



ELSEVIER

Physica A 235 (1997) 19–33

**PHYSICA A**

# Dynamics of density fluctuations in colloidal gels

A.H. Krall\*, Z. Huang, D.A. Weitz

*Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, USA*

---

## Abstract

We use dynamic light scattering to measure the dynamic structure factor of density fluctuations occurring in colloidal suspensions that have attained a quiescent state long after aggregation. We find a stretched-exponential decay to a finite plateau. Our interpretation of the arrested decay is that these systems are gels, i.e., systems possessing a finite elastic modulus  $G$ . We develop a theory for the internal elastic modes of a fractal cluster and use it to derive  $G$  and the arrested, stretched-exponential behavior of colloidal gel dynamics. Good agreement between experiment and theory is obtained.

*Keywords:* Gels; Colloidal aggregation; Fractal dynamics

---

*Dedicated to our friend and colleague, Prof. Rudolf Klein on the occasion of his sixtieth birthday*

## 1. Introduction

Colloidal aggregation is an outstanding example of a process that produces fractal objects [1,2]. Many studies have investigated the growth and morphology of particle clusters aggregating in dilute suspensions where encounters between clusters are relatively rare events, i.e., the volume of the system occupied by clusters remains small. These studies have investigated, for example, the different cluster-size distributions and fractal dimension values that result in the limiting cases that the rate of the colloidal aggregation is controlled by the diffusion of the clusters [3–5] or, conversely, by the low probability of the formation of a permanent bond [6,7]. Recent work has turned to more concentrated suspensions where cluster growth can proceed to a late stage in which the clusters occupy most of the system's volume and are therefore in continual proximity with their neighbors. In the case of aggregation tending toward the diffusion-limited colloidal aggregation limit (DLCA), light scattering experiments have revealed a low-angle scattered intensity ring which implies the existence of spatial ordering among the clusters [8–10]. One can explain the ordering by

---

\*Corresponding author.

assuming that, under DLCA conditions, the clusters are relatively monodisperse with an average radius  $R_c$ , so that neighboring clusters are typically separated by the average cluster diameter  $2R_c$ , i.e., the clusters order like the molecules of a dense fluid. This picture leads us to expect for the final state of the aggregating colloid a *gel* in which clusters of a characteristic size pack and bond with their neighbors in a network that spans the system. In this paper, we use dynamic light scattering to study the relaxation of density fluctuations of such fractal colloidal gels. Gels of all types have received much attention recently because of their fascinating dynamic behavior [11–15]. Gels of the type considered here are particularly interesting since the arrest of the rigid motions of their fractal clusters constituents removes the contribution made by translations and rotations to the signal detected in a dynamic light scattering experiment, allowing us to observe for the first time the internal motions of fractal colloidal clusters. The importance of internal motions is that they are the elementary excitations analogous to sound waves in homogeneous systems. The much-studied polymeric gels do not permit these motions inside the fractal to be resolved with light scattering, since for them  $R_c$  is much smaller than the wavelength of light.

Information about the density fluctuations of a system may be obtained by dynamic light scattering (DLS) through a measurement of the normalized dynamic structure factor  $f(q, t) = S(q, t)/S(q, 0)$  [16], where

$$S(q, t) = \frac{1}{M} \sum_{j,k=1}^M \langle \exp \{ i\mathbf{q} \cdot [\mathbf{r}_j(0) - \mathbf{r}_k(t)] \} \rangle. \quad (1)$$

Here  $S(q, t)$  is the normalized autocorrelation function of the Fourier transform at wave vector  $\mathbf{q}$  of the position-dependent number density of the particles  $j = 1, \dots, M$  contained in the scattering volume. The angle brackets denote a statistical-mechanical ensemble average. In liquid-like systems, the position  $\mathbf{r}_j(0)$  of particle  $j$  at an arbitrary time  $t = 0$  becomes uncorrelated with the position  $\mathbf{r}_k(t)$  of any particle  $k$  after a sufficiently long delay time  $t$ . For such systems,  $f(q, t)$  decays to zero at long times, the ensemble average is equivalent to an average over time, and identical results are obtained from different scattering volumes. By contrast, in a gel, the interconnection of clusters throughout the system results in a solid-like material in which clusters that are neighbors at any instant remain neighbors indefinitely. Accordingly, the decay of  $f(q, t)$  may saturate at a finite value,  $f(q, \infty)$ , indicating the presence of static spatial non-uniformity, even though the system is macroscopically homogeneous. This inhomogeneity of the system at the microscopic level implies that averaging over space as well as time is now required in order to realize the ensemble average. Techniques, now standard, are available that allow us to obtain  $f(q, t)$  with the proper averaging for such *non-ergodic* systems [17,18]. When this is done,  $f(q, \infty)$  becomes meaningful as a quantity that characterizes the ability of the gel to remain rigid in the presence of thermal agitation. In fact, we relate  $f(q, \infty)$  to the macroscopic elasticity of the gel. In this article, we report measurements of  $f(q, t)$  of fractal colloidal gels as a function of the volume fraction,  $\phi$ , of the unaggregated colloidal particles. We introduce a model for gel dynamics that fits the data and which allows us to infer the elastic modulus,  $G$ ,

of the gel. We find that  $G$  has a power-law dependence on  $\phi$ . To obtain a functional form for  $f(q, t)$ , we identify a set of elastic distortions of the interior of a cluster. A thermal sum over these modes yields a form for  $f(q, t)$  similar to the result obtained in the classical model of a harmonically bound Brownian particle [11,15], but with stretched-exponential dynamics; the predicted stretching exponent is in good agreement with the measured one. The characteristic time of the relaxation,  $\tau$ , is expressed in terms of the gel's macroscopic elastic modulus  $G$  and the viscous drag coefficient  $6\pi\eta R_c$  of the typical cluster. Here  $\eta$  is the viscosity of the solvent. Over the range of volume fractions we measure, we infer a variation of  $G$  through six orders of magnitude with a power-law dependence  $G(\phi) \propto \phi^{3.9}$ .

