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# Diffusion Limited Aggregation

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# 1 Introduction

In nature exist several phenomena with amazing structures. For example in nonliving nature is known snowflake growth, mineral deposition, lightning paths etc. and in living nature corals, lichen, trees etc. These structures are fractal-like.

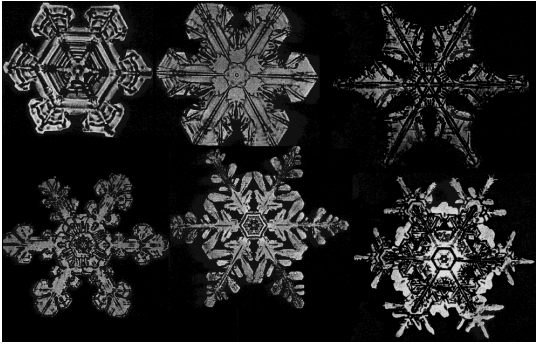


Figure 1: Snowflakes occur in vast multitude forms and have 6 similar branches [1].



Figure 2: Lightning path is fractal-like [2].

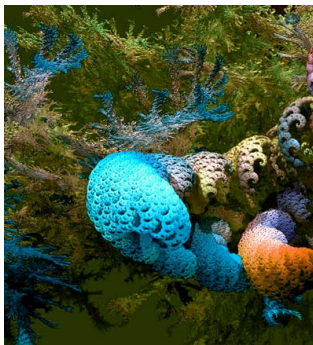


Figure 3: Fractal sea life in colours [3].



Figure 4: Lichen grows like fractals [4]. The cleaner the air, the bigger ratio between surface and perimeter.

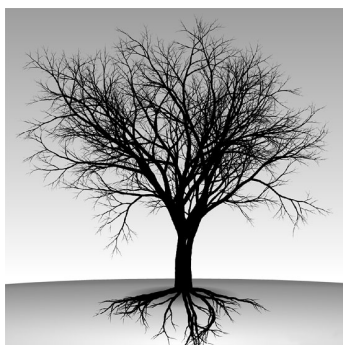


Figure 5: Tree. Fractal roots and crown [5].



Figure 6: Leaf's venation is fractal-like.



Figure 7: Romanesco broccoli has more fractional structure than other vegetables [6].

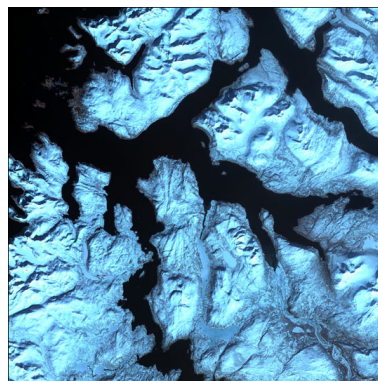


Figure 8: Norwegian fjords made by glaciers activity [7].

Snowflakes grow from the particles from the environment. Model for formation of fractals grown from particles from environment was introduced in 1981 by T. A. Witten and L. M. Sander. It is called Diffusion Limited Aggregation (DLA) (see chapter 2). Many different compounds were synthesised in laboratories with DLA, there are also several programs for simulating the growth.

### 1.1 Diffusion

Diffusion is a random motion in fluid systems as well in solid phases.

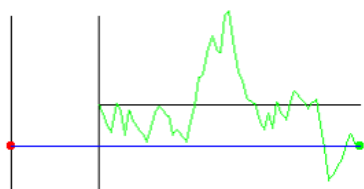


Figure 9: Brownian motion. Red dot moves randomly up and down. It's motion on y-axis is plotted with respect to time [1].

