

A dynamical light scattering technique and its application in viscoelastic networks in soft matter

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ABSTRACT

In this paper, we present a dynamic light scattering technique using diffusing wave spectroscopy to track the dynamics of colloidal particles embedded in a complex fluid which allows us to obtain structural and dynamical information of a transparent viscoelastic material. Scattered light of a single speckle is detected by a photomultiplier tube and the time correlation function of light intensity is calculated using a temporal average. If the particles can not explore the entire phase space, temporal average and ensemble average are not the same. This is a necessary condition to relate ensemble average from the scattering by many particles to intensity temporal fluctuations. To overcome non-ergodicity for large lag times, a CCD camera is used for the acquisition of the scattered light where pixels form an array of detectors which enables us to perform thousands of simultaneous experiments. In this manner, the time correlation function is obtained directly by taking the ensemble average instead of using a temporal average. For short lag times, the non-ergodicity problem can be avoided by remixing the scattered light coming from the sample by the use of a slowly rotating diffuser disk placed before the collection optics of the photomultiplier tube. This procedure provides a true ensemble-averaged time correlation function over ~ 7 -8 decades of time. As an example of the application of this technique, the dynamics of microspheres embedded in cross-linked polymer matrix, namely, an acrylamide-bisacrylamide gel is studied. This polymer network is known to swell or shrink by changing the solvent composition. The description of the arrested dynamics of the microspheres can be obtained, as well as the viscoelastic properties of the polymer network at different cage sizes.

Keywords: Dynamic Light Scattering, Microrheology, Polymer Network

1. INTRODUCTION

Dynamic light scattering techniques had been widely used in several fields to extract dynamical and structural information in complex fluids. Initially, these techniques were constrained to transparent samples, where a single scattering event is a good approximation.¹ However, in the past fifteen years, new developments allowed to take into account multiple scattering, leading to diffusive wave spectroscopy (DWS).^{2,3} This technique extends the single scattering experiment to multiple scattering assuming that light transport in the sample can be treated as a diffusive process. Using DWS, it is possible to measure the mean square displacement, $\langle \Delta r^2(t) \rangle = \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle$, where $\langle \rangle$ denotes an ensemble average, of embedded colloidal particles in a fluid. These particles interact with the surrounding fluid which can be a pure viscous or a viscoelastic fluid. The rheological properties of a fluid under study can be estimated from the mean square displacement measurement.⁴

In a DWS experiment, a laser beam strikes a slab formed by a turbid suspension made of the liquid under study and probe colloidal particles, embedded for that purpose, which scatter light. The temporal autocorrelation function of a small fraction of the light that passes through the slab is measured. The transport of light through the slab is treated as a diffusive process and photons are treated as random walkers, with a random walk step length equal to the transport mean free path l^* and a resultant diffusion coefficient $D = vl^*/3$, where v is

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the speed of light in the suspension. The transport mean free path results equal to the inverse of the reduced scattering coefficient μ'_s . The diffusion approximation is valid for calculating transport of light only over distances much longer than l^* .² When scattering is not isotropic, which is the case for particle sizes close to, or larger than the photon wavelength, the random walk step length is longer than the photon mean free path length $l = 1/\mu_s$, where μ_s is the scattering coefficient. These lengths are connected by $l^*/l = 2k_0^2/\langle q^2 \rangle$, where $k_0 = 2\pi n/\lambda$ is the photon wave vector in the solvent, λ is the laser wavelength in vacuum, n is the effective index of refraction in the sample, and $\langle q^2 \rangle$ represents the angle average for the squared scattering vector for a typical scattering event experienced by the photon in the medium.

