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Anomalous diffusion in gelatin-surfactant solutions and gels

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A photon correlation spectroscopy study carried out on semidilute 4% (wt./vol) aqueous gelatin sols and gels with the anionic surfactant sodium dodecyl sulphate (SDS) showed three relaxation processes in the dynamic structure factor data. First an exponential process $S(q,t) \sim \exp(-D_f q^2 t)$ at $t \leq 20\ \mu$s, referred to as the collective mode, was observed, followed by an intermediate power-law regime $S(q,t) \sim t^{-\alpha(q)}$ at 20 $\mu\text{s} \geq t \leq 1$ ms, and finally a stretched exponential decay $S(q,t) \sim \exp-(t/\tau_c)^{\beta}$ was observed for $t \geq 1$ ms. The power-law exponent α and characteristic time τ_c in the stretched part were found to be q dependent: $\alpha \sim q^x$, with $x = 1.80 \pm 0.09$ in the sol state and $x = 0.98 \pm 0.05$ in the gel state, and $\tau_c \sim q^{-y}$, with $y = 2.05 \pm 0.08$ and 3.0 ± 0.2 in the sol and gel states, respectively, but independently of SDS concentrations. In the fast mode the relaxation time was measured to be the same in the pure gelatin sol and gel states. It is proposed that the different q dependences observed in the gel and sol states with and without SDS indicate the presence of different characteristic length scales. Our results agree with the predictions of the anomalous Gaussian diffusion model in the sol state, but differ significantly in the gel state. [S1063-651X(98)03407-2]

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I. INTRODUCTION

The relaxation and dynamics of polymers have been widely studied by many workers recently [1–4]. Gelatin that forms physical gels in a semidilute regime presents a topological hindrance to the motion of individual chains and a variety of complex phenomena have been observed [5]. The complexity in motion starts when individual chains undergo a coil-helix transition leading to the onset of gelation where triple helices tend to form. This physical process is significantly altered when an anionic surfactant forms complexes with gelatin.

Gelatin is a polypeptide obtained from denatured collagen. Above ~30 °C it is a linear random coil biopolymer and when cooled it transforms to a gel state when the concentration exceeds ~0.5% (wt./vol). In the sol state, gelatin is characterized as a random coil with a persistence length of ~20 Å, radius of gyration $R_g \sim 300$ Å, and an effective hydrodynamic radius $R_h \sim 220$ Å [6–10]. Gelation is preceded by the formation of interconnected triple helices. As the helix fraction grows beyond a critical helix concentration, the whole dynamics is governed by both intermolecular and intramolecular hydrogen bonds formed between adjacent peptide bonds and ultimately a thermally reversible gel forms [11,12]. Around $p\text{H}=7$ the gelatin chain is amphoteric and some groups (e.g., lysine and argenine $\simeq 7.5\%$ of residues) are positively charged and these make complexes with the polar head group of the anionic surfactant. About 12% of the chain, mostly comprised of glutamic and aspartic acids, is negatively charged. Glycine, proline, and hydroxyproline are neutral. Other (6%) residues are strongly hydrophobic in nature, leaving about 58% of the chain to be neutral [6].

Photon correlation spectroscopy (PCS) is very useful in studying the relaxation processes in complex systems. Early PCS studies on pure gelatin sol and gel showed pure exponential relaxation of the correlation function in the dilute regime, which moved to nonexponential relaxation as the semidilute regime was approached [5]. However, the detailed relaxation study of gelatin–sodium dodecyl sulphate (SDS) complexes in sol and gel states has not been reported, to our knowledge. Amis and co-workers observed the two-mode relaxation phenomena where both relaxations were individually exponential and these were interpreted as fast and slow mode relaxations [13–15]. After their work, many more elucidations of this problem have occurred, but no concrete understanding has been established to explain the origin of these modes. Borsali *et al.* [16] studied the gelatin solutions and gels and detected the fast and slow modes as exponential and stretched exponential relaxations. Martin, Wilcoxin, and Odinek [2] observed three stepwise relaxations in a system of colloidal particles. Ren *et al.* [1,5] studied the quenched gelatin system in sol and gel states and reported three types of relaxation processes: the fast mode relaxation frequency, which was inversely proportional to the solvent viscosity; cooperative diffusion due to segmental motion of the polymer chain, and the power-law relaxation behavior in an intermediate time domain and the autocorrelation function as a stretched exponential decay at longer time scales. When the system was set to a gel the slow mode froze and only the fast mode remained.

In this paper we shall be concerned with the study of relaxation in gelatin-SDS sols and gels with the objective of characterizing these complex states through PCS studies. It is well known that a significant change in the conformation of polymers arises due to polymer-surfactant interactions. In this work we have used PCS to study gelatin-surfactant solutions at two temperatures: $T < T_{\text{gel}}$ ($T_{\text{gel}} \simeq 30$ °C) and $T > T_{\text{gel}}$ with four SDS concentrations (0.5, 0.8, 2, and 4 mM) both at and above CMC (0.8 mM) of SDS. Qualitatively, our work is similar to the work of Ren *et al.* [5], which reported on pure semidilute gelatin samples for $T < T_{\text{gel}}$ and $T > T_{\text{gel}}$ and that of Martin, Wilcoxin, and Odinek, which reported on silica particles [2]. However, the quantitative features differ

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significantly from those reported by Ren *et al.* [1,5]. We have interpreted the data through anomalous diffusion of gelatin-SDS complexes in the aqueous solution environment. The physical chemistry of binding surfactants to gelatin has been reported separately [17].