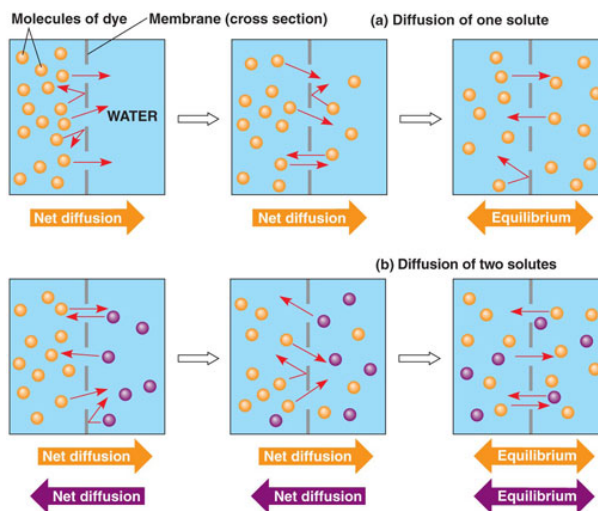


Figure 10: Diffusion of (a) one type of particles and (b) two types of particles in the solution [8].

However, particles can walk far relative from the starting point. The driving force for spreading process is completely statistical.

Diffusion is the macroscopic result of random thermal motion on a microscopic scale. If the distribution of all types of particles in the solution are not uniform, there will be a net flux even though the

motion of each individual molecule is completely random. The flux is proportional to the gradient in concentration (molar or molecular).

$$\vec{j} = -D\vec{\nabla}n, \quad (1)$$

where  $D$  is diffusion constant and  $n$  concentration. It is also known

$$\vec{\nabla} \cdot \vec{j} = -\frac{\partial n}{\partial t} + q, \quad (2)$$

where  $q$  stands for sources. From equations 1 and 2 and with consideration that  $D$  is constant it is possible to write diffusion equation

$$\frac{\partial n}{\partial t} = D\nabla^2 n - q. \quad (3)$$

## 1.2 Aggregation

If particles have the possibility to attract each other and stick together, they form aggregates. The forces between the particles may be weak or strong. For particles which carry electrical charge the forces are strong. Aggregates represent a preferred state compared to spread particles that can stick together. Aggregates are usually well ordered.

Without an electrical charge the forces are much weaker i.e. the sticking force is Van der Waals force. Each aggregate is unique because there is no ordering force of the electrical field. Such a building is also named a cluster.

## 1.3 Fractals

Cluster is a group of particles of somewhere between 3 and  $10^7$  stars/atoms/protons and neutrons within nuclei. Fractal on the other hand is more than group of particles. There are several facts/demands:



Figure 11: Hubble view of one of the globular clusters [9].

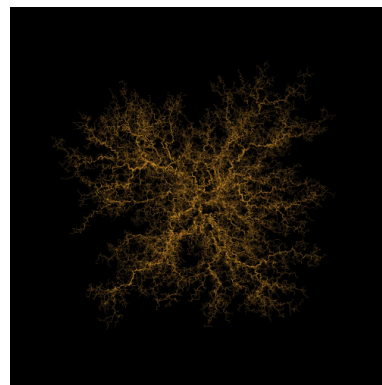


Figure 12: Computer simulated DLA fractal from initial seed in 3D open space [10].

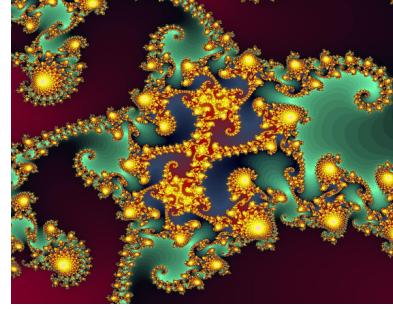


Figure 13: Computer simulated DLA fractal from initial seed over a sphere [10]. Figure 14: Computer simulated 2D fractal [11].

- The geometric pattern of the fractal is repeated at ever smaller scales - irregular shapes and surfaces that can not be represented by classical geometry are produced. Fractals are scale invariant and self-similar.
- Fractal has a finite area but an infinite perimeter - it has a fractional dimension  $D$ . This is a statistical quantity that gives an indication of how complete fractal appears to fill space.

$$N_n = Cr_n^{-D}, \quad (4)$$

where  $N_n$  is number of objects with a characteristic linear dimension  $r_n$ ,  $C$  is proportional constant. From equation 4 it is easy to express fractional dimension or so called similarity dimension formula [7]

$$D = \frac{\ln \frac{N_{n+1}}{N_n}}{\ln \frac{r_n}{r_{n+1}}}. \quad (5)$$

Plot of  $\ln(N_n)$  with respect to  $\ln(r_n)$  is a linear function with a negative slope which yields the fractal dimension. For most objects relationship holds true over a finite range of  $r_n$ . At small  $r_n$  this relationship is limited by the size of the particles that make up the object. At large  $r_n$  this relationship is limited by the size of the object.