## 2. Experiment

We study colloidal gels of the type whose behavior as aggregating systems has been discussed extensively by Giglio and his group [8,9]. We prepare them by mixing equal volumes of a suspension of polystyrene spheres, diameter 19 nm, and a solution of  $\text{MgCl}_2$ . In each case, the solvent is a  $\text{D}_2\text{O}/\text{H}_2\text{O}$  mixture,  $\text{D}_2\text{O}$  mass fraction 0.70, whose density equals that of polystyrene [19]. This practice prevents gravitational settling of the aggregating clusters, and is essential to form a gel. After mixing, a portion of the aggregating suspension is transferred to a scattering cell. We use cell thicknesses of 1 mm for the more concentrated samples and 5 mm for the more dilute ones. This keeps the transmission of the unscattered beam above 0.3 which we believe is sufficient for us to neglect multiple scattering. At the colloidal concentrations under study here, aggregation in the strict DLCA limit proceeds too rapidly to allow us time for the mixing and transfer. We therefore choose a standard salt concentration of 6 mM in the final gel, such that the colloids aggregate somewhat more slowly. The aggregation is nevertheless close enough to the DLCA limit to result in the appearance of the low-angle intensity ring [9]. We use a multiple delay-time correlator to measure the normalized scattered intensity autocorrelation function  $g_2(t) \equiv \langle I(0)I(t) \rangle / \langle I \rangle^2$ , which is related to  $f(q, t)$  by the Siegert relation [20]. For fluid systems, including the aggregating colloid, the amplitude  $g_2(t=0)$  of  $g_2(t)$  is close to 2 provided that the detector receives light from within a single laser speckle, as is the case for our instrument. During the aggregation, we obtain the average hydrodynamic radius,  $R_h$ , of the growing clusters from a cumulants analysis of  $g_2(t)$ . We find that the clusters grow until a time of the order of  $10^3$  to  $10^4$  s, depending on the colloidal concentration. For colloid volume fractions above  $\phi \approx 10^{-3}$ , the end of the growth of  $R_h$  coincides with the appearance of a nonexponential behavior for  $g_2(t)$  and a reduction of the amplitude  $g_2(0)$ . Also at this time, the values of  $R_h$  begin to vary more from run to run. The amplitude loss and noisiness of  $R_h$  are typical features of nonergodic systems. In particular, the decrease of  $g_2(0)$  is closely related to the saturation of the decay of  $f(q, t)$  to a finite value  $f(q, \infty)$ , and thus indicates gelation of the system. The aggregation of more dilute colloids with  $\phi < 10^{-3}$  ends when the values of  $R_h$  become

constant without an increase of run-to-run fluctuations and  $g_2(t)$  acquires a non-exponential character without loss of its amplitude. That these more dilute colloids also form gels is suggested by the observation that an aggregated sample, initially homogeneous as judged by the eye, fragments into coarse pieces if it is gently tapped or vibrated. We shall therefore assume that the aggregation of all of our samples ends with the formation of a gel, even though, in principle, our measurements imply gelation of only the more concentrated systems with volume fractions  $\phi > 10^{-3}$  such that the decrease of  $g_2(0)$  can be observed.

### 3. Behavior during gelation

We obtain interesting qualitative information on the kinetics of gelation from correlation functions that are measured in runs of short duration made during the aggregation and gelation. Here, and for this purpose only, we ignore the issue of nonergodicity, since the methods we use to obtain the proper ensemble averaging are difficult to apply to a system which is not in equilibrium. Fig. 1 shows the behavior of  $g_2(0)$  and the apparent hydrodynamic radius  $R_h$  as functions of the time since the initiation of the aggregation of a colloidal suspension with particle volume fraction  $\phi = 5 \times 10^{-3}$ . These values have been obtained by fitting the initial decay of  $g_2(t)$  with the form  $g_2(t) = 1 + A \exp(-2Dq^2t)$ , where  $A$  and  $D$  are fitting parameters. During the period of free growth of the aggregating particles,  $D$  is the diffusion coefficient of the randomly moving clusters from which their average hydrodynamic radius  $R_h$  may be found from the Stokes–Einstein relation  $D = k_B T / 6\pi\eta R_h$ . Initially  $R_h$  increases, reflecting the growth of the aggregates. However, about 1500 s after initiation of the aggregation,  $R_h$  is seen to attain a maximum. At about the same time,  $g_2(0)$  shows a drop from the initial value, close to 2, that occurs in fluid systems. The interpretation of Fig. 1 is that this sample has gelled at the gel time  $t_{\text{gel}} = 1500$  s; subsequently  $R_h$  should be viewed as a quantity that characterizes the dynamics of density fluctuations in the gel and not as the radius of any aggregates of colloidal particles. The decrease of  $R_h$  shows that the time scale of such dynamics shortens in the curing gel, while the behavior of  $g_2(0)$  indicates that their amplitudes decreases. Both trends may be due to the stiffening of the gel. This behavior is consistent with that reported for a polymeric gel whose dynamics also showed a divergent characteristic time at the gel time [13]. This analysis is only qualitative because of the neglect of ensemble averaging; however, some ensemble averaging is actually provided by occasional rearrangements of the early gel as it sets. These re-arrangements are the source of the noisiness of the data shown in Fig. 1.

### 4. Dynamics of quiescent gels

For the remainder of this article we discuss only quiescent gels. Typically, we take data during a two-day period beginning one day after the preparation of the samples.