II. EXPERIMENTAL PROCEDURE

A. Materials and methods

Gelatin was purchased from Biorad Co. (U.S.) with a sharp molecular weight M_w distribution at $\simeq 10^7$ g mol^{-1}. Aqueous solution was prepared by soaking the sample nearly for 1 h at ~50 °C to remove the historical effects [7]. The solvent was 0.1M of NaCl in double distilled water containing 0.1 mM of sodium azide to prevent bacterial contamination. Noting that gelatin itself has 12% residual water, we made the sample to 4% (wt./vol). The sample was gently stirred for about 2 h to make a homogeneous solution. To obtain a dust-free stock solution, the hot sol was first centrifuged for 30 min and the aliquots were loaded directly into a 5-ml cylindrical quartz scattering cell. A photon correlation spectroscopy study was done on these samples after 10–15 h of sample preparation. The quartz cell was kept in a home-made goniometer thermostated to an accuracy of ±0.1 °C [18]. An Aerotech He-Ne randomly polarized laser (10 mW) with $\lambda = 6328$ Å was used as light source and a Brookhaven Instrument Corp. (BIC) 9000AT correlator (1024 channels) was used to measure the intensity autocorrelation function of the scattered light. Before starting the experiments, the goniometer was calibrated by using a dilute suspension of standard polystyrene latex particles (size equal to 900 Å) kept in an identical quartz cell supplied by the BIC. The data collected were analyzed through four software packages supplied by the BIC (CUMULANT, EXPONENTIAL SAMPLING, NNLS, and CONTIN). The calibration was iterated until we obtained the desired diameter with ~2% error using all data analysis softwares. During these experiments we explored the angles from 30° to 110° by rotating the goniometer arm smoothly and repeating 3–4 times by focusing the scattered light on a THORN EMI (B2FBK/RFI) photomultiplier tube properly such that we obtained maximum counts. To obtain a very good set of data the following precautions were undertaken. First, the count rate was maintained at 10^4-10^5 counts per second. Second, the pinhole size in front of the photomultiplier tube was fixed at 100 μm to minimize the sample volume and we chose fewer coherence areas from the scattering volume to reduce the multiply scattered light. At lower scattering angles noticeable broadening of the correlation function may occur because a finite range of wave numbers contributes to the scattered light as ''seen'' by the photomultiplier. This was minimized in our experiments by placing a narrow-band interference filter in front of the photomultiplier tube, which had a bandwidth of less than 3% of the wavelength of the incident laser source. This reduced the above-mentioned artifact considerably.

Finally, the percentage difference between the calculated and measured baselines was monitored continuously and preset at less than 0.1% for the correlograms to be acceptable. Any correlogram that did not satisfy this criterion was rejected. The background was estimated from measured baseline statistics. Experiments were performed in two steps. First, the free gelatin sol at $T = 55$ °C [4% (wt./vol)] was loaded into the scattering cell and the correlograms were recorded at different scattering angles. The sol was allowed to cool to room temperature ($T = 20$ °C) in regulated decreasing steps of 5 °C. As the sol cooled, correlograms were recorded continuously at temperature intervals of 5 °C. At each of these set temperatures, the scattering intensity was measured between $30° \leqslant \theta \leqslant 110°$ at an interval of 5°. Hence, at each of these temperatures, 17 correlograms were recorded to extract the q dependence of relaxations in finer detail. Again, each of these experiments was carried out at least thrice to observe data reproducibility. Thus, at each of these preset temperatures more than 50 correlograms were recorded. Each correlogram was recorded over a typical period of 10 min and over this experimental duration a good signal statistics was seen to build up. The temperature controller provided temperature regulation better than ±0.1 °C of the preset temperature and this completed a cycle of experiment. Next the temperature controller was set to a new temperature that is lower than the previous one by 5 °C and the entire experimental cycle was repeated. The analysis that follows is based on the interpretation of more than 1000 correlograms.

B. Data analysis

The salient theoretical and experimental features of PCS have been discussed in detail elsewhere [19,20]. The normalized dynamic structure factor was defined as $S(q,t) = [\{\langle I(0)I(t)\rangle - B\}/(\langle I^2\rangle - B)]^{1/2}$. The B was the measured baseline. All the data were analyzed through the software supplied by the BIC and some developed by us. The fast mode was analyzed through the CONTIN [21] analysis method and an intermediate power law with stretched exponential fittings was done by a FORTRAN program written by us. This FORTRAN program is based on the least-squares minimization between raw data and fitting curves. The first two points in correlograms were not used in the calculation to avoid the electronic dead time effect.

III. RESULTS AND DISCUSSION

A typical set of correlation functions $S(q,t)$ is shown in Fig. 1 for a free gelatin sample in aqueous solution. The correlation function for temperatures $T > T_{\mathrm{gel}}$ distinctly shows three relaxation regimes, one for $\tau \leqslant 20$ μs, followed by a characteristic power-law relaxation regime up to 20 μs$\leqslant \tau \leqslant 1$ ms, and beyond this a stretched exponential relaxation for $\tau \geqslant 1$ ms. As the sol evolved to a gel state, the intermediate relaxation mode disappeared ($T < T_{\mathrm{gel}}$) and only the fast and stretched exponential modes remained in the $S(q,t)$ data.

Figure 2 shows the plot of the dynamic structure factor $S(q,t)$ as a function of delay time in the gel state of free and SDS bound gelatin samples. When SDS was added to the gelatin at concentrations below and at critical micellar concentration (CMC) values, $S(q,t)$ recovered its three-stage relaxation features. For SDS concentrations above the CMC, $S(q,t)$ was observed to regain the characteristic of the gel state behavior where the intermediate relaxation mode was found to be absent. However, compared to the free gelatin sample, the samples with SDS added (above the CMC)

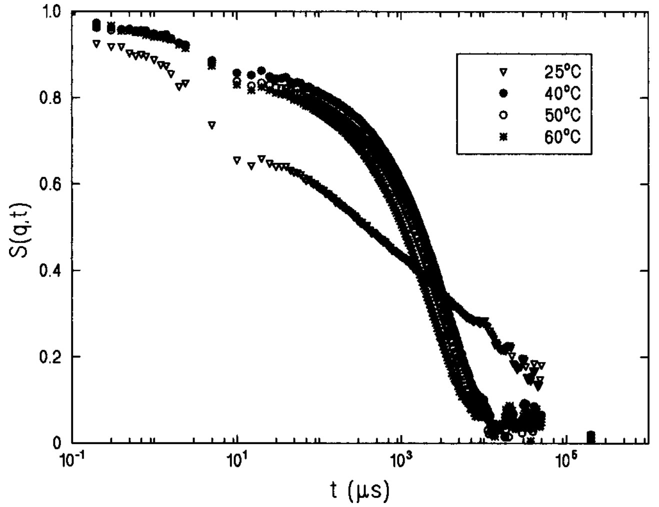

FIG. 1. Dynamic structure factor $S(q,t)$ as a function of delay time t, for below and above the gelation temperature $T_{\mathrm{gel}} \simeq 30$ °C. The sample was pure gelatin 4% (wt./vol) in $0.1M$ of NaCl, pH $=7$ aqueous solution. The characteristic decay frequency in the stretched exponential part converges as the sol evolves to the gel state.

showed a much slower relaxation in the stretched exponential domain of the $S(q,t)$ data.

