PHYSICAL REVIEW A VOLUME 39, NUMBER 8 APRIL 15, 1989

# Growth of fractal aggregates in water solutions of macromolecules by light scattering

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(Received 1 July 1988; revised manuscript received 27 September 1988)

We present experimental results showing that such macromolecules as bovine serum albumin (BSA) and deoxyribonucleic acid (DNA) in water solutions build aggregates of fractal structure. We use light scattering techniques, including dynamic (light-beating spectroscopy) and static (intensity) measurements. The BSA results show a behavior similar to that of polystyrene solutions, while for DNA we have observed a restructuring process analogous to those occurring in colloidal silica and gold aggregates.

## I. INTRODUCTION

Many efforts have been made in recent years to understand the kinetic process of growth by random aggregation, i.e., the mechanism of cluster formation from small isolated subunits. Aggregation processes are of paramount interest in many fields of science,[1] such as medicine (growth of tumors), physics, chemistry, polymer physics, metallurgy, meteorology, and ecology, with important implications in industrial processes. In particular, the geometrical properties (shape and size) of such clusters can be utilized to obtain a clear display of the typical features in an aggregation process such as self-similarity, scaling, and universality.[2] In other words, fractal geometry describes such phenomena, showing that it is not necessary to make reference to statistical mechanics. The concepts of fractal geometry are explained in terms of the fractal dimension $D$ (Hausdorff dimension) that quantifies the way in which the mass $M$ of a cluster increases with its length $R$:[3,1]

$$M \sim R^D .$$

Different growth processes (e.g., lattice animals and diffusion-limited, percolation, reaction-limited, and diffusion-limited cluster-cluster aggregations) differ in $D$, so that the fractal dimension contains information about such mechanisms.

Several models have been proposed to explain growth mechanisms, ranging from the simplest Eden model,[4] a lattice model in which particles are added one at a time at random times to the adjacent site to occupy sites (the resulting clusters are relatively compact and their density correlations are independent of distance in the limit of large size), to the models in which the aggregate is built up from the diffusional motion.

Models that utilize the Brownian diffusion are the diffusion-limited aggregation model (DLA) (formulated by Witten and Sander[5]) and the diffusion-limited cluster-cluster aggregation[6,7] (DLCCA). For both, computer simulation allows the study of the density correlation function and a calculation of the fractal dimension $D$, that is 2.5 and 1.75 in a three-dimensional lattice for DLA and DLCCA, respectively. The value 1.75 for DLCCA has also been obtained in the numerical solution of the Smoluchowski equation for cluster-cluster aggregation limited by Brownian diffusion.[8]

Another interesting model for the aggregation process is reaction-limited aggregation (RLA), where the aggregation process starts after the constitutive monomer is somehow activated.[9] For example, in a protein solution the macromolecules are converted from the native $N$ state to the denatured $D$ state according to the revisible reaction $N \rightleftarrows D$, and in the simplest case only the denatured monomers participate in the aggregation process. The appropriate solution of the Smoluchowski equation for this process furnished a value for the fractal dimension that is $D=2.1$.[10]

An interesting process has been observed in silica and gold colloid aggregates.[9,11] These systems are characterized by two classes of aggregation: diffusion limited and reaction limited; the first one is obtained when very rapid aggregation occurs ($D=1.75$), the second one when the aggregation process is slow ($D=2.1$). Clusters for which $D=1.75$ always restructure themselves after a certain time, changing their fractal dimensionality from 1.75 to 2.1 after they are completely stable.

We are interested in biological macromolecular solutions, such as lysozyme, bovine serum albumin (BSA), and deoxyribonucleic acid (DNA), that have been investigated from a structural point of view using many different techniques, such as viscosity, acoustic absorption,[12] and light scattering.[13–15] The results clearly show that these macromolecules tend to form quite a stable, solidlike lattice composed of interacting clusters. As a rule, the structure builds up in a time that ranges between minutes and hours, depending on the kind of macromolecules. A comparison of results for these macro-

 

molecules seems to indicate a common behavior, although the characteristic dimension implied in the structure (the size of the cluster) changes from one macromolecular solution to another[13,15] (0.1 $\mu$m for lysozyme, 0.2 $\mu$m for BSA, and 2 $\mu$m for DNA). In particular, it seems that this characteristic dimension roughly scales like the dimension of the single macromolecule.

