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# A new method for calculating kinetic constants within the Rayleigh–Gans–Debye approximation from turbidity measurements

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**Abstract.** Using the Rayleigh–Gans–Debye (RGD) approximation and a von Smoluchowski kinetics, a simple theory has been developed which provides a complete fitting of the absorbance versus time curve in a homocoagulation process. Contributions from pairs of particles with zero, one, and two particles between them have been taken into account for aggregates of any size. A description of the curve in the first 20 seconds is obtained for all cases, and in general it is possible to reproduce the curve correctly for the first minute. Finally, we present a technique based on this theory for adjusting the kinetic constant in a homocoagulation process.

## 1. Introduction

Turbidity measurements of the aggregation of colloids are widely used in colloidal science, since they can easily be performed, and information on the kinetic constant is readily obtained from them using the initial slope of the curve [1, 2]. However, adjusting this initial slope is not easy, due to experimental fluctuations in the early stages of coagulation, and in some cases little reproducibility is obtained [3–5].

In this work, the Rayleigh–Gans–Debye (RGD) approximation has been used to explain theoretically the form of the whole turbidity curve in a homocoagulation process. To estimate the turbidity of a suspension of particles, it is necessary to calculate the light scattering cross section of the particles and aggregates.

In previous work [6, 7] the calculation of the scattering cross section of the aggregates was performed assuming fixed structures—linear or closed ones—of the aggregates, which simplifies the calculation, but this assumed form can be far from the actual structure of the aggregates that are formed. Also, a finite number of aggregates are considered in the evolution, so measurements can be reproduced only in the early stages (obviously, the more aggregates one takes into account, the longer the time period that one can reproduce). In this work we have tried to include some of the structure contributions in calculating the scattering cross section, and have included all of the aggregates that are formed.

Thus the contributions from structures of pairs of particles have been considered, as well as the total cross section of each particle, in calculating the scattering cross section of any aggregate, without restrictions on its structure or size. Also, a von Smoluchowski kinetics has been assumed for calculating the concentration of any aggregate at time  $t$ . As a result,

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it has been possible to describe the absorbance versus time curve for a homocoagulation process for the first minute.

Finally we present a new method of obtaining kinetic constants from turbidity measurements based on this theory. The method consists in adjusting the theoretical curve to the experimental one, using the kinetic constant as a fitting parameter.

## 2. Total cross sections of aggregates

To begin with, the definition of turbidity for a colloidal suspension is given as

$$\tau = \sum_{k=1}^{\infty} n_k(t) \sigma_k$$

where  $n_k(t)$  is the number of aggregates of  $k$  particles, and  $\sigma_k$  is the total light scattering cross section of one of these aggregates.

When the RGD approach is used to calculate the light scattering cross section of a particle in a dispersive medium, the fundamental approximation is that

$$4\pi a/\lambda(m-1) \ll 1$$

where  $\lambda$  is the wavelength of light in the medium,  $a$  is the characteristic length of the particle, and  $m$  is the relative refractive index. The total light scattering cross section for a sphere of radius  $a$  can be calculated as follows [8, 9]:

$$\sigma_1 = \frac{4}{9} \pi a^2 \alpha^4 (m-1)^2 \int_0^\pi P_1(\vartheta) (1 + \cos^2 \vartheta) \sin \vartheta \, d\vartheta$$

where  $\alpha = 2\pi a/\lambda$ ,  $\vartheta$  is the scattering angle, and

$$P_1(\vartheta) = \frac{9\pi}{2u^3} J_{3/2}^2(u) = \left\{ 3 \frac{\sin u - u \cos u}{u^3} \right\}^2$$

with  $J_{3/2}(x)$  the (3/2)th-order bessel function, and  $u = 2\alpha \sin \vartheta/2$ .

