DYNAMIC LIGHT SCATTERING FROM COLLOIDAL GELS

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Abstract

We present a brief, preliminary account of the interpretation of dynamic light scattering from fractal colloidal gels. For small scattering angles, and for high initial colloid particle volume fractions, the correlation functions exhibit arrested decay, reflecting the non-ergodic nature of these systems and allowing us to directly determine the elastic modulus of the gels. For smaller initial volume fractions, the correlation functions decay completely. In all cased, the initial decay is not exponential, but is instead described by a stretched exponential. We summarize the principles of a model that accounts for these data, and discuss the scaling behavior of the measured parameters.

When colloidal particles are destabilized and made to aggregate, highly tenuous and disordered structures result. However, despite their disorder, the structure of these colloidal aggregates can be quantitatively described as fractals, allowing relatively simple yet quantitative characterization of their structure [1]. In particular, the growth of their mass with their size follows a power law, $M \sim R^{d_f}$, where the exponent is the fractal dimension, d_f, which characterizes the structure, and reflects how tenuous it is; a lower fractal dimension corresponds to a more tenuous structure. The scaling behavior of fractal aggregates is not limited to their structure; fractal objects are also predicted to have other scaling properties. For example, their internal dynamics should also exhibit scaling properties, but should be sensitive to a different scaling exponent reflecting the connectivity of the structure [2]. Thus, measurement of the internal dynamics of fractal objects should provide both new information about their properties as well as their structure.

An ideal experimental method for studying the internal dynamics of a colloidal aggregate is dynamic light scattering. It probes the motion of an object over length scales comparable to the wavelength of light, which is ideal for the internal dynamics of colloidal aggregates. Unfortunately, however, dynamic light scattering probes all motion of the aggregates, and the normal contribution due to the diffusive motion of the aggregates dominates all other contributions, precluding the measurement of their internal dynamics [3]. However, if the aggregates can be held rigidly in place, and not allowed to undergo translational diffusion, the remaining dynamics would allow the determination of their internal dynamics. This is possible by exploiting a unique property of colloidal aggregates; since their density decreases as their size grows, if a colloid system is allowed to aggregate,

and if it continues to form fractal structures indefinitely, the aggregates will ultimately fill all space to form a colloidal gel [4]. This will pin the individual aggregates in place, allowing dynamic light scattering to be used to measure their internal dynamics. To form such gels, it is essential for the fractal aggregates to continue to grow unimpeded. The major limitations to continued growth is the sedimentation of the aggregates as their mass increases. This can be reduced by slowly tumbling the sample, but true gelation is still not observed. There is, however, one system that can be made to gel. This is polystyrene latex particles; their density is only about 5% above that of water, and thus they can be buoyancy matched by the addition of heavy water to the solution, obtaining isopicnic conditions [4]. This allows colloidal gels to be made and their properties to be studied.

Ultimately, the challenge will be to adjust the important parameters of these colloidal gels. These include the strength of the bonds between the individual particles, which must scale the overall strength and properties of the fractals, and the scattering properties of the individual particles, which determine the range over which they can be studied using light scattering. The control of these different features will require the use of different materials. For example, one fundamental question to be addressed is whether there is a fundamental limit on the extent of a fractal cluster, and hence on the lowest initial volume fraction of particles that can be used to form a gel. The experimental limitation in the investigation of this question is the time it takes for the gel to form. Since the gelation is ultimately limited by diffusion, and since the diffusion coefficient of the growing clusters decreases as their radius increases, the gelation time increases rapidly as the initial volume fraction is decreased, and can soon exceed any reasonable length of experiment. However, the gelation time also depends on the size of the initial particles, and much lower initial volume fractions can be explored using very small colloidal particles. In addition, because their scattering cross section is reduced, the use of very small particles will also allow higher initial volume fractions to be studied with light scattering without running into the problems of multiple scattering. A particularly useful material to use to meet these criteria is silica, which is available in the form of very small particles. Finally, for the study of very low volume fraction gels, it will also become essential to use particles that have very strong interparticle bond strengths, and metallic particles may provide the optimum choice. However, both the silica and the metallic particles are too dense to allow them to be buoyancy matched. Thus, these studies must be performed in microgravity. The study of the properties of these gels will be accomplished using light scattering, and thus it is essential to establish the theoretical underpinnings for the correct interpretation of the light scattering by using gels made with buoyancy matched polystyrene. Here, we summarize

some preliminary results of these studies, and will provide a more complete account elsewhere [5].