Scattering techniques are a powerful way of studying fractal structures. Depending on the characteristic length scale to be observed and on the nature of the aggregate, it is possible to use neutron scattering, x-ray, and light scattering. It can be shown that the scattered intensity, on a length scale much smaller than the cluster radius, is related to the transfer wave vector, $k$ [$k=4\pi n\lambda^{-1}\sin(\theta/2)$], through the simple relation $I(k)\alpha k^{-D}$. This power-law relation for the scattered intensity provides a simple and accurate experimental method of determining the fractal dimension.

The object of this work is the analysis of these aggregated structures in terms of the current models of the aggregation phenomena in order to obtain a detailed view of the growth mechanism in these macromolecular water solutions. We have measured, at different times, the scattered intensity as a function of different scattering angles. The mean linewidth, obtained as the first cumulant of the intensity correlation function, has also been measured as a function of $k$ by a quasielastic light scattering experiment at long times (when the systems were at equilibrium). In the first case we have direct information about the fractal dimension; in the second one the information concerns the $kR$ dependence of the average linewidth (where $R$ is the radius of the cluster).

As predicted by the kinetic models for the random aggregation in terms of scaling arguments[16] the $kR$ dependence of the linewidth is important because three dynamical regimes will be observed, depending on the value of $kR$: for $kR \ll 1$, the fluctuations in concentration relax by the center-of-mass motion so that the linewidth shows the well-known $k^2$ dependence; for $kR \gg 1$, this scaling law predicts a $k^3$ dependence for $\langle \Gamma \rangle$, so that in this region it is possible to probe the fractality of the clusters by intensity measurements. In fact, at a given value of $k$ one probes the motion of the subclusters of size $R \sim k^{-1}$. At $kR=1$, a crossover is observed at the regime where $\langle \Gamma \rangle \sim k^3$. As a result, utilizing experimental values for the radius [13,15] we are for lysozyme in the so-called Guinier region ($kR \ll 1$), where the obtained linewidth is $\langle \Gamma \rangle = D_0 k^2$ ($D_0$ is the Brownian diffusion coefficient) and the intensity shows a Gaussian decay; for BSA and DNA we are in the Porod regime ($kR \gg 1$), where the cited arguments predict for $\langle \Gamma(k) \rangle$ a $k^3$ dependence, so that by intensity measurements it is possible to extract directly the fractal dimension $D$.

## II. EXPERIMENT

Highly polymerized calf-thymus DNA sodium salt was purchased from the Sigma Chemical Company and the solutions were prepared according to a well-established procedure.[14,15] DNA was dissolved in phosphate buffers containing 0.007$M$ $Na_2HPO_4$, 0.002$M$ $NaH_2PO_4$, and 0.001$M$ $Na_2ETDA$ ($p$H $=7.2$, ionic strength $\simeq 0.026$), filtered and dialyzed in order to eliminate foreign particles. The hyperchromicity of the obtained solution at 260 nm was checked and suggests that the solution proved to be free from denatured DNA. The DNA was used without further purification. A DNA concentration of 150$\mu$M (moles of phosphate) as determined by optical absorbance (molar extinction coefficient at 260 nm $=6412M^{-1}$ cm$^{-1}$) was employed. In the used solution, the DNA, with a molecular weight $M_r$ of about[15] $10^7$, assumes a globular configuration with a hydrodynamic radius of about 260 Å.

High-purity crystallized lysozyme and BSA, purchased from the Miles Research Division, were dissolved in doubly distilled deionized gas-free water at 1% by weight concentration. The resulting $p$H readings were 5.1 and 5.6 respectively. For BSA we have also utilized solutions with different $p$H values, namely, 3 and 10.9, obtained by adding an appropriate quantity of NaOH and HCI to each solution. Before the measurements, the samples were filtered.

Great care was taken to avoid dust contamination. The sample cell was washed for a long time in running distilled, filtered water in a dust-free chamber in which the preparation of the solution and the filling of the cell were performed. The measurements were made at the constant temperature of 20 °C in an optical thermostat that allows temperature regulation better than $10^{-2}$ °C. The light source was a 10-mW He-Ne laser operating at a wavelength of 6328 Å. Our measurements were divided into two parts.