Light scattering techniques usually assumes that the particle can explore the entire space phase during the experiment, i.e. the medium under investigation must be ergodic, such that the ensemble averaged properties can be measured by a time average. This assumption is not satisfied if the particle is bounded or if the sample presents inhomogeneities. The most direct method of performing ensemble average of scattered light from non-ergodic samples is based in the idea of collecting light scattered by different parts of the sample, performing the real ensemble averaging.⁵ Experimentally the sample is slowly moved or rotated, while the autocorrelation function of the scattered light is collected. This extra movement leads to an additional decay in the autocorrelation function. This method has the important disadvantage of experimental complexity, besides it is not well suited for fragile turbid systems, since moving or rotating the sample can led to its disturbance or even breakdown. Sheffold et al.⁶ proposed another way of performing diffusing-wave spectroscopy in non-ergodic media. This method is based on that transmitted light through a sandwich of two turbid cells can be considered as ergodic even if only the second cell is ergodic. These authors demonstrated that under some particular conditions, the field autocorrelation function of transmitted light through the double-layer sample can be written as a product of autocorrelation functions corresponding to the individual layers.⁶ Consequently, it is sufficient to measure the intensity autocorrelation functions of the two-cell setup and of the second ergodic layer, in order to obtain the properly averaged intensity autocorrelation function of the non-ergodic layer. This method solves the problem of non-ergodic signal coming from the sample. However as shown below, because we can only retrieve the information of the non-ergodic medium at times where the autocorrelation function of the ergodic layer is not zero, we can lose information at long times.

Other technique for dealing with detecting signals coming from non-ergodic samples is to use a CCD array as a light detector. This method allows the intensity from a large number of speckles to be simultaneous and independently measured. A time series of images of scattered light obtained from the CCD camera is processed such that each pixel in the CCD array can be considered as an input to its own correlator. This method of processing scattered intensity data collected with a CCD camera is like having N independent samplings of the data, where N is the number of speckles in the field of the CCD array. If N is sufficiently large, then a complete ensemble average is obtained without any need to sample the system over time any longer than the actual dynamical time that are under study.⁷ Thus, a direct ensemble average can be obtained without any need for time averaging. This approach solves the non-ergodicity problem because a full ensemble average is obtained. The limitation of this technique is due to the minimum delay time for which the correlation function can be measured, set by the frame rate of the camera. However, by using both the two-cell technique, and a CCD camera as a light detector, we can measure a true ensemble-averaged time correlation function over ~ 7 -8 decades of time, allowing the measurement of the mean square displacement of the scattering particles in a large range of lag times.

The aim of this paper is to use the two-cell technique in conjunction with multispeckle DWS to track the motion of polystyrene microspheres embedded in a network of acrylamide and bis-acrylamide polymers. We will show that this system presents a viscoelastic behavior due to the formation of a cross-linked network. Because this polymer network can undergo an equilibrium transition of volume with changing solvent composition, we could measure the effective cage size where particles are trapped when solvent composition is varied.

2. DIFFUSING WAVE SPECTROSCOPY ²

In a DWS experiment light from a laser is incident on one side of a planar sample of thickness $L \gg l^*$ and scattered light is collected from a small area on the opposite side. A single photon passing through the sample

undergoes n scattering events and emerges with a phase that depends on its total path length s . An example of such trajectory is shown in figure 1.

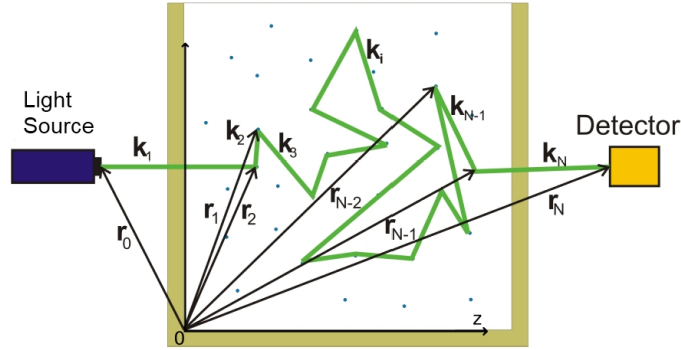


Figure 1. A single path through a sample of multiply-scattered light.