For an aggregate of  $k$  spheres of radius  $a$ , the total cross section can be expressed as

$$\sigma_k = \frac{4}{9} \pi a^2 \alpha^4 (m-1)^2 \int_0^\pi P_k(\vartheta) (1 + \cos^2 \vartheta) \sin \vartheta \, d\vartheta$$

where now  $P_k(\vartheta)$  is defined as

$$P_k(\vartheta) = P_1(\vartheta)(k + A_k) \quad \text{with} \quad A_k = \sum_{\substack{i,j \\ i \neq j}}^k \frac{\sin h s_{ij}}{h s_{ij}}$$

where  $s_{ij}$  is the centre-to-centre distance between spheres  $i$  and  $j$ , and  $h = u/a = (4\pi/\lambda) \sin(\vartheta/2)$ .

The differences between the cross sections for different aggregates come uniquely from the geometrical factor  $A_k$ , so we can write

$$\begin{aligned} \sigma_k &= k\sigma_1 + \frac{4}{9} \pi a^2 \alpha^4 (m-1)^2 \sum_{\substack{i,j \\ i \neq j}}^k \int_0^\pi P_1(\vartheta) \frac{\sin h s_{ij}}{h s_{ij}} (1 + \cos^2 \vartheta) \sin \vartheta \, d\vartheta \\ &= k\sigma_1 + \frac{4}{9} \pi a^2 \alpha^4 (m-1)^2 \sum_{\substack{i,j \\ i \neq j}}^k I_{ij}. \end{aligned}$$

For two adjacent spheres, the centre-to-centre distance,  $s_{ij}$ , is  $2a$ , but this distance for two non-contiguous (e.g. spheres A and C in figure 1) spheres is not so easy to calculate. Also, the difficulty in calculating  $s_{ij}$  is greater for a bigger number of spheres between particles  $i$  and  $j$ . This can be seen from figure 1.

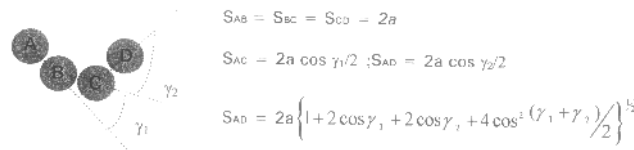


Figure 1. Calculating  $s_{ij}$ .

Since the distances depend on the aggregate structure, we have to average over all possible angles between particles. So, the integrals  $I_{ij}$  defined above must be redefined as follows:

$$I_{ij} = \int_0^\pi \left\{ \int \cdots \int \rho(\gamma_1, \dots, \gamma_n) \frac{\sin h s_{ij}(\gamma_1, \dots, \gamma_n)}{h s_{ij}(\gamma_1, \dots, \gamma_n)} d\gamma_1 \cdots d\gamma_n \right\} \times P_1(\vartheta)(1 + \cos^2 \vartheta) \sin \vartheta d\vartheta$$

where  $\rho(\gamma_1, \dots, \gamma_n)$  is a distribution function.

The distribution function that we have chosen is a flat one—that is, all of the configurations are equally probable. We could choose another distribution function—for example, a function with gaussians centred on the linear and closed configurations—but there is little difference in the final value of  $I_{ij}$ .

In any case, several authors [6, 10] have reported that the aggregate structure is intermediate between the linear and closed ones. Also, experimentally the structure of the aggregate has been observed to depend on the velocity of the reaction. Thus, selecting a flat distribution function is the easiest way to average over all of the dependences, and probably the most realistic situation.

Now, with this new definition,  $I_{ij}$  does not depend on the form of the aggregate. The only important thing is how many particles there are between particles  $i$  and  $j$ . From now on, we will call the integrals  $I_n$ , where  $n$  represents the number of particles between  $i$  and  $j$ .

Therefore, the total cross section of an aggregate of  $N$  particles can be written as follows:

$$\sigma_N = N\sigma_1 + \frac{4}{9}\pi a^2 \alpha^4 (m-1)^2 \sum_{n=0}^{N-1} (N-n-1)I_n = k_{CS} \sum_{n=-1}^{N-1} (N-n-1)I_n$$

since there are  $N - n - 1$  pairs of particles with  $n$  particles between them.  $k_{CS}$  has been introduced as a constant which is equal to the factors appearing in front of the sum. Also, we have defined  $I_{-1}$  so as to ensure that  $k_{CS}I_{-1} = \sigma_1$ .