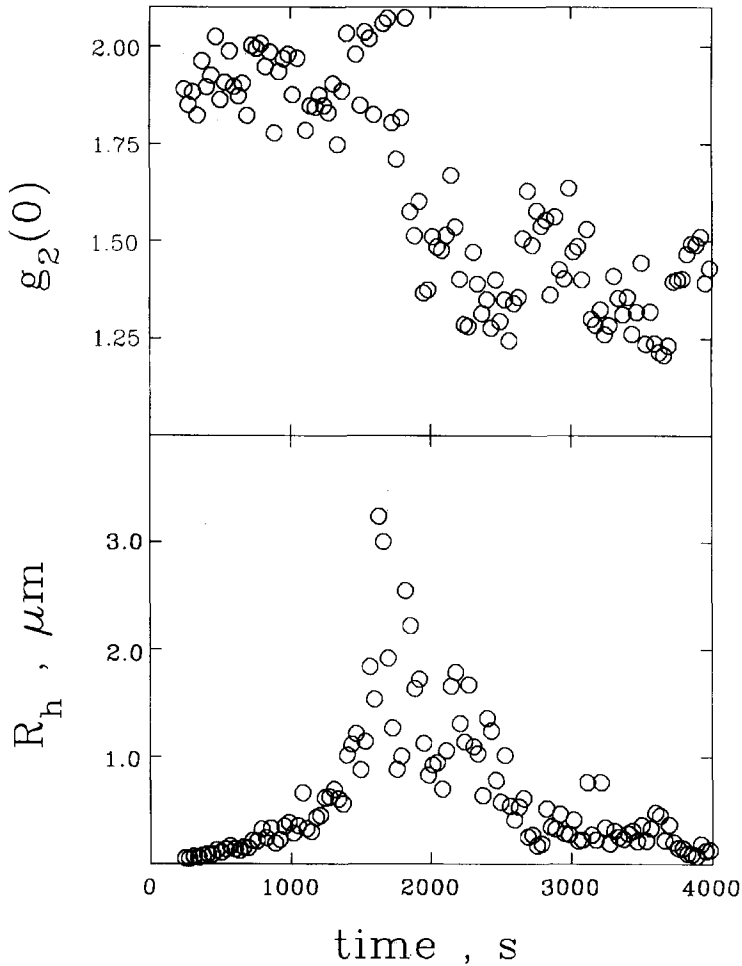


Fig. 1. Aggregation and gelation of a suspension of 19 nm diameter polystyrene spheres,  $\phi = 5.0 \times 10^{-3}$ ,  $[\text{MgCl}_2] = 6 \text{ mM}$ . The upper and lower curves are respectively the intensity autocorrelation function amplitude  $g_2(0)$  and the apparent hydrodynamic radius  $R_h$  as functions of the time since the initiation of the aggregation. The system gels at  $t_{\text{gel}} \cong 1500 \text{ s}$ .

During this time, the gels exhibit steady-state behavior. The correlation functions  $g_2(t)$  taken from samples with  $\phi > 10^{-3}$  have reduced values of  $g_2(0)$ . For these samples, we make a supplementary measurement of the scattered intensity averaged over speckles so that we can apply the modified Siegert relation derived by Pusey and van Megen to reduce  $g_2(t)$  to the properly averaged  $f(q, t)$  [18]. Gels with  $\phi < 10^{-3}$  yield values for  $g_2(0)$  that are experimentally indistinguishable from those of fluid systems. We therefore calculate  $f(q, t)$  using the usual Siegert relation to which the modified one reduces in this case, assuming that here effects of structural arrest are too small to cause a time average to differ appreciably from an ensemble average.

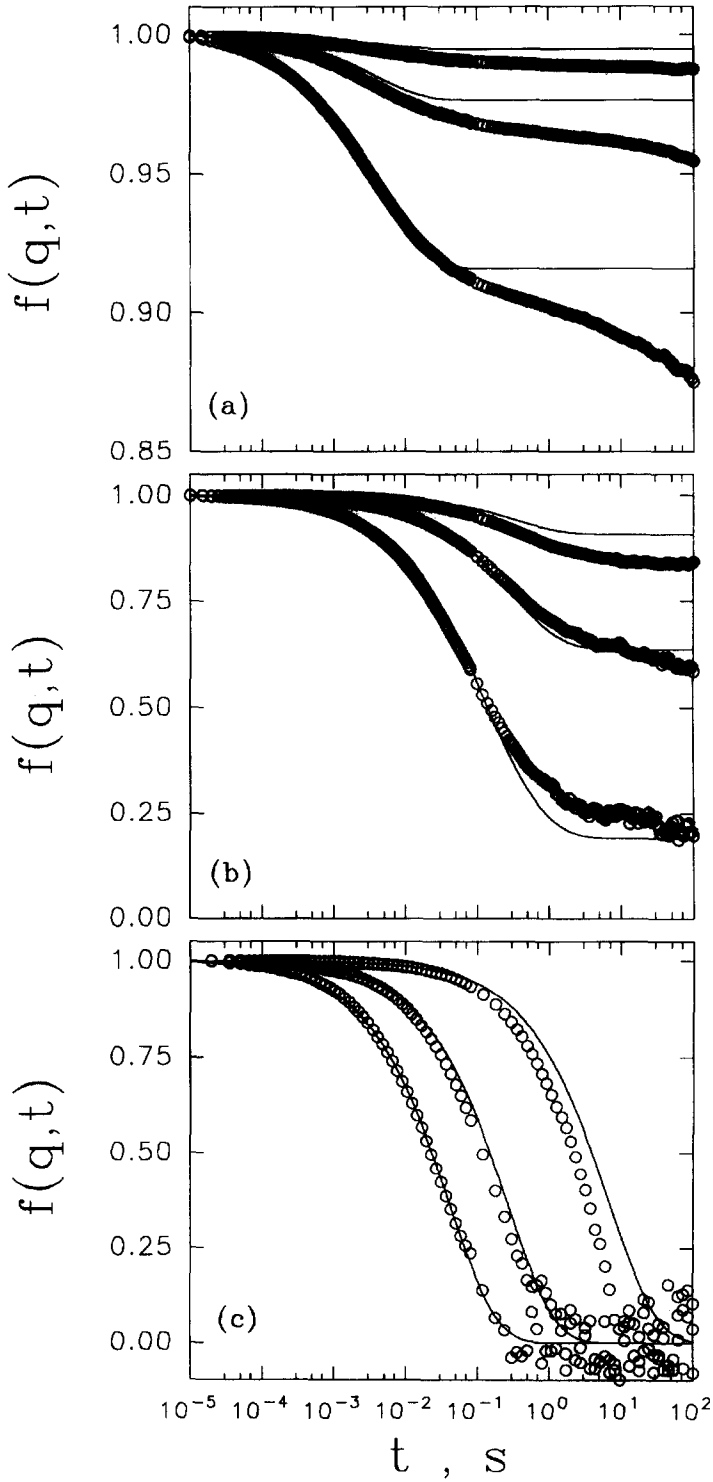


Fig. 2.

