Test of the Physical Interpretation of the Structural Coefficient for Colloidal Clusters

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I. Introduction

It is well established that random mesoscopic aggregation leads to clusters with internal structure described by a fractal geometry. Branched clusters grow under pure diffusive conditions, exhibiting a fractal dimension around 1.75. Although clusters seem to be good fractals, discussion is actually held on the unicity of the fractal dimension for describing the whole aggregate morphology.1-4

The fractal dimension, \( d_f \), links the number of primary particles per cluster, \( n \), to the aggregate radius of gyration, \( R_g \), according to the relationship \( n = k_0 R_g^{d_f} \), where \( R_0 \) is the monomer radius. The structural coefficient, \( k_0 \), has proven to contain additional information on cluster morphology. In fact, for fractal aggregates with identical \( d_f \), \( R_g \), and \( R_0 \) but different structural coefficient, the lower the \( k_0 \) value, the smaller the number of primary particles contained in a cluster. Larger distance should then exist among them, being the structural coefficient related to that distance. Hence, both structural coefficient and fractal dimension parametrize how fractal objects fill space. O and Sorensen5 found dependence of the structural coefficient on the monomer overlapping in a cluster: \( k_0 = k_0^{(3D)} \delta \), where \( \delta = 2 R_0 / l \), with \( l \) being the center-to-center distance. Thus, \( k_0 \) should increase as overlap increases. This description coming from simple arguments, agrees with simulations and experiments from stereoviews of three-dimensional (3D) aggregates for which high \( k_0 \) values were found.1

In the present paper, that correlation is extended for systems in which an extra separation is considered between monomers. The relationship presents a similar form, with \( \delta = 2 R_0 / (2 R_0 + S) \), where \( S \) is the surface-to-surface distance. An experimental test is performed using surfactant-covered particles aggregating under diffusive conditions. Thus, monomers into the clusters are forced to be located at a certain distance. The mean diffusion coefficient, assessed by dynamic light scattering (DLS), was employed to monitor the aggregation processes. Fractal dimensions were measured by static light scattering (SLS). The structural coefficient, \( k_0 \), was determined for bare and surfactant-covered particles. Results not only support a physical interpretation of the structural coefficient in terms of a separation among monomers, but also allow that separation to be calculated.

II. Theoretical Background

The average diffusion coefficient for aggregating colloidal particles is experimentally assessed from light scattering as5

\[
\bar{D}(t) = \frac{1}{\sum_{n=1}^{N} n^2 S(q R_g(n)) D(n)} \sum_{n=1}^{N} n^2 S(q R_g(n))
\]

The cluster structure factor, \( S(q R_g) \), accounts for the spatial distribution of individual particles within the clusters (\( q \) is the scattering vector and \( R_g \) is the radius of gyration for a cluster formed by \( n \) monomers). The diffusion coefficient, \( D(n) \), describes the system hydrodynamics as a function of the particle size and the cluster size distribution, \( N(n,t) \), containing information on the aggregation mechanism. The cutoff size, \( n_c \), is the upper limit of particles per aggregate, which rises as clusters grow up.

The cluster structure factor, \( S(q R_g) \), is related to the mean light scattered intensity according to \( I(q,t) \sim S(q R_g) \). The characteristic length scale is determined by the cluster size, \( R_g \). For fractal clusters, the structure factor shows a long-time asymptotic power law behavior, \( S(q R_g) \sim (q R_g)^{-\alpha_g} \), valid in the range \( q R_g \leq 1 \). The size and structure of the aggregates determine cluster motion.7,8 The diffusion coefficient depends on the translational and rotational diffusion coefficients, \( D(t) \) and \( D(t) \), respectively. The total diffusion coefficient is then written as \( D(n) = D(t) + D(t) \), where coupling effects have been neglected. Assuming fractal structure for clusters, the average translational diffusion coefficient, \( \langle D(t) \rangle \), is expressed as a function of the number average mean cluster size, \( \langle n \rangle \), according to \( \langle D(n) \rangle = \bar{B}(n) \langle R_g \rangle^2 \). The constant \( \bar{B} \) is a constant containing the cluster fractal dimension and the structural coefficient, \( k_0 \), and the diffusion coefficient for free monomeric particles, \( D_0 \). For certain experimental conditions (described below), the rotational contribution is negligible and the overall diffusion coefficient is identified only to the translational coefficient.