The total phase shift $\phi(t)$ of the photon after passing from the laser to the detector is

$$\phi(t) = k_0 s(t) = \sum_{i=0}^N \mathbf{k}_i(t) \cdot [\mathbf{r}_{i+1}(t) - \mathbf{r}_i(t)]. \quad (1)$$

The total field at the detector is the superposition of the fields from all light paths through the sample to the detector

$$E(t) = \sum_p E_p \exp[i\phi_p(t)], \quad (2)$$

where \sum_p represents the sum over paths, and E_p is the amplitude of the field from path p at the detector. It can be shown that under the assumption of independence of light paths, the field autocorrelation function can be written as

$$g_1(t) = \frac{\langle E(0)E^*(t) \rangle}{\langle |E|^2 \rangle} = \int_0^\infty P(s) \exp \left[-\frac{1}{3} k_0^2 \langle \Delta r^2(t) \rangle \frac{s}{l^*} \right]. \quad (3)$$

Here $P(s)$ is the fraction of scattered intensity in path of length s , or path length distribution. Thus, the calculation of the autocorrelation function is reduced to determining the path-length distribution function. This distribution can be calculated using the diffusion approximation of transport of light within the sample. For a plane wave through a slab of thickness $L \gg l^*$ and infinite transverse extent, the field autocorrelation function takes the form:

$$g_1(t) = \frac{\frac{L/l^* + 4/3}{\alpha^* + 2/2} (\sinh[\alpha^* x] + \frac{2}{3} x \cosh[\alpha^* x])}{(1 + \frac{4}{9} x^2) \sinh[\frac{L}{l^*} x] + \frac{4}{3} x \cosh[\frac{L}{l^*} x]}, \quad (4)$$

where $x = [k_0^2 \langle \Delta r^2(t) \rangle]^{1/2}$ and $\alpha^* = \frac{z_0}{l^*}$. The field autocorrelation function is related to the measured intensity correlation function $g_2(t)$, through the Siegert relation: $g_2(t) = 1 + \beta |g_1(t)|^2$, where β is an instrumental factor determined by collection optics. As can be seen from eq. 4, experimental measurement of the intensity correlation function, and numerical inversion of equation 4 allows us to measure the mean square displacement of the scattering particles. The numerical inversion of eq. 4 requires the knowledge of the transport mean free path l^* . Usually, l^* is measured by comparing the total transmitted intensity through a sample of interest relative to a reference sample, of known l^* .⁸ We used a method that allowed us to obtain absolute values for the transport mean free path of light just measuring in an integrating sphere both the transmittance and the reflectance in this kind of systems. This technique is described elsewhere.⁹

3. TWO-CELL TECHNIQUE AND MULTISPECKLE DWS

As can be seen from eq. 4, the field autocorrelation function is related with the ensemble average of the mean square displacement. Indeed, ensemble-averaged quantities are commonly calculated theoretically, while it is the time averaging that is most easily obtained in experiments. If the particles are bounded near a fixed position, or if part of the sample is solid-like, time averaging and ensemble averaging are not equivalent. Experimentally, one finds that a series of time-averaged measurements of a given sample yields a set of different results. To overcome this situation, Scheffold et al.⁶ proposed a method for obtaining true-ensemble average autocorrelation function without rotating of moving the sample. This method is based on the idea that light transmitted through a sandwich of two turbid cells can be considered as ergodic even if only the second cell is ergodic. The use of a second cell modifies the intensity correlation function of transmitted light, which now exhibits an additional decay. In order to simplify the analysis of the experimental data, the parameters of the double-cell sample can be optimized. Namely, moderate absorption and/or leakage of light should be introduced between the two cells, and the optical thickness of the second, ergodic cell should be reduced well below the optical thickness of the cell containing the non-ergodic medium, while the dynamics of scatterers in the second cell should be chosen slow. Under these conditions, Scheffold et al.^{6,10} shown that the field autocorrelation function of light transmitted through the double-layer sample can be written following the multiplication rule:

$$g_1^M(t) = g_1^E(t) * g_1^S(t), \quad (5)$$

where the M holds for mixed signal, E for ergodic sample and S for the sample under study. The two-cell geometry can be also realized using a very slowly rotating diffuser disk, as suggested by Viasnoff et al.¹¹ As can be seen from 5, the ensemble average autocorrelation function of the sample can be extracted from the mixed signal, prior measurement of the ergodic sample. This method provides a procedure of obtaining accurate autocorrelation functions in turbid, non-ergodic media in time scales below the characteristic decorrelation time of the second ergodic cell. In our case, we used a rotating diffuser disk made of ground glass connected to a slow-working motor. The decay correlation time was found to lie around the 20 ms.

