$$

then the fractal dimension of this object is d_f. Fractals can be obtained, for instance, by self-replication of its elements so any part of the fractal object has the same structure as the entire object. Such object show an interesting relation between the density and size of the object. The larger the area of the object, the smaller its density. When such an object has an infinite area its density reaches zero.

An example of a fractal – the Sierpiński triangle

The Sierpinski triangle is a fractal described in 1915 by Wacław Sierpiński. The Sierpiński triangle (d_f =1.585) can be constructed as follows:

1. Draw an equilateral triangle with a side length of 1. Find the centres of the sides and draw lines joining them. In this way you get four equilateral triangles, each of them has a side length of 1/2. Remove the middle triangle to get:

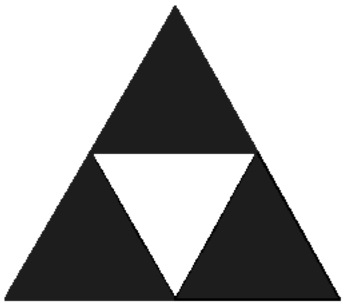


Fig. 1 Generation of the Sierpiński triangle: step1

2. Divide each of the three smaller triangles into four equilateral triangles as above. Their vertices are at the centres of the sides of the triangles obtained in the previous step. Again remove the middle triangles to get:

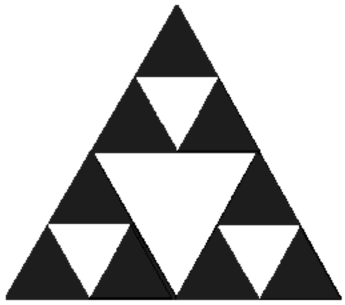


Fig. 2 Generation of the Sierpiński triangle: step2.

3. Repeat the procedure in 2.

After *k* steps the initial triangle will have $1+3+3^2+...+3^{k-1}$ empty triangles of different sizes. The figure given below illustrates the result obtained after 5 iterations:

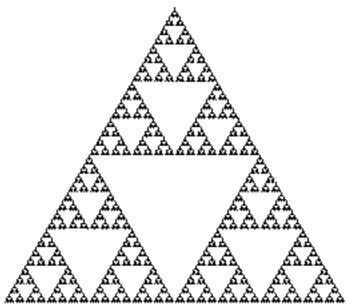


Fig. 3 Generation of the Sierpiński triangle: step 5.

Diffusion Limited Aggregation (DLA)

For the sake of simplicity let consider diffusion in a two-dimensional square lattice. At the centre of the lattice place an immovable nucleus. Draw a large circle whose centre is the nucleus, and place a particle on the circle at a random location. The generated particle performs a random walk which represents the process of diffusion. If the particle is at a site next to the nucleus or to the aggregate formed around the nucleus, the particle is incorporated into the aggregate and another particle is generated on the circle. This new particle begins a random walk. If the new particle moves outside the circle it is removed and a new particle is generated on the circle.

The following algorithm describing this process can be implemented in computer languages such as C++ or python.

1. Draw a square lattice. Empty nodes are assigned a value of 0.
2. At the centre of the lattice place a nucleus, this node is assigned a value of 1 (occupied node).
3. Choose at random a starting position of a new particle on the circle around the nucleus.
4. Choose at random the direction of stepwise random walk the particle (N, E, W, S) and move the particle to the new site.
5. Check if the new site is outside the circle, if so, break the process and generate a new particle, as described at 3.

6. Check if the new site is next to any particle belonging to the aggregate. If so, the particle joins the aggregate, repeat 3, if not, repeat 4.

One of the experimental methods for obtaining DLA aggregates is electrolysis of a water soluble salt. In the process we observe aggregation of mass around the central point (nucleus). As a result of the process we obtain a DLA fractal of a shape similar to that shown in the figure below.

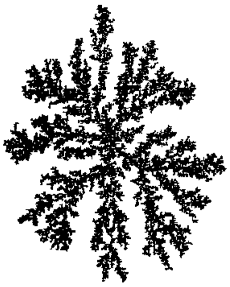


Fig. 4 DLA fractal.