The cluster size distribution, \( N(n,t) \), is usually described for diluted systems by Smoluchowski’s equation. The physical information on the aggregation mechanism is contained into the aggregation kernels, \( k_n \), which parametrize the rate at which \( i \)-mers bind to \( j \)-mers.

Diffusion-limited cluster aggregation is modeled by a Brownian kernel9 but no analytical solutions are known for the Smoluchowski equation. However, constant kernel has proven to be a good approximation.10 For monomeric initial conditions the cluster size distribution for constant kernel (the kernel is size independent, i.e., \( k_{ij} = k_{ii} = c \))

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3 To whom correspondence should be addressed.
7 Sorensen, C. M.; Roberts, G. J. Colloid Interface Sci. 1997, 186, 447.
9 Oh C.; Sorensen, C. M. J. Colloid Interface Sci. 1997, 193, 17.
Table 1: Characteristics of the Colloidal Systems

<table>
<thead>
<tr>
<th>Samples</th>
<th>$D_0$ (m$^2$/s)</th>
<th>$d_0$ (nm)</th>
<th>$\phi$ (cm$^{-3}$)</th>
<th>ccc (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lx1</td>
<td>(1.19 ± 0.02) · 10$^{-11}$</td>
<td>40 ± 2</td>
<td>2 · 10$^{-6}$</td>
<td>996 ± 2</td>
</tr>
<tr>
<td>Lx2</td>
<td>(2.70 ± 0.02) · 10$^{-12}$</td>
<td>184 ± 5</td>
<td>1.3 · 10$^{-8}$</td>
<td>437 ± 30</td>
</tr>
<tr>
<td>Lx3</td>
<td>(2.01 ± 0.03) · 10$^{-12}$</td>
<td>242 ± 8</td>
<td>1.2 · 10$^{-3}$</td>
<td>394 ± 7</td>
</tr>
</tbody>
</table>

is given by\textsuperscript{11} $N(t/t_{agg}) = N_0[(t/t_{agg})^{1/\lambda}(1 + t/t_{agg})^{n-1}]$, where $N_0$ is the initial monomer concentration and $t_{agg} = 2k_{ij}N_0$ is the characteristic aggregation time at which particle concentration falls to half its initial value. Combining all previous information, the average diffusion coefficient can be written as

$$D(t) = B \frac{\sum n^{-1-1/\lambda} N(n, t/t_{agg})}{\sum nN(n, t/t_{agg})}$$

which is valid for fractal clusters in fast aggregation. As expected, $D(t)$ is $q$ independent. Note that the time evolution of the average diffusion coefficient contains information on both the reaction kinetics ($t_{agg}$) and cluster morphology ($d_0$ and $k_{ij}$).

Most kernels reported in the literature are homogeneous functions of $i$ and $j$.\textsuperscript{12-14} Many features depend on a homogeneity exponent, $\lambda$, which allows kernels to be written as $k_{ij} \propto a^{\lambda}$.\textsuperscript{15} That exponent describes the tendency of a large cluster to bind to other large clusters, governed by the overall rate of aggregation. The exponent should take the value 0 for diffusion-limited cluster aggregation (DLCA), and 1 for reaction-limited cluster aggregation (RLCA).\textsuperscript{16} $\lambda$ will be used in this work to check the aggregation mechanism and to calculate the characteristic aggregation time. This parameter is related to the exponent from the long time power law for the mean diffusion coefficient ($D \sim t^{1/(1-\lambda)}$), predicted from the dynamic scaling solution for the cluster size distribution.\textsuperscript{11}

### III. Materials and Methods

Three monodisperse aqueous suspensions of spherical polystyrene particles were used as experimental systems. Table 1 summarizes the diffusion coefficient and particle size, determined by DLS. The particle concentration and critical coagulation concentration (ccc) are also included. Sodium dodecyl sulfate molecules (SDS) were adhered on system Lx1 to keep particle surfaces separated at a certain distance. Moreover, these molecules bestow an extra stability to the smallest particles. Samples Lx2 and Lx3 are surfactant-free.