For the slow dynamics, we used a CCD camera as a light detector. With this approach is possible to record simultaneously a large number of speckles and thereby obtain direct multi-speckle ensemble-averaged autocorrelation functions. The autocorrelation function at a lag time τ is calculated by an algorithm comparing the speckle field image at a time τ to the image at a given fixed reference time. The intensity in a pixel at a time t_0 is multiplied by the intensity in the same pixel at a time τ after. The intensity correlation function is calculated by averaging over pixels

$$g_2(t) = N \frac{\sum_{k=0}^N I_k(0)I_k(t)}{\left[\sum_{k=0}^N I_k(0)\right]^2}. \quad (6)$$

Experimentally, in transmission geometry, the image of the speckle pattern on the back side of the sample cell is focused by a lens into a pinhole and the transmitted pattern is directly imaged onto the CCD chip. If D is distance from the pinhole to the CCD camera, λ is the wavelength of the light, and A is the diameter of the diaphragm, the size of the speckles of scattered light formed in the CCD chip is $\approx D\lambda/A$. By changing D and/or A , the size of the speckles relative to the size of a pixel on the CCD chip can be controlled. If the speckles are too small, for example if several speckles occupy a single pixel, optical contrast is lost. We adjusted the speckle size to obtain a satisfactory optical contrast with as many speckles as it was possible to be analyzed.⁷ The frame rate of the camera is around 100 frames/second, allowing detection of the autocorrelation function at delay times as small as 10 milliseconds.

The experimental setup es shown in Fig. 2. A laser beam is sent through a spacial filter, and a beam expander (BE). Afterwards the beam is deviated depending on the kind of experiment to be done by a mirror (M). In the case of l^* measurements, the beam is sent into the sample and the scattered light is collected by the integrating sphere.⁹ In the case of DWS measurements, the beam is sent into the sample (S) through a pinhole to assure a planar wave incident to the sample (P1). The sample is in a temperature controlled bath (TB). The scattered light is collected, with the aid of an achromatic doublet (AD) and a beam splitter (BS), by a couple of photomultipliers in cross correlation and by a CCD camera to make multispeckle DWS. Prior the light enters

the photomultiplier, the light strikes the diffusing rotating disk (DD) which is before the fiber optics entrance. In the multispeckle DWS, the achromatic doublet forms an image 1:1 of the back side of the sample in the Iris (I). The distance from the iris to the CCD camera was changed to optimize optical contrast.