In Fig. 2, we plot the normalized dynamic structure factors  $f(q, t)$  of three gels with colloidal monomer volume fractions in the range  $1.7 \times 10^{-4} \leq \phi \leq 5.0 \times 10^{-3}$  as functions of  $q$  and  $t$ . Data taken at three scattering angles  $\theta$  are shown for each concentration. The lowest angle,  $\theta = 15^\circ$ , is in all cases much larger than the angle where occurs the intensity peak corresponding to cluster ordering. The wave number of the probed density fluctuation is related to the scattering angle  $\theta$  by  $q = (4\pi n/\lambda)\sin(\theta/2)$ , where  $b = 1.33$  is the refractive index of the solvent and  $\lambda = 530$  nm is the wavelength of the laser. It is seen that the gel with the highest concentration  $\phi = 5 \times 10^{-3}$  has highly arrested dynamics with  $f(q, t) > 0.85$  for delay times  $t$  out to 100 s. The intermediate gel,  $\phi = 1.5 \times 10^{-3}$ , shows much larger amplitudes for temporal density fluctuations; nevertheless the saturation of  $f(q, t)$  to finite values indicates that this sample also lacks the complete relaxation of a liquid-like system. With the most dilute gel,  $\phi = 1.7 \times 10^{-4}$ , we obtain at all angles decays of  $f(q, t)$  to values below 0.1. Given the level of noise in the data, these decays cannot be reliably distinguished from decays to zero. The time scale for these decays decreases by about two orders of magnitude as  $q$  increases over the range of our measurements. The decays of the two more concentrated gels, on the other hand, occur on time scales that depend on  $q$  much less strongly but are quite different for the two concentrations, being of the order of  $10^{-3}$  s for the most concentrated sample and 0.1 s for the intermediate sample. In all cases, the range of times over which  $f(q, t)$  has an appreciable variation is very broad, say three decades. For comparison, the times over which a decaying exponential varies appreciably cover a range of only about one decade.

## 5. Model for the dynamics of fractal gels

To explain these observations, we introduce the following model for the internal dynamics of gelled fractal clusters. It has been shown that a good approximation for the dynamic scattering of a fractal cluster is obtained if one ignores the details of its structure on length scales shorter than  $q^{-1}$  [21]. The reason is that colloidal particles that are this close to each other scatter the incident radiation nearly coherently. We therefore treat the cluster as an assembly of sub-clusters of radius  $q^{-1}$ , regarding these sub-clusters as the elementary units that scatter the incident radiation. Throughout, we shall call these sub-clusters “blobs”. We then apply Eq. (1) to the assembly of blobs,



Fig. 2. Ensemble-averaged dynamic structure factors  $f(q, t)$  of quiescent colloidal gels. The two more concentrated gels are stiff enough that thermal motions are localized to distances of the order  $1/q$  or less; consequently the decay of  $f(q, t)$  saturates at long times. The least concentrated gel is floppy enough that a full decay is observed. (a) Colloidal monomer volume fraction  $\phi = 5.0 \times 10^{-3}$ ; the three data sets, from top to bottom, correspond to scattering angles  $\theta = 15^\circ, 32^\circ$ , and  $64^\circ$ ; the smooth curves are calculated from Eq. (7) with  $\delta^2 = 3.1 \times 10^{-4} \mu\text{m}^2$  and  $\tau = 3.9 \times 10^{-3}$  s. (b)  $\phi = 1.5 \times 10^{-3}$ ;  $\theta = 15^\circ, 32^\circ$ , and  $64^\circ$ ;  $\delta^2 = 5.9 \times 10^{-3} \mu\text{m}^2$ ,  $\tau = 0.36$  s. (c)  $\phi = 1.7 \times 10^{-4}$ ;  $\theta = 15^\circ, 45^\circ$ , and  $90^\circ$ ;  $\delta^2 = 2.2 \mu\text{m}^2$ ,  $\tau = 1850$  s.

having re-interpreted the coordinate  $r_k(t)$  in Eq. (1) as the center of mass of blob  $k$ . As a further approximation, we ignore the terms of Eq. (1) that describe the product of fields scattered from distinct blobs, i.e., we restrict the sum to the terms  $j = k$ . This step yields a good approximation because colloidal particles separated by distances greater than  $q^{-1}$  scatter the incident radiation nearly incoherently [21]. Under these approximations, the normalized dynamic structure factor becomes [16]

$$f(q, t) = \exp \{ - q^2 \langle \Delta r^2(t) \rangle / 6 \}, \quad (2)$$

where  $\langle \Delta r^2(t) \rangle$  is the mean squared displacement of the center of mass of a typical blob of radius  $q^{-1}$ . In writing Eq. (2), we have neglected rotations since we expect them to be suppressed in the case that the clusters are packed in a gel. In any case, it is known that the effect of rotations is only to change the time scale of  $f(q, t)$ , relative to the prediction of Eq. (2), by a factor of the order of 2 [21]. The saturation of the decay of  $f(q, t)$  indicates that the motions of a given blob are localized in that there exists a characteristic value, say  $\delta^2$ , for the mean squared displacement at long times. That is,  $\langle \Delta r^2(t) \rangle \approx \delta^2$  as  $t \rightarrow \infty$ . Now although the blob's motions are local in this sense, since the particles in a cluster may interact it is also true that the blob's motion are coupled to the motions of particles throughout the cluster. In general, a large number of distinct types of such collective motions, or modes, may contribute to the motion of the given blob. By assumption, the amplitude of the net contribution of all these modes is the blob's maximum mean squared displacement  $\delta^2$ . However, each mode may make its contribution on a time scale characteristic of that mode. In this case, the buildup of  $\langle \Delta r^2(t) \rangle$  to its final value is a process occurring over a range of characteristic times. The measured decay of  $f(q, t)$  occurs over a wide range of times. This observation suggests that a large number of collective modes of internal motion within the fractal cluster, covering a wide range of characteristic times, contribute to the observed dynamics.

To this point, the discussion is quite general. To make progress, we need a schematic picture of these collective motions. Let us imagine that the given blob is carried along by the motion of some "sub-cluster" in which it is imbedded; this sub-cluster is itself imbedded in and carried along by a larger sub-cluster, and so on. Thus we imagine a hierarchy of local modes each of which contributes to the motion of the blob. The succession goes on up to include the motions as a unit of the entire cluster of radius  $R_c$ . We enumerate the modes by the radii  $R_i$  of the sub-clusters  $i = 0, 1, \dots, N$ , where sub-cluster 0 is the blob with  $R_0 = q^{-1}$ , sub-cluster  $N$  is the entire cluster with  $R_N = R_c$ , and in general sub-cluster  $R_i$  is contained within sub-cluster  $R_{i+1}$ . Since within the fractal no preferred length scale can be singled out, we have  $R_{i+1}/R_i \equiv f$ , where  $f$  is a fixed scale factor. This relation fixes the number of modes,  $N$ , in terms of the scale factor through  $f^N \approx qR_c$ . We treat each mode as an independent, over-damped harmonic oscillator characterized by a spring constant  $\kappa_i$  and a relaxation time  $\tau_i$  for an exponential return to equilibrium. We assign  $\tau_i$  in terms of  $\kappa_i$  as  $\tau_i = 6\pi\eta R_i/\kappa_i$ , assuming that a Stokes drag coefficient  $6\pi\eta R_i$  applies to the sub-cluster of radius  $R_i$ . The first mode,  $i = 0$ , is the fastest and stiffest and the only mode that can