Experiment

Method

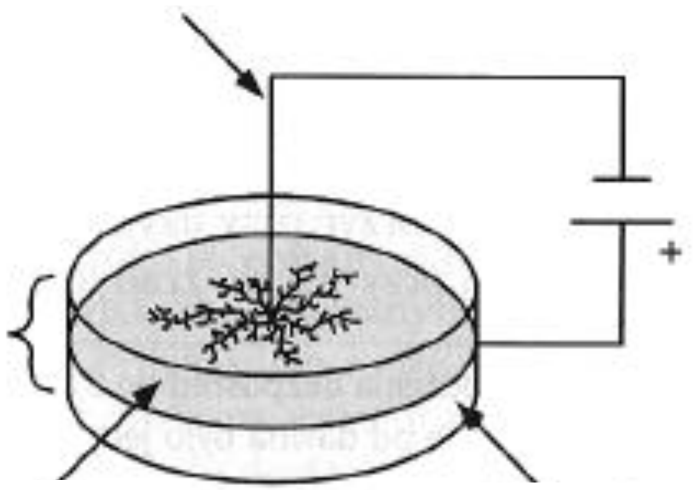
The experiment is divided into 2 parts. In part I, an aggregate is obtained by electrolysis of an aqueous water solution of $ZnSO_4$ using zinc electrodes. In part II, a computer simulation of DLA is performed.

Reagents and equipment
- $ZnSO_4 \cdot 7H_2O$;
- 2 Petri dishes
- 1 volumetric flask of 100 cm^3
- 1 beaker of 50 cm^3
- 1 pipette of 2 cm^3
- 1 wash bottle
- transparent foil
- zinc anode in the shape matching the Petri dish
- zinc cathode
- 2 clamps
- 1 retort stand
- sheet of paper with concentric circles with the radii increasing by 0.005 m (as many as it fits to a given Petri dish)
- power supply
- 2 stopwatches.

Procedure

Experiment

1. Make 100 cm^3 of 0.5 $mol \cdot dm^{-3}$ water solution of zinc sulphate(VI).
2. Wash carefully the electrodes with distilled water and dry them.
3. Assembly the setup for electrolysis according to the scheme presented below.



4. Place the zinc anode in the Petri dish so that it matched the internal edge of the dish.
5. Pour some of the solution made to a beaker of 50 cm^3.
6. With the help of a pipette draw some of $ZnSO_4$ solution from the beaker and spread homogeneously on the Petri dish to get a thin (1mm to 1.5 mm) layer of the solution on the dish.
7. Cover the solution placed on the Petri dish with a circle cut out of the transparent foil. The diameter of the circle must be the same as the inner diameter of the Petri dish. At the centre of the circle make a hole of a diameter close to 1 mm.
Caution: Make sure that there are no air bubbles between the foil and the solution. If they appear, they should be removed by e.g. a glass rod.
8. Place the Petri dish with the solution covered with foil on the paper with the concentric circles whose diameters differ by 5 mm.
Make sure that the hole in the foil coincides with the centre of the circles on the paper.
9. Mount the zinc cathode in the clamp screwed on the retort stand and place its end in the hole of the foil covering the solution, making sure that the electrode was in contact with the solution.
10. Before connecting the power supply to the power socket, both potentiometers on the right hand side of the device, marked “Voltage” should be turned to the right till resistance is felt. It ensures that the maximum output voltage of the power supply will be used.
Connect one of the electrodes with the power supply (anode – a positive pole; cathode – a negative pole). At this stage of the system preparation, push the button “Power” to connect the power supply device with the electrical grid. Now, connect the second electrode with the power supply device and immediately set the desired current intensity, e.g. 0.1 A, by shifting slightly to the right the potentiometer marked “coarse”, and then shifting the potentiometer marked as “fine” to set the accurate current intensity (the current intensity in Ampere is displayed on the screen of the digital display. Immediately start the stopwatch.
11. At the moment of switching on power supply, aggregation starts and a Zn fractal begins to grow. Measure the time in which fractal arms grow and reach subsequent circles. Measurements are made for two selected arms. Put the data in the table below:

Table 1

R/m	t_1/s	t_2/s	m_1/g	m_2/g	ln R	lnm_1	lnm_2
0,005							
0,010							
0,015							
0.020							
0.025							
0.030							
0.035							
0.040							

R - the radii of the circles drawn on the sheet of paper
t - time in which the fractal's arm reaches subsequent circles
m - mass of liberated zinc.

12. After the measurements, switch off the power supply by pressing the button "Power" on the power supply unit. Disconnect the electrodes from the clamps (+) and (-), wash them in distilled water and dry them.
13. Repeat the experiment, using a clean Petri dish, for another value of current intensity, e.g. 0.5 A. Put down the results in a separate table.

Calculations

1. For a given series of measurements, for each time t_1 and t_2, calculate the mass of liberated zinc from the Faraday's law:

$$m = kit, \tag{2}$$

where $k = M_{Zn}/(zF)$, M_{Zn}= 65.4 g·mol^{-1}, z – is the number of moles of the electrons needed for liberation of 1 mole of Zn, F = 96485 C·mol^{-1} – the Faraday`s constant. Put down the calculated mass in a table.
2. Calculate the values of ln$R$ and ln$m$, and plot the dependence ln$m$ = f(ln$R$) for the two observed arms of the fractal, 1 and 2. The fractal dimension d_f is calculated with the use of linear regression, it is equal to the slop of the linear plot.
3.On the basis of the values of d_f obtained for two arms of the aggregate calculate the mean value.
4. Perform the calculations described above (1-3) for 2 series of measurements for different current intensities.

