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Evolution of non-ergodicity during gel transition studied through probe particle diffusion

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Abstract

We report ergodic to non-ergodic transition as studied through the evolution of dynamic structure factor during a sol to gel transition process. The experimental system was 5% (w/v) aqueous solution of gelatin with latex spheres of diameter 90 nm added to it to a concentration of 10 μg/cc. We have measured the kinetic properties of the medium from dynamic light scattering measurements and the results discussed within the frame work of the model proposed by Pusey and Van Megen [Pusey PN, Van Megen W. Physica A 1989;157:705]. The ergodicity parameter Y was measured to be $Y = 1$ in the sol state, but as the onset of gelation took place it deviated strongly from its sol state value, signalling the transition to a non-ergodic state. The microscopic local viscosity, "seen" by the probe particle, η_l was observed to increase from its sol state value of $\eta_l = 1$ to 5000 cP as the gel state was reached. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Probe diffusion; Light scattering; Gelatin; Non-ergodicity

1. Introduction

The diffusion of probe particles in a confined geometry has evoked considerable interest in the past [1–8]. In solution phase the probe particle can explore the entire configurational space of the system, and hence, the time averaged dynamic structure factor measured through dynamic light scattering (DLS) gives a good ensemble averaged picture of the system [9–11]. There are situations, where due to geometrical constraints offered by the crosslinked networks of a gel, the probe particle gets confined and can execute only local excursions about its mean position. Thus, it cannot explore the entire configurational space and the time averaged dynamic structure factor no longer is a representative of the whole ensemble of the system. Here the data interpretation of DLS measurements become too ambiguous [9]. The non-Markovian Brownian motion of probe particles was investigated by Ohbayashi et al. [1]. The probe particles were used to measure microviscosity and channel size of sickle-cell haemoglobin gels by Madonia et al. [2]. Allain et al. [3] studied the diffusion of probe particles in gelling, copolymerization of acrylamide and bisacrylamide, solutions and deduced the evolution of micro-viscosity. The wavevector k dependence of the probe diffusion was explored by Nishio et al. [4] in polyacrylamide gels and the pore size of the gel network where the crosslink content was varied through the gelation threshold was deduced from the DLS data. Djabourov et al. [5] adopted a similar approach and explored colloidal probe diffusion in a physical gel. Subsequently, Reina et al. [6] reported observation of a complex dynamical behavior ranging from the purely translational diffusion of the probe particles in the medium to a relaxational behavior associated with the local motion of probe particles in a confined space inside the

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gel. The dynamics of probe particles in a semidilute polymer solution was quantified through a set of phenomenological scaling laws by Phillies et al. [7]. The molecular weight dependence of probe diffusion in polyacrylamide gels was studied in details by Tokita et al. [8].

Pusey and Van Megen [9] proposed the ergodic to non-ergodic transition as seen by the probe particles during the sol to gel transition process through an elegant mathematical model which was almost overlooked until then. Subsequently, they could apply their model to a chemically crosslinked gel (polyacrylamide) and studied the dynamics of probe particle diffusion in these gelling solutions [11,12]. The effect of inhomogeneities in gels was explored by Suzuki and Nozaki [12] through DLS studies.

In spite of the simplistic approach provided by Pusey and Van Megen [9] in dealing with non-ergodicity, not much has been done in the experimental front to extend this idea to other gelling systems and re-examine the older results. The purpose of this work was to study the evolution of dynamic structure factor of the light scattered from the probe particles in a gelling solution. The transport properties, such as diffusivity of the probe and microscopic viscosity, "seen" by the probe, as the medium goes from an ergodic system (solution phase i.e. one which, when given enough time, evolves through all representative fractions of all spatial configurations) to a non-ergodic system (gel state) where the spatial configurations explored do not span the whole configurational space have been explored in detail. DLS technique was used to study the transport properties of the medium.