The integrals  $I_n$  have been calculated for  $n = -1, 0, 1$  and  $2$  by numerical integration with a flat distribution function. The values obtained are represented in figure 2 as functions of  $\alpha$ . It is important to notice that not only is the value of  $I_n$  smaller for bigger  $n$ , but also the factor  $N - n - 1$  that multiplies  $I_n$  in the summation is smaller for greater  $n$ . Thus, the total cross section can be correctly evaluated using just a few terms of the summation.

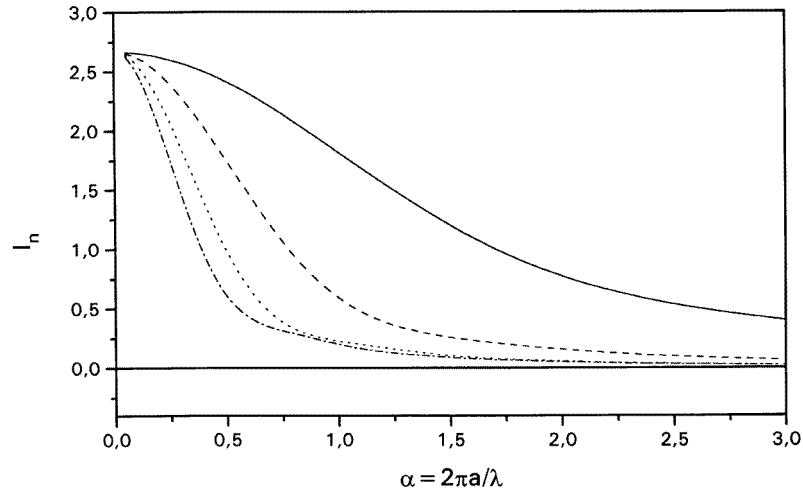


Figure 2. The integrals  $I_n$  for:  $n = -1$ , —;  $n = 0$ , - - -;  $n = 1$ , ·····;  $n = 2$ , — ···.

### 3. The theoretical turbidity curve

We have used a von Smoluchowski kinetics [11]—that is, a unique kinetic constant for coagulation,  $k_{kin}$ , independent of the aggregate form or size. The evolution of the aggregates is described by the equation

$$\frac{dn_k(t)}{dt} = \frac{1}{2}k_{kin} \sum_{\substack{i,j=1 \\ i+j=k}}^N n_i(t)n_j(t) - k_{kin}n_k(t) \sum_{i=1}^{\infty} n_i(t)$$

where the  $k$ -particle aggregate concentration as a function of time ( $n_k(t)$ ) can be obtained analytically [11, 12]:

$$n_k(t) = n_0 \frac{t_p^{k-1}}{(1+t_p)^{k+1}} \quad t_p = k_{kin}n_0t$$

where  $n_0$  is the initial particle concentration.

Going back to the definition of turbidity, and considering the calculations made for the aggregate concentration and the light scattering cross section, it can be expressed as follows:

$$\begin{aligned} \tau &= \sum_k \sigma_k n_k(t) = \sum_{k=1}^{\infty} \left\{ k_{CS} \sum_{n=-1}^{k-1} (k-n-1) I_n \right\} n_0 \frac{t_p^{k-1}}{(1+t_p)^{k+1}} \\ &= k_{CS} \sum_{n=-1}^{\infty} \sum_{k=n+2}^{\infty} (k-n-1) I_n n_0 \frac{t_p^{k-1}}{(1+t_p)^{k+1}} = k_{CS} n_0 \sum_{n=1}^{\infty} I_{n-2} \frac{t_p^{n-1}}{(1+t_p)^{n-1}}. \end{aligned}$$

In practice, we will truncate this series at the fourth term, since this retains the most important contributions to the summation.

