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# Microrheology of Chemically Crosslinked Polymer Gels by Diffusing-Wave Spectroscopy

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**Summary:** The Brownian motion of probe particles in aqueous solutions of poly(vinyl alcohol)(PVA) and in chemically crosslinked PVA gels has been studied by diffusing-wave spectroscopy (DWS). At long time scales the measurements allow us to determine the effect of the crosslinking ratio on the macroscopic viscosity of sols and the shear modulus of gels. The local shear modulus of gels as obtained from the characteristic length of the Brownian cage was found to agree with that measured by classical rheometry and dynamic light scattering (DLS). These microrheological techniques were applied to two polymer gel systems. Substrate induced gradient structure of hydrogels was studied from a microrheological point of view using DLS. It is clearly seen that hydrophobic substrate induces weakly crosslinked network formation at the interface region up to a few millimeters as expected from other experimental facts. Magnetic particle motion in gels under external magnetic field was investigated by DWS. The translational motion of the magnetic particles in gels due to the alternating magnetic force can be detected and found to be superimposed on the relaxation due to the thermal motion.

## I. Introduction

Microrheological techniques have been applied to the study of soft-matter systems since the late 1920s. Recently, several advanced techniques such as diffusing-wave spectroscopy (DWS), particle-tracking microrheology or atomic force microscopy measurements have been developed.[1] The main advantage of these microrheological techniques over the macroscopic rheometry is the possibility to study the "in situ" viscoelastic behavior of materials in a large range of frequencies extending up to 1 kHz. DWS measurements are sensitive to fluctuations in the multiple-scattering media at length scales as small as 1 nanometer, which is smaller than the wavelength of the light, because the decorrelation of speckle patterns of multiply scattered light intensity requires only very small displacement of the scatterers. By single and multiple dynamic light scattering measurements, it is possible to determine the mean-square displacement $<\Delta r^2(t)>$ of probe particles from the autocorrelation function of the scattered light

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intensity, over a wide range of time (from $10^{-6}$ to $10^{3}$ s) and length (larger than 100 nm for single, from 0.3 to 300 nm for multiple, approximately) scales.[2]

Experimental studies using single and multiple dynamic light scattering of the viscoelasticity of synthetic and biological polymer solutions, emulsions, colloidal suspensions, and gels have been reported.[3-8]

In this paper we report DWS measurements in chemically crosslinked gels under three different experimental conditions. We first compare the values of the shear modulus determined by DWS and classical rheometry in the bulk of the sample. We then present two specific applications of the microrheological techniques to gel systems: micro-rheological investigation of gradient gel structure induced by substrates, and microscopic motion of magnetic particles in gels under an external magnetic field.

## II. DWS Measurements of Probe Particle Motion in Chemically Cross-linked Gels: Elasticity of the Gels

We have performed DWS measurements on poly(vinyl alcohol) (PVA) solutions and chemically crosslinked gels containing latex probe particles. Chemically crosslinked PVA (molecular weight: 95.000, degree of deacetylation: 95 mol%, from Acros Organics, USA) gels were prepared from PVA solutions at the desired concentration (2 – 10 %) by adding glutaraldehyde (GA, 8 % aqueous solution, from Sigma, USA), at acidic condition (pH = 2, adjusted by HCl). The crosslinking ratio, $R_c$, was defined as the molar ratio of GA to repeating units of PVA. DWS measurements were carried out on PVA samples containing polystyrene microspheres (diameter: 107 or 535 nm, from PolySciences). The particles were dispersed in PVA solutions at a concentration of 1 % prior to crosslinking. PVA gels were prepared in light scattering cells (21 mm in diameter, 2 mm in thickness).

