



Morphology and mobility of synthetic colloidal aggregates



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ABSTRACT

The relationship between geometric and dynamic properties of fractal-like aggregates is studied in the continuum mass and momentum-transfer regimes. The synthetic aggregates were generated by a cluster–cluster aggregation algorithm. The analysis of their morphological features suggests that the fractal dimension is a descriptor of a cluster's large-scale structure, whereas the fractal prefactor is a local-structure indicator. For a constant fractal dimension, the prefactor becomes also an indicator of a cluster's shape anisotropy. The hydrodynamic radius of orientationally averaged aggregates was calculated via molecule–aggregate collision rates determined from the solution of a Laplace equation. An empirical expression that relates the aggregate hydrodynamic radius to its radius of gyration and the number of primary particles is proposed. The suggested expression depends only on geometrical quantities, being independent of statistical (ensemble-averaged) properties like the fractal dimension and prefactor. Hydrodynamic radius predictions for a variety of fractal-like aggregates are in very good agreement with predictions of other methods and literature values. Aggregate dynamic shape factors and DLCA individual monomer hydrodynamic shielding factors are also calculated.

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1. Introduction

Aerosol and colloidal particles may form complex structures via agglomeration [1] and flocculation. The morphology and hydrodynamic properties of these structures have been studied extensively in the literature, e.g., Refs. [2,3], due to their numerous technological applications: for example, the mobility of power-law aggregates influences their size distribution, their precipitation behavior, and their agglomeration. Even though many studies have investigated the relationship between geometric and dynamic properties, the prediction of the hydrodynamic radius from aggregate structural properties remains elusive.

Forrest and Witten [4], in their analysis of the agglomeration of ultrafine smoke particles, first suggested that the resulting agglomerates are power-law objects obeying the scaling law (over a finite size range)

$$N = k_f \left(\frac{R_g}{R_1} \right)^{d_f}, \quad (1)$$

where N is the number of primary particles that form the aggregate, d_f the fractal (or Hausdorff) dimension, k_f the fractal prefactor (also

referred to as lacunarity [5] or structure factor [6]), R_g the radius of gyration, and R_1 the radius of the primary particles. We refer to aggregates satisfying the scaling law Eq. (1) as "power-law" aggregates [7] (equivalently, fractal-like or quasi-fractal) because the scaling law relation is independent of whether the aggregate has a real scale-invariant (self-similar) morphology. The fractal dimension provides a quantitative measure of the degree to which a structure fills physical space beyond its topological dimension. The fractal prefactor, a parameter whose importance is increasingly being appreciated [6,8–10], is an essential ingredient for a complete description of a power-law aggregate, as suggested by the scaling law. According to Wu and Friedlander [8] it is a descriptor of packing of the primary particles, becoming an indicator of the aggregate local structure. The radius of gyration is a geometric measure of the spatial mass distribution about the aggregate center of mass.

The calculation of the Stokes friction coefficient of a fractal-like aggregate, and consequently of its hydrodynamic radius, is analytically and computationally demanding as it requires the solution, analytical or numerical, of the creeping-flow Stokes equations. The hydrodynamic radius of an aggregate is defined as the radius of a sphere with the same mobility (or equivalently, the same diffusion coefficient) under identical flow conditions, ensemble-averaged over many aggregates and orientationally averaged [8]. Several methods have been proposed to calculate it.

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Kirkwood and Riseman [11] in their pioneering analysis of the translational diffusion coefficient of flexible macromolecules derived a purely geometrical expression for the polymer friction coefficient. The derived expression depends only on monomer–monomer distances in the chain. Their analysis was based on a double average of the Oseen tensor, a tensor that describes the perturbed fluid velocity on a surface due to a point source: an initial average over the internal configurations of the chain is followed by an orientational average. Hubbard and Douglas [12] modified their analysis by avoiding the configurational pre-averaging approximation, retaining the angular average of the Oseen tensor. The remaining angular average corresponds to the physical average over the orientational Brownian motion of the aggregate. They realized that the orientationally averaged (spherically symmetric) Oseen tensor is the free-space Green's function of the Laplace operator. Thus, they concluded that the orientationally averaged hydrodynamic friction of an arbitrarily shaped Brownian particle may be obtained from the solution of a Laplace equation. Hogan and co-workers in a series of papers [13–15] calculated the so-called Smoluchowski radius, the point mass-transfer analog of the hydrodynamic radius, via stochastic simulations of point mass–aggregate collision rate. Their calculations are, in a sense, equivalent to the discrete stochastic simulations of the Hubbard and Douglas [12] continuum approach. Filippov [16] avoided the previously described approximations, at the expense of significant numerical effort, by developing a full multipole expansion of the Stokes velocity field to obtain the fluid stress tensor on the aggregate surface. The friction coefficient was subsequently calculated by integrating the stress tensor over the aggregate surface.

