



Fractal-like structures in colloid science

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ABSTRACT

The present work aims at reviewing our current understanding of fractal structures in the frame of colloid aggregation as well as the possibility they offer to produce novel structured materials. In particular, the existing techniques to measure and compute the fractal dimension d_f are critically discussed based on the cases of organic/inorganic particles and proteins. Then the aggregation conditions affecting d_f are thoroughly analyzed, pointing out the most recent literature findings and the limitations of our current understanding. Finally, the importance of the fractal dimension in applications is discussed along with possible directions for the production of new structured materials.

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1. Introduction

Freely rephrasing Mandelbrot’s words, nature exhibits fascinating geometrical patterns and shapes, which cannot be captured by Euclidian geometry. In order to be able to describe clouds, lightning, or the blood vessel architecture, a new mathematical instrument was developed, namely, fractal geometry. Ideal fractal objects are usually described as exhibiting self-similarity over an infinite range of length scales. In other words, the same geometrical pattern is identified over any scale one looks at fractals. Well-known examples for ideal fractals are the Koch snowflake and the Sierpinski triangle. On the other hand, there are natural fractals, which still exhibit self-similarity, but only on a limited number of scales: below their smallest repeating unit, no fractal scaling is observed. Among this category, one can find the most diverse objects, e.g., trees, lungs, river networks, and colloidal fractals.

Colloidal fractals are built-up starting from a colloidal suspension of primary particles aggregating in a finite-sized cluster. Note that henceforth, the terms “aggregate” and “cluster” will be used interchangeably as synonyms. It is worth recalling that most colloidal suspensions are only kinetically stable, in the sense that spontaneous (van der Waals forces-induced) aggregation of particles can only be delayed by an electrostatic or steric barrier, but eventually (i.e., thermodynamically) they will aggregate and phase separate from the continuous phase they were suspended into [1]. This implies that, in the vast majority of cases, fractal aggregates are non-equilibrium structures and are as such only kinetically stable. Other forms of structures obtained from the spontaneous organization of colloidal particles, such as colloidal glasses and colloidal crystals, the latter being stable equilibrium structures, are out of the scope of the present review [2].

It is accepted, since the work of Forrest and Witten [3], that large enough aggregates (or clusters) of colloidal particles follow a fractal scaling, i.e., their mass *i* (that is their number of primary particles) scales

with any characteristic cluster size, for example, the gyration radius *R_g*, according to a typically non-integer power law:

$$i = k \left(\frac{R_g}{R_p} \right)^{d_f} \tag{1}$$

where *R_p* is the primary particle radius; *d_f* is the fractal dimension of the colloidal aggregates, comprised between 1 (linear aggregates) and 3 (spherical aggregates); and *k* is the fractal prefactor, a number which typically ranges between 1 and 1.2 and that has been reported to be a function of the fractal dimension itself [4,5]. A correlation providing a *d_f*-dependent prefactor, *k* = *k*(*d_f*), has been proposed by Gmachowski [6]. Some of the colloidal fractals reported in the literature can be appreciated in Fig. 1. More details about the aggregation conditions and mechanisms are discussed in Section 3.

One should note that Eq. (1) holds for any characteristic size of the clusters, obviously with different values of the prefactor *k*. Several sizes have been used in the literature, including the hydrodynamic radius, the radius of the smallest sphere encompassing the cluster, the size of smallest box enclosing the cluster, etc. [5,10,11]. The radius of gyration is one of the most commonly used sizes because it is a purely geometrical property of the cluster and can be easily determined by static scattering methods. If the relative positions of the particles belonging to it are known, the radius of gyration can be computed from the following equation (valid for clusters made of identical primary particles):

$$R_g = \sqrt{\frac{1}{2N^2} \sum_{i,j=1}^N (r_i - r_j)^2} \tag{2}$$

where *N* is the number of particles constituting the aggregate, while *r_i* and *r_j* are the positions of the *i*th and *j*th particles’ centers. Although

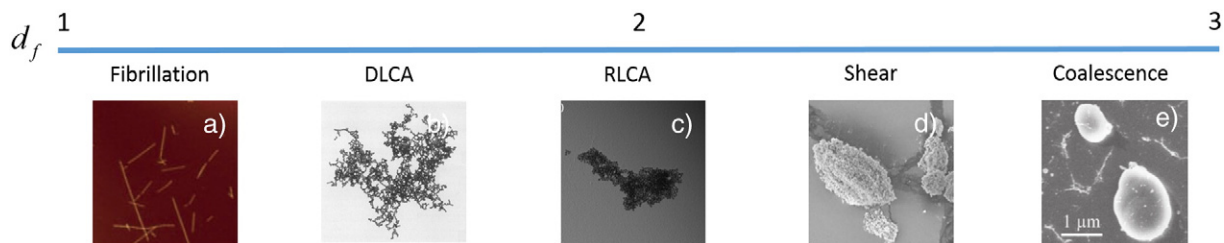


Fig. 1. Colloidal fractals exhibiting very different structures according to the aggregation conditions and mechanisms. (a) Protein fibrils [7]; (b) gold particles [8]; (c) gold particles [107]; (d) PMMA particles, ad hoc prepared; (e) rubbery polymer aggregates [9]. Fig. 1a), 1b), 1c) and 1e) are reprinted (adapted) with permission from their respective sources.

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