The laser beam at $\lambda$ = 488 nm from an argon ion laser (SpectraPhysics 2020) was expanded to about 1 cm diameter at the sample. The diffused light was collected by a single-mode optic fiber placed in the axis of the beam for transmission geometry, or placed in the backscattering cone for backscattering geometry. The intensity autocorrelation function of the diffused light was calculated using a BI9000 correlator. In order to obtain the ensemble average of the scattered intensity, the optical fiber detecting the light was oscillated at 10 mHz, so that the scattering signal from different positions was recorded. A detailed theoretical presentation of DWS in non-ergodic systems was reported previously.[8,9]

The experimentally determined quantity is the intensity autocorrelation function of the scattered intensity $I(t)$,

$$g_T^{(2)}(\tau)=\frac{<I(t+\tau)\cdot I(t)>}{<I(t)>^2}. \tag{1}$$

The dynamic structure factor obtained in the transmission geometry from the Siegert relation, $g_T^{(2)}(t)=1+\beta\left|g_T^{(1)}(t)\right|^2$, where $\beta$ is an experimental factor ($\approx 1$), is given by:

$$g_T^{(1)}(t)=\frac{\left(\dfrac{L/l^*+4/3}{z_0/l^*+2/3}\right)\left[\sinh\left(\dfrac{z_0}{l^*}\sqrt{k_0^2\Delta r^2(t)}\right)+\dfrac{2}{3}\sqrt{k_0^2\Delta r^2(t)}\cosh\left(\dfrac{z_0}{l^*}\sqrt{k_0^2\Delta r^2(t)}\right)\right]}{\left(1+\dfrac{4k_0^2\Delta r^2(t)}{9}\right)\sinh\left(\dfrac{L}{l^*}\sqrt{k_0^2\Delta r^2(t)}\right)+\dfrac{4}{3}\sqrt{k_0^2\Delta r^2(t)}\cosh\left(\dfrac{L}{l^*}\sqrt{k_0^2\Delta r^2(t)}\right)} \tag{2}$$

where $L$ is the thickness of the sample, $l^*$ is the scattering mean free path (determined experimentally), $l_T$ is the characteristic length scale probed by DWS in the transmission geometry, which is expressed as $l_T = l^*/k_0L$, $z_0$ is the penetration depth, and $k_0 = 2\pi/\lambda$.

Figure 1(a) shows the dynamic structure factors obtained in transmission geometry for dispersions of latex particles in water, a PVA solution and gels. For water and the polymer solution the structure factor goes to zero at long time, which means that the relaxation of the concentration fluctuations is total in the experimental time scale so that the system can be considered as ergodic. For the polymer solution, the representative curve is shifted towards the right with respect to that of water, indicating a slower diffusion of the particles through the medium. For the gels however, the dynamic structure factor does not go to zero at infinite time, which indicates the existence of frozen-in concentration fluctuations. In that case the systems are non-ergodic, the time average of the correlation function of the field scattered by a given scattering volume differing from the ensemble average obtained by scanning the sample. It is the latter quantity which has a physical meaning for the analysis of the gel dynamics. The plateau value increases upon increasing the crosslinking ratio, indicating that the particle motion is more restricted due to an increased modulus of the gel.

The dynamic structure factor was numerically inverted, using eq.(2) into the mean-square displacement of the probe particles, $<\Delta r^2(t)>$.[10] Figure 1(b) shows $<\Delta r^2(t)>$ as a function of time for the latex particles in PVA systems.