(i) The measurements of the scattered intensity as a function of the scattering angle $\theta$ (wave vector k) were carried out with different experimental apparatus for BSA and DNA solutions. In the first case we used a simple goniometer with an angular resolution of 0.01°, a single-photon counting photomultiplier, and a counter. In the case of the DNA solution the scattered intensity turns out to be strongly anisotropic and mainly directed forward (because of the relatively large size of the single molecules). Therefore it becomes necessary to make precise measurements at very low scattering angles. For this reason we utilize a technique that makes use of the optical Fourier transform.[13] The intensity measurements are repeated at different times in order to study the kinetic behavior of the aggregation process of the macromolecules. The transmitted light was not significantly attenuated, so multiple-scattering effects are in our case negligible, and therefore do not influence the measured fractal dimension.[17]

(ii) We measured the photocurrent autocorrelation function with a 128-channel single clipped homemade correlator in the homodyne technique. The correlation of the intensity fluctuations in such a light scattering experiment is[18]

$$C_K(\tau)=\left[\frac{1+K}{1+\langle n\rangle}f(A,T)|g^{(1)}(k,\tau)|^2+1\right]N_B\ , \qquad (1)$$

where $\tau$ is the delay time, $k$ is the exchanged wave vector, $K$ is the clipping level, $N_B=\langle n_K\rangle\langle n\rangle N$ is the theoretical

value of the correlation function at $\tau \to \infty$, $\langle n_K \rangle$ and $\langle n \rangle$ are, respectively, the averaged values of the clipped signal and of the signal, $N$ is the total number of sampling times $T$, and $f(A,T)$ is a function that depends on the coherence area $A$ and on the sample time $T$. The

$$g^{(1)}(k,\tau)=\frac{\langle \Delta\rho(\tau)\Delta\rho(0)\rangle}{\langle \Delta\rho^2\rangle}$$

in the first-order correlation function of the density fluctuations of the macromolecules.

The background contribution to the correlation function $C_K(\tau)$ was measured in each run by delaying the last few channels of the correlator for a suitable time. In this way a reliable estimate of the uncorrelated contribution is obtained. After the subtraction of this "background" in $C_K(\tau)$ and the normalization for its value at $\tau=0$, we have the $g^{(1)}(k,\tau)$. The first cumulant in the obtained first-order density correlation function gives us the average linewidth $\langle \Gamma \rangle$. The measurements were taken after a long time from the sample preparation when solutions were in a stable structural phase and the growth mechanism was at its conclusion.

## III. RESULTS AND DISCUSSION

### A. Elastic scattering (intensity measurements)

The fractal dimension is in general defined as[3]

$$N(R)=\left[\frac{R}{R_0}\right]^D , \tag{2}$$

where $N(R)$ is a quantity obtained by measuring a fractal medium with a gauge $R_0$. In our case, $N(R)$ can be identified as the number of particles of radius $R_0$ which lie within a sphere of radius $R$ centered on an arbitrary particle.

A general and useful way of determining the fractal dimension of an aggregate observed in the real space uses the notion of the density correlation function that is directly connected with the measured scattered intensity. Fractal objects are self-similar structures[5,19] whose geometrical properties are scale invariant, that is, the pair correlation function is homogeneous:

$$\langle \rho(\lambda r_1)\rho(\lambda r_2)\rangle = \lambda^{-A}\langle \rho(r_1)\rho(r_2)\rangle , \tag{3}$$

where $\rho(r)$ is the concentration of monomers at the position $r$; this implies $\langle \rho(r_1)\rho(r_2)\rangle \sim |r_2-r_1|^{A}$. The exponent $A$ is related to the fractal dimension $D$. If $N(R)$ is the number of monomers within radius $R$, then

$$N(R)=\int_0^R d^d r \langle \rho(0)\rho(r)\rangle / \langle \rho\rangle \sim \int_0^R d^d r\, r^{-A} \sim R^{d-A}=R^D , \tag{4}$$