Computations

Simulations

Diffusion limited aggregation (DLA) is simulated with the program `dla-2d.exe` for aggregates of different size. Before starting a simulation the program asks for the aggregate size and writes down the results in the file `dla-2d.data`.

Visualisation and analysis

The figures of the fractals and analysis of their structure (determination of the fractal dimension) can be made using data analysis software, e.g. `Origin`, or using a spreadsheet (see below).

1. Draw aggregates made of increasing number of particles (e.g. 10^2, 10^3, 10^4, 10^5).
2. Determine the fractal size of an aggregate with a large number of particles. Select a square that covers the fractal around the nucleus of the aggregate. Find out the number of particles (number of occupied nodes) that are in the square. Calculate the density ρ by dividing the number of occupied nodes M by the total number of nodes within the square L^2. Repeat the procedure for a smaller L (e.g. L/2). Write the results in a table, e.g.:

Table 2

L	M	$\rho = M/L^2$
...		
161		
81		
41		
21		
...		

Plot ρ as a function of L. Determine the fractal dimension d_f of the aggregate from a plot of the logarithm of the density ρ versus the logarithm of L. If the formula:

$$\rho \propto L^{d_f - 2} \tag{3}$$

holds, then the plot $\ln\rho = f(\ln L)$ is a straight line with slope d_f -2 and the aggregate is a fractal of the fractal dimension d_f. Compare the result with the theoretical value d_f = 1,66.

Determination of the fractal dimension in a spreadsheet

The file `dla-2d.data` obtained in simulations is a text file where the coordinates x and y of particles are arranged in two columns.

1. Load data from the file `dla-2d.data` to a spreadsheet. Column A contains the abscissas x, while column B the ordinates of the particles. Check if the number of lines in columns A and B is equal to the number M of points set in the simulation. Determine the maximum and minimum values of x and y and find the length L_0 of the side of the smallest square $-L_0/2 \le x \le L_0/2$, $-L_0/2 \le y \le L_0/2$, that covers the fractal object around the nucleus of aggregation.
2. Draw the simulated fractal object and, using the figure, determine the side of the smallest square covering the fractal object around the nucleus of aggregation.

Note: the values of L_0 determined at 1 and 2 should be the same. If the number of particles (points) in the fractal is high, e.g. $M = 10^4$, scrolling the sheet with the figure can become slow. If so then delete the figure when L_0 has been determined.

3. Calculate the density $\rho_0 = M/L_0^2$. Write the results in a table.
4. Select L smaller than L_0 (e.g. reduce L_0 by half, $L = L_0/2$) and find the number of points inside a smaller square with side L:

a) Sort columns A and B in ascending order with respect to the data in column A.
b) Mark the rows where $x < -L/2$ and delete them, the other rows will shift upwards. Similarly, delete the rows where $x > L/2$.
c) Sort the modified columns A and B in ascending order with respect to the data in column B .
d) Mark the rows where $y < -L/2$ and delete them, the other rows will shift up. Delete the lines for which $y > L/2$.
e) Read off the index of the last data row, which is the number of molecules M in a square of side L.

Note: The number of particles in the square $L/2 \le x \le L/2$, $-L/2 \le y \le L/2$, can be found in several ways. For instance, by marking the columns and using the tool Data->Filter->Standard Filter... . Setting the ranges Column A > $-L/2$, Column A < $L/2$, Column B > $-L/2$, Column B < $L/2$, the tool will automatically perform the operations described in the above points b)-d).

5. Calculate the density $\rho = M/L^2$. Write the results in a table.
6. Reduce L (e.g. by half) and repeat the procedure described at 4 and 5.
7. Plot $\ln \rho = f(\ln L)$ and fit a straight line whose slope is d_f - 2. Compare the value of d_f with the theoretical value of d_f = 1,66.

Discussion

1. Write chemical equations for the reaction taking place at the electrodes upon Zn fractal formation.
2. Identify the factors determining the rate of formation of Zn fractal.

3. What are the similarities/differences between the mechanism of fractal generation in this experiment and the mechanism of fractal generation in computer simulations?

References

[1] M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo, Y. Sawada, Phys. Rev. Lett. 53 (1984) 286.
[2] T. A. Witten, Jr., L. M. Sander, Phys. Rev. Lett. 47 (1981) 1400.

Additional topics

Electrolysis, Faraday’s laws, diffusion.