The most important achievement in this theory is that we are taking into account all of the aggregates, and not only the smaller ones, as was done in previous work [6, 7]. It has been possible to calculate the total cross section of all of the aggregates, and this leads us to a description of the turbidimetric curve with just the restrictions arising from the RGD approximation.

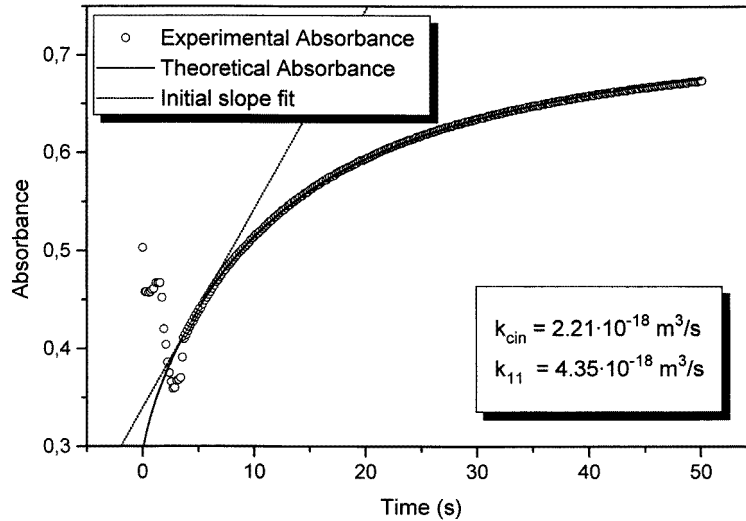


Figure 3. Fitting for the latex MP3 (185 nm).  $n_0 = 5 \times 10^{10} \text{ cm}^{-3}$ .

#### 4. Curve fitting

Using the theoretical model of turbidimetric evolution of aggregates given above, a new technique for calculating kinetic constants has been developed. We have taken as fitting parameters the kinetic constant, and a time ( $t_0$ ) that should be thought of as the time at which the aggregation begins. It is important to calculate exactly when the reaction begins, because it is very fast, and an incorrect start time would lead to a bad fitting and an incorrect value for the kinetic constant.

To prove the efficiency of the method, we have used polystyrene latexes as the model colloidal system due to their high monodispersity, which is quite important when a light scattering technique is used.

In this work, cationic amidine (called MP3) and carboxylated (called AM2) polystyrene latexes were used as model colloids. The latexes were synthesized and cleaned following the recipes and methods described in references [13] and [14]. The particle sizes, as obtained by transmission electron microscopy (TEM) were  $298 \pm 9 \text{ nm}$  and  $185 \pm 7 \text{ nm}$  for the AM2 and MP3 latexes, respectively.

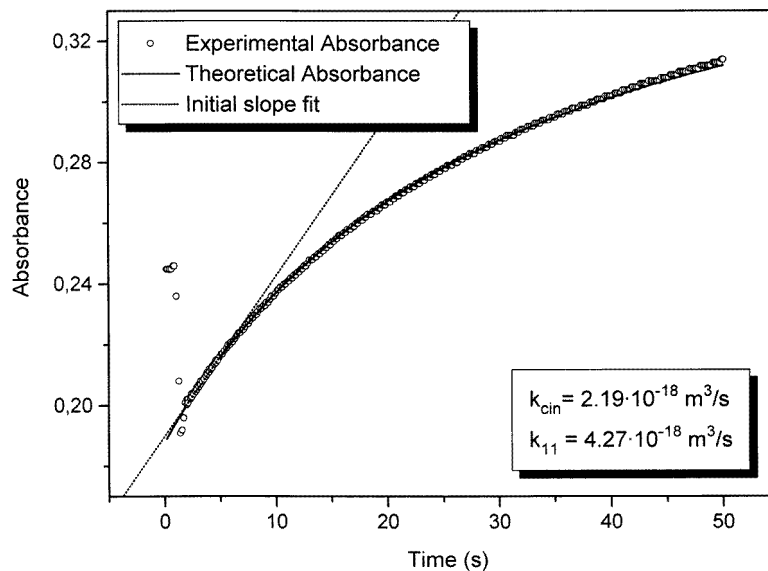
Since the latexes used here had weak acid (AM2) and basic (MP3) groups, it was necessary to carry out the experiments at constant pH, so that no changes in the surface charge would occur during the coagulation process. In this work, the samples were adjusted to a pH of 6 in all cases. The critical coagulation concentrations in this environment were measured for both latexes using NaCl as the electrolyte.

