Dynamic light scattering as a probe of the evolution of a self-preserving size distribution in a fractal system

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We consider the behavior of the dimensionless ratio of the first two cumulants that would be observed in a dynamic light-scattering experiment on a coagulation system of particles. This cumulant ratio evolves with time to a limiting value independent of time representing a self-preserving distribution. The limiting value is a function of the fractal dimension of the clusters.

Considerable effort has been made in the past few years to understand the kinetic process of growth by aggregation of colloidal particles. This renewed interest has been aroused by the use of the fractal concept[1] to describe the morphology of the aggregate particles. As first shown by Forrest and Witten[2] and subsequently by others, the aggregated particle may display spatial self-similarity characterized by a fractal dimension D, which may be noninteger. Hence the number of monomers i in a given cluster is related to the aggregate radius by $i \sim R^D$. This static property has been found in numerous real colloids[3–6] as well as in computer simulations.[7,8]

The dynamics of the growth is also affected by the fractal nature of the clusters.[9,10] The growth process is thought to obey the Smoluchowski equation[11]

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} K(i,j) n_i n_j - n_k \sum_i K(i,k) n_i \ . \tag{1}$$

In Eq. (1) n_i is the concentration of clusters made up of i monomers and $K(i,j)$ is the coagulation kernel. Growth by aggregation naturally leads to a size distribution of the clusters; thus this is an important quantity in describing the coagulation process. Friedlander, and co-workers[12] showed that Eq. (1) leads to a "self-preserving" size distribution which keeps a time-independent shape regardless of the initial distribution. This occurs after a long time compared to the coagulation time, $t_c = (4\pi RND)^{-1}$, where in this expression only D is the cluster diffusion constant and N is the total number concentration. More recently, Kolb, Botet, and Jullien[13] have found an explicit expression for the self-preserving size distribution

$$N(x) = \frac{(1+\beta)^{1+\beta}}{\Gamma(1+\beta)} x^{\beta} e^{-(1+\beta)x} \ . \tag{2}$$

Here $x = V/\langle V \rangle$ where V is the Archimedean volume of the cluster particle, $\langle V \rangle$ is the average cluster volume, β is the degree of homogeneity of the coagulation kernel, $K(\lambda i, \lambda j) = \lambda^{\beta} K(i,j)$, and Γ is the gamma function. Despite the recent activity in this area, no measurement of the size distribution has been presented for a fractal system.

In this paper we wish to predict the results of hypothetical experiments that use the dynamic light-scattering technique photon correlation spectroscopy[14] (PCS) to measure the size distribution of aggregating systems, fractal or not, using the method of cumulants.[15] We shall calculate the ratio of the first two cumulants of the PCS spectrum of light scattered from a system of aggregating particles obeying Eq. (1) in a computer simulation. The spectrum is the intensity autocorrelation function assuming the Siegart relation. This will allow us to watch the evolution to a self-preserving size distribution. We also will calculate the cumulant ratio using Eq. (2) and find that it is a strong function of the fractal dimensionality.

Our simulation involves solving Eq. (1) using standard numerical techniques. We assumed a Stokes-Einstein Brownian coagulation kernel, modified to include the fractal dimensionality,

$$K(i,j) = K_0 (i^{1/D} + j^{1/D})(i^{-1/D} + j^{-1/D}) \ ,$$

with homogeneity $\beta = 0$ and a zeroth-order log normal initial distribution. To calculate the first two cumulants of the PCS spectrum, we also assumed the light scattering from the cluster particles could be expressed as a power of the cluster volume V^p with $1 \leq p \leq 2$. Then the dimensionless ratio of the first two cumulants is

$$Q = \frac{C_2}{C_1^2} = \frac{\langle V^p R^{-2} \rangle \langle V^p \rangle}{\langle V^p R^{-1} \rangle^2} - 1 \tag{3a}$$

$$= \frac{M_{p-2/D} M_p}{M_{p-1/D}^2} - 1 \ . \tag{3b}$$

Here M_k is the kth normalized moment of the distribution in Eq. (2), and we used the fact that $i \sim V \sim R^D$. The moments were calculated numerically using the size distribution at various times generated during the computer simulation.

The cumulant ratio Q was calculated as a function of reduced time $t^* = t/t_c$ for two different fractal dimensions, $D = 2$ and 3 ($D = 3$ represents a nonfractal system, e.g., a system of coalescing droplets), for $qR \ll 1$ hence $p = 2$, and a number of different initial distribution widths. Figure 1 displays our results. Q accurately reflects the various initial distributions[16] at $t = 0$ but evolves to a constant value independent of the initial distribution after a few reduced time units. This represents the self-preserving size distribution. Our result for an initially monodisperse system agrees well with that given by Versmold and Hartl[17] who considered this function for Smoluchowski coagulation when the kernel $K(i,j) = 1$. In this case Eq. (1) is exactly solvable. Note that while narrow distributions broaden, broad distributions actually narrow to the same self-preserving size distribution as reflected in Q. It is also interesting to note that the value of the cumulant ratio in the long-time, self-preserving regime Q_{SP} is a function of the fractal dimensionality. This suggests that measurement of Q_{SP} in a real system could yield D.