where the exponent $d$ is the Euclidean space dimension and $d-A=D$ (analogously $M=R^D$ if $M$ is the mass of the cluster). In terms of these arguments it can easily be shown[20] that, for a fractal system, the structure factor, namely, the Fourier transform of the pair correlation function, satisfies the following general expressions:

$$S_M(k)=S(kR) ,$$

where $S_M$ is the structure factor for a generic cluster of mass $M$, and in a $d$-dimensional expansion:

$$S(kR)=1-\frac{k^2R^2}{d} \quad \text{for } kR \ll 1 , \tag{5a}$$

$$S(kR)=(kR)^{-D} \quad \text{for } kR \gg 1 . \tag{5b}$$

Therefore in the Porod region, we have the possibility of a direct measurement of the fractal dimension $D$ (only for small distances compared with the radius of gyration of the fractal).

Since the measured intensity $I(k)$ is proportional to the structure factor $S(k)$, we have

$$I(k)\sim S(k)\sim k^{-D} . \tag{6}$$

We use this simple relationship to measure $D$. A logarithmic representation of the measured scattered intensity $I(k)$ as a function of $k$ will be a straight line with slope $D$. However, when the system is highly polydispersed, it has been shown in terms of the scaling theory of percolation clusters[20] that the structure factor and hence the scattered intensity at the gel point obeys the following relation: $I(k)\sim S(k)\sim k^{-\mu}$, where $\mu=D(3-\tau)$ and $\tau$ is the percolation exponent. In this case, a separate determination of the exponent $\tau$ would be required to extract $D$ from the measured exponent $\mu$. But, in our case, we are in the presence of a nonpercolating system with a little polydispersity in the particles forming the aggregate; therefore, Eq. (6) is again valid[17] and the exponent extracted from the logarithmic plot of the scattered intensity is the true fractal dimension.

### B. Dynamic scattering

In our homodyne experiment we measure the dynamic structure factor $S(k,\tau)$ proportional to the autocorrelation function of the scattered field $g^1(k,\tau)$; from this the mean decay rate, or Rayleigh linewidth, is obtained as the first cumulant:[21]

$$\langle \Gamma \rangle = -\left.\frac{d \ln g^{(1)}(k,\tau)}{d\tau}\right|_{\tau=0} = -\left.\frac{d \ln S(k,\tau)}{d\tau}\right|_{\tau=0} .$$

For linear or branched polymers the first cumulant is[21]

$$\Gamma = -\left.\frac{d \ln S(k,\tau)}{d\tau}\right|_{\tau=0} = D_0 k^2 + A(kR)\Theta \Big| ,$$

where $\Theta$ is the rotational diffusion coefficient. The amplitude function $A(kR)$ for $kR \ll 1$ decays like[21] $(kR)^4$, if the aggregated structures are essentially spherical in shape and its value is small; therefore, the translational term dominates $\langle \Gamma \rangle \sim k^2$. For $kR \gg 1$ rotational effects will obscure the $k^2$ dependence.

Clusters of different sizes contribute to the experimentally observed first cumulant; therefore, we have a mean linewidth weighted by the number distribution of the cluster sizes $P(M)$ [$P(M)=N(M)/cv$ where $N(M)$ is the number of aggregates of molecular weight $M$ in the scattering volume $v$, and $c$ is the mass concentration for unit volume. In any case $\sum_M MP(M)=1$]. In terms of the structure factor $S_M(k)$, for a cluster of molecular

weight $M$ (the scattering strength is proportional to $M^2S_M(k)$, we have

$$\langle\Gamma\rangle=\frac{\int M^2P(M)S_M(k)[D_0k^2+A(kR)\Theta]dM}{\int M^2P(M)S_M(k)dM} . \quad (7)$$

The scaling form of the structure factor and precise models of kinetic growth suggest the form of $P(M)$, giving us the solution of Eq. (7); two different distributions of cluster sizes, calculated, respectively, from a percolation model and from the solution of the Smoluchowski equation in the kinetic cluster-cluster aggregation model furnish an analogous result:[22]

$$\langle\Gamma\rangle=k^2D_zF(kR_z) ,$$

where $D_z$ is the average diffusion coefficient and $R_z$ the average radius of gyration; the function $F(kR_z)$ takes into account the internal modes. However, in contrast with the percolation model, the obtained function $F(kR_z)$ for the kinetic cluster-cluster aggregation is complex and not universal.[22]

However, it is shown[16,22] that, for $kR_z \ll 1$, $F(kR_z)=1$ and $\langle\Gamma\rangle=k^2D_z$; under these conditions the intensity measurements are insensitive to the fractal nature of the system. The obtained diffusion coefficient is due to fluctuations in concentration and therefore represents the cluster diffusion constant.