In the coagulation experiments, we collected experimental data for 50 seconds after the beginning of the reaction. The initial monomer concentration was adjusted in order to obtain a value of the absorbance during coagulation within the range of the spectrophotometer. The mixing process was performed using a specifically designed device, consisting of a syringe containing the electrolyte. The syringe is shot by releasing a spring, and the electrolyte is driven into the latex solution inside the spectrophotometer cell [15]. The electrolyte concentration was higher than the critical coagulation concentration. Thus, the reaction takes place in the diffusion-limited aggregation regime, and the kinetic constant governing

the process should be the rapid one.

In figure 3 we show a fitting of the experimental curve for the 185 nm diameter latex as well as the linear fit for the early stages of coagulation. It can be seen that our fitting is really good for the time period for which we have obtained experimental data. In this experiment, we used a wavelength of 600 nm, and the initial concentration of particles was  $n_0 = 5 \times 10^{10} \text{ cm}^{-3}$ .

We have compared the kinetic constant obtained in this way with the monomer–monomer reaction constant ( $k_{11}$ ), calculated from the initial slope which corresponds to the dimer formation process [2]. Since we are using a von Smoluchowski kinetics, in which all of the constants are the same, the relation  $k_{11} = 2k_{kin}$  should be fulfilled. The values for  $k_{kin}$  and  $k_{11}$  obtained for the smaller-particle-size latex are also shown in figure 3. It can be seen that they completely agree with the theoretical relationship. Also it is important to point out that the values obtained for  $k_{kin}$  are similar to those reported in the literature for negatively charged polystyrene latexes obtained using different techniques [4, 12], which lie in the range  $k_{11} = 5 \times 10^{-18} - 8 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ , and for cationic latexes [15].



**Figure 4.** The fitting for the latex MP3 (185 nm).  $n_0 = 2.5 \times 10^{10} \text{ cm}^{-3}$ .

Nevertheless it should be noticed that although this new method provides values of the kinetic constant in agreement with those obtained by adjusting the initial slope, in doing the latter it is necessary to use the data from the four or five seconds after the beginning of the coagulation, when uncertainties about the selection of appropriate initial experimental points are appearing [16], whereas in this new method we are using all of the experimental data to fit the curve. This situation can be observed in figure 3 and figure 4, where the initial points display a great dispersion due to the turbulences in the sample occurring during the mixing process.

To prove the reliability of the method, we have performed some experiments using other initial particle concentrations. In figure 4, we present an absorbance curve for a reaction where the particle concentration was a half of the previous one ( $n_0 = 2.5 \times 10^{10} \text{ cm}^{-3}$ ). All of the other measurement conditions were the same as in figure 3. The fitting is also

really good, and the value obtained for the kinetic constant agrees completely with that calculated for the other case and with those obtained using the linear fit. The initial particle concentration was also increased up to  $n_0 = 10^{11} \text{ cm}^{-3}$ , but in this case multiple scattering occurs due to the high solid concentration in the cell.