A. Fast mode relaxation

All the measured $S(q,t)$ data were fitted to $S(q,t) \sim e^{-\Gamma(q)t} \sim e^{-D_f q^2 t}$ up to $t \leqslant 20$ μs, where a single exponential fitting was found to be adequate. The fitting procedure was the following. The fast modes were fitted by taking the average value of $S(q,t)$ of those channels where the fast mode almost decayed to a constant value and this was used as the base line ($t \sim 60$ μs). The first three to four points were avoided to nullify the dead time effect. Next the entire first mode region was normalized with respect to the baseline value with the dead time effect almost eliminated.

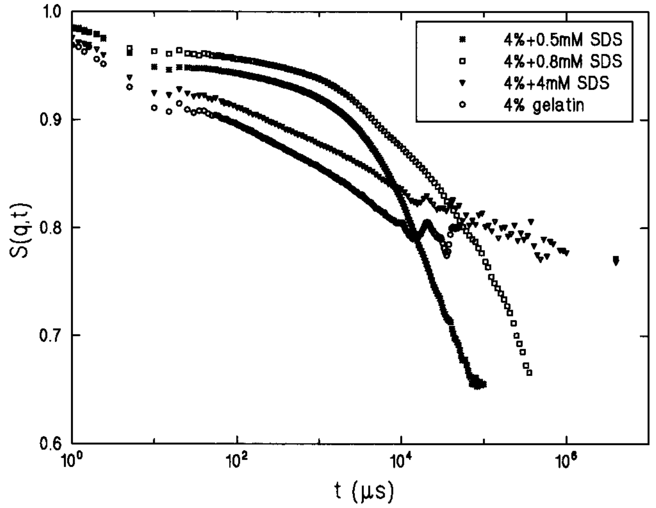

FIG. 2. Evolution of $S(q,t)$ in the gel state ($T=20$ °C) as a function of SDS concentration. As the SDS concentration increases the stretched exponential behavior becomes pronounced for SDS concentrations above the CMC (0.8 mM) of the surfactant, indicating surfactant induced softening of the gel.

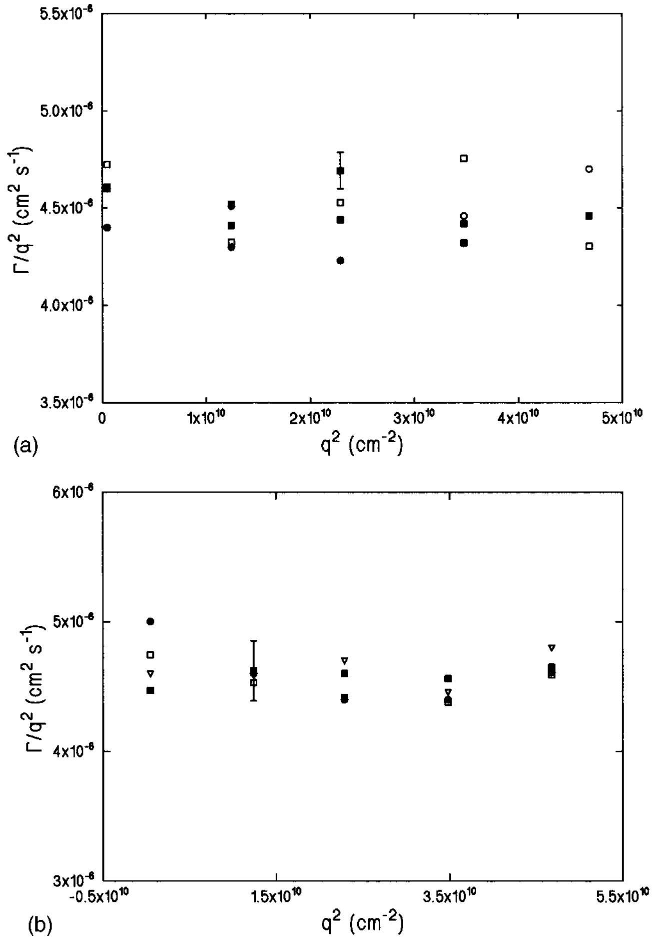

FIG. 3. Linewidth $\Gamma(q)$ of the fast mode of $S(q,t)$ of Fig. 2 as a function of q^2 for different concentrations of SDS in the (a) sol state ($T=55$ °C) and (b) gel state ($T=20$ °C). Pure gelatin (○), 0.5 mM of SDS (■), 0.8 mM of SDS (□) and 4 mM of SDS (●) in an aqueous medium with pH$=7$ and an ionic strength of $0.1M$ of NaCl. $\Gamma(q)$ is linear with q^2. A representative error bar is shown on only one data point.

The initial relaxation part in Fig. 1 implied that for free gelatin sols at almost all temperatures $S(q,t)$ followed a universal feature where $\Gamma(q)$ was observed to be independent of T ($T > T_{\mathrm{gel}}$) and this showed a significant change in the gel state. This regime was analyzed through the CONTIN regression routine and the deduced $\Gamma(q)$ values are plotted in Figs. 3(a) and 3(b) for sol and gel states for various concentrations of SDS.

For free gelatin and gelatin with surfactant sols, the fast mode relaxation frequency $\Gamma(q)$ was observed to show $\Gamma(q)=D_f q^2$ behavior with the fast mode diffusion coefficient value $D_f=(0.46\pm0.06)\times10^{-5}$ cm^2 s^{-1} for both free gelatin and surfactant-added gelatin sols, which remained constant for all concentrations of SDS studied. The $\Gamma(q)=D_f q^2$ has the characteristic of the fast mode being diffusive in nature. For translational diffusion of free gelatin chains in the solvent medium D_f should show an inverse proportionality to the solvent viscosity (η_0). The measured value of D_f and $\eta_0=0.65$ cp will yield a hydrodynamic radius R_h of the diffusing entity as $\simeq 8$ Å, which is an unreal-