Water for sample preparation was purified by inverse osmosis using Millipore equipment. Prior to aggregation, samples were sonicated for 15 min in order to break up any initial clusters, thus guaranteeing initial monomeric conditions. Aggregations were induced by adding KBr solution to stable colloids. A Y-shaped device was used for monitoring aggregations simultaneously by DLS and SLS. The working volume fractions appearing in Table 1 were set attending to several constraints: the upper limit was carefully chosen to avoid multiple scattering. The lower limit was determined taking into account that (i) the intensity of scattered light must be larger than noise from static scatterers and undesired contamination, and (ii) the aggregation kinetics should be fast enough to ensure reasonable run time.

### IV. Results and Discussion

The main experimental aim of this work is to obtain the structural coefficient $k_0$ for clusters growing under diffusion conditions. Aggregation experiments were performed at a high electrolyte concentration for the three colloidal systems. To ensure that rotational contribution can be neglected from the light scattering measurements, the angular dependence of the first cumulant from the light autocorrelation function was determined. As an example, Figure 1 shows $\mu_1$ as a function of $q^2$ for sample Lx2. Straight lines appeared for every aggregation time, with $\mu_1$ tending to zero at the $q = 0$ limit, as expected for pure translational detection. Thus, the first cumulant can be converted into mean translational coefficient (also plotted in Figure 1).

Monotonically decreasing long-time asymptotic power laws are reached, as theory predicts, from dynamic scaling arguments. The kinetic exponent, $-1/\lambda(1-\lambda)$, contains structural and dynamic information. An independent technique is required to determine $d_0$ or $\lambda$. Table 2 shows the fractal dimensions determined by SLS. Fractal dimensions for the surfactant-free systems (Lx2 and Lx3) are in the range commonly accepted for diffusion-limited cluster aggregation.\textsuperscript{17} However, fractal dimensions are significantly higher for sample Lx1. This difference is

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\textsuperscript{11} Ziff, R. M. Kinetics of Aggregation and Gelation; North-Holland: Amsterdam, 1984.
\textsuperscript{16} Broide, M. L.; Cohen, R. J. J. Colloid Interface Sci. 1992, 153, 493.
\textsuperscript{17} Carpineti M.; Giglio M. Adv. Colloid Interface Sci. 1990, 46, 13.
Table 2: Summary of Results

<table>
<thead>
<tr>
<th>Systems</th>
<th>$d_i$</th>
<th>$\lambda$</th>
<th>$t_{agg}$ (min)</th>
<th>$B$ ($10^{-11}$ m²/s)</th>
<th>$k_0$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lx1</td>
<td>2.41 ± 0.12</td>
<td>0.06 ± 0.03</td>
<td>0.38 ± 0.07</td>
<td>10.50 ± 0.04</td>
<td>0.73 ± 0.09</td>
<td>0.97 ± 0.12</td>
</tr>
<tr>
<td>Lx2</td>
<td>1.79 ± 0.07</td>
<td>0.05 ± 0.01</td>
<td>2.40 ± 0.08</td>
<td>2.69 ± 0.13</td>
<td>0.99 ± 0.09</td>
<td>1</td>
</tr>
<tr>
<td>Lx3</td>
<td>1.74 ± 0.02</td>
<td>0.03 ± 0.01</td>
<td>5.50 ± 0.08</td>
<td>1.95 ± 0.17</td>
<td>0.95 ± 0.16</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 2. Time evolution of the normalized first cumulant as a function of the scaled time for sample Lx2. From the scaled time, the characteristic aggregation time is determined.

explained by rearrangement of the monomeric particles within the aggregates because, in this case, the surfactant molecules adhered on the particle surface make the binding weaker, thus allowing monomers to change their positions. The fractal dimension change is responsible for the different slope observed in Figure 1 for sample Lx1. Once the fractal dimensions were determined, the homogeneity exponents were easily calculated (Table 2). All values are close to zero, as expected for diffusion-controlled aggregation. Thus, the cluster reactivity is size independent. Furthermore, the aggregation mechanism was not altered by the presence of adsorbed surfactant molecules, as predicted from the short-range character of the involved steric force. Nevertheless, the cluster structure becomes more compact, thus differing from DLCA.