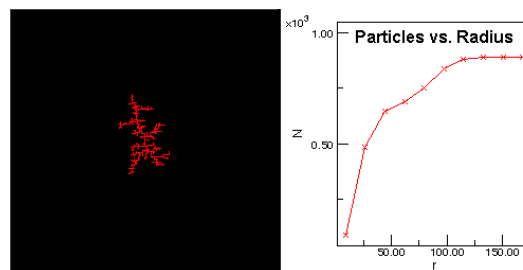


Figure 15: Simulation of the fractal growth. Particles in fractal versus radius of fractal shows logarithmic dependency [12].

From equation 4 can be written



$$C = N_n r_n^D = N_{n+1} r_{n+1}^D = N r^D = r^D + \dots + r^D. \quad (6)$$

For fractals made of different size particles it is possible to express Moran equation [1] from equation 6

$$C = r_1^D + \dots + r_N^D. \quad (7)$$

Fractals can be classified according to their self-similarity [6]

- **Exact self-similarity** is the strongest type of self-similarity. The fractal appears identical at all scales.
- **Quasi self-similarity** is a loose form of self-similarity. The fractal appears approximately identical at different scales.
- **Statistical self-similarity** is the weakest type of self-similarity. The fractal has numerical or statistical measures which are preserved across scales. All DLA fractals belong to this type.

## 2 Diffusion Limited Aggregation

DLA theory, proposed by Witten and Sander in 1981, is applicable to aggregation in any system where diffusion is the primary mean of transport in the system. DLA can be observed in laboratory in many systems such as electrodeposition and dielectric breakdown.

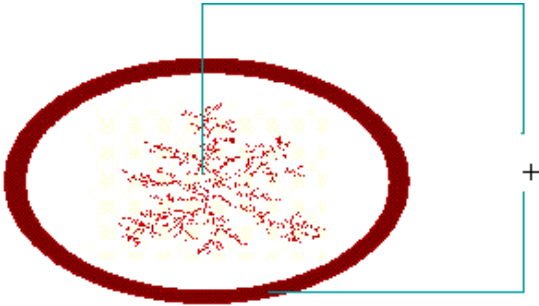


Figure 16: A fractal structure via electrodeposition is possible if solution of copper sulfate or zinc sulphate is sandwiched between glass plates and a voltage between a central cathode wire and an outer ring anode is applied [13].



Figure 17: A DLA cluster grown from a copper (II) sulphate solution in an electrodeposition cell [6]. Fractals are tree-like. The shapes depend on the applied voltage and the concentration of electrolyte. A linear geometry can also be adopted with growth between parallel electrodes.

DLA-cluster (also known as Brownian tree) is a fractal aggregate made by DLA, where the shape of the cluster is controlled by the possibility of particles to reach the cluster via Brownian motion. Starting with a uniform distribution, some particles might meet. The aggregates may grow as long there are particles moving around. “Arms” of the cluster “catch” particles so that they can’t reach inner parts of the cluster. During the diffusion of a particle through the solution it is more likely, that the particle attaches to the outer regions than to the inner ones of the cluster - a fluffy shape occurs, with many arms (see picture 17).



Figure 18: High-voltage dielectric breakdown (HVDB) within a block of plexiglas creates a fractal pattern [6]. Dielectric breakdown refers to the formation of electrically conducting regions in an insulating material exposed to a strong electric field. HVDB represents the negative of DLA when fractal grows from particles from the environment.

A single-particle bump on a straight edge of the cluster is more likely to catch a wandering particle also due to the fact that it has three unoccupied neighbours while each particle along the edge has only one unoccupied neighbour (see picture 19).

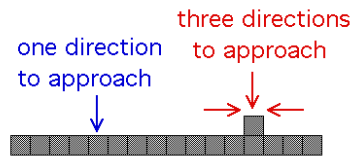


Figure 19: Higher probability to glue to the cluster onto the bulk goes to more unoccupied [1].