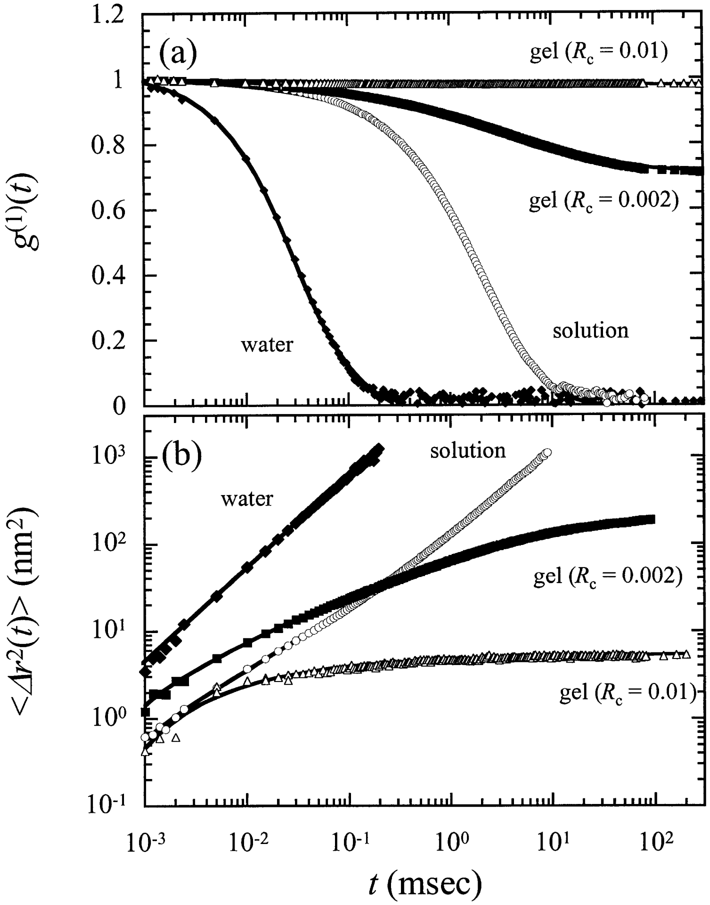

Figure 1. (a) Normalized dynamic structure factors for a PVA solution at $C_p = 5$ % and gels at the same concentration containing latex particles (radius: 535 nm) measured by DWS. (b) Mean-square displacement of latex particles in PVA solutions and gels.

For solutions, $<\Delta r^2(t)>$ is proportional to the time at long times, indicating that the particles undergo Brownian diffusion with $<\Delta r^2(t)> = 6Dt$ where $D$ is the translational diffusion constant of the latex in the solution.[3] One can estimate the macroscopic viscosity of the system by using the Stokes-Einstein equation. The results thus obtained agree with those measured by macroscopic rheometry (data not shown). At short times, the shape of the $<\Delta r^2(t)>$ curves reflects the viscoelasticity of the sample.[3,11] For concentrations larger than 5 %, which correspond to the regime where the polymer chains are entangled, one observes an inflexion point in the curve reflecting a confinement of the latex particles in the entanglement network.

For gels, at long time scales, $<\Delta r^2(t)>$ levels off at a certain value that decreases upon increasing crosslinking ratio. The mean square displacement of the particles in gels is limited due to caging, and the maximum displacement is determined by the competition between the thermal energy of the particles and the elasticity of the network that is considered as a continuous medium since the particle size is much larger than the mesh size. $<\Delta r^2(t)>$ can be expressed by this equation,[12]

$$< \Delta r^2(t) >= 6\delta^2 \left[1 - \exp\left[-(t/\tau_c)^\gamma\right]\right], \tag{3}$$

where $\delta$ and $\tau_c$ are respectively the characteristic size and time of the Brownian cage, which are the characteristic spatial length and time required for the particles to explore the cage. The short time behavior of the particles is subdiffusive, and expected to reflect the local dynamics of the gels.

The local shear modulus $\mu$ of the medium can be estimated from the plateau value of the mean-square displacement $\delta^2$, arguing that the work necessary for a particle of radius $R$ to move over $\delta$ is equal to the thermal energy $k_BT$ of the particle, so that[3]

$$\mu = \frac{k_BT}{6\pi R\delta^2} . \tag{4}$$

As discussed by Schnurr et al,[13] the above expression is strictly valid only at time scales that are short enough so that the solvent and the network move as one at scales large when compared with the mesh size of the network. In this limit the gel behaves as an incompressible fluid.

In order to evaluate the validity of the DWS measurements of the shear modulus, a comparison of the values of the local storage shear modulus obtained by DWS with those measured by macroscopic rheometry was made.

Figure 2 shows a comparison between the modulus $\mu$ and the macroscopic value $G'$ measured by classical rheometry for PVA gels at two concentrations and various crosslinking ratios. One observes a good agreement between the two sets of data for gels with $C_p = 8$ %. For these gels the increase of the modulus with crosslinking ratio is slightly less than the linear dependence expected from rubber elasticity theory.

