

AGGREGATION AND FRACTAL AGGREGATES

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PREFACE

Aggregation phenomena are of great importance in many scientific areas: physics, chemistry, biology, medicine, engineering... Due to the introduction of the concept of **fractal** and the access to big computers, this field has literally exploded in the last six years. We think that it is the appropriate time to give a presentation of these recent progresses in a version readable by a wide range of scientists.

The material presented here is largely inspired by the recent thesis of one of the authors (R.B.) and by the series of lectures given at Orsay by the other (R.J.). A shorten version has already been published in French ("Les phénomènes d'agrégation et les agrégats fractals", R. Julien, Annales des Télécommunications, 41, 343, 1986).

We would like to apologize to all colleagues whose works have not been cited for our aim was primarily pedagogical and we would rather write a book on **lecture notes** than have an exhaustive review. We acknowledge all people who have directly or indirectly helped us, in particular Max Kolb and Jean-Claude Toledano. We thank Paul Meakin, Catherine Allain, Johann Nittmann and Eugene Stanley who gave us their beautiful photographs. Most of the figures illustrating our simulations were realized at CIRCE (Centre Inter-Régional de Calcul Electronique), Orsay. Finally, we would like to acknowledge support from the CNRS (Centre National de la Recherche Scientifique), France.

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CONTENTS

PREFACE

v

I—INTRODUCTION

1

I-1—PRESENTATION

1

I-2—COLLOIDS AND AEROSOLS

2

I-3—MACROSCOPIC AGGREGATION

7

I-4—FIELD-INDUCED AGGREGATION

10

—Electrolysis

10

—Sedimentation

11

—Filtration

11

—Similar structures

12

II—BEFORE FRACTALS

14

II-1—KINETICS (SMOLUCHOWSKI EQUATION)

14

II-2—STRUCTURE

23

III—FRACTALS

24

III-1—DEFINITIONS

24

III-1-1—Fractal dimension

24

III-1-2—Self-similarity

27

III-1-3—Random fractals

28

III-1-4—Self-affine fractals and multifractals

29

III-2—PHYSICAL PROPERTIES OF FRACTALS

31

III-2-1—Mass repartition

31

III-2-2—Connectivity

32

III-2-3—Dynamical properties

34

III-2-4—Elasticity

35

III-2-5—The hierarchy of exponents

35

III-3-SOME EXAMPLES OF FRACTALS	
IN STATISTICAL PHYSICS	36
III-3-1-The random walk	36
III-3-2-The self avoiding walk	37
III-3-3-Lattice animals and percolation clusters	39
III-3-4-The concept of universality	40
III-3-5-Fractal aggregates	41
III-4-EXPERIMENTAL DETERMINATION OF THE FRACTAL	
DIMENSION OF AGGREGATES	42
III-4-1-Analysis of digitalized micrographs	42
III-4-2-Scattering experiments	46
III-4-3-Pore size distribution	50
IV-PARTICLE-CLUSTER AGGREGATION	52
IV-1-THE EDEN MODEL	52
IV-1-1-Definition and general properties	52
IV-1-2-Properties of the surface of Eden clusters	54
IV-1-3-Analytical investigations	58
IV-1-4-Anisotropy of Eden clusters	59
IV-1-5-The off-lattice Eden model	59
IV-2-THE WITTEN-SANDER MODEL	61
IV-2-1-Definition and general properties	61
IV-2-2-Extensions of the Witten-Sander model	65
a-Introduction of a sticking probability.	65
b-Straight line trajectories	66
c-Different geometries	68
IV-2-3-The Experimental realizations of the Witten-Sander	
Model and the Pietronero-Wiesman model	68
IV-2-4-Properties of the surface	71
IV-2-5-Internal structure and lattice anisotropy effects	72
IV-2-6-Analytical investigations on the Witten-Sander	
Model	74
V-CLUSTER-CLUSTER AGGREGATION	77
V-1-THE MODEL AND ITS HIERARCHICAL VERSION	78
V-1-1-The original brownian model in a box	78
V-1-2-The hierarchical model	80
V-1-3-Anisotropy of cluster-cluster aggregates	83