2. Theoretical background

The essence of Pusey and Van Megen proposition is summarized here. We have also performed an ab initio derivation of these results [13]. The assumptions made are the following:

1. Time averaged properties of a particular volume of a non-ergodic medium is equivalent to the one averaged over a sub-ensemble $\{m\}_p$ of m configurations achieved by restricted displacements $\{\Delta_j(k)\}$ of the scatterers about fixed positions $\{\vec{R}_j\}$.
2. The total field scattered by a particular volume is written as the sum of fluctuating (effectively ergodic) component and a constant (non-ergodic) component.
3. The diffusion coefficient D is k dependent and yields the gradient diffusion coefficient in $k \to 0$ limit.

The intensity correlation function (ICF) measured by DLS is defined as

$$\mathrm{ICF} = \langle I(0)I(\tau)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathrm{d}t\, I(t)I(t+\tau).$$

In an ergodic medium, the scatterers are highly delocalized. Hence, on given enough time any particular sub-ensemble of the system would evolve through all the spatial configurations of the system. Thus we can say that the time average of the intensity correlation function ($\langle\mathrm{ICF}\rangle_\mathrm{T}$) and the ensemble averaged intensity correlation function ($\langle\mathrm{ICF}\rangle_\mathrm{E}$) are equal.

As a consequence, the information obtained from studying the time averaged intensity correlation function of a particular sub-ensemble of the system is applicable to the entire system. However, as the system moves towards non-ergodicity the scatterers become more and more localized and suffer fluctuations about their mean positions only. Hence, by just studying the time averaged intensity correlation function of a sub-ensemble of the system one does not get knowledge of the system as a whole. If one wants to study $\langle\mathrm{ICF}\rangle_\mathrm{E}$ of the system then a huge amount of experimental time and averaging over a lot of sub-ensembles of the system would be required. A very tedious and impractical proposition. They showed that from a single shot DLS measurement performed on a non-ergodic medium, it was possible to extract the exact dynamic structure data.

Let us recapitulate some of the useful relations that have been used in our studies from Refs. [9,13]. The suffices E and T imply ensemble and time average, respectively. The ICF measured by the correlator is designated as $g_\mathrm{T}^2(\tau)$ and the dynamic structure factor is $f(k,\tau)$. The non-ergodicity parameter Y is defined as

$$Y = \frac{\langle I(k)\rangle_\mathrm{E}}{\langle I(k)\rangle_\mathrm{T}}, \tag{1}$$

and consequently, the normalized ICF, g_T^2 can be written as

$$g_\mathrm{T}^2 = \frac{\langle I(k,0)I(k,\tau)\rangle}{\langle I(k)\rangle_\mathrm{T}^2} = Y^2[f(k,\tau)-f(k,\infty)]^2+1. \tag{2}$$

From Eq. (2), at $\tau = 0$

$$\frac{\langle I^2(k)\rangle_\mathrm{T}}{\langle I(k)\rangle_\mathrm{T}^2} - 1 = Y^2[1-f(k,\infty)]^2.$$

Define $\langle I^2(k)\rangle_\mathrm{T}/\langle I(k)\rangle_\mathrm{T}^2 - 1 = \sigma_I^2$.

Note that σ_I is an experimentally determined parameter.

$$\sigma_I^2 = Y^2[1-f(k,\infty)]^2. \tag{3}$$

Hence, one can show that

$$g_\mathrm{T}^2(k,\tau) - 1 = Y^2\left\{f(k,\tau) - 1 + \frac{\sigma_I}{Y}\right\}^2, \tag{4}$$

$$f(k,\tau) = \frac{\sqrt{(g_\mathrm{T}^2-1)}}{Y} + 1 - \sigma_I. \tag{5}$$

In macromolecular and colloidal systems, the forces constraining the scatterers are usually weak and their motions can be defined by coupled overdamped Langevin equations. Then, a short time expansion of the dynamic structure factor can be written as

$$f(k,\tau) = 1 - Dk^2\tau + \cdots. \tag{6}$$

In general, D is an effective diffusion coefficient which depends in a complicated fashion on the scattering amplitudes and both self and collective Brownian motions. However, for identical scatterers (colloids or polymers) D can be identified as k dependent collective diffusion coefficient which, in the limit $k \to 0$ is equal to the gradient diffusion coefficient. Further,

$$\begin{aligned} g^2(k,\tau) - 1 &= Y^2\left\{\mathrm{e}^{-Dk^2\tau} - 1 + \frac{\sigma_I}{Y}\right\}^2 \\ &= Y^2\left\{1 - Dk^2\tau + \cdots + \frac{\sigma_I}{Y}\right\}^2. \end{aligned} \tag{7}$$