contribute to the motion of the given blob if all parts of the cluster except for the blob and its immediate surroundings are held fixed. The last mode,  $i = N$ , is the slowest and floppiest and the only mode that can contribute if the cluster is rigid. We assume that the spring constant  $\kappa_c$  of this last mode sets the scale for the gel's macroscopic elastic modulus  $G$  through  $G \propto \kappa_c/R_c$ . The reason for this identification is that  $2R_c$  is the average spacing between clusters, while  $\kappa_c$  is the average effective spring constant describing the elastic bond between clusters. Since we assume the modes are independent, the mean squared displacement,  $\langle \Delta r^2 \rangle$ , of the given blob is the sum  $\sum_{i=0}^N \langle \Delta r_i^2 \rangle$  of the amplitudes of each mode. According to the equipartition of energy principle, these satisfy  $\kappa_i \langle \Delta r_i^2 \rangle = 3k_B T$ , where  $k_B$  is Boltzmann's constant. To obtain the full dynamic behavior,  $\langle \Delta r^2(t) \rangle$ , of the mean squared displacement of the blob, we similarly sum the time-dependent mean squared displacements,  $\langle \Delta r_i^2(t) \rangle = \langle \Delta r_i^2 \rangle [1 - \exp(-t/\tau_i)]$ , contributed by each mode. These have exponential relaxations from their initial values of zero to their final values  $\langle \Delta r_i^2 \rangle$ . Thus our model becomes complete once we assign the spring constants  $\kappa_i$  characteristic of the collective motion executed by the sub-cluster of size  $R_i$ . To do this, we invoke a power-law relation between spring constant and size that is due to Kantor and Webman [22, 23]:

$$\kappa_i = \kappa_c (R_i/R_c)^{-\beta}. \quad (3)$$

Here the exponent  $\beta$  is given by  $\beta = 2 + d_B$ , where the backbone dimension  $d_B \approx 1.1$  is the fractal dimension of the space of paths remaining on the cluster that connect pairs of points on the cluster. Thus we have  $\tau_i = \tau_c (R_i/R_c)^{\beta+1}$ , where  $\tau_c = 6\pi\eta R_c/\kappa_c$  is the system's slowest relaxation time and describes how the typical cluster, acted on by the restoring forces provided by its neighbors, relaxes to its equilibrium position. We pass from a discrete sum over the modes  $i = 0, 1, \dots, N$  to an integration over the sizes  $R$  of the modes to obtain finally

$$\langle \Delta r^2(t) \rangle = \frac{3k_B T}{\kappa_c} \int_{R=0}^{R_c} \frac{dR}{R \ln f} \left( \frac{R}{R_c} \right)^\beta \left\{ 1 - \exp \left[ -\frac{t}{\tau_c} \left( \frac{R_c}{R} \right)^{\beta+1} \right] \right\}. \quad (4)$$

Here, since  $qR_c \gg 1$  strongly holds in our measurements, we have extended the lower limit of the integral from  $R = q^{-1}$  to  $R = 0$ . This approximation allows us to express the integral in terms of the incomplete gamma function,  $\gamma(a, x)$  [24], but has a negligible effect on the final results, as we have verified by evaluating Eq. (4) numerically as written and from the finite lower limit  $R = q^{-1}$ . There now appears in Eq. (4) the quantity  $1/R \ln f$ , which is the number of modes per unit increment of the mode size  $R$ . This particular form for the density of modes is the direct consequence of our identification of the system's normal modes as the local motions of sub-clusters whose sizes satisfy the relation  $R_{i+1}/R_i = f$ . Eq. (4) becomes

$$\langle \Delta r^2(t) \rangle = \frac{3k_B T}{\beta \kappa_c \ln f} \left\{ 1 - [ps^p (\Gamma(-p) - \gamma(-p, s))] \right\}, \quad (5)$$

where  $p = \beta/(\beta + 1)$  and  $s = t/\tau_c$ . Here  $\Gamma$  is the usual gamma function. The quantity in square brackets is a function that decays to 0 from an initial value of 1. The beginning

of its expansion in powers of  $s$  is  $1 - \Gamma(1 - p)s^p + \beta s - ps^2/(4 - 2p) + \dots$ . Therefore, at early times  $t \ll \tau_c$ , Eq. (5) is identical with the stretched exponential form

$$\langle \Delta r^2(t) \rangle = \frac{3k_B T}{\beta \kappa_c \ln f} \left\{ 1 - \exp \left[ - \left( \frac{t}{b\tau_c} \right)^p \right] \right\}, \quad (6)$$

where  $b = [\Gamma(1 - p)]^{-1/p}$ . By integrating Eq. (4) numerically, we find that Eq. (6), with  $b$  so specified and with  $p = \beta/(\beta + 1)$ , is a good approximation only for very early times such that  $s = t/\tau_c$  is of the order  $10^{-2}$  or less. However, if  $p$  and  $b$  are treated as free parameters, Eq. (6) is an excellent approximant to the computed integral for all times less than about  $10\tau_c$ . In this sense, our theory predicts a stretched exponential form for fractal gel dynamics. We have evaluated Eq. (4) using various choices for  $\beta$  and find that the effective stretching exponent  $p$  is always somewhat less than  $\beta/(\beta + 1)$ , while the effective value for  $b \approx 0.3$  does not vary much as a function of  $\beta$ .