V-2- EXTENSIONS OF THE CLUSTER-CLUSTER MODEL	84
V-2-1- Influence of the lattice and cluster rotations	84
V-2-2- Extensions to large space dimensions	85
V-2-3- Influence of the nature of the cluster trajectory	86
V-2-4- The chemical model	87
V-2-5- Influence of cluster polarizability	89
V-2-6- Influence of the initial concentration	91
V-2-7- Cluster-cluster aggregation in two monomer systems	92
V-3- KINETICS OF THE CLUSTER-CLUSTER MODEL	92
V-3-1- The use of the Smoluchowski equation	92
V-3-2- Connection between Cluster-Cluster and Particle-Cluster aggregation	96
V-3-3- Kinetics in presence of sources and sinks	98
V-4- THE CLUSTER-CLUSTER MODEL IN HIGH SPACE DIMENSION	99
VI- RESTRUCTURING IN AGGREGATION MODELS	103
VI-1- PARTIAL RESTRUCTURING	103
VI-2- REVERSIBLE AGGREGATION	105
VII- CONCLUSION	109
REFERENCES	111

I-INTRODUCTION

I-1-PRESENTATION

Aggregation is an irreversible physical process in which initially dispersed basic units (particles, or **microaggregates**) stick together, under the action of given attractive forces, to build characteristic structures, the **aggregates**, whose size increases with time. Two fundamental aspects will retain our attention all along these lecture notes: first the **kinetics**, i.e. the quantitative description of the time evolution of their mean size and of their size-distribution, and second the **geometry**, i.e. the quantitative description of the structure of the aggregates. The first aspect has been studied since a long time, mainly after the introduction of a very useful kinetic equation by **Smoluchowski** in 1916. The second aspect, however, has been, only very recently, the subject of a great amount of studies⁽¹⁾, providing interesting new insights on the first aspect. These recent progresses are essentially due to the introduction of the mathematical concept of **fractal**, which permitted a quantitative description of the structure of the aggregates, generally considered as too complicated in the past.

Right now, we would like to define with precision the limits of our purpose. In many experimental examples, the aggregation phenomenon is mixed with other phenomena, such as the creation process of the basic units. This is for example the case of the clouds formation. In all what

follows, we shall assume that the formation of the basic units, generally called **nucleation**, is completely achieved when the aggregation phenomenon starts to take place. We shall also never be interested in the description of the internal structure of the basic units. Very often, these basic units are quite compact, i.e. **not fractal**. However, sometimes, metallic microaggregates can exhibit very fascinating amorphous structures⁽²⁾.

After this introduction devoted to the description of several experimental examples, we shall describe the status of the field before the introduction of the concept of fractal (chapter II). Then we shall introduce fractals and discuss the main physical properties of fractal aggregates (chapter III). In the following chapters, we shall give a detailed review of the two main theoretical models of aggregation: the **particle-cluster** (chapter IV) and the **cluster-cluster** (chapter V) aggregation models, which generally lead to such fractal structures. At last we shall discuss the problem of restructuring and readjusting in both models (chapter VI) which is presently one of the most interesting open questions (at least in our opinion).

1-2-COLLOIDS AND AEROSOLS

Colloids are spherical particles in suspension in a liquid. They are often, but not necessarily, metallic. Gold colloids are known since a very long time. In the middle-age, the alchemists knew how to prepare

them and to use them to colour glass. When reducing a gold salt, one can obtain a suspension of microscopic gold spheres, all of the same diameter, of order some nanometers. The surface of these spheres is generally electrostatically charged, so that, when not in a ionized solvent, the **short range Van der Waals attraction** is inefficient against the **strong electrostatic repulsion** which maintains the spheres far away from each other. The figure 1 gives the shape of the potential energy versus distance curve.