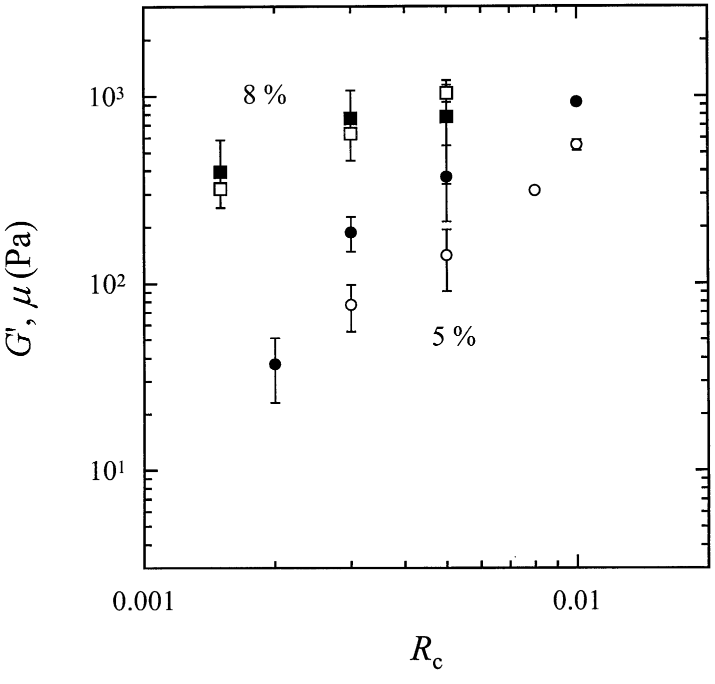

Figure 2. Comparison of the microscopic shear modulus $\mu$ with the macroscopic storage modulus $G'$ measured at 92 Hz of PVA gels as a function of the crosslinking ratio $R_c$. Open circles: $C_p = 5$ %, macroscopic (without latex); filled circles: $C_p = 5$ %, microscopic; open squares: $C_p = 8$ %, macroscopic (without latex); filled squares: $C_p = 8$ %, microscopic.

For the gels with $C_p = 5$ % the agreement between $G'$ and $\mu$ is not as satisfactory. This might be due to the increased difficulty in performing accurate measurements by mechanical rheometry when the gels are soft, that is when the polymer concentration and/or the crosslinking ratio are low. The large variation of $G'$ and $\mu$ with the crosslinking ratio, already reported for other systems[14] is generally explained by the formation of dangling chains at low crosslinking ratio and trapped entanglements at high crosslinking ratio.

We also performed a comparative study using DWS and DLS techniques. It is possible to investigate the cage dynamics by DLS when the characteristic length of the cage is large enough, that is for gels with low crosslinking ratio and/or low polymer concentration provided that the size of the probe particle is small enough. Usually, the decay function of DLS for a gel containing probes is bimodal, as the fluctuations of polymer concentration and the motion of confined particles are observed simultaneously. The characteristic time of the cage is independent of $q$, while the fluctuations of the gel are diffusive as inferred from the $q^2$ dependence of the relaxation time. The fluctuating and frozen-in components of light scattered by both the latex and gel were determined by fitting a two component exponential function. The fraction of the frozen-in intensity scattered by the latex $A_G$ can be related to $\delta$, according to

$$A_G = \exp(-q^2\delta^2)\,. \qquad (5)$$

From the value of $\delta$, the shear modulus $\mu$ was determined by DLS and compared with that obtained by DWS. In Table 1, the shear moduli $\mu$ of a PVA gel ($C_p$ = 2 %, $R_c$ = 0.01), measured by DWS and DLS using various sizes of probes, are shown. The comparison between the values of $\mu$ for a PVA gel with $C_p$ = 2 % and $R_c$ = 0.01 measured by DLS and those determined by DWS, indicates that the two methods are equivalent and that the addition of concentrated latex to the gel does not affect significantly the modulus.

| method | latex conc. (%) | latex diameter (nm) | µ (Pa) |
|---|---|---|---|
| DLS | 0.01 | 107 | 36 |
| DWS | 1 | | 43 |
| | | 535 | 31 |

Table 1. Local shear modulus $\mu$ of PVA gel (2 %, $R_c$ = 0.001) determined by DWS and DLS using latexes with different size.