If our attention is restricted to the "Porod" regime $kR_z \gg 1$, scaling arguments[16] give $F(kR_z)\sim kR_z$ and, in this large-$kR_z$ limit, the mean linewidth $\langle\Gamma\rangle$ becomes independent of the correlation range:

$$\langle\Gamma\rangle\sim k^3 . \quad (8)$$

This $k^3$ dependence could be found by the interpretation of the experimental data. If we obtain such a wave-number dependence in a real experiment we are in the Porod regime, and light scattering intensity experiments can give detailed information about the properties of the structures and about the growth mechanism determining them. Equation (8) is expected to fail when $ka_0\sim 1$, where $a_0$ is the chemical length that characterizes the monomer size. At these lengths the only possible technique is neutron scattering.

When $kR_z\sim 1$ we are in the crossover regime and all processes (c.m.) diffusion, rotation and configurational relaxation) have the same rate $\langle\Gamma\rangle_0\sim 1/R_z^3$ where $\langle\Gamma\rangle_0$ is called the fundamental relaxation rate.

The time evolution of the aggregation process has been analyzed[8] in terms of the Smoluchowski rate-equation approach for a cluster-cluster aggregation limited by Brownian diffusion. The use of the scaling properties in the resulting equations allows the expression of the asymptotic time exponent in terms of the fractal dimensionality of the cluster. For very long times, the radius of the cluster (obtained like the gyration radius from the Brownian diffusion coefficient $D_B$ via the well-known "Einstein-Stokes" law) is given by

$$R\sim D_B{}^{-1}\sim t^{1/D} , \quad (9)$$

while, for short times, the behavior of the system is characterized by a continuous increase in the hydrodynamic radius with a fractal dimensionality a little lower than those obtained in the asymptotic regime.[8] The asymptotic scaling in time and the short-time behavior have been experimentally verified in many systems and particularly in colloidal polystyrene water solutions[8] where the fractal dimension, obtained in the time asymptotic limit, is $D=1.75$.

In Fig. 1 we show the normalized relaxation rate $\langle\Gamma\rangle/k^2$ versus $kR$ for lysozyme, BSA, and DNA. It is evident that in the utilized $k$ range these data show that for the lysozyme we are in the condition $\langle\Gamma\rangle_{lys}\sim k^2$, while for BSA and DNA we are in the $\langle\Gamma\rangle\sim k^3$ case. For $R$ we have used the values of previous works,[13,15] that is, 0.05$\mu$m for lysozyme, 0.1$\mu$m for BSA, and 1$\mu$m for DNA.

Therefore, we can conclude that for the lysozyme solutions we are in the Guinier regime $kR \ll 1$ where the light scattering intensity is insensitive to the fractal structure of the scattering clusters; for DNA and BSA solutions we are in the Porod regime $kR \gg 1$ or in the intermediate one $kR\sim 1$ where the angular dependence of the scattering intensity contains useful information about both the cluster-size distribution and the cluster structure.

In Figs. 2 and 3 we show our intensity scattering profiles for BSA and DNA, respectively, at different times, starting from the instant in which the sample is prepared and the aggregation process begins to take place. Note that all the data points are used for the determination of the properly weighted linear least-squares fit.