To summarize, DLA is called “Diffusion” because the particles forming the structure wander around randomly before attaching themselves (“Aggregating”) to the structure. “Diffusion-limited” because the particles are considered to be in low concentrations so they don’t come in contact with each other and the structure grows one particle at a time rather than by chunks of particles.

## 2.1 Differential equation for DLA

The dynamics of deformable bodies with a well defined surface can be represented by a gauge field  $\Psi$  [14]: inside the body is  $\Psi \leq 0$ , outside  $\Psi > 0$ , on the surface, which grows by deposition of diffusing particles, is

$$\Psi(x, y, z; t) = 0. \quad (8)$$

Equation of motion of  $\Psi$  (changing of surfaces topology) is

$$\frac{\partial \Psi}{\partial t} + (\vec{V} \cdot \vec{\nabla}) \Psi = 0, \quad (9)$$

where  $\vec{V}(\vec{r}, t)$  is velocity field.



In the region  $\Psi > 0$  particles with concentration  $n$  around nuclei particle/surface diffuse and are absorbed at the surface boundary. The surface absorbs all the particles that hits it. This is described with equation 3. The boundary conditions on the surface are  $n = 0$ . The particles that disappear from surface's environment become part of the solid and change the surface which has "concentration"  $n_0$ . The equation 3 changes when considering a given rate of absorption per unit time  $\Phi(\vec{r}, t)$  at a given boundary point  $\vec{r}$  and time  $t$  into

$$\frac{\partial n}{\partial t} = D\nabla^2 n - q - \lim_{\epsilon \rightarrow 0^+} \Phi(\vec{r}, t) \delta(\Psi - \epsilon) |\vec{\nabla} \Psi|, \quad (10)$$

The amount of material absorbed from environment at a point  $\vec{r}$  of the boundary per unit time and unit area is

$$\Phi(\vec{r}, t) = D(\vec{\nabla} n)_+ \cdot \vec{m}, \quad (11)$$

where  $+$  denotes approaching the boundary from the region of positive  $\Psi$  and  $\vec{m}$  is a unit vector normal to the surface and pointing into the region of positive  $\Psi$ . The normal velocity  $\vec{V}_m(\vec{r})$  of the growing surface is then

$$V_m(\vec{r}) = \frac{1}{n_0} D(\vec{\nabla} n)_+ \cdot \vec{m}. \quad (12)$$

The velocity field  $\vec{V}(\vec{r})$  throughout the space is so

$$\vec{V}(\vec{r}) = \frac{1}{n_0} D(\vec{\nabla} n)_+. \quad (13)$$

With equations from 10 to 13 it is possible to write solution for  $n$

$$n = n^s + \lim_{\epsilon \rightarrow 0^+} dt' d\vec{r}' G[\vec{r} - \vec{r}', t - t'] \frac{\partial \Psi}{\partial t'}(\vec{r}', t') \delta[\Psi(\vec{r}', t') - \epsilon], \quad (14)$$

where  $n^s$  is the concentration that would have existed just in the presence of the sources,  $G$  is the Green function. The equation 9 can at last be rewritten into

$$\frac{\partial \Psi}{\partial t} - \lim_{\epsilon \rightarrow 0^+} D \int dt' d\vec{r}' \vec{\nabla} G(\vec{r} - \vec{r}', t - t') \cdot \vec{\nabla} \Psi(\vec{r}, t) \frac{\partial \Psi}{\partial t'}(\vec{r}', t') \delta[\Psi(\vec{r}', t') - \epsilon] = -\frac{1}{n_0} D \vec{\nabla} n^s \cdot \vec{\nabla} \Psi. \quad (15)$$

Solution of the equation 15 gives the description of the surface growth.

## 2.2 Computer simulations of DLA

Computer simulation of DLA is one of the primary means of studying DLA model. Simulations can be done on a lattice or along the lines of a standard molecular dynamics simulation where a particle is allowed to freely random walk until it gets within a certain critical range at which time it is pulled onto the cluster. Of critical importance is that the number of particles undergoing Brownian motion in the system is kept very low so that only the diffusion controls the aggregation.