This further reduces to

$$\begin{aligned} g^2(k,\tau) - 1 &= \sigma_I^2\left\{1 - \frac{YDk^2\tau}{\sigma_I^2} + \cdots\right\}^2 \\ &= \sigma_I^2\left(\mathrm{e}^{-YDk^2\tau/\sigma_I}\right)^2. \end{aligned} \tag{8}$$

Finally, the effective diffusion coefficient is given as

$$D = -\frac{\sigma_I}{k^2\tau Y}\ln\left\{\frac{g^2(k,\tau) - 1}{\sigma_I^2}\right\}. \tag{9}$$

3. Experimental details

The light scattering experiments were performed with an 80 mW diode pumped frequency doubled Nd:YAg laser emitting at a wavelength of 532 nm. This laser has long coherence time, ~1 min and hence, has a very narrow linewidth. A 5% (w/v) gelatin solution was prepared in a neutral buffer medium as follows. This material procured from M/S. Loba Chemie (Indo-Astranal, India) batch no. 2930 with maximum nominal impurities as follows: Sulphate ash = 1.5%, $SO_2 = 2.4 \times 10^{-4}\%$ and heavy metals (Zn, Cu, Pb) in concentrations less than SO_2 concentration. The preparation is devoid of any *E. coli* or liquifier presence. The material was used without further purification. The solvent chosen was deionized double distilled water. The solvent was centrifuged at 8000 rpm for 1 h to remove dust. Gelatin powder was allowed to swell overnight in this solvent. The solvent was heated to 60°C to dissolve the solute material. The pH of the solution was maintained at 6.8 in a 0.1 M sodium phosphate buffer ($Na_2HPO_4 + NaH_2PO_4 \cdot 2H_2O$). To this solution latex particles (Fluka Scientific, USA, nominal size $= 90 \pm 5$ nm) was added. The latex particle volume fraction based on the data supplied by the manufacturer was calculated to be $\sim 5 \times 10^{-5}$. The differential scattering observed from latex particles was at least 10 times larger than the gelatin solutions. The sample was then kept in an ultrasonic vibrator for about 30 min to ensure that the latex particles were homogeneously spread in the medium. The clean solution was collected using a micropipette and transfered directly into optical quality borosilicate glass cell and then sealed. The sample was allowed to undergo self gelation through self cooling and was used only after 24 hours. Sol state studies were performed on melted gels. The temperature of the system was maintained $\sim(20 \pm 1)$°C. A digital correlator (Brookhaven Instruments, USA, model-9000AT) was used to measure the intensity correlation function of the scattered light. The entire scattering assembly was mounted on a Newport vibration isolation table. Further details of the experimental setup and data handling can be found elsewhere [14]. For measuring $\langle I(k)\rangle_\mathrm{E}$, the sample cell was rotated, and also translated vertically to scan as many scattering volumes as possible and the scattering intensity measured. The measured intensity gave the ensemble averaged values. The same procedure was adopted by Joosten et al. [10,11]. The $\langle I(k)\rangle_\mathrm{E}$ values thus measured were highly reproducible and the maximum error was $\sim\pm 2\%$.

4. Results and discussions

The ergodicity parameter Y was calculated using Eq. (1) and is plotted as function of gelation time in Fig. 1. For an ergodic medium Y was very well defined and was almost equal to 1, but after ~3 h the onset of gelation took place and the medium was rendered non-ergodic. This made Y highly undefined (Fig. 1) and started