## III. Applications

In this section we present two examples of microrheological measurements of gels that emphasize the specific possibilities of the light scattered based microrheological techniques .

### *III-1. Gradient Gel Structure Induced by Substrate Effect*

The interfacial properties of hydrogels made by radical polymerization of water soluble vinyl monomers depend on whether the substrate used for the preparation of the gel is hydrophobic (tetrafluoroethylene, polystyrene, hydrophobically modified glass, etc) or hydrophilic (glass, mica, etc).[15-17] In particular, gels synthesized on hydrophobic substrates exhibit a reduced friction coefficient against glass.[15] This behavior was interpreted by assuming that the surface of the gel made on a hydrophobic substrate consists of a loosely crosslinked network structure with dangling chains.

In situ monitoring of the refractive index change of solutions under polymerization reaction by electronic speckle pattern interferometry showed the presence of a polymer concentration gradient over a spatial range extending up to 1 mm from the interface between the gel and the substrate.[18] However, the refractive index profile does not give any information on the actual structure of the gel.

Viscoelastic measurements in gels allow us to probe directly the network structure since the presence of dangling chains should contribute to increase the local viscosity and decrease the modulus. In this section, we report on microrheological measurements by dynamic light scattering (DLS) of confined probe particles along the concentration gradient within the gel, taking advantage of the spatial resolution of the microrheological technique.

Measurements of the single scattering from a small amount of trapped particles dispersed within polyacrylamide (PAAm) gels before crosslinking reaction were performed. PAAm gel was synthesized by redox radical polymerization of acrylamide (2.5 %) in the presence of methylene bis(acrylamide) as a crosslinker (1 mol% of acrylamide), ammonium persulfate as an initiator (1 mM) and tetramethylethylene diamine as a redox initiator (0.6 v%) under nitrogen atmosphere at room temperature. All the chemicals were used as received. Before the redox initiator was added, oxygen in the solution was removed by purging nitrogen for 5 min. All the solutions were filtered through 0.45 μm Millipore filter. Polystyrene microspheres (Polysciences, Inc., USA) with radius 535 nm was used as probe particles (volume fraction $\phi = 10^{-4}$). For DLS measurement, the gel was prepared in a glass tube (12 mm in diameter). As a hydrophilic substrate, the bottom of the glass tube was used, and as a hydrophobic substrate, a piece of tetrafluoroethylene (teflon) plate was set at the bottom. The glass tube and the teflon plate were sonicated in ethanol and then in detergent aqueous solution, followed by rinsing in distilled water. All the DLS measurements were made at 25 °C, at scattering angle 60°, triplicated and averaged. The scattering cell was vertically moved with a resolution of 10 μm from the surface of the substrate up to 6 mm within the gel. An arrangement using two pinholes (diameter 200 μm) and a lens in front of the photomultiplier, provides a detection volume of $(200\ \mu\mathrm{m})^3$. This determines the spatial resolution of the depth profiling. The experimental setup for the DLS measurements is shown in Figure 3(a).

Height profiles of mean-square characteristic length $\delta^2$, (which is inversely proportional to the local shear modulus) and the characteristic time $\tau_c$ (proportional to the local friction coefficient of the network which the particles experience) were determined and plotted in Figure 4. Both the characteristic length and time in the gel made on glass are