Once the aggregation mechanism was identified, the characteristic aggregation time was determined from the time evolution of the first cumulant:

$$ \mu_1(t) = \mu_1(0) \left(1 + \frac{t}{t_{agg}}\right)^{-1/d_0(1-\delta)} \tag{3} $$

Figure 2 shows $\ln[\mu_1(t)/\mu_1(0)]$ as a function of the scaled time, $\ln[(t/t_{agg})+1]$, for system Lx2. $t_{agg}$ was fitted considering that a straight line with slope unity should be obtained. The fitted values appear in Table 2. Differences are related to the different particle size and initial monomer concentration employed for experiments.

The theoretical mean diffusion coefficient (eq 2) was calculated from values appearing in Table 2. Figure 1 plots continuous curves fitted to the experimental data.

The fitting parameter, $B$, contains the structural coefficient. The cutoff size in eq 2, $n_0$, was set attending to convergence criteria. Data presented in this work coincide over the whole time range from a cutoff size of 250 upward, hence a value of 500 was set to guarantee convergence in all cases.

Time-independent $B$ values were obtained indicating that only static information is contained, as predicted from $B = D_0 k_0^{1/2}$. Figure 3 plots the time evolution for the three experimental systems. Table 2 includes the mean values for each system. The structural coefficient $k_0$ was calculated directly from the fitted $B$ values. For surfactant-free particles, the structural coefficient is very close to unity. This value is in accordance with other experiments ($k_0 = 1.23$ for soot particles and DLCA simulations ($k_0 = 1.19$, averaged over off-lattice simulations). The value also agrees with the qualitative conclusions reported in ref 2. However, the values are significantly smaller than those in the range of 2.0 through 2.4, reported in ref 21 for carbonaceous soot aggregates in laminar diffusion flames. Nevertheless, $k_0$ decreases significantly for SDS-covered particles. This result agrees with prediction from $k_0 = k_0^{(1)}(\delta^{(1)}$, where $\delta = 2R_g(2R_0 + S)$. $S$ is the distance between surfaces of two adjacent primary particles and $R_0$ is the monomer radius. $k_0^{(1)}$ is the structural coefficient when particles are in contact, $S = 0$. This result supports the physical interpretation of the structural coefficient in terms of a monomer separation.

In addition, this relationship allows the thickness of the adsorbed SDS layer to be calculated. With this purpose, the structural coefficient $k_0^{(1)}$ was identified as the average $k_0^{(1)}$ value for the free surfactant systems, Lx2 and Lx3 (because monomer separation must be $\delta = 1$), yielding $k_0^{(1)} = (0.97 ± 0.12)$. However, for aggregates with surfactant adsorbed (sample Lx3), a separation between monomers of $S \sim 4.5$ nm is found. The steric barrier introduced by the presence of SDS prohibits particles from getting in contact because the distance between particles must be at least two times the surfactant layer thickness. The obtained value agrees with the value reported for SDS adsorbed on polystyrene particles, $1–2$ nm.

Notes


Evidence that $k_0$ is related to packing of spheres into space confirms that the structural coefficient contains useful additional information on the inner cluster structure and, hence, the fractal dimension is insufficient for characterizing cluster morphology.

**V. Conclusions**

The fractal dimension and structural coefficient were determined for clusters growing under diffusion conditions. Dependence between the structural coefficient on the monomer separation within the clusters was found by comparison between clusters from bare and surfactant-covered particles. The relationship $k_0 = k_0^{(2)} \delta_0$, valid for monomer overlapping, has proven to be also valid for describing separation between monomers. Assuming that bare latex particles are in close contact, the distance between adjacent primary particles was calculated for the surfactant-covered particles. The obtained value for SDS-covered particles is on the order of twice the thickness of the adsorbed surfactant layer. This result agrees with the high fractal dimension obtained in the presence of SDS, which may be explained by a rearrangement within the cluster due to the presence of a short-range repulsive steric force. Results support a physical interpretation of the structural coefficient, based on monomer packing into the clusters.

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