The simplest computer growth (using a lattice) starts with an initial seed particle at some origin and another particle somewhere on the lattice (see pictures 20 and 21). Then the second particle moves around in random motion (in 2D up, down, left, right), step by step from lattice site to lattice site. It can meet the first particle or move out from the lattice and another particle is introduced (the first particle either bounces off the edge or the image is toroidally bound; however, new points can

be seeded anywhere in the image area). If the particle touches the initial particle, it is immobilized instantly and becomes part of the aggregate. Then another particle is thrown onto the lattice, it walks around and after a while meets the first two or moves out from the lattice. The action is repeated as long as particles are available.

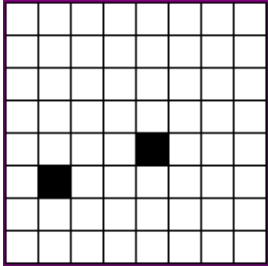


Figure 20: Initial seed particle is in the middle of the lattice. Second particle is introduced [1].

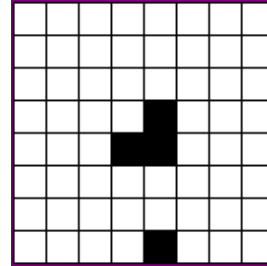


Figure 21: Fourth particle is introduced to a three-particle aggregate [1].

Within DLA simulation models, there are some variations:

- The point of view can be changed from the moving particle onto the grid, where it moves on and handle only the states of the grid. This is called a External linkcellular automaton. Here it is possible to have more than one particle moving in one iteration.

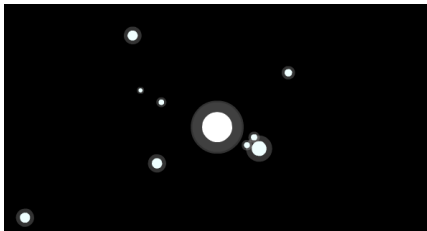


Figure 22: More than one particle moving in junior step of the iteration. Particles have different diameters and linksticking coefficients [15].

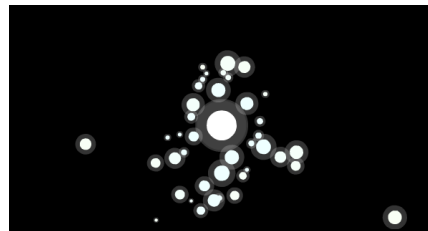


Figure 23: Older step of the iteration. Fractal structure is starting to appear [15].

- External linksticking coefficient can be introduced - when a particle reaches the cluster it will not always stick. Thus, when it doesn't stick immediately, it moves along in the vicinity of the cluster's arms, until it either finally sticks somewhere or gets lost.

If the wandering particle strikes part of the existing structure and always sticks, then stickiness is 1. Otherwise is less than 1. Low stickiness probability gives rise to more dense clusters. The fractal dimension does not change much until the sticking coefficient becomes less than 0.1. As the sticking coefficient vanishes the fractal dimension becomes close to the spatial dimension - close to 2 in 2D.

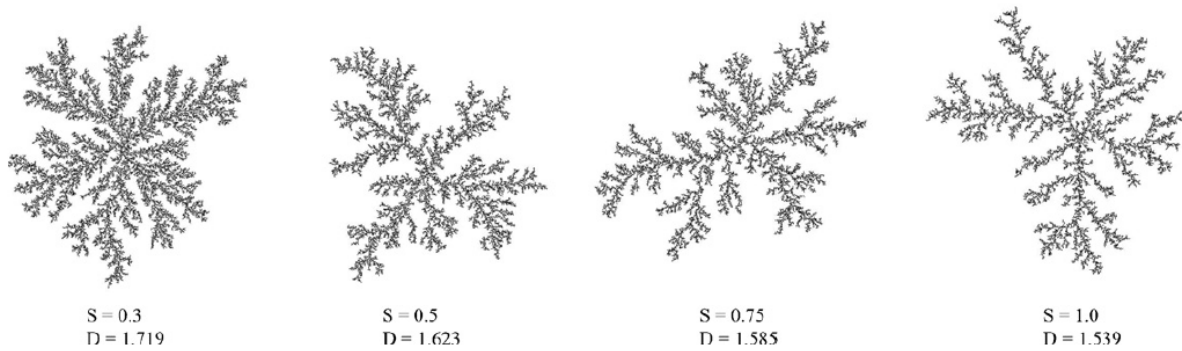


Figure 24: Fractal grown from a point with different stickiness probability. The higher the stickiness, the lower the fractal dimension, the lower the density of the fractal [16].