In this study we use the methodology introduced and validated by Isella and Drossinos [17] who calculated, approximately but accurately, the friction coefficient and the hydrodynamic radius of straight chains by solving a Laplace equation with appropriate boundary conditions. Their approach is similar to the continuum approach of Hubbard and Douglas [12] and the single-particle discrete simulations performed by Hogan and collaborators [14]. Its advantages are the numerical solution of a simpler equation and easy computational implementation. The method as originally proposed is limited to colloidal aggregates or aerosol particles where mass and momentum transfer occurs in the so-called continuum regime. In the continuum transfer regime rarefaction effects, quantifiable by the Knudsen number, $\text{Kn} = \lambda/R_1$ where λ is the gas mean free path, are negligible as $R_1 \gg \lambda$ ($\text{Kn} = 0$).

The power-law aggregates we use in this work are synthetic in that they were generated by an algorithm that does not simulate a physical agglomeration mechanism. Instead, the algorithm allows the construction of power-law aggregates with specific properties. In the following, we study the morphology of these synthetic aggregates in an attempt to identify the geometrical factors that determine their small- and large-scale structure. We propose an empirical fit that relates their dynamical properties (hydrodynamic radius) to structural properties (radius of gyration).

2. Hydrodynamic radius of synthetic fractal-like aggregates

2.1. Methodology

In the continuum regime the Stokes friction coefficient of a N -monomer aggregate is [2]

$$f_N = \frac{1}{B_N} = \frac{k_B T}{D_N} \equiv 6\pi\mu R_h, \quad (2)$$

where B_N is the aggregate mechanical mobility, D_N the Stokes–Einstein diffusion coefficient, k_B the Boltzmann constant, μ the fluid viscosity, and R_h the hydrodynamic radius. Eq. (2) defines the

aggregate hydrodynamic radius, which equals the mobility radius in the continuum regime.

Isella and Drossinos [17] argued that the ratio of two aggregate-to-monomer friction coefficients, and correspondingly of their hydrodynamic radii, is related to a ratio of two molecular collision rates: the molecular collision rate with the N -aggregate (K_N) and the molecular collision rate with a monomer (K_1). Accordingly,

$$\frac{f_N}{Nf_1} = \frac{K_N}{NK_1} = \frac{R_h}{NR_1}. \quad (3)$$

The collision rates may be calculated from the steady-state molecular diffusion equation [$\nabla^2 \rho(\mathbf{r}) = 0$], via integrating the molecular diffusive flux $\mathbf{J}_N = -D_g \nabla \rho$ over the aggregate surface, where D_g is the molecular diffusion coefficient and ρ the gas density. The appropriate boundary conditions are total absorption on the aggregate surface [$\rho(\mathbf{r}_{\text{sur}}) = 0$, i.e., neglect of multiple scattering events] and constant fluid density far away from the aggregate ($\rho \rightarrow \rho_\infty$ for $|\mathbf{r}| \rightarrow \infty$). For a monomer, the molecular collision rate evaluates to $K_1 = 4\pi D_g R_1 \rho_\infty$. Thus, the friction coefficient may be determined from the numerical solution of a diffusion equation. For the diffusion calculations we used the finite-element software COMSOL Multiphysics [18].

Isella and Drossinos [17] validated the methodology for straight chains ($d_f = 1, k_f = \sqrt{3}$) by solving the diffusion equation in cylindrical coordinates. We reproduced their calculations in three dimensions. The size of the spherical computational domain was chosen to be at least two orders of magnitude larger than a characteristic dimension of the aggregate to ensure that the condition $\rho_\infty = \text{constant}$ hold at the computational-domain boundaries. We also tested the mesh-independence of the solutions. Fig. 1 shows a power-law aggregate with the corresponding normal diffusive flux, whose integral over the aggregate surface gives the molecule–aggregate collision rate. The aggregate hydrodynamic radius is obtained through Eq. (3) and the appropriate normalization via K_1 .

Furthermore, we validated our calculations for two three-dimensional objects by comparing them to literature values. We calculated the perpendicular friction coefficient of two 3d, symmetric shapes composed of 8 particles: a cube and a rectangle. Our results are compared to the numerically evaluated, analytical calculations of Filippov [16] in Table 1. The highly accurate collision-rate results provide additional support that the method is general enough to be extended to power-law aggregates (with $d_f \neq 1$).

2.2. Generation

The power-law aggregates used in our simulations were created with the tunable cluster–cluster aggregation algorithm proposed by Thouy and Jullien [19] and modified by Filippov et al. [20]. The use of a “mimicking” algorithm, i.e., an algorithm that is not based on a physical agglomeration mechanism, allows us to generate aggregates that have prescribed number of primary particles, fractal dimension, and fractal prefactor. The synthetic aggregates satisfy exactly the scaling law by construction. They share many features with aggregates generated by physical process-based algorithms, and, more importantly, they provide an ensemble of well characterized aggregates to investigate the relationship between their static and dynamic properties.

We consider equal-sized, spherical, and non-overlapping monomers (primary particles). The creation of a fractal-like object starts by specifying the desired total number of primary particles $N = 2^n$ where n is the number of generations. Initially we create $N/2$ dimers; the dimers stick together to form 4-mers by choosing randomly a sticking point and a sticking angle, a process that

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