Insertion of Eq. (6) into Eq. (2) yields our model equation for the dynamic structure factor of fractal colloidal gels:

$$f(q, t) = \exp \{ - q^2 \delta^2 [1 - e^{-(t/\tau)^p}] \}, \quad (7)$$

where we treat  $\delta^2$  and  $\tau$  as volume-fraction-dependent fitting parameters. We assign the effective stretching exponent  $p$  a fixed value independent of volume fraction but optimize  $p$  in order to obtain the best agreement between the data and the model. If we set  $\beta = 3.1$ , the theoretical value for  $p$ , found by fitting the numerically computed integral Eq. (4) to the approximant Eq. (6), is 0.70, which may be compared with  $\beta/(\beta + 1) = 0.756$ . From our theory may be derived two relations linking the fitting parameters  $\delta^2$  and  $\tau = b\tau_c$  to the gel's properties  $G$  and  $R_c$ . These are  $G \propto \kappa_c/R_c = 6\pi\eta b/\tau$  and  $\delta^2/\tau = D_c/2\beta b \ln f$ , where  $D_c = k_B T/6\pi\eta R_c$  is the Stokes–Einstein diffusion coefficient for the typical cluster taken in isolation in the solvent of viscosity  $\eta$ . Below, in numerical expressions for  $G$  and  $R_c$ , we have used  $b = 0.3$ ,  $\beta = 3.1$ , and  $f = 2$ . We have also set  $G \equiv \kappa_c/R_c$  identically. Thus our values for  $G$  are only estimates holding to within an underdetermined factor of the order of one.

## 6. Application of the model

The smooth curves of Fig. 2 have been computed from Eq. (7) with the stretching exponent  $p$  assigned a best-fit, universal value of 0.66, close to the theoretical value of 0.70 that results from the choice  $d_B = 1.1$  for the backbone dimension. Generally, Eq. (7) gives quite a good description of the data. The fine scale of Fig. 2(a), however, allows us to see long-time deviations of the behavior of the stiffest, highly arrested gel from our model. Specifically, the dynamic structure factor of the most concentrated gel continues to decay weakly at times much longer than the characteristic time  $\tau$ , whereas the model predicts a decay to a flat plateau. The observed sloping plateau suggests that the full behavior of density fluctuations in colloidal gels includes a second, slow process that partially completes the arrested decay of the first process

which is the one modeled by our theory. The two-step decay qualitatively resembles the beta and alpha decays of systems close to a glass transition. This analogy has already been made for polymeric gels [14]. Here, for all but the most concentrated gels, the final decay seems to be a small effect occurring only at extremely long times.

Fig. 3 summarizes the behaviour of gels with volume fractions covering the range  $1 \times 10^{-4} \leq \phi \leq 5 \times 10^{-3}$ . Saturation of the decay of  $f(q, t)$  is measurable only for sufficiently concentrated gels in the range  $1 \times 10^{-3} \leq \phi \leq 5 \times 10^{-3}$ . Accordingly, both  $\delta^2$  and  $\tau$  have been adjusted in fitting Eq. (7) to the correlation functions we obtained from the samples in this range. Their values appear in Fig. 3 as circles. The values for the parameter  $\delta^2$  are well represented by a power-law form in the volume fraction:  $\delta^2 = 1.8 \times 10^{-10} \mu\text{m}^2 \phi^{-2.7}$ . We cannot detect saturation of the correlation functions of the weaker gels with concentrations in the range  $1 \times 10^{-4} \leq \phi < 1 \times 10^{-3}$ . Therefore, in order to represent them with Eq. (7), we fix  $\delta^2$  by extrapolating it from the power-law fit to the values of  $\delta^2$  obtained from the more concentrated samples. Only  $\tau$  is then adjusted in the fit to correlation function data. Values for  $\delta^2$  and  $\tau$  so obtained for the more dilute gels appear in Fig. 3 as squares. Over the full volume fraction range  $1 \times 10^{-4} \leq \phi \leq 5 \times 10^{-3}$ ,  $\tau$  has a power-law dependence on  $\phi$  given by  $\tau = 3.5 \times 10^{-12} \text{ s } \phi^{-3.9}$ ; the behavior of  $\tau$  is continuous across the two ranges we have defined in our analysis. The inferred variation of  $\tau$  (and  $G \propto \tau^{-1}$ ) over a six-decade

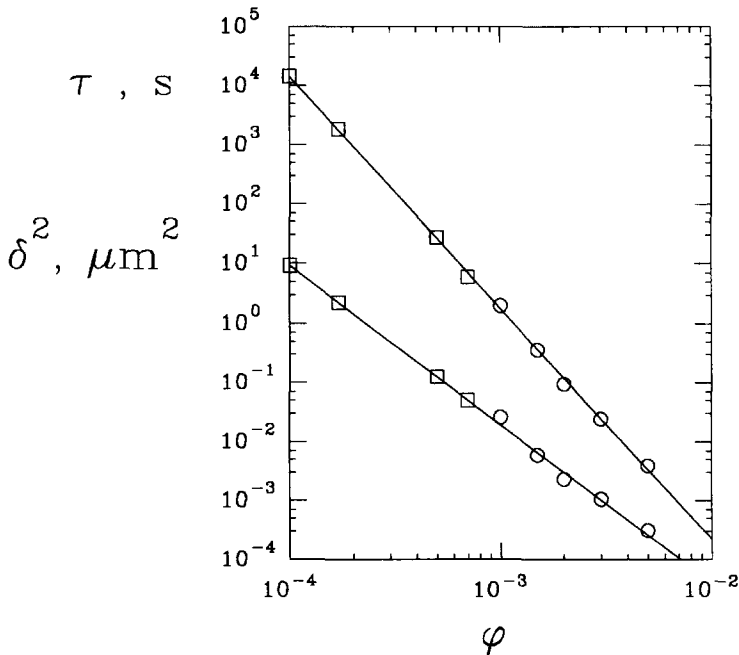


Fig. 3. The parameters  $\delta^2$  and  $\tau$  as functions of  $\phi$ . Circles: both parameters adjusted in fits of Eq. (7) to measured  $f(q, t)$ . Squares: only  $\tau$  adjusted;  $\delta^2$  assigned from the power-law fit to the lower set of circles.

range is remarkable. We point out, however, that this wide variation of  $\tau$  is not observed directly, since the correlation functions of weak gels typically attain values experimentally indistinguishable from zero in times much less than  $\tau$ . (For example, see Fig. 2(c) and note that  $\tau = 1850$  s for this concentration.) The reason is that  $\tau$  is the characteristic time required for the mean-squared displacement of a typical blob in the cluster to relax to its saturated thermal value (which  $\delta^2$  to within factors of order one); provided  $\delta^2 q^2$  is of order one or less, the saturation is observable in the scattering experiment and  $\tau$  is also the characteristic time for the decay of  $f(q, t)$ . For a sufficiently dilute gel, however, we have  $\delta^2 q^2 \gg 1$  at all but inaccessibly low angles and the scattered light is completely decorrelated by blob displacements much smaller than  $\sqrt{\delta^2}$ . These displacements occur in times of the order  $1/D_c q^2 \ll \tau$ . Here  $D_c \approx \delta^2/\tau$  is the free diffusion coefficient of an isolated cluster. This remark explains the behavior noted above, i.e. that the time scale of the correlation function of the least concentrated gel of Fig. 2 shows more  $q$ -dependence than do those of the more concentrated gels.