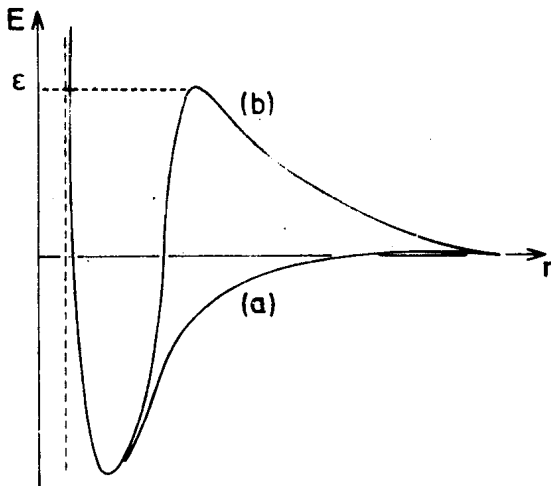


Fig.1: Shape of the interaction energy curve between two colloidal particles as a function of their center-to-center distance in the case of strong electrostatic screening (a), and in the case of partial electrostatic screening (b).

In general the repulsive barrier ϵ is larger than kT , giving a remarkable stability to the colloidal suspension. Some gold colloids, prepared by Faraday 130 years ago are still conserved today! When dissolving a salt into the suspension, one can introduce mobile ions. Ions of opposite sign to the surface charges come around the sphere to realize an **electrostatic screening**. This reduces the electrostatic barrier ϵ , which may become of order kT . For very large ionic concentration, one can obtain a complete electrostatic screening of the surface charges and entirely restore the Van der Waals interaction (figure 1a). Other experimental techniques can be used to realize this partial or complete screening: one can replace the surface charges by neutral organic molecules (as done by Weitz and al.⁽³⁾ at Exxon, Annandale, USA). In these two cases, the suspension loses its stability. Particles begin to aggregate to build clusters whose size increases with time. Aggregates may eventually contain up to some thousands of particles and reach sizes of order micron. At this stage, they begin to diffuse light and the solution exhibits a characteristic "milk-like" appearance. Figure 2 shows electronic micrographs of gold colloid aggregates recently grown by David Weitz⁽³⁾. Figure 2a corresponds to complete screening while figure 2b corresponds to partial screening ($\epsilon \approx kT$).

How can one explain the formation of these aggregates? As long as colloidal particles remain far away from each other, they diffuse inside the solution, undergoing the so-called **brownian motion**. In the case of complete screening, they ignore themselves until by chance they come so

close that they "feel" the Van der Waals attractive forces. In that case, they irretrievably stick together to form a doublet which also diffuses inside the solution, sticks other particles or other doublets, etc.... In the case of partial screening, the thermal agitation must be sufficiently large to win the electrostatic repulsive barrier, of height ϵ , defined in fig.1b. Particles bounce on each other many times before being able to win the electrostatic barrier, after what they irretrievably stick. In that case the overall process is slower.

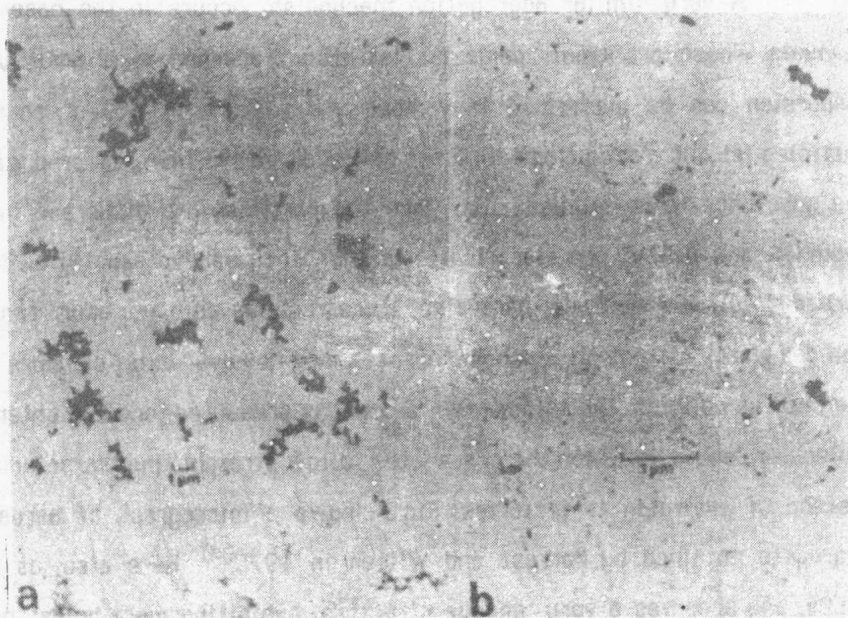


Fig.2: Gold colloids photographs obtained by David Weitz and collaborators, using an electron microscope. The two cases of rapid aggregation (a) and slow aggregation (b) are shown, which correspond to the cases of complete screening or partial screening, respectively.