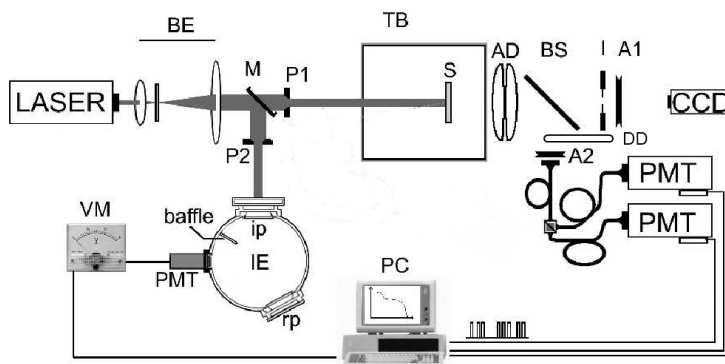


Figure 2. Experimental setup. Adapted from.¹²

As a test for our experimental setup, we analyzed the scattered light coming from a turbid suspension of colloidal polystyrene microspheres dispersed in a water-glycerol mixture (85% glycerol). In this case, the sample is ergodic. Although the particle's dynamics is slow enough to be detected by the multispeckle DWS. The red line in Fig. 3 corresponds the intensity correlation of the rotating diffuser disk. By measuring the total autocorrelation function and using the multiplication rule (eq. 5) an ensemble averaged autocorrelation function of the scattered light due to the embedded particles was obtained (red filled circles in fig. 3). The autocorrelation function measured by multispeckle DWS is shown in fig. 3 in red hollow circles. In this particular case, where light comes from the diffuser disk, the correlation function goes to zero at a time ~ 20 ms. There is an overlap region between the rotating diffuser disk autocorrelation measurement and the multispeckle DWS measurement. There is no substantial difference between them within the experimental error. The black line in Fig. 3 is the autocorrelation function measured directly, e.g. without the rotating diffuser disk. Because the water-glycerol mixture is an ergodic system, measurements using both methods, rotating diffusing disk in conjunction with multispeckle DWS and just simple DWS method, gave analogous results.

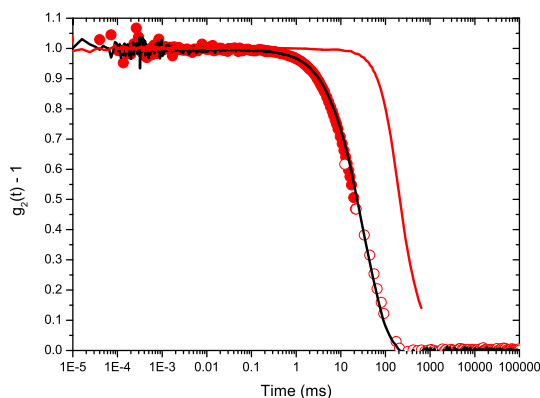


Figure 3. Intensity correlation function of polystyrene microspheres embedded in water-glycerol mixture, measured by DWS and multispeckle DWS.

4. MICRORHEOLOGY

One of the most fundamental properties of any material is its mechanical susceptibility as a response to a shear excitation. A solid is elastic and stores energy whereas fluids dissipate mechanical energy and they are viscous. However, many materials of interest are viscoelastic, they both store and dissipate energy, with relative proportions depending on the frequency (ω) of a sinusoidal deformation applied to the material. The mechanical susceptibility is characterized by the complex shear modulus $G^*(\omega)$, which determines the shear stress induced in a material upon application of an oscillatory shear strain at a frequency ω . The real part of $G^*(\omega)$, which is called the storage modulus, $G'(\omega)$, it is in phase with the applied shear strain. The imaginary part of $G^*(\omega)$, called the loss modulus, $G''(\omega)$, it is in phase with the shear strain rate.¹³ Complex fluids usually presents a rich viscoelastic behavior due to the large length scale of the supra-molecular structures embedded in them. Traditionally, $G^*(\omega)$ is determined mechanically, by applying a shear strain and measuring the induced shear stress. However, because the measurements are mechanical, their frequency range is limited. However, in the past decade, microrheological techniques have successfully matured.^{3,14,15} The response can be measured either by actively manipulating the probe particles or by passively measuring the mean square displacement, $\langle \Delta r^2(t) \rangle$, of them, as in the case of DWS. The bulk mechanical susceptibility of the fluid determines the response of the probe particles excited by the thermal stochastic forces, which lead to Brownian motion. The measured $G^*(\omega)$ can be related to $\langle \Delta r^2(t) \rangle$ by describing the motion of the particles with a generalized Langevin equation incorporating a memory function to take into account the viscoelasticity of the fluid.⁴ Here, in contrast to mechanical rheometers, there is no strain applied on the material during the measurement. This is particularly useful in complex fluids in which even small imposed strains can cause structural reorganization of the material and, consequently, a change in the viscoelastic properties. The relation between $\langle \Delta r^2(t) \rangle$ of probe particles embedded in the complex fluid and the $G^*(\omega)$ can be written as⁴

$$G^*(\omega) = G'(\omega) + iG''(\omega) = \frac{k_B T}{\pi a i \omega \mathcal{F}_u [\langle \Delta r^2(t) \rangle]}, \quad (7)$$

where k_B is the Boltzmann's constant, T is the temperature, a is the radius of the particle and \mathcal{F}_u represents the unilateral Fourier transform.