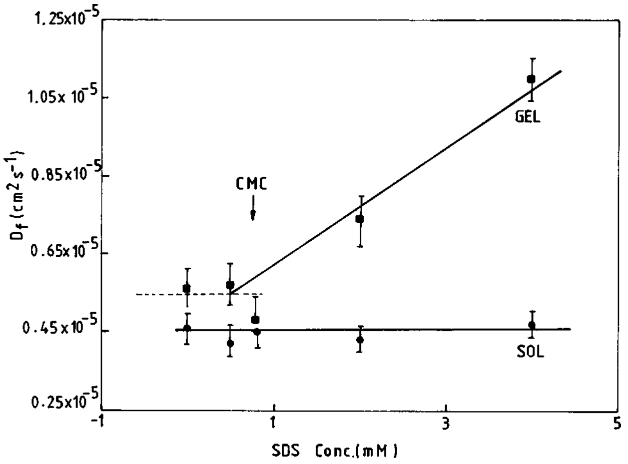

FIG. 4. Variation of the fast mode diffusion coefficient D_f as a function of SDS concentration. In the sol state D_f was observed to remain independent of SDS concentration, but D_f increased with SDS concentration in the gel state, beyond the CMC of the surfactant. The dotted line is the fitting below the CMC.

istic value. If D_f were to be interpreted as a self-diffusion coefficient of gelatin and gelatin surfactant bound chains, D_f should show an inverse proportionality to the solution viscosity η and a similar calculation with $\eta = 13$ cp [10] will yield a still smaller hydrodynamic radius value.

Hence it can be conjectured that the fast mode could be the collective mode (gel mode) arising out of density fluctuations occurring in the gel network of gelatin solutions [22]. Hence D_f can be defined as the diffusion coefficient of the collective mode related to the shear modulus G and osmotic modulus K through the friction coefficient f as $D_f = (K + \frac{4}{3}G)/f$. Ren *et al.* [1,5] used this D_f value to arrive at the effective hydrodynamic radius of gelatin as 170 Å. Our studies are at variance with their results to a large extent. Our D_f values are two orders of magnitude larger than their values. It was observed that as the SDS concentration in the gelatin sol was raised from 0 to 4 mM, no significant change in D_f values in the sol state could be noticed (see Fig. 4).

In the gel state the fast mode diffusion coefficient D_f value increased from $(0.50 \pm 0.07) \times 10^{-5}$ cm^2 s^{-1} at zero surfactant concentration to $(1.1 \pm 0.1) \times 10^{-5}$ cm^2 s^{-1} at a SDS concentration of 4 mM (Fig. 4). This implied that the gel network became more and more rigid as the SDS concentration was increased since D_f is directly proportional to the rigidity modulus of the network. We shall not discuss the fast mode relaxation further, with the remark that this singular diffusive motion could be clearly observed in both sol and gel states and this cannot be attributed to either self- or mutual diffusion of gelatin chains (or gelatin-SDS complexes) in the diffusion medium. D_f values are listed in Table I.

B. Intermediate power-law relaxations

In the intermediate time domain 20 μs$\leq t \leq$1 ms the dynamic structure factor $S(q,t)$ plotted in Figs. 1 and 2 clearly shows a distinct relaxation regime that is nonexponential. As the sols were cooled and the gel state evolved this intermediate relaxation regime slowly disappeared (Fig. 1). On the other hand, when SDS was added to a matured gel, this relaxation regime reappeared for SDS concentrations below the CMC values. Beyond the CMC of SDS this relaxation regime could not be observed (see Fig. 2). However, the SDS-added gelatin gel exhibited a wider dynamic structure factor curve for $t \geq 1$ ms as compared to that of the free gelatin gel sample. This $S(q,t)$ regime was least-squares fitted to

TABLE I. Summary of results estimated and their specified features. In cases where the tabulated parameters showed a dependence on SDS concentrations the reported values pertain to results from a pure gelatin sample 4% (wt./vol) in the sol state at $T = 55$ °C and corresponding to a gel state $T = 20$ °C.

Phenomena	Parameter		Remarks
	sol	gel	
Fast mode	D_f (cm^2 s^{-1}$\times 10^5$)		
$S(q,t) \sim e^{-D_f q^2 t}$	0.46 ± 0.06	0.50 ± 0.07	D_f is independent of SDS concentrations in the sol state D_f linearly increases with SDS concentrations in gel states
Intermediate mode	exponent x		
$S(q,t) \sim t^{-\alpha(q)}$ $\alpha \sim q^x$	1.80 ± 0.09	0.98 ± 0.05	x is independent of SDS concentration in both sol and gel states
Stretched exponential mode	exponent β		
$S(q,t) \sim e^{-(t/\tau_c)^\beta}$	0.85 ± 0.09	0.85 ± 0.09	β is independent of q and SDS concentrations
	exponent y		
$\tau_c \sim q^{-y}$	2.05 ± 0.08	3.0 ± 0.2	$y = 2/\beta$ as per Refs. [1,5] y is independent of SDS concentrations.

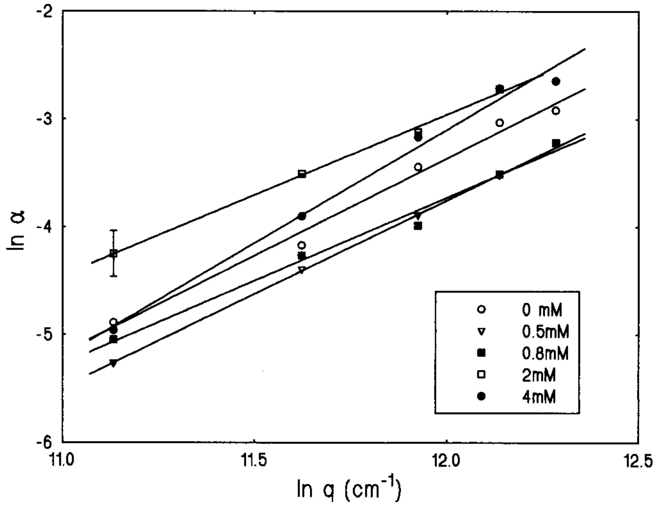

FIG. 5. Variation of the power-law exponent $S(q,t) \sim t^{-\alpha}$ in the intemediate regime of $S(q,t)$ of Fig. 2 as a function of q, in the sol state of the gelatin-SDS system, at $T=55$ °C. The fitting yields $\alpha \sim q^{1.80\pm0.09}$. This exponent is the average of all the curves.