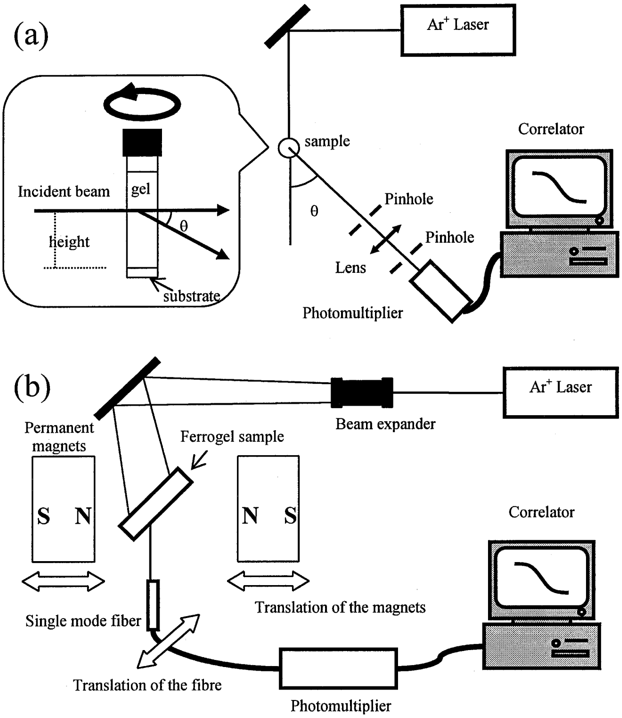

Figure 3. (a) Schematic illustrations of the experimental setup for DLS measurements of substrate induced gradient structure of PAAm gels. A gel is synthesized in a glass tube having a teflon substrate at the bottom (or the bottom was used as a glass substrate). In order to obtain ensemble average over different positions of the gel at the same height, the tube was continuously rotated. (b) DWS measurements under external oscillating magnetic fields. Ferrogel samples are fixed between two permanent magnets mounted on a piezoelectric actuator. Then the magnets were sinusoidally oscillated to create an alternating magnetic field. In order to obtain an ensemble average, a single-mode optical fibre was periodically translated to scan the sample.

independent of the distance to the substrate. On the other hand, those of the gel made on teflon increase upon approaching the substrate. This suggests that the crosslinking density of the network decreases in the vicinity of the interface since $\delta^2$ depends on the crosslinking density. The characteristic length increases over a 4 mm depth, while the characteristic time increases in a 1 mm thick layer close to the substrate. The local viscosity is likely to be less sensitive to the variation of crosslinking density except in the very close vicinity of the interface where the presence of many dangling chains might increase the friction exerted on the probe particles.

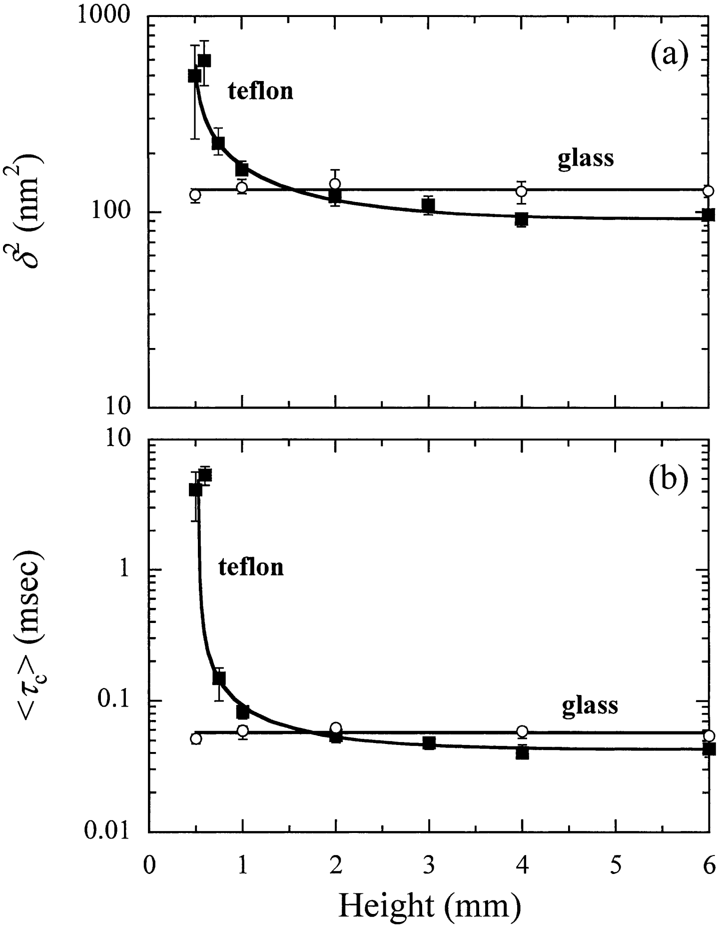

Figure 4. Height dependences of (a) the local mean square characteristic length and (b) the local characteristic time of PAAm gels (1 mol%) made on glass (open symbols) and teflon (filled symbols).