The method of applying directly the Laplace transform of the $\langle \Delta r^2(t) \rangle$ and using analytical continuity ($s \rightarrow i\omega$) may be very accurate well inside the frequency extremes, but introduces errors near the frequency extremes due to the truncation of the data set. We used another method based on Mason.¹⁵ Expanding $\langle \Delta r^2(t) \rangle$ locally around the frequency of interest, using a power law and retaining the leading term, the viscoelastic modulus can be calculated using:¹⁵

$$G'(\omega) = |G^*(\omega)| \cos(\pi\alpha(\omega)/2), \quad (8)$$

$$G''(\omega) = |G^*(\omega)| \sin(\pi\alpha(\omega)/2), \quad (9)$$

where

$$|G^*(\omega)| \approx \frac{k_B T}{\pi a \langle \Delta r^2(1/\omega) \rangle \Gamma[1 + \alpha(\omega)]}. \quad (10)$$

Here, Γ is the gamma function and

$$\alpha(\omega) \equiv \left. \frac{d \ln \langle \Delta r^2(t) \rangle}{d \ln t} \right|_{t=1/\omega}. \quad (11)$$

As mentioned use the combination of rotating diffuser disk and multispeckle DWS to measure the autocorrelation function. The, numerical inversion of eq. 4 give us the $\langle \Delta r^2(t) \rangle$ of the probe particles and eqs. 8 to 11 allow us to estimate the complex shear modulus of the viscoelastic material under study.¹⁶

5. DYNAMICS OF SCATTERING PARTICLES IN POLYMERIC GELS

Acrylamide and bis-acrylamide gels were prepared as follows. Acrylamide monomers were mixed with N,N,N',N'-tetramethylethylenediamide (TEMED) that is a initiator, and with ammonium persulfate, which acts as a catalyst for the polymerization reaction.¹⁷ Cross-linking is achieved when methylenebisacrylamide is added to the mixture. Bisacrylamide is essentially two acrylamide monomer units bridged by a covalent bond.^{17,18} To characterize the concentration, we used the total weight of both polymers (T) and the ratio (C) of bisacrylamide to the total polymer weight. Polystyrene probe particles (diameter 400nm) were added to the solution before the samples were polymerized. To avoid, interparticle interactions as well as hydrodynamic correlation, particle volume fractions were kept low, ~ 0.015 . At this volume fraction, $l^* = 150\mu\text{m}$. L/l^* was around 12 and 20, ensuring that the diffusive approximation for light transport within the sample was accurate enough, and without significant light absorption. Samples were polymerized in a cylindrical teflon container, taking a disk-like shape after the polymerization. Then, we placed these gels in a water solution of 0.4 v% TEMED (pH 12) to hydrolyze a portion of the acrylamide groups into acrylic acid groups. We use a hydrolyzation time of about 72 hr.¹⁷ The gels were washed with water and placed in water-acetone mixtures at various compositions. Lowering the acetone concentration from 40% to 0% the gel can shrink by a factor of 4.

Fig. 4 presents the mean square displacement of probe particles embedded in a gel sample at two different volumes obtained by changing the acetone concentration, measured using DWS with a rotating diffuser disk in conjunction with multispeckle DWS. The mean square displacement was obtained from numerical inversion of eq. 4, in 8 decades of time which is the result of the interaction of particles with the network formed by the acrylamide and bis-acrylamide gel. The experimental results in fig. 4 present three regions. A sub-diffusive region at short times, a plateau-like region at intermediate times, and a diffusive or super-diffusive region at long times. As can be observed the particle's dynamics changes substantially depending on the volume of the gel which is determined with the acetone-water composition. Increasing the acetone concentration the mesh size is smaller and particles are trapped in a smaller cage, because the available volume in the gel is lower. This can be observed in the range of 1 to 10 ms, where the mean square displacement presents a change in curvature to abruptly reach a plateau, which is related to the particle trapping. We used a recent theoretical development to explain the dynamics of particles embedded in the gel, that is based in a thermokinetic description of anomalous diffusion of particles in a viscoelastic medium in terms of a non-Markovian diffusion equation involving memory functions.¹⁹ By modeling the particle's host fluid as a structured viscoelastic medium acting on the particle with a sinusoidal force on the average, an analytical description for the dynamics of the particle can be explicitly realized (see eq. 29 in [19]). Red line in fig. 4 shows the best fit of this theoretical description to our experimental results. As we can see, the model captures completely the dynamics of the particles in this kind of gels. In particular, the trapping of the particle is very well described. However, when the gel is swollen, the model is not suitable for the description of the particle's dynamics, as can be seen in the blue line in Fig. 4. Apparently the trapping in the cage formed by the polymer network is not so important at this expanded volume, so the contribution of short times is more important for the particles in this case. This short time contribution ($t < 1\text{ms}$) is not taken into account in the thermokinetic description.¹⁹