We use polystyrene colloids with a radius of $a = 9.5$ nm, suspended in a mixture of H_2O and D_2O to buoyancy match the particles as much as possible. Their aggregation is initiated by adding a solution of $MgCl_2$ to make the final concentration 6 mM. While the ultimate aggregation process is diffusion-limited, we adjust the salt concentration to slightly slow the rate to allow sufficient time to prepare the sample and study its behavior before it gels. Thus, for the higher initial volume fractions, the aggregation is initially in the reaction-limited regime, although it ultimately becomes limited by diffusion [1]. Our preliminary experiments focus on initial volume fractions of $1 \times 10^{-4} \le \phi_0 \le 5 \times 10^{-3}$, and measurements performed after the sample had been allowed to aggregate for several days, so that the properties no longer changed with time, and a gel had been formed. We measure the intermediate structure factor, $f(q,t)$, as a function of scattering wave vector, q, properly performing an ensemble average where required. We find that the method suggested by Pusey and van Megen [6] was preferable to that used by Xue et al [7], as the former method enabled decays at longer time scales to be discerned, limited only by the total measurement time, rather than by the rotation rate.

The measured $f(q,t)$ depend strongly on the initial volume fraction of the particles, and on the scattering vector. For the higher concentrations, the samples were non-ergodic for all q, in that $f(q,t)$ did not decay to zero. By contrast, as the initial volume fraction decreased, the total decay in $f(q,t)$ increased, with the higher q becoming ergodic first. Finally, for the lowest volume fraction samples, $f(q,t)$ decayed completely for all scattering wave vectors measured. Interestingly, for all cases, the initial decay of the correlation function was not exponential, but instead was well described by a stretched exponential, decaying as $\exp[-(t/\tau)^p]$, where the stretching exponent, p, was approximately 0.7 and was essentially independent of both ϕ_0 and q. For the lower volume fraction samples, the stretched exponential form provided a good description of $f(q,t)$ over the full range of its decay. By contrast, for the higher volume fraction samples, it provided a good description only for the early time decay, as $f(q,t)$ saturated at a non-zero values at longer times.

We found empirically that $f(q,t)$ could be well fit for all q and all ϕ_0 using a functional form reminiscent of that which describes a harmonically bound Brownian particle. Thus, we fit the data to

$$f(q,t) = \exp\left\{-q^2\delta^2\left[1 - e^{-(t/\tau)^p}\right]\right\}$$ (1)

where the characteristic decay time, τ, and the maximum excursion, δ^2, were used self-consistently as fitting parameters for each value of ϕ_0. This described the data quite well.

Although empirical, this functional form can be derived with a simple model that describes the dynamics of a fractal aggregate [5]. We assume that the scattering probes the motion of small subunits within each aggregate, of size q^{-1}. The motion of each of these subunits is determined by the total motion of all the other portions of the aggregate to which it is attached, up to the motion of largest fractal cluster which makes up the gel. Because of the contribution of motions of many different length scales, the initial decay is comprised of many different time scales, leading to the observed non-exponential behavior. By performing an appropriate sum over all the contributions, we find a functional form that is empirically similar to Eq. (1). The value of the stretching exponent depends on d_s, the bond or connectivity fractal dimension, which determines the scaling of the connected regions [2]. Thus, this provides the only experimental measure of this dimension for a colloidal gel. When $f(q,t)$ does not decay to zero, the extent of the total decay, δ^2, provides a measure of the effective spring constant of the gel, $\kappa = k_B T / \delta^2$ [7]. This spring constant also determines the effective time constant of the decay, provided we know the size of the characteristic cluster in the gel, R_c. This can be determined directly from the position of the peak of the ring of the static scattering pattern; alternatively this can be calculated from the initial volume fraction of particles, assuming that the gelation process is diffusion-limited cluster aggregation [4]. Then, the time constant is given by $\tau = 6\pi\eta R_c / \kappa$. Thus, both the time constant and the spring constant of the colloidal gel are determined. Finally, we can also determine the elastic modulus of the gel; it is related to the spring constant through an additional length scale, which we again take as the characteristic cluster size, giving $G = \kappa / R_c$.

An important question about the scaling of these quantities is their dependence on ϕ_0. We can directly determine the scaling of the modulus for those gels whose correlation functions are non-ergodic, allowing δ^2 to be measured. For the lower volume fraction samples, we can only determining the time constant, and from it infer the modulus. We find that the modulus scales as $G \sim \phi_0^{3.9}$, which is consistent with expectations. This is the first experiment measure of this scaling behavior for these low volume fraction colloidal gels. In addition, this establishes our ability to measure the mechanical properties of colloidal gels through light scattering alone. This is of particular importance as the moduli of the colloidal gels become very weak and mechanical measurement would be strongly biased by the contribution of the surrounding fluid, making it difficult to measure the contributions of the colloidal gel network itself.

These light scattering experiments establish the essential theoretical basis required to interpret the dynamic light scattering from colloidal gels. This will enable these studies to be performed in microgravity. Furthermore, it will be possible to use light scattering measurements, rather than mechanical measurements, to determine the elastic modulus of these colloidal gels.

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