One can see, on fig.2, that the shape of the potential interaction curve has a great influence on the structure of aggregates. While the aggregates obtained in slow aggregation (fig.2b) are (apparently) compact, those of fig.2a exhibit a characteristic stringy structure. Such typical effect: **the influence of aggregation mechanism on the structure of resulting clusters**, will be one of the main studies of these lecture notes.

A very similar aggregation mechanism occurs in the case of aerosols. These are small particles initially dispersed in a gas. Such dispersion can be performed in various ways. One can collect smoke particles let out from a flame. One can suddenly heat a wire covered with the substance to be studied, etc.. Once the particles are dispersed in a chamber, and if they are electrically neutral, they behave exactly as the screened colloids, because, here also, there remains only the short range Van der Waals attraction. Some differences may however exist compare to the case of colloids: for sufficiently small gas pressures, one can enter a molecular regime in which the aggregates follow straight line trajectories instead of brownian trajectories. Fig.3 shows a micrograph of aerosol aggregate obtained by Forrest and Witten in 1979⁽⁴⁾. Here also, as in fig.2a, one observes a very tenuous structure, exhibiting more holes than matter! This photograph has a great historical importance in the field, since this is from this picture that Forrest and Witten have, for the first time, pointed out the **fractal** character of such aggregates. This was the starting point of a great amount of studies that we will review here.

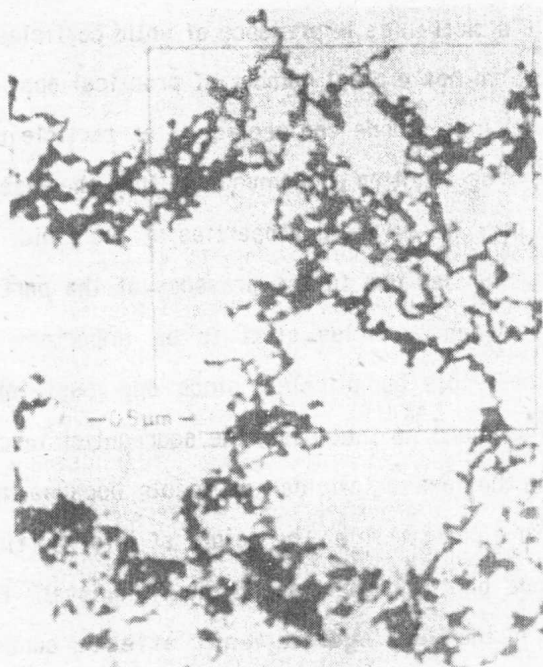


Fig.3: Photograph of an aerosol aggregate (iron smoke) observed with an electron microscope. By analysing a digitalized version of this photograph, Forrest and Witten⁽⁴⁾ have for the first time proven the fractal character of such aggregate.

I-3-MACROSCOPIC AGGREGATION

Experiments with colloids or aerosols essentially deal with submicronic particles. However, there exist many interesting experiments

where particles, in suspension in a fluid, can reach sizes of order one millimeter. Fluid mechanics in presence of solid particles is a large field of research, which has a great number of practical applications, such as lubrication. As long as one can neglect inter-particle interactions, one does not observe aggregation phenomena and then the essential problem is to understand how the physical properties of the fluid, for example its viscosity, are modified due to the presence of the particles. But when interactions between particles start to be important, the preceding problem becomes more complicated, since one must take into account aggregation phenomena. In that case, the aggregation mechanism is more complex than in the case of colloids or aerosols, because the fluid does not keep itself into a passive role. The nature of inter-particle interactions strongly depends on the properties of the fluid itself. Furthermore the driving motion of the fluid (**hydrodynamic effects**) cannot be neglected. We shall only quickly describe two bidimensional model-experiments which have been performed in France (Ecole Supérieure de Physique et Chimie Industrielle, Paris⁽⁵⁾, and Université de Marseille⁽⁶⁾). One of the interest of such experiments is that they realize some kind of experimental simulation, on a macroscopic scale, of what happens in colloids or aerosols: one can directly see the aggregates and, by the way, better understand their behavior.