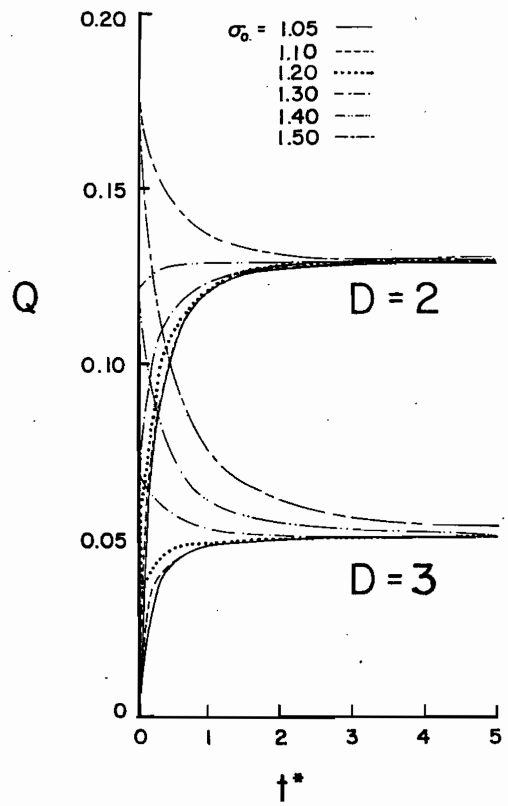

FIG. 1. Evolution of the dimensionless ratio of the first two cumulants, $Q=C_2/C_1^2$, as a function of reduced time, $t^*=t/t_c$. The initial size distribution was taken to be a zeroth-order log normal, $N(R)=\exp[-\ln^2(R/R_0)/2\ln^2\sigma_0]$ with various initial geometric widths σ_0. Results for two different fractal dimensions, $D=2$ and 3, are shown.

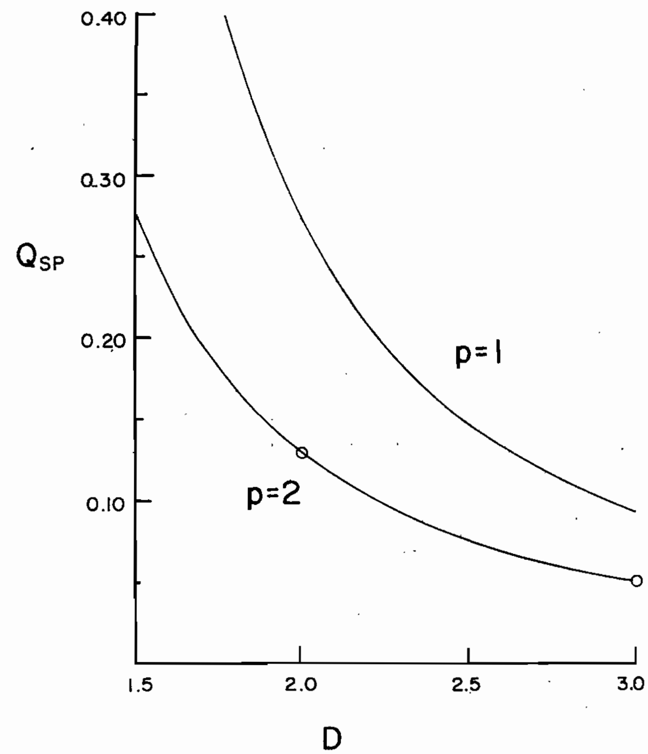

FIG. 2. The limiting self-preserving cumulant ratio Q_{SP} as a function of fractal dimensionality of the aggregates D. Two light-scattering regimes are shown, $p=1$ and 2, where the scattered intensity behaves $I\propto V^p$. The two data points are the computer simulation results in Fig. 1 for large t^*.

To explore this latter result further, we calculated Q_{SP} using Eqs. (2) and (3). The normalized kth moment of the size distribution is

$$M_k(t)=\frac{\Gamma(1+\beta+k)}{\Gamma(1+\beta)(1+\beta)^k}M_1^kM_0(t)^{1-k} . \tag{4}$$

The zeroth and first moments are the number density and total volume, respectively. Applying Eq. (4) to (3) yields Q_{SP} as a function of D. These results are plotted in Fig. 2 for both the "Porod," $qR>>1$ hence $p=1$, and "Guinier," $qR<<1$ hence $p=2$, regimes. We have also assumed $\beta=0$ in Fig. 2, since this is expected in the simple Brownian diffusion case. Q_{SP} displays a strong dependence on D which should be easily distinguished in a dynamic light-scattering experiment. Values for Q_{SP} when $p=2$ for $D=2$ and 3 also agree well with the simulation values at long time in Fig. 1.

Our results assume that clusters of equal mass have the same hydrodynamic radius. Nonsphericity of clusters could lead to different hydrodynamic radii for different particles of the same mass. This would result in a larger Q than we have predicted here. Furthermore, we have assumed as others before us[9,13] that the diffusion coefficient is proportional to $i^{-1/D}$. Chen, Deutch, and Meakin[18] have shown the value $1/D$ may be too small. If so, our results can be easily modified to cover this change.

An experimental procedure might be to measure the fractal dimension D using the first cumulant which contains mean size information. Such experiments have been performed. Concurrently, the second cumulant and hence Q could be measured as a function of time to watch the evolution of the distribution. This would be most successfully carried out in the $qR<<1$ regime where the scattering is isotropic, and hence there would be no angular dependence for Q. This is the region described in Fig. 1. When $qR>1$, there is only a small region where $R<<\lambda$, to give isotropic scattering, is satisfied as well; outside this region our results must be modified.

In conclusion, measurement of the ratio of the first two cumulants in a dynamic light-scattering experiment should allow for study of the evolution with time of the particle size distribution to its self-preserving form. Furthermore, the limiting value of the cumulant ratio is strongly dependent on the fractal dimensionality of the resulting aggregates and hence should allow for another method for determination of this quantity.

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