In Fig. 4 we report the obtained values of the dimension $D$ at different times both for the macromolecules BSA (triangles) and DNA (circles). It is clear that the measured fractal dimension $D$ changes with time, ranging for BSA from 1.65±0.02 just after the sample preparation (a few minutes) to the value of 1.76±0.03 after a very long time (21 h). For DNA we have the following values 2.19±0.02 for very low times and 1.75±0.03 30 h after the sample preparation. The long-time values are

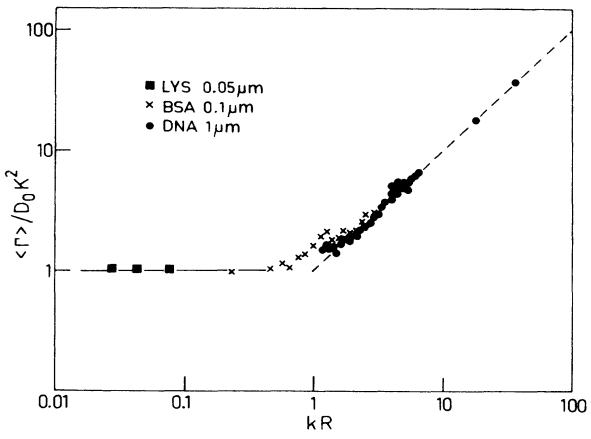


FIG. 1. Normalized relaxation rate for lysozyme (squares), BSA (crosses), and DNA (circles) water solutions.

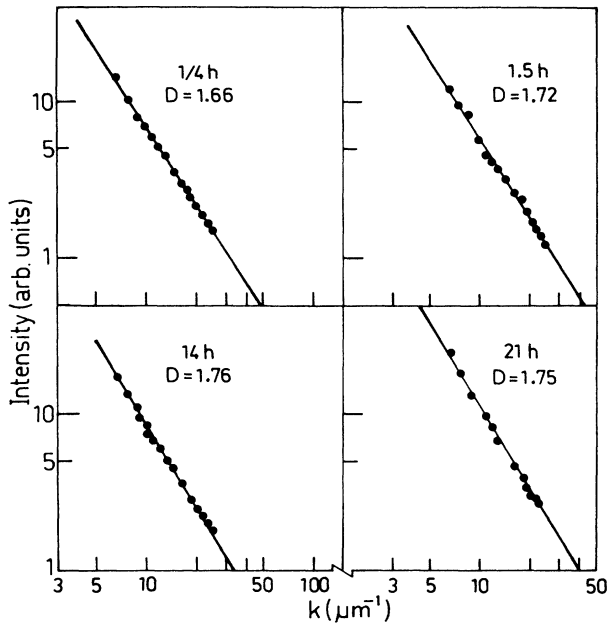


FIG. 2. Intensity scattered profiles at different times for BSA solution.

referred to the asymptotic limit, i.e., when the system is in a stable state and its properties do not change.

The long-time value $D=1.75$ is the same as that obtained by the diffusion-limited cluster-cluster aggregation[6,7] by computer simulation experiments and by quasi-elastic light scattering experiments in a colloidal system.[8]

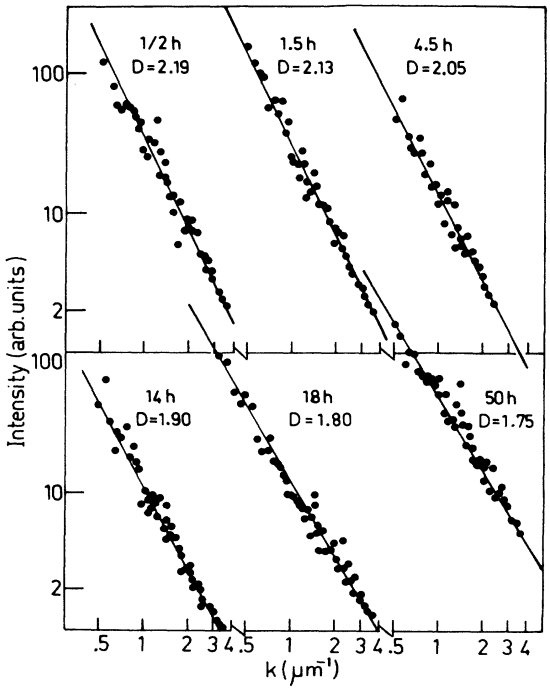


FIG. 3. Intensity scattered profiles at different times for DNA solution.