Plate 1 shows the experiment done in Paris. These are wax balls, of 1.6 mm diameter, floating on the surface of water. Due to its weight, a given ball weakly depresses water surface on very short distances, and

this is enough to attract other balls, if they are sufficiently close. At the beginning of the experiment, the balls are dispersed by agitating the surface. Once agitation is stopped, the aggregation phenomenon starts to take place. The plate 1 shows a photograph of the surface taken 1 700 seconds after stopping agitation. Here also one observes very tenuous structures which strongly resemble those observed in colloids or aerosols. One must however remember that this is a **two-dimensional** experiment. The figure 4 shows a photograph of a similar experiment, but under shear forces (using a Couette apparatus). The aggregates are apparently more compact. Many loops can be seen inside their structure.

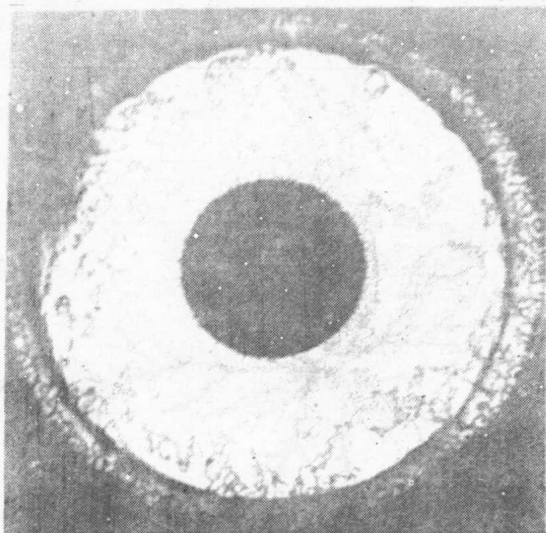


Fig.4: Aggregation of wax balls on the surface of water in the presence of shear forces (Experiment done by Camoin and Blanc⁽⁶⁾ in Marseille).

I-4-FIELD-INDUCED AGGREGATION

We call field-induced aggregation all aggregation experiments in which inter-particle interactions are not the unique cause of aggregation but there exists some external field which forces particles to aggregate. Let us only give some examples:

-**Electrolysis:** when an electric current runs into a metallic salt solution, metal atoms deposit on cathode. The structure of the deposit strongly depends on the experimental conditions but when the experiment is performed very slowly, in a diluted solution, under a weak potential, aggregates may exhibit tiny opened branched structures⁽⁷⁾.

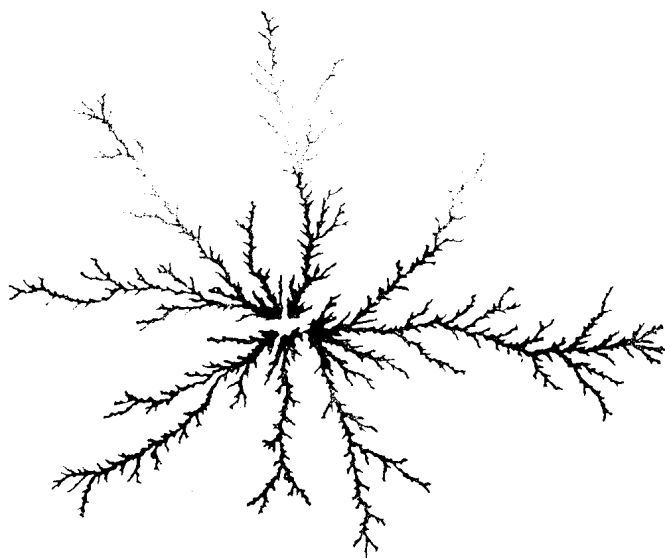


Fig.5: Cathodic deposit obtained by Matshushita et al.⁽⁷⁾.