This study is a striking illustration of the potential of the microrheological techniques to investigate the local viscoelasticity of materials. Also the results reported here confirm the intriguing observation that the hydrophobicity of the substrate perturbs the gelation process over a surprisingly large spatial range, producing a gradient of the crosslink density.

### *III-2. Magnetically Sensitive Gels*

In DWS measurements, one observes usually the thermal fluctuations of the confined probes. Motion of the probes induced by macroscopic external forces such as an oscillating shear flow have been reported.[6] However, DWS experiments using direct microscopic manipulation of the probe by external forces have not been reported. Here we present a study of the particle displacement induced by an external magnetic field. This work is the microscopic analogue of the rheological studies of magnetic field-sensitive gels containing magnetic particles dispersed homogeneously in a polymeric network. The particle motion in response to a non-uniform magnetic field induces elongation, contraction or bending of the gels with short response time.[19,20]

Chemically crosslinked PVA gels containing magnetic particles were studied. Magnetic particles were prepared by emulsion polymerization of styrene monomers in the presence of magnetite particles. Magnetite ($Fe_3O_4$) sol was prepared from $FeCl_2$ and $FeCl_3$ in aqueous solution using sodium hydroxide as a precipitating agent. Obtained stabilized magnetite sol has a concentration of 15.2 m% and an average particle diameter of 10 nm. 60 $cm^3$ of styrene monomers was emulsified in 120 $cm^3$ of distilled water, in the presence of 1.89 g of dihexyl sodium sulfosuccinate, 0.25 g of potassium hydrogen carbonate and 5 g of the magnetite sol under gentle stirring for 2 hours at constant temperature of 60 °C. The solution was then heated to 80 °C and an initiator solution (1.6 g of potassium peroxidisulfate dissolved in 20 $cm^3$ of distilled water) was added. The polymerization reaction was carried out for 20 h at 80 °C. After polymerization the magnetic particles were purified by evaporating the unreacted monomers and by dialyzing against water. The obtained particles have average radius of 1.3 $\mu$m. The particles were homogeneously dispersed in PVA solutions prior to the crosslinking reaction.

We have analyzed the particle motion induced by the inhomogeneous magnetic field, with a set-up in which the gel was fixed between two permanent magnets translated by means of a piezoelectric actuator, at various frequencies (Figure 3(b)). To perform an ensemble averaging of the correlation function of the multiple scattered intensity, the sample was scanned periodically at a frequency of $10^{-4}$ Hz over a displacement of 1 mm by means of an optical fiber. Dynamical structure factors obtained both in the absence of magnetic field and with a magnetic field of intensity $B$ = 25 mT at various frequencies are presented in Figure 5.

In the absence of magnetic field the dynamical structure factor exhibits only the classical relaxation mode corresponding to the Brownian diffusion of the magnetic