Using Eqs. 8 to 11 allowed us to calculate the elastic and viscous modulus for the acrylamide and bis-acrylamide gel. Fig. 5 presents the viscoelastic spectra for the shrunken gel presented in Fig. 4. The loss modulus is larger at lower frequencies than the storage modulus, i.e., the gel has a liquid-like behavior at these frequencies. At intermediate frequencies, the storage modulus presents a plateau and the loss modulus a dip. At higher frequencies, both modulus are relatively similar, although the elastic modulus is larger. This rheological data is difficult to be obtained with mechanical rheometry, because it can destroy the polymer network. In contrast, with this optical technique we could obtain rheological data at low and very high frequencies.

6. CONCLUSIONS

We presented a dynamical light scattering technique that allow us to measure the mean square displacement of scattering probe particles embedded in a viscoelastic fluid for over 7 decades of time. This technique deals with a non-ergodic sample by using an CCD array and averaging over pixels instead of a temporal averaging at long lag times, and by mixing the scattering with the signal coming from an ergodic sample at shorter times. In addition, with this technique it is possible to obtain the elastic and loss modulus in a very wide frequency

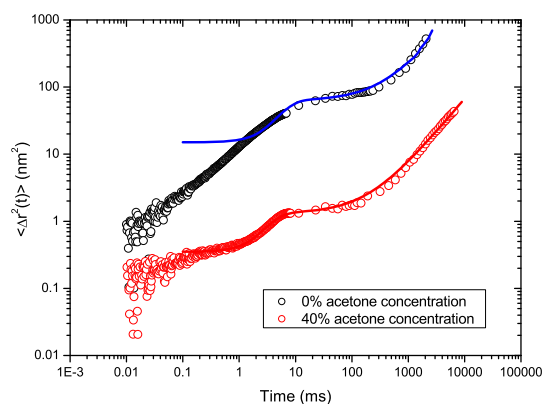


Figure 4. Mean square displacement of probe particles embedded in a gel at different swelling ratio ($T=0.07$, $C=0.02$).

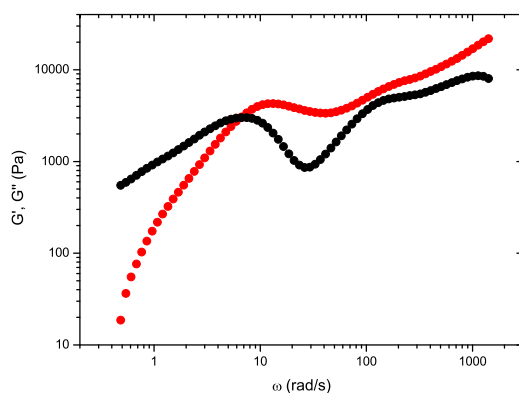


Figure 5. Microrheological viscoelastic spectra of a swollen gel. Elastic modulus: black circles, viscous modulus: red circles.

range. In particular, we measured the mean square displacement of particles embedded in an acrylamide and bis-acrylamide gel, and with this information we obtained the viscoelastic spectra of the gel. It is important to remark that in this case, mechanical rheometry is not a good option, because it can destroy the polymer network in the gel, on the contrary the optical techniques are well suited to get rheological information.

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