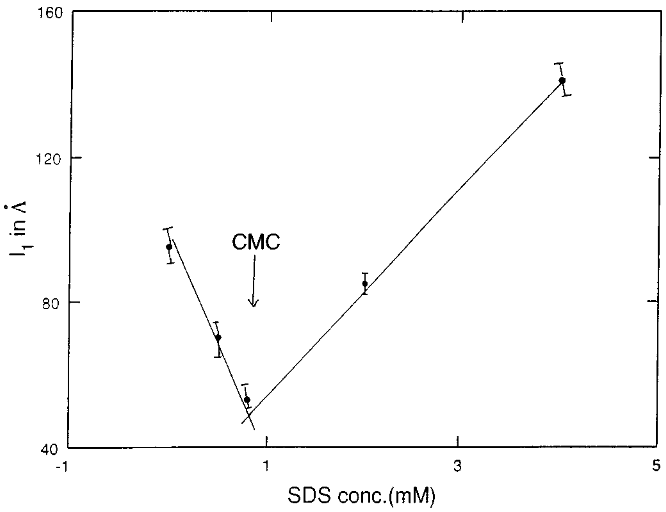

FIG. 7. Variation of the length scale l_1 with SDS concentration in the sol state of gelatin at $T=55$ °C. l_1 decreased up to the CMC and then showed a continuous increase, implying the SDS induced contraction of the gelatin chain due to specific binding up to the CMC and formations of necklace-bead structures in the solution [23,24] beyond the CMC. The crossover occurs at ~0.8 m*M*.

a power law $S(q,t) \sim t^{-\alpha(q)}$ and the deduced values are listed in Table I. The deduced q dependence is plotted in Figs. 5 and 6 for sol and gel states for various concentrations of surfactant.

The fitting yielded $\alpha(q) \sim q^{0.98\pm0.05}$ for the gel state and $\alpha(q) \sim q^{1.80\pm0.09}$ for the sol state. Since $\alpha(q)$ is a dimensionless parameter, a characteristic length scale l_1 can be introduced at this stage, which is defined as

$$\alpha(q) = l_1^x q^x, \quad x = \begin{cases} 1.80\pm0.09 & \text{for the sol state} \\ 0.98\pm0.05 & \text{for the gel state.} \end{cases} \tag{1}$$

When the experimental value of q was substituted the value of l_1 obtained was 95 Å for the free gelatin sol and 50 Å for the gel state. When the surfactant was added to the 4% (wt./vol) gelatin solution, l_1 showed a significant dependence on the SDS concentration where its value was minimum (42 Å) at ~0.8 m*M* (the CMC of free SDS) concentration of the surfactant. This increased to a value of ~150 Å as the SDS concentration reached 4 m*M*. Almost the opposite trend was observed in the gel state, where l_1 fell from ~65 Å at the CMC of SDS to ~15 Å as the surfactant concentration was raised to 4 m*M*.

Ren *et al.* [1,5] showed that this length scale varied with the concentration of gelatin in the sol state as $l_1 \sim C^{-0.75}$ (see Figs. 7 and 8). When our data were combined with this, we obtained a value of $l_1 \simeq 450$ Å for a diluted solution of 0.3% (wt./vol) of gelatin. This is close to the radius of gyration R_g value of the free gelatin chain measured below the gelation concentration [~0.5% (wt./vol)] of this biopolymer. Hence

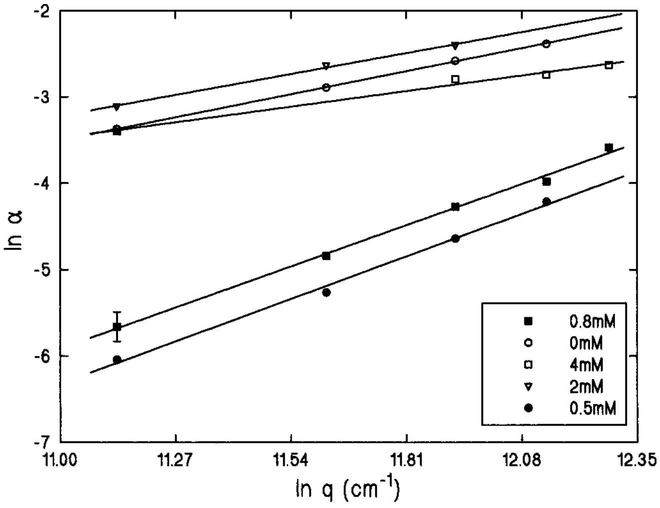

FIG. 6. Variation of the power-law exponent $S(q,t) \sim t^{-\alpha}$ in the intemediate regime of $S(q,t)$ in Fig. 2 as a function of q, in the sol state of the gelatin-SDS system, at $T=20$ °C. The fitting yields $\alpha \sim q^{0.98\pm0.05}$. This exponent is the average of all the curves.

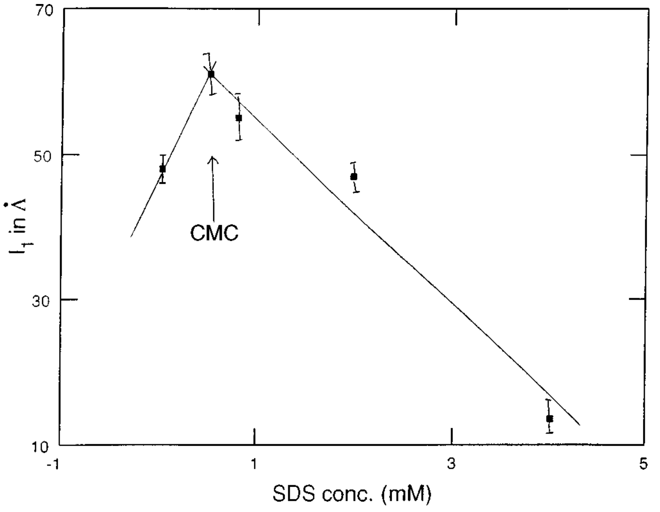

FIG. 8. Variation of the length scale l_1 with SDS concentration in the gel state of gelatin at $T=20$ °C. l_1 increased up to the CMC and then showed a continuous decrease. The crossover occurs at ~0.8 m*M*.

l_1 can be taken as indicative of the R_g value of the free gelatin or SDS bound gelatin chains in the sol state.