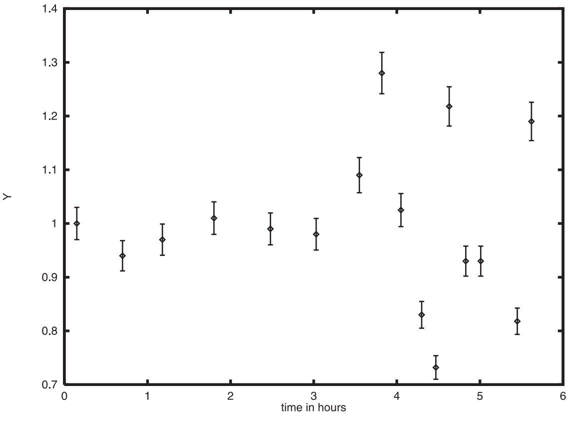

Fig. 1. Variation of the ergodicity parameter Y with gelation time. The hot sol at 60°C was allowed to cool to 20°C and the Y parameter was measured continuously. Note that after ~180 min, the onset of gelation renders the Y parameter completely undefined about its ergodic state value of 1.

fluctuating about 1. In fact Y takes a value depending upon the sub-ensemble of the medium under study. One can associate this observation to the evolution of the non-ergodic nature of the medium. This has further bearing on the ICF measured by the digital correlator. When the medium is ergodic, the scatterers execute unrestricted Brownian motion, the intensity $I(k,t)$ of the speckle pattern will fluctuate with time. Furthermore, with time a representative fraction of all possible configurations of the scatterers will eventually be sampled so that in turn the speckle pattern will undergo full range of Gaussian fluctuations. Hence, for a perfectly ergodic state, $g_T^2(k,0)$ will have its maximum value. As the process of gelation onsets, the scatterers suffer only limited fluctuations about some fixed points and get localized. Now, the probes do not evolve through all possible spatial configurations hence only a restricted range of fluctuations is sampled causing $g_T^2(k,0)$ to steadily decrease with progress of gelation. This phenomenon can be clearly observed from Fig. 2.

Study of the dynamic structure factor, $f(k,\tau)$ versus the correlation delay time τ (Fig. 3) shows that as $\tau \to \infty$, $f(k,\tau)$ decays to a lower value for sol state but remains almost constant in the gel state (Fig. 3). Let us visualize this. As $\tau \to \infty$ the jth particle looses all correlation with the kth particle. Consequently, the dynamic structure factor $f(k,\tau)$ will be

$$f(k,\infty) \sim \sum_{j=1}^{N}\sum_{k=1}^{n_j}\left\langle b_j b_k \mathrm{e}^{i\vec{k}\cdot(\vec{R}_j-\vec{R}_k)}\right\rangle_{\mathrm{T}} \left\langle \mathrm{e}^{i\vec{k}\cdot\Delta_j}\right\rangle_{\mathrm{T}} \left\langle \mathrm{e}^{i\vec{k}\cdot\Delta_k(\tau)}\right\rangle_{\mathrm{T}}. \tag{10}$$

Going by assumption (2), we can write

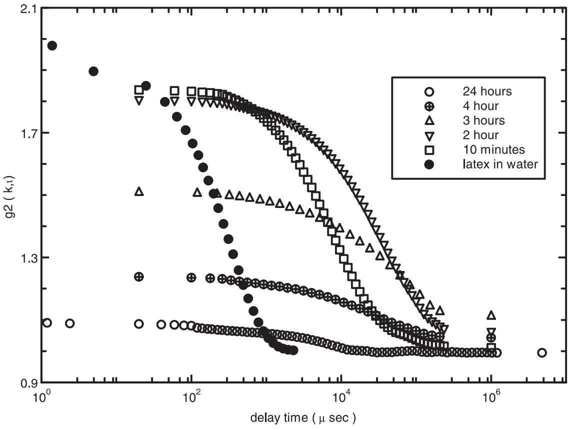

Fig. 2. The evolution of normalized ICF, $g_T^2(\tau)$ with time. For latex solution, $g_T^2(k,0)$ had a value ∼2 which slightly falls to ∼1.9 for the sol state in the begining, and gradually it kept reducing and after 24 h, it showed a value of ∼1.1. The $g_T^2(k,0)$ value is a measure of range of fluctuations "seen" by the probe particle in the medium. See text for details.