A further modification is using different attaching probabilities depending on the current geometrical environment i.e. the more neighbours are already present, the more likely it is for a particle to attach.

- The lattice geometry can be varied: a square lattice with four neighbour sites, a triangular lattice with six neighbours (snowflakes). Overall shape of the cluster is related to the shape of the lattice.
- A starting line can be used instead of a starting point as a seed line, thus resulting in forest like clusters (diffusion-limited deposition, DLD).

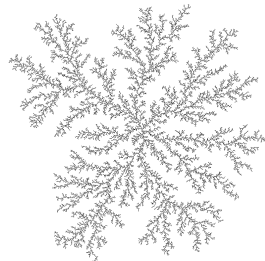


Figure 25: Initial seed is a point [10].

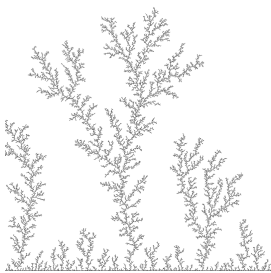


Figure 26: Initial seed is a line [10].

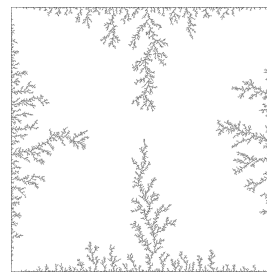


Figure 27: Initial seed is inner part of a square [10].

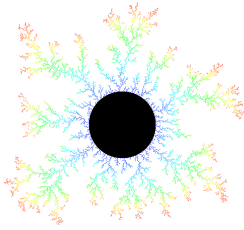


Figure 28: Initial seed is outer part of a circle [10].

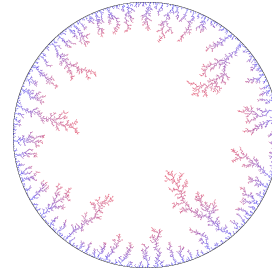


Figure 29: Initial seed is inner part of a circle [10].

- Movement over any distance (off-lattice DLA) is allowed (there is no lattice). This approach allows the creation of very large clusters.
- If there are several simultaneously growing clusters within a "solution" cluster-cluster-aggregation (CCA) is introduced.

Fractal growth has been observed after certain growth time under a field emission scanning electron microscope (SEM) which gave direct proof of the DLA process.

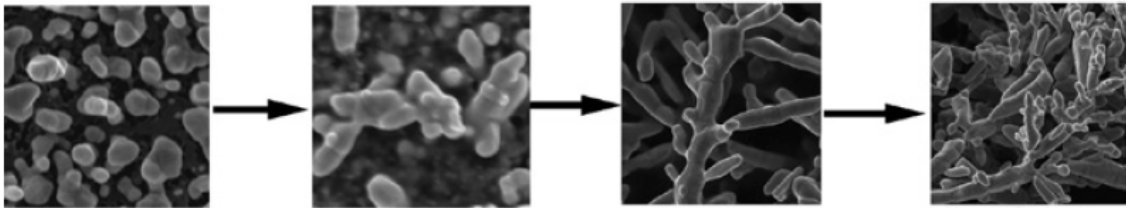


Figure 30: The growth-time dependent morphology of the silver structures, demonstrating DLA process. The growth time is 1, 5, 10 and 60 min from left to right [17].

### 2.3 DLA and nanotubes

Van der Waals force is not present only when we are dealing with spherical particles, but also when shape of particles is non-spherical. Nowadays are "in" all materials which are nanotube-like. They also aggregate due to mentioned force and DLA. But when investigating nanotube's properties it is better to have a single nanotube than a whole aggregate of nanotubes. This is the reason why physicist started to investigate the Van der Waals interaction between two nanotubes at arbitrary angle  $\Theta$  (see picture 31).