SDS tends to bind to the positive polar groups (comprising nearly 7.5% of the chain length), thereby reducing these charge groups and screening the electrostatic interactions [23]. This continues until the saturation binding process that occurs approximately at the CMC of SDS is completed [24]. The net effect of this is the reduction in the chain size and hence a lower R_g value. Beyond the CMC of SDS, micelles form in the sol state and the interaction between SDS micelles and the gelatin chain is dominated by intermicellar repulsion within the gelatin-SDS complexes resulting in the expansion of the chain. This is often referred to as the cooperative binding domain and the geometrical shape can be represented through the necklace-bead model [25]. These are low-energy states of SDS-gelatin complexes at surfactant concentrations higher than the CMC. So as the SDS concentration increases, a long-range correlation develops in the solution through intermicellar interactions. The exponent $\alpha(q)$ always had values higher than that of the sol. Ren *et al.* [1,5] conjectured that intermediate relaxation could be due to the motion of the polymer segment along the reptation tube of the molecule. This implies that the length scale in the sol state, i.e., the diameter of the tube in the sol state, is higher than that in the gel state. Though our values of l_1 were found to be larger in the sol state than in the gel state, in conformity with the assertion of Ren *et al.* [5], we could not ascribe the origin of this to the reptation dynamics. For the reptation model to be applicable, it is necessary to have either definite or transient cross-links or entanglements in the polymer solution giving rise to networks and the diameter of the reptation tube is typically equivalent to the mesh size or correlation length. In gelatin solutions in the absence of cross-links no definite networks are known to form [11,12]. Above the gelation temperature, the molecular conformation of gelatin is known to be a random coil and below this there is a propensity to form helices. In view of this, invoking a network model to discuss the intermediate mode appears questionable at this stage. This calls for further in-depth study of the power-law domain of the structure factor.

C. Stretched exponential decay

For times $t > 1$ ms, the measured dynamic structure factor $S(q,t)$ exhibited stretched exponential behavior: $S(q,t) \sim \exp-(t/\tau_c)^\beta$ with a characteristic time scale τ_c and width parameter β. This could be observed in both the sol and gel states at all surfactant concentrations. A typical stretched exponential curve of $S(q,t)$ is shown in Fig. 9. The parameters τ_c and β determined through least-squares fitting of $S(q,t)$ to $\exp-(t/\tau_c)^\beta$ showed an interesting **q** and surfactant concentration dependence. β is plotted as a function of SDS concentration in Fig. 10 for both sol and gel states of gelatin and β was found to be equal to 0.85 ± 0.09, showing no surfactant concentration dependence. Figures 11 and 12 show the q dependence of the relaxation time $\tau_c(q)$. Least-squares fitting to the data yielded $\tau_c(q)$ scaling as $q^{-2.05\pm0.08}$ and $q^{-3.0\pm0.2}$ in sol and gel states, respectively. Ren *et al.* [5] saw a q dependence of -2.5 in the sol state and -3 in the gel state of free gelatin. Hence the presence of SDS did not seem to have altered the gel sate dynamic structure factor behavior in the long time limit. However, in the sol state we observed a much smaller exponent (-2.05 ± 0.08) as compared to their value of -2.5. The surfactant concentration dependence of τ_c has been plotted in Fig. 13. In the sol state no concentration dependence was observed whereas in the gel state τ_c showed a peak close to the CMC of SDS and then it decreased substantially.

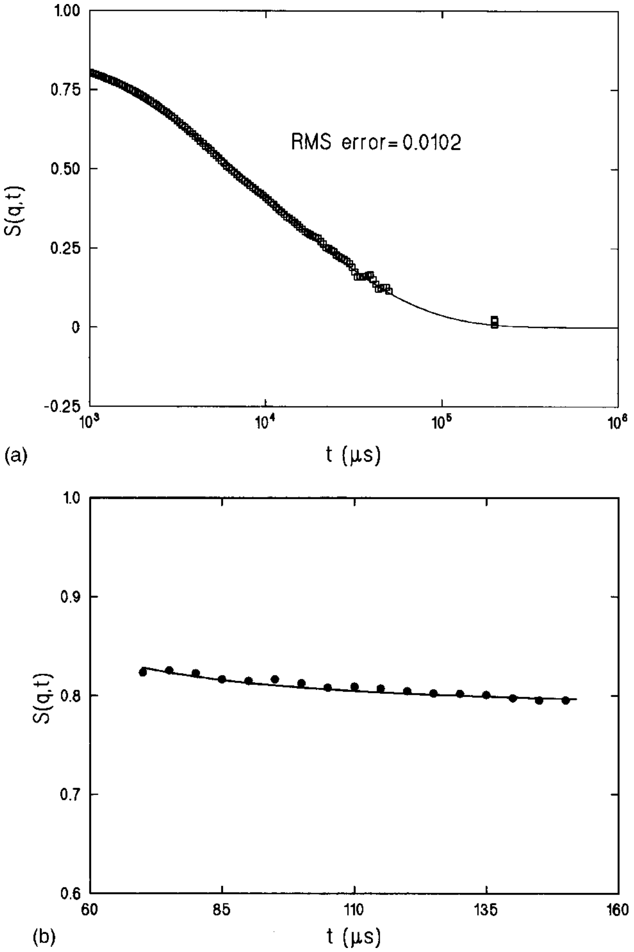

FIG. 9. (a) Stretched exponential regime of the structure factor $S(q,t)$ for 4% (wt./vol) gelatin solution and its fitting to $S(q,t) \sim e^{-(t/\tau_c)^\beta}$ (solid line). For all the samples we observed an excellent fitting. (b) Power-law regime of the structure factor $S(q,t)$ for 4% (wt./vol) gelatin solution and its fitting to $S(q,t) \sim t^{-\alpha(q)}$ (solid line). For all the samples we observed an excellent fitting.

The width parameter β did not show any difference as the sol state evolved to a gel state; unlike in the case of Ren *et al.* [5], β did not show any dependence on SDS concentration either. In case of nonthermoreversible gels β was measured [2] to be 0.65, whereas our value is $\beta=0.85\pm0.05$. Ren *et al.* [5] have measured a value much smaller than this for free gelatin solutions and gels. Another interesting feature of this slow mode is that most of the polymer solutions were shown to exhibit a **q**-independent slow mode, which does not seem to be true in our case [16,28].