These remarks can be made more quantitative. For early delay times satisfying  $t \ll \tau$ , Eq. (7) becomes

$$f(q, t) \cong \exp(-D_p q^2 t^p), \quad (8)$$

where  $D_p \equiv \delta^2/\tau^p$  may be called a “stretched” diffusion coefficient. In dilute gels, the numerical values of  $D_p$  and  $q$  can be such that most of the decay of  $f(q, t)$  occurs while  $t \ll \tau$  holds and Eq. (8) applies. A sensitive test for this stretched-exponential behavior is a plot of  $\ln[f(q, t)]$  versus  $D_p q^2 t^p$ , which should yield a straight line, independent of angle and volume fraction. Fig. 4 is a plot of this form for two volume fractions,  $1.0 \times 10^{-4}$  and  $7.0 \times 10^{-4}$ , and several angles. The smooth curves have been calculated from the full form of our model (Eq. (7)); in the case of the higher concentration, terms neglected in Eq. (8) are important enough to cause the curves to depart slightly from linearity and to show a small angle dependence. Most noteworthy is how straight the data are at early times. This behavior indicates that the initial motion of clusters in colloidal gels is a free but anomalous diffusion, i.e.,

$$\langle Ar^2(t) \rangle = 6D_p t^p \quad (9)$$

for times  $t \ll \tau$ . Such anomalous or stretched diffusion has been reported in polymeric gels [13,14], but only as a secondary process that occurs after an initial regime of linear diffusion. Such a regime would appear as rounding off of the curves of Fig. 4 and is not observed. Here, moreover, we have accounted for the stretching as the consequence of the superposition of collective motions that occur within a fractal object.

Fig. 4 also shows that the measured behavior of colloidal gels deviates slightly from our model with respect to the dependence of  $f(q, t)$  on  $q$  or angle: the data indicate a small increase of  $D_p$  as  $q$  decreases. Fig. 2 shows that the saturation behavior of  $f(q, t)$  with respect to  $q$  also departs slightly but systematically from our model: the

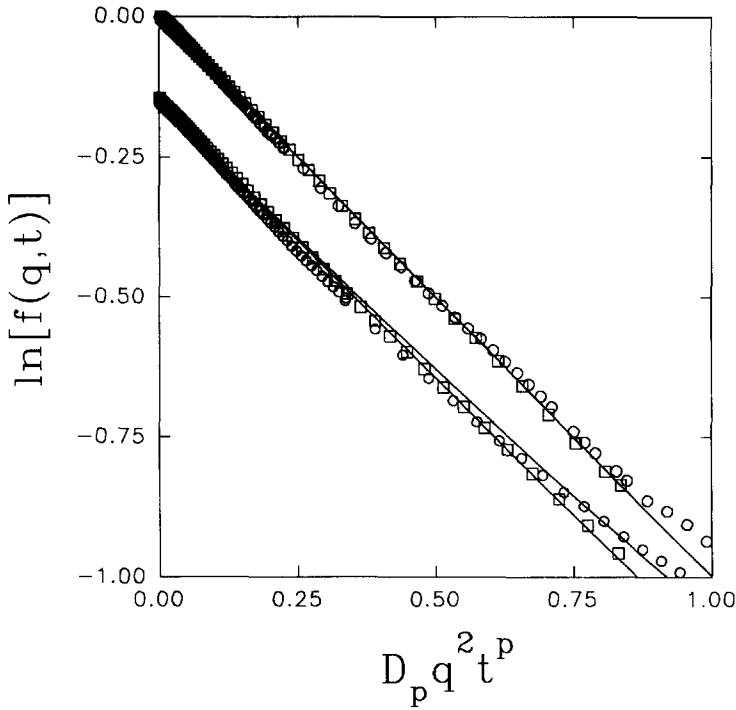


Fig. 4. Dynamic structure factors  $f(q, t)$  of dilute colloidal gels. Stretched-exponential dynamics occur down to even the earliest delay times of  $10 \mu\text{s}$ . The smooth curves are computed from Eq. (7);  $D_p$  is defined by  $\delta^2/\tau^p$  with  $p = 0.66$ . Upper data and curves:  $\phi = 1.0 \times 10^{-4}$ ; circles denote  $\theta = 30^\circ$  and squares denote  $60^\circ$ ;  $\delta^2 = 9.2 \mu\text{m}^2$ ,  $\tau = 1.4 \times 10^4 \text{ s}$ . Lower data and curves (with  $f(q, t)$  shifted down by a factor for clarity):  $\phi = 7.0 \times 10^{-4}$ ; circles denote  $\theta = 40^\circ$  and squares denote  $90^\circ$ ;  $\delta^2 = 0.050 \mu\text{m}^2$ ,  $\tau = 6.1 \text{ s}$ .

low-angle correlation functions of the more concentrated gels tend to decay more than is predicted by the self-consistent fit of the model to the data taken over all angles. This trend could be expressed as a small increase of  $\delta^2$  as  $q$  decreases. Our model assumes that  $f(q, t)$  depends on  $q$  only through the  $q^2$  that occurs explicitly in Eq. (7). The data show that this is indeed the dominate dependence.

From the above power-law expressions for the parameters  $\delta^2$  and  $\tau$ , together with the relations given below Eq. (7) for the gel properties  $G$  and  $R_c$ , we find  $G \approx (1.6 \times 10^{10} \text{ dyn/cm}^2)\phi^{3.9}$  and  $R_c \approx (0.38)R_1\phi^{-1.2}$ . Here  $R_1 = 9.5 \text{ nm}$  is the radius of a colloidal monomer. For comparison, Buscall et al. considered the shear modulus of a close pack of fractal structures and predicted  $G \propto \phi^v$  with  $v = 3.5 \pm 0.2$  and  $4.5 \pm 0.5$  for cluster growth by, respectively, diffusion-limited and reaction-limited aggregation [25]. According to our finding, the modulus attains values that are within the measurement capabilities of conventional mechanical rheometers for colloidal volume fractions near the upper end of the range where we have made spectroscopic measurements. For example, our expression gives  $G = 17 \text{ dyn/cm}^2$  for  $\phi = 5 \times 10^{-3}$ .