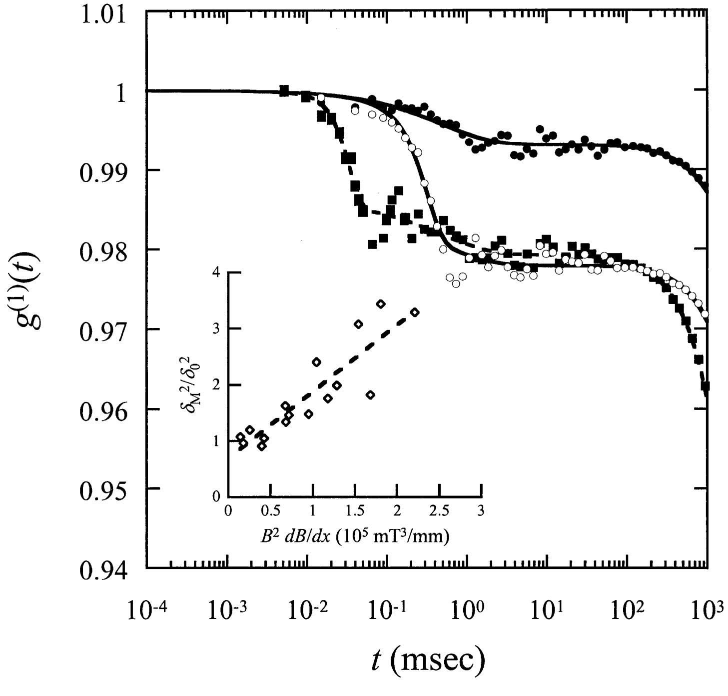

Figure 5. Normalized field correlation function of a ferrogel under oscillatory magnetic field of various frequencies. The oscillatory magnetic field is made by translating a pair of permanent magnets (in a sinusoidal wave with amplitude 500 µm). The frequencies are: 3 Hz (open squares); 1 Hz (closed squares); 0.1 Hz (open circles). Results without magnetic field: closed circles. The translation of the detection fiber that allows to measure ensemble averages, leads to a cut off of the correlation function at about $10^3$ msec. Inset: Normalized mean square characteristic spatial length $\delta_M^2$ as a function of $B^2dB/dx$.

particles. This mode can be fitted by a stretched exponential with an exponent $\beta = 0.7$ and an average relaxation time $\tau_0 \cong 1$ msec. At low frequencies of the magnetic fields ($\leq 0.1$ Hz ) we still see a single decay mode but it becomes sharper upon increasing the frequency. At frequencies larger than 0.1 Hz one observes ,in addition to the Brownian motion, a second faster decay, sharper than a single relaxation process.

The sharpness of this mode increases upon increasing the frequency of the magnetic field whereas the characteristic time $\tau_M$ (taken as the time at half decay) is inversely proportional to the frequency. This mode is likely associated with the uni-dimensional motion of the particles along the field gradient.

From the curves of Fig. 5, one can also determine the intermediate value $g_{int}$ of the plateau following the faster decay. By analogy with what was previously discussed for particles undergoing Brownian motion, $g_{int}$ can be described as a function of the characteristic spatial length $\delta_M$ explored by the particles:

$$g_{\mathrm{int}} = \exp\left( -\sqrt{\frac{\delta_M{}^2 L^2}{6 l^{*2}} \frac{2\pi}{\lambda}} \right), \qquad (6)$$

where $L$ is the thickness of the gel, $l^*$ is the scattering mean free path, that is determined as explained in the literature,[21] and $\lambda$ is the wavelength of the laser, respectively.

From the dynamical structure factors given in Fig. 5, we have calculated the values of $\delta_M{}^2$ as a function of the magnetic force $F$, which at low field intensity $B$ can be written as:

$$F \propto B^2 \, \mathrm{d}B/\mathrm{d}x. \qquad (7)$$

The inset of Figure 5 shows normalized mean square characteristic spatial length, $\delta_M{}^2$ as a function of $B^2$ d$B$/d$x$. It is found that within the experimental accuracy the mean square length explored by the particles varies linearly with the magnetic force. Also $\delta_M{}^2$ was found to be independent to the first order of the frequency of the magnetic field.

## IV. Conclusions

Single and multiple dynamic light scattering can be a powerful tool for a microrheological investigation of polymer gels. We studied cage dynamics of probe particles confined in chemically crosslinked gels. We found that the value of the local shear modulus of the chemically crosslinked PVA gels determined by diffusing-wave spectroscopy is equivalent to that obtained by classical mechanical rheometry and single light scattering.

These techniques were used to investigate the gradient structure of polymer gels induced by the substrates. We determined the height profiles of the mean-square characteristic length and the characteristic time of the probe particles motion in polyacrylamide gels made on hydrophobic and hydrophilic substrates. It is shown that the gel surface region made on hydrophobic substrates has