D. Origin of power-law and stretched exponential regimes

Ren *et al.* [1,5] have attributed the origin of the power law and stretched exponential regimes to anomalous diffu-

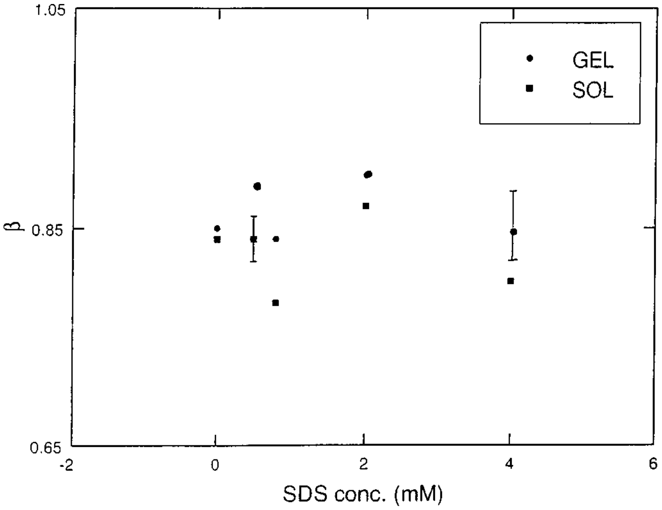

FIG. 10. Width parameter β of the stretched exponential $S(q,t)$ as a function of SDS concentration in sol ($T = 55$ °C) and gel ($T = 20$ °C) states of gelatin. Within experimental error $\beta = 0.85 \pm 0.09$ for both the sol and gel states. Only representative error bars are shown.

sions, where the mean-squared displacement of a random walker on a fractal lattice was given as

$$\langle R^2\rangle = \begin{cases} l_1^2 \ln(t/t_1), & t<\tau_c \\ 2l_2^2(t/t_2)^{\beta}, & t\geqslant \tau_c, \end{cases} \tag{2}$$

where the elementary time and step length of the two random walks are t_1, l_1 and t_2, l_2. Based on simulation results, they derived the dynamic structure factor $S(q,t)$ assuming a Gaussian diffusion model given by

$$S(q,t) \sim \begin{cases} t^{-\alpha(q)}, & t<\tau_c \\ e^{-(t/\tau_c)^{\beta}}, & t\geqslant \tau_c. \end{cases} \tag{3}$$

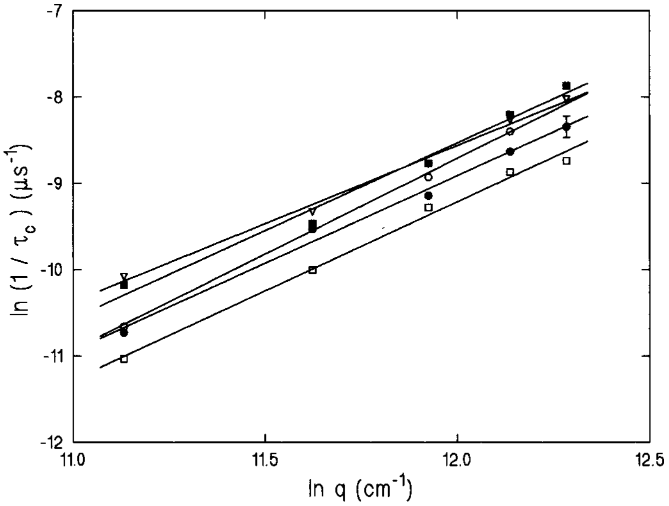

FIG. 11. Variation of stretched mode relaxation frequency ($1/\tau_c$) as a function of q for the sol state of the gelatin-SDS system at $T = 55$°C. Pure (○), 0.5 mM of SDS (▽), 0.8 mM of SDS (■), 2 mM of SDS (□), and 4 mM of SDS (●). The fitting yielded $\tau_c(q) \sim q^{-2.05\pm0.08}$. Only representative error bars are shown.

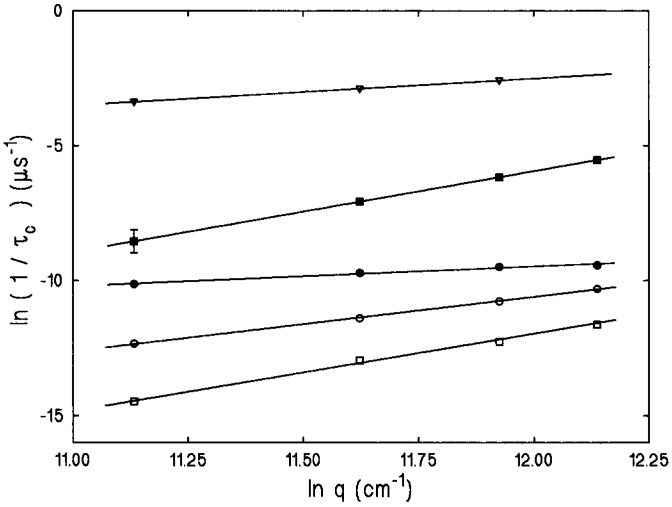

FIG. 12. Variation of stretched mode relaxation frequency ($1/\tau_c$) as a function of q for the gel state of the gelatin-SDS system at $T = 20$ °C. Pure (○), 0.5 mM of SDS (▽), 0.8 mM of SDS (■), 2 mM of SDS (□) and 4 mM of SDS (●). The fitting yielded $\tau_c(q) \sim q^{-3\pm0.2}$. Only representative error bars are shown.

Here the first length scale l_1 was assigned as $\alpha = l_1^2 q^2$ and the second length scale came from the definition $D_s = l_2^2/t_2 = t_2^{\beta-1}\tau_c^{-\beta}q^{-2}$. The slow mode diffusivity D_s defined here could not be determined since t_2 was not known. This model predicts that $\alpha = l_1^x q^x$ with $x = 2.0$ for both sol and gel states. Our measurements showed $x = 1.80 \pm 0.09$ in the sol state, which is not far away from these predictions. However, in the gel state this exponent x was measured to be only 0.98 ± 0.05, which does not concur with the results of this model.