Thus, it should be possible to test directly the validity of this optical method for the determination of gel elasticities. The optical method then extends the range of measurements to much more dilute gels. Our result for the characteristic cluster radius  $R_c$  can be compared with the expression  $R_c \approx R_1 \phi^{-1/(3-d_f)}$  where  $d_f$  is the fractal dimension. This formula estimates  $R_c$  as the average cluster size at the moment when the volume fraction occupied by clusters attains 1 in diffusion-limited aggregation. Static scattering measurements on our samples give a fractal dimension  $d_f = 2.1$ , closer to the value expected for reaction-limited aggregation. With this value, the estimated exponent for  $R_c$  is  $-1.1$ , close to the exponent  $-1.2$  we find from our analysis of dynamic scattering data.

## 7. Discussion

The dynamics of colloidal gels are undoubtedly influenced by the mode of the aggregation process in which they are formed. As discussed above, in order to keep the rate of aggregation sufficiently slow to permit mixing, we have primarily studied systems that aggregate in a regime intermediate between the reaction- and diffusion-limited extremes. However, we can achieve the strict DLCA regime for those suspensions at the lowest colloidal monomer concentrations. Thus, in one experiment we initiated aggregation of a dilute suspension,  $\phi = 1.0 \times 10^{-4}$ , by adding  $\text{MgCl}_2$  to a final concentration of 30 mM. Over several hours, we observed growth of  $R_h$  consistent with the power-law behavior  $R_h \propto t^{1/d_f}$  expected in DLCA [5]. After a few days, the system reached a quiescent state which we assume is a gel. We then obtained data similar to those shown in Fig. 4. We found, however, that this diffusion-limited gel required a higher value,  $p = 0.71$ , for the stretching exponent. The change improves the agreement with the value 0.70 predicted by our model of gelation and gel dynamics, which is partly based on a DLCA picture of colloidal aggregation. We take the fact that the change is, however, rather small as an indication that our model applies to the rest of our gels, which were formed in aggregation processes that were partly limited by the rate of reaction.

In this paper, we have described dynamic light scattering measurements performed on colloidal suspensions that have attained a quiescent state long after aggregation. We argue that such systems are gels; we show how the elastic modulus of the gel can be inferred from the amount of arrest of thermal density fluctuations. The relaxation of density fluctuations is of a stretched exponential form. We show that the origin of this behavior is the hierarchy of elastic internal motions occurring within the fractal clusters. We have modeled the structure of the gel as a close pack of clusters whose radius is the radius at which clusters growing by the diffusion-limited aggregation process occupy all the system's volume. We propose that this simple model may provide a unified picture for analyzing colloidal gel behavior as it is exhibited by various experimental techniques including dynamic and static light scattering and mechanical rheology.

## Acknowledgements

We thank R. C. Ball, T. Witten, and M. E. Cates for fruitful discussions.

## References

- [1] F. Family and D.P. Landau, eds., *Kinetics of Aggregation and Gelation* (North Holland, Amsterdam, 1984).
- [2] M.Y. Lin, H.M. Lindsay, D.A. Weitz, R.C. Ball, R. Klein and P. Meakin, *Proc. Roy. Soc. London A* 423 (1989) 71.
- [3] D.A. Weitz, J.S. Huang, M.Y. Lin and J. Sung, *Phys. Rev. Lett.* 54 (1985) 1416
- [4] D.A. Weitz and M.Y. Lin, *Phys. Rev. Lett.* 57 (1986) 2037.
- [5] M.Y. Lin, H.M. Lindsay, D.A. Weitz, R. Klein, R.C. Ball and P. Meakin, *J. Phys.: Condens. Matter* 2 (1990) 3093.
- [6] A. Vailati, D. Asnaghi, M. Giglio and R. Piazza, *Phys. Rev. E* 48 (1993) R2358.
- [7] A.E. Gonzalez, *Phys. Rev. E* 47 (1993) 2923.
- [8] M. Carpineti and M. Giglio, *Phys. Rev. Lett.* 68 (1992) 3327.
- [9] M. Carpineti and M. Giglio, *Phys. Rev. Lett.* 70 (1993) 3828.
- [10] M.D. Haw, W.C.K. Poon and P.N. Pusey, *Physica A* 217 (1995) 230.
- [11] J.G.H. Joosten, E.T.F. Gelade and P.N. Pusey, *Phys. Rev. A* 42 (1990) 2161.
- [12] J.G.H. Joosten, J.L. McCarthy and P.N. Pusey, *Macromolecules* 24 (1991) 6690.
- [13] J.E. Martin, J. Wilcoxon and J. Odinek, *Phys. Rev. A* 43 (1991) 858.
- [14] S.Z. Ren and C.M. Sorensen, *Phys. Rev. Lett.* 70 (1993) 1727.
- [15] J.-Z. Xue, D.J. Pine, S.T. Milner, X.-I. Wu and P.M. Chaikin, *Phys. Rev. A* 46 (1992) 6550.
- [16] P.N. Pusey, in: *Liquids, Freezing and the Glass Transition*, eds. J.P. Hansen, D. Levesque and J. Zinn-Justin (Elsevier, Amsterdam, 1991).
- [17] P.N. Pusey and W. van Meegen, *Physica A* 157 (1989) 705.
- [18] W. van Meegen, S.M. Underwood and P.N. Pusey, *Phys. Rev. Lett.* 67 (1991) 1586.
- [19] Z. Huang, A.H. Krall and D.A. Weitz, *J. Coll. Interface Sci.* 170 (1994) 170.
- [20] B.J. Berne and R. Pecora, *Dynamic Light Scattering* (Krieger, Malabar, FL, 1990).
- [21] H.M. Lindsay, R. Klein, D.A. Weitz, M.Y. Lin and P. Meakin, *Phys. Rev. A* 38 (1988) 2614.
- [22] Y. Kantor and I. Webman, *Phys. Rev. Lett.* 52 (1984) 1891.
- [23] We are indebted to R.C. Ball for suggesting this line of reasoning.
- [24] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
- [25] R. Buscall, P.D.A. Mills, J.W. Goodwin and D.W. Lawson, *J. Chem. Soc. Faraday Trans. I* 84 (1988) 4249.