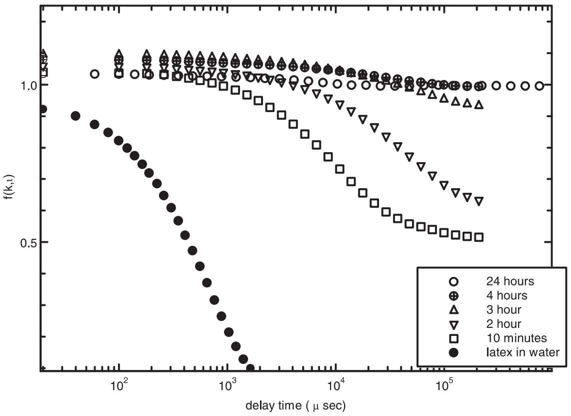

Fig. 3. The evolution of dyanamic structure factor $f(k,\tau)$ with time for the data reported in Fig. 2. The structure factor relaxes to its equilibrium value for an ergodic medium for latex solution. However, for a gelling solution, the relaxation is incomplete and for matured gel (after 150 min), it hardly relaxes at all, implying that the fluctuations are highly confined. This is clearly seen in these curves.

$$\left\langle \mathrm{e}^{i\vec{k}\cdot\Delta_j}\right\rangle_{\mathrm{T}} = 1 - \left\langle \frac{(\vec{k}\cdot\Delta_j)^2}{2} + \cdots \right\rangle_{\mathrm{T}}. \tag{11}$$

For a completely fluctuative medium $\Delta_j \to \infty$.

Hence,

$$\left\langle \mathrm{e}^{i\vec{k}\cdot\Delta_j}\right\rangle_{\mathrm{T}} \to 0. \tag{12}$$

From Eq. (10) it is obvious that for a fluctuative medium as $\tau \to \infty, f(k,\infty) \to 0$.

If the system shows restricted small fluctuations (i.e. $\Delta_j \to 0$);

$$\left\langle \mathrm{e}^{i\vec{k}\cdot\Delta_j}\right\rangle_{\mathrm{T}} \to 1. \tag{13}$$

Hence, $f(k,\tau) \to$ constant value.

Thus, from the above analysis, we can conclusively state that the sol state is a fluctuative medium, whereas the gel state shows restricted small fluctuations. In fact, Fig. 3 provides a manifestation of this phenomenon.

To study the diffusion curves (Fig. 4) from Eq. (9) one needs to understand the morphology of the sol and gel structures. In the sol state, one has monomers of gelatin moving freely in the solution, whereas the gel state is a three dimensional network of polymer strands which are physically crosslinked by functional groups [15,16]. The solvent gets either trapped in its interstitial space as bound solvent or (and) remains attached to the polymer as a hydration layer. In fact, a smaller fraction of the solvent constitutes the hydration layer.

Qualitatively, from Fig. 4, we can state that the particle is suffering unrestricted Brownian motion in the sol state where as in the gel state it shows strong re-

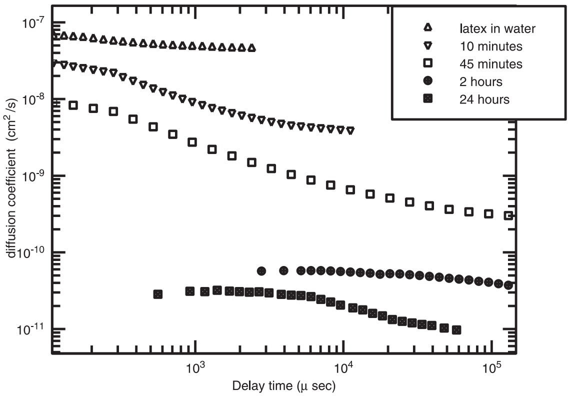

Fig. 4. The time dependence of k-dependent diffusion coefficient derived from Eq. (9). For latex in water there is only one diffusivity. For the gelling solution, the probe particle sees two diffusivities over two time scales. At short times, the probe does not see the presence of barriers and executes free Brownian motion. At longer time durations, the probe particles can execute only restricted Brownian motion since these are highly confined in space. The long time diffusion coefficient in the limit of $k \to 0$ gives the gradient diffusivity.