For the stretched exponential mode they predicted $\tau_c \sim q^{-2/\beta}$. Our measured β value for both sol and gel states was $\beta = 0.85 \pm 0.09$, which implied that we should have observed $2/\beta = 2.38$. From Fig. 11, at $T = 55$ °C, the fitted exponent obtained was 2.50 ± 0.09, which is not very different from the theoretical value. Again in the gel state this expo-

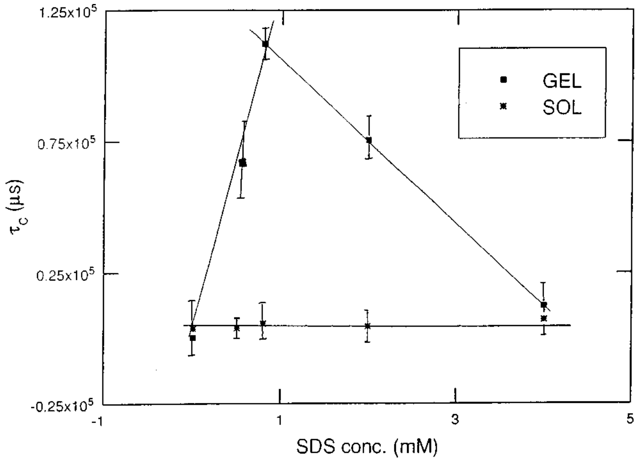

FIG. 13. Variation of τ_c as a function of SDS concentration in sol ($T = 55$ °C) and gel ($T = 20$ °C) states of gelatin. In the gel state τ_c remained the same independently of surfactant concentration, whereas in the sol state τ_c increased up to the CMC of the surfactant and then decreased.

nent was measured to be 3.0 ± 0.09 in Fig. 12, whereas the theoretical value predicted for this was 2.38. Here again we observed that in the sol state the Gaussian distribution model provided a proper description of the observed experimental data, but this failed to account for the results obtained in the gel state of gelatin in the presence of an added surfactant.

The physical origin of the intermediate and stretched exponential relaxation modes was often attributed to the motion of the polymer topologically constrained to a tube along its length due to intermolecular interactions. For average displacements comparable to the tube diameter, the segmental motion towards the walls becomes severely hindered and this dynamics has been proposed to have been reflected by $S(q,t) \sim t^{-\alpha}$ behavior [1,2]. In addition, l_1 was identified with the mesh size of the gelatin network. The stretched exponential mode was explained as full chain reptation along the tube [25–28].

Let us discuss this proposition. The dynamic structure factor under the Gaussian approximation can be written for the Rouse, Zimm, and reptation models of relaxation [29–31] as

$$S(q,t)=S(q,0)\exp\left[-\left(\frac{t}{\tau_c}\right)^n\right], \tag{4}$$

with

$$n=\begin{cases}\frac{1}{2} & \text{for the Rouse model}\\ \frac{2}{3} & \text{for the Zimm model}\\ \frac{1}{4} & \text{for the reptation model.}\end{cases} \tag{5}$$

Here τ_c is the appropriate relaxation time constant of the model concerned. This implies that the stretched exponential mode relaxation should behave as $S(q,t) \sim e^{-(t/\tau_c)^\beta}$, with $\beta=\frac{1}{2}$ for relaxations obeying Rouse dynamics. Ren *et al.* have reported $\beta=0.81$ for the sol state and 0.67 for the gel state of gelatin [5]. Our values for both the sol and gel states were the same, $\beta=0.85\pm0.09$. Hence the stretched exponential decay cannot be attributed to Rouse-type relaxation in the dispersion medium. The Zimm relaxation model does not predict the appropriate β values for sol and gel states either. For a similar reason the dynamic structure factor given by Eq. (5) for the local reptation of the polymer chain in the gel state fails to describe the observed gel state behavior. Maybe a hierarchically constrained dynamics where the relaxation time at any stage depends on its precedent in a constrained way would provide an adequate description of the observed relaxations in power-law and stretched exponential regimes [32]. Empirically, we have observed that beyond the fast mode the entire relaxation regime could be least-squares fitted to the expression

$$S(q,t)=\frac{At^{-\alpha}}{B+C\ \exp(t/\tau_c)^\beta}, \tag{6}$$

where A, B, and C are adjustable parameters.

IV. CONCLUSIONS

The dynamic structure factor showed three distinct relaxation regimes for both free and surfactant (SDS) containing sols and gels of the polypeptide, gelatin. The initial fast mode showed exponential relaxation up to $t \leqslant 20\ \mu$s. This mode was found to be diffusive in nature with a diffusion coefficient D_f that was neither proportional to nor the inverse of the solvent or solution viscosity. We interpret this fast mode as characteristic of the collective mode where the osmotic bulk K and shear modulus G determine the relaxation time through $D_f=(K+\frac{4}{3}G)/f$. Hence this mode could not possibly be interpreted as occurring due to either self- or mutual diffusion of free gelatin chains or their SDS bound complexes.

The intermediate power-law and long time stretched exponential power-law features observed in the measurements of $S(q,t)$ have been explained through anomalous diffusion by Ren *et al.* [1,5]. Our results with SDS being present as a third component qualitatively concur with the initial observation of Ren *et al.*; we compared our results with the theoretical model reported by them. We concluded that the dynamic structure factor beyond the fast mode ($t \geqslant 20\ \mu$s) originates from the Gaussian diffusion of scattering entities in the dispersion medium. Representing this diffusion as $P(r,t)=(2\pi\langle r^2\rangle)^{-1/2}\exp(-r^2/2\langle r^2\rangle)$, $S(q,t)$ can be computed by taking the Fourier transform of $P(r,t)$. Consequently, a length scale l_1 can be associated with the intermediate relaxation regime such that $\alpha(q)=l_1^x q^x$. Ren *et al.* [5] observed $x=2$, which is in complete disagreement with our results, where we obtained $x=0.98\pm0.05$ for gels and 1.80 ± 0.09 for sols. For the sol state the exponent 1.80 is not far off the theoretical predictions of 2, but for the gel state the measured exponent is almost half of this value. This implies that the anomalous diffusion model is inadequate to explain the gel state behavior completely. The anomalous diffusion model predicts that for stretched exponential relaxation, the relaxation time $\tau_c \sim q^{-2/\beta}$. In our experiments β was 0.85 ± 0.09, hence τ_c should vary as $\sim q^{-2.35}$; in the sol state we observed $\tau_c \sim q^{-2.05\pm0.08}$ and in the gel state this was $\sim q^{-3.0\pm0.2}$. Again, there was a discrepancy between our values and the theoretical values predicted by the anomalous diffusion model.

Gelatin is known to form helices even at temperatures above T_{gel}, though the degree of helicity is small. Hence, in order to understand the dynamics of diffusion in gelatin solutions and gels a more rigorous theoretical framework is needed. Simple polymer theory models and conjectures would be inadequate to describe the dynamic structure factor relaxations in this system, as has been clearly seen in our studies. Furthermore, gelation occurs due to systematic formation of intermolecular and intramolecular hydrogen bonds between peptide linkages of adjacent gelatin molecules. A percolation-type model is unlikely to address the observed dynamics and relaxations in complete detail.

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