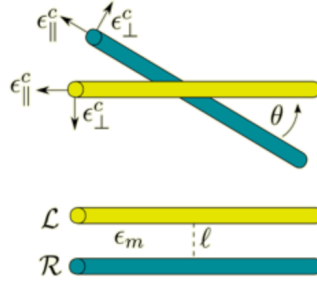


Figure 31: Two cylinders at arbitrary angles [18].

The interaction free energy  $G$  for two cylinders with anisotropic dielectric properties yields [18]

$$G(l, \Theta) = -\frac{(\pi a^2)^2 (\mathcal{A}^{(0)} + \mathcal{A}^{(2)} \cos^2 \Theta)}{2\pi l^4 \sin \Theta}, \quad (16)$$

$$G(l, \Theta = 0) = -\frac{3(\pi a^2)^2 (\mathcal{A}^{(0)} + \mathcal{A}^{(2)})}{2\pi l^5}, \quad (17)$$

where  $a$  is radius of the cylinders,  $l$  is the separation,  $\mathcal{A}$  is the Hamaker coefficient which quantifies magnitude of Van der Waals interaction. This coefficients represent the material properties of the interacting bodies and are tabled.

The molecular structure of the nanotubes was ignored and the interactions between them were derived in terms of dielectric constant and indices of refraction. See below

$$\mathcal{A}^0 = \frac{3}{2} k_B T \sum_{n=0}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} \Delta_{\mathcal{L}m}(\Phi) \Delta_{\mathcal{R}m}(\Phi - 90) d\Phi, \quad (18)$$

$$\mathcal{A}^0 + \mathcal{A}^2 = \frac{3}{2} k_B T \sum_{n=0}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} \Delta_{\mathcal{L}m}(\Phi) \Delta_{\mathcal{R}m}(\Phi) d\Phi, \quad (19)$$

where spectra functions are

$$\Delta_{\mathcal{L}m}(\Phi) = -(\Delta_{\perp}(\mathcal{L}) + \frac{1}{4}(\Delta_{\parallel}(\mathcal{L}) - 2\Delta_{\perp}(\mathcal{L})) \cos^2 \Phi), \quad (20)$$

$$\Delta_{\mathcal{R}m}(\Phi) = -(\Delta_{\perp}(\mathcal{R}) + \frac{1}{4}(\Delta_{\parallel}(\mathcal{R}) - 2\Delta_{\perp}(\mathcal{R})) \cos^2 \Phi), \quad (21)$$

$$\Delta_{\mathcal{R}m}(\Phi - 90) = -(\Delta_{\perp}(\mathcal{R}) + \frac{1}{4}(\Delta_{\parallel}(\mathcal{R}) - 2\Delta_{\perp}(\mathcal{R})) \sin^2 \Phi), \quad (22)$$

where anisotropy parts are

$$\Delta_{\perp} \equiv \frac{\epsilon_{\perp}^c - \epsilon_m}{\epsilon_{\perp}^c + \epsilon_m}, \quad (23)$$

$$\Delta_{\parallel} \equiv \frac{\epsilon_{\parallel}^c - \epsilon_m}{\epsilon_m}. \quad (24)$$

This is the physics behind the aggregating dielectrical nanotubes.

### 3 Conclusion

With DLA and usage of computers it is possible to construct models of natural objects with irregular shapes that approximate fractals: clouds, coastlines, mountain ranges, lightning bolts, snowflakes etc.

DLA was proven with observing growth of the silver structures under SEM. It is important that density of particles is low enough because diffusion in fractal growth should represent the main transport.

My research work is connected with fractal growth of  $\text{TiO}_2$  via hydrothermal synthesis. I am trying to make fractal nanotubes using small percentage of impurities. First step was to produce non-aggregated nanotubes. Since now I made nanotubes which aggregated into inseparable nests. My next step will be, according to DLA, lowering the concentration of initial compounds to maximally avoid aggregation and to find optimal hydrothermal synthesis temperature for combined growth of fractals and crystals.



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