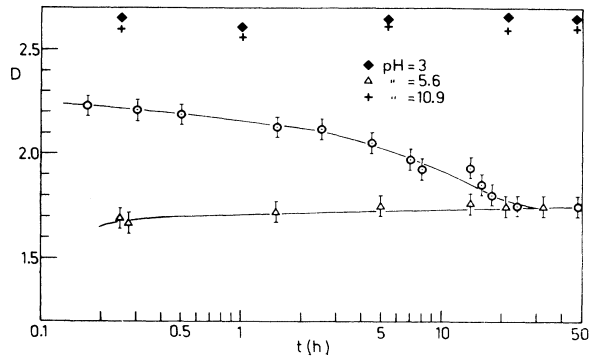


FIG. 4. The obtained fractal dimension $D$ as a function of time; circles refer to DNA solution and triangles to BSA solution at $p$H = 5.6; squares and crosses refer to BSA solutions at $p$H levels of 3 and 10.9, respectively.

In these latter measurements, the value of the fractal dimension $D=1.75$ is the asymptotic (long-time) numerical solution of Smoluchowski's equation for a cluster-cluster aggregation limited by Brownian diffusion.

Our results are in good agreement, in the long-time regime, with the values predicted by DLCCA. The time behavior of our data can be explained by the following simple arguments.

(i) The BSA results suggest that this protein of radius 25 Å is very sensitive to collisions with the solvent showing a pure Brownian character. In fact, the $p$H of the solution, 5.6 in our case, inhibits reaction processes, so the monomers are always in the native $N$ state [for different $p$H values like 10.9 and 3, where the protein is in a denatured state, we have values of $D$ such as 2.65 or 2.6 (see Fig. 4) and the system doesn't show any time dependence]. This fact explains the values obtained in the initial phase and in the long-time limit of the aggregation process ($D=1.65$ after 15 min from the sample preparation and $D=1.75$ at long times) that are very close to the values predicted by the solution of the Smoluchowski equation in the DLCCA model. In any case, the behavior of our solution is in complete agrement with that of polystyrene particles in water, where the value of $D$ goes from about 1.6 at short times to 1.75 at long time.[8]

(ii) As can be seen in Fig. 4, the $D$ values obtained for DNA monotonically decrease with time starting from 2.2 at short times and reach the asymptotic value of 1.75 at $t=31$ h. This behavior can be explained in terms of a restructuring mechanism similar to the one observed in gold and silica colloids. In these cited cases, the systems have two regimes of irreversible aggregation: RLA and DLCCA. In our system the situation is reversed: The final state is the DLCCA, contrary to the silica colloidal aggregates where it is the RLA. In fact, in the first stage of the aggregation process (short times) the globular DNA macromolecules of mean dimension 0.52$\mu$m have active sites, and consequently the mechanism of growth is dominated by RLA, The single macromolecule is a long chain of the constitutive double-helix coil aggregate in a threadlike form. Interactions among internal coil parts

and their fragments are possible, as are interactions among different macromolecules via such active sites. It is possible that the interactions of the thread with the solvent disarm in time and the mechanism that begins with the reaction-limited aggregation process gives way at long times to the simplest diffusion-limited cluster-cluster aggregation.

## IV. CONCLUSIONS

We have measured the properties of water solutions of biological macromolecules lysozyme, BSA, and DNA by quasielastic and intensity light scattering. By these techniques, in the available ranges of $k$ we have shown that for BSA and DNA solutions it is possible to analyze the nature of the aggregates forming in such solutions. As a result, it is shown that the intensity profiles give us an indication that these clusters have a fractal nature and that the time behavior is different for the different macromolecules.

The BSA solutions show the same temporal evolution as polystyrene solutions. At long times the structure exhibits a diffusion-limited cluster-cluster aggregation, while the transient behavior is characterized by a continuous change in the measured fractal dimension with values a little lower than those obtained in the time asymptotic limit.

The DNA solutions show a restructuring process typical of colloidal silica and gold aggregates. The initial state is, in our case, driven by the reaction-limited aggregation and the final one by the cluster-cluster diffusion-limited aggregation. This result can be attributed to the interactions among the macromolecules and the solvent.

## ACKNOWLEDGMENTS

Three of us (S. M., G. M., and F. M.) are affiliated with the Gruppo Nazionale di Struttura della Materia (Italy) and Centro Interuniversitario di Struttura della Materia (Italy).

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