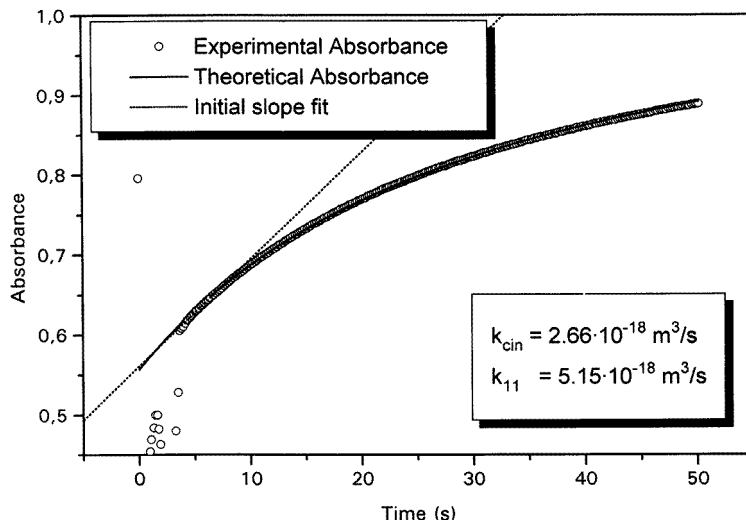


Figure 5. The fitting for the latex AM2 (298 nm).

With the objective of checking the method for systems with different particle sizes, we have used other type of latex. Figure 5 shows the fitting for the 298 nm diameter latex, and the kinetic constant and the monomer–monomer reaction constant values. The fitting is also quite good, and the constant again fulfilled the theoretical relationship. In this case, the initial particle concentration was smaller,  $n_0 = 1.5 \times 10^{10} \text{ cm}^{-3}$ , and the wavelength of light was taken to be larger (800 nm), in order to get a value for  $\alpha$  that was small enough,  $\alpha = 1.56$ . Several authors have tested the validity of the RGD approximation [2, 8], reporting errors in the determination of optical factors within 10% for  $\alpha < 1.5$ , and within 20% for  $1.5 < \alpha < 3.0$ .

However, if we try to fit a curve for a longer time, problems arise due to the large aggregates which do not fulfil the RGD approximation conditions. This can be seen in figure 6, where the experimental data were fitted for 100 seconds, again using the smaller latex and for the same measuring conditions as described above for this latex.

## 5. Conclusions

Calculations of the total light scattering cross section of the aggregates have been made, taking into account structures of two particles with zero, one, and two particles between them. Also a von Smoluchowski kinetics was used to describe the aggregate evolution. Theoretical calculations were compared with the experimental aggregation of latex particles; a good agreement between them was found. This method has also been checked for several particle concentrations and two latexes with different particle sizes.

Hence, a new technique for obtaining kinetic constants from turbidity measurements of aggregation has been developed, fitting all of the experimental data and not only those for



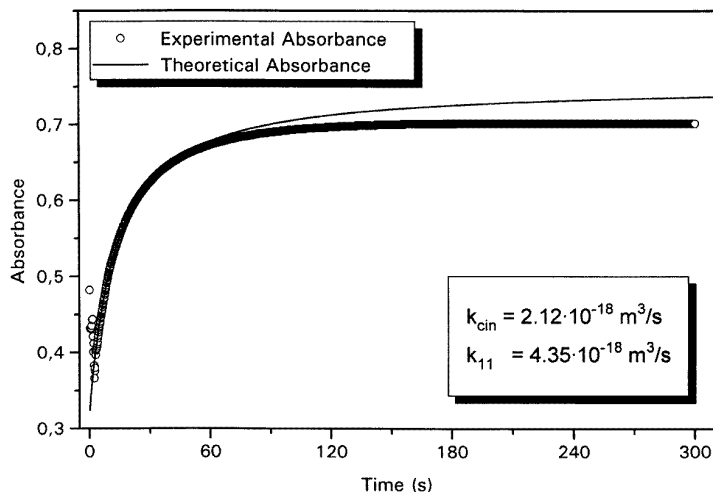


Figure 6. The long-time fitting for the latex MP3 (185 nm).

a few seconds. It permits us to fit the curve for the first minute—that is, up to the time at which the aggregates become too big and no longer fulfil the conditions of the RGD approximation. The kinetic constants obtained are in good agreement with those calculated from the initial slope, and with those reported in the literature, indicating that the von Smoluchowski kinetics is a good approximation to the real kinetics.

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