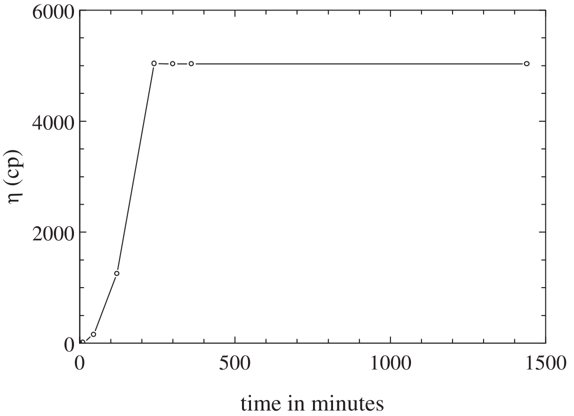

Fig. 5. Evolution of microscopic viscosity as seen by the probe particle in the gelling solution deduced from the long time diffusivity data of Fig. 4 (after 24 h). The microscopic viscosity increases from the sol state value (at 60°C) of ~1 cP to ~5000 cP for the matured gel (at 20°C).

duction in particle mobility. It can be inferred from the experimental data that there are two modes of diffusion: one, fast at short correlation time and the other slow at long correlation time. This can be attributed to the fact that at short correlation times the diffusing particle is insensitive to the presence of polymer strands. Hence, the diffusion of the particle is more prominent at short correlation times, whereas at long correlation time the collective motion of both the particles and the medium comes into play. Since the medium in gel state is less fluctuative, the relaxation time of this state is much smaller than the relaxation time of the sol state. This can also be observed from Fig. 4 by noting the onset of the plateau region of the diffusion coefficient. Hence, we can say that only the long time behavior of the diffusion coefficient carries the signature of the collective motion of the medium as well as the probe particles. As the long time diffusion coefficient is a measure of the collective motion of both the medium and the probe particles, it gets lowered as one moves from a completely fluctuative medium to a medium where the bulk movement of the network and the solvent trapped in it takes place. It can thus be argued that the long term diffusion coefficient is associated with the local viscosity of the medium through Strokes–Einstein relation:

$$\eta_l = \frac{k_B T}{6\pi r D}, \tag{14}$$

where η_l is the coefficient of local viscosity observed by the probe particle (microscopic viscosity), r is radius of the probe particle, k_B is Boltzmann constant, T is absolute temperature and D is long time diffusion coefficient. From Fig. 5 it is observed that after gelation, the coefficient of viscosity remains almost constant. The evolution of η_l can be effectively probed if we assume that there was no polymer adsorption on the surface of the latex particles. This allows us to use $r = 90$ nm and we could estimate the value of "microscopic viscosity" (the viscosity of the region where the probe particle has been trapped) from Eq. (14). The result is plotted in Fig. 5. The η_l had a sol state value of almost 1.10 ± 0.05 cP (at 60°C) which gradually increased to almost 5000 ± 200 cP (at 20°C) as the onset of gelation takes place at time ~180 min. Beyond this time the viscosity retained a plateau value. This high viscosity is responsible for arresting the center of mass motion of the latex spheres. In this calculation, we neglect the effect of solvent adsorption on the latex surface.

5. Conclusions

These experiments clearly establish that as the sol state evolved to a gel phase, non-ergodicity was introduced in a significant manner. The solution phase allows the concentration fluctuations to pervade the entire space uniformly, thereby making the time and ensemble averages to be identical. In a non-ergodic medium, this is no longer possible because only restrictive fluctuations are permitted. This does not allow these fluctuations to relax to equilibrium over a finite time. Due to this, the probe particle sees a microscopic viscosity that is very very large as compared to that of an ergodic medium. Thus, one observes a reduced center of mass diffusivity. Here, it must be borne in mind that the gel network more or less experiences the same hydrodynamic hindrance in its normal modes of fluctuations. The hyperdiffusive regimes observed by Djabourov et al. [5] were not seen in our experiments. Studies of non-ergodic systems are challenging, since these provide an insight into the underlying dynamics prevailing in many physically important systems and processes. Hence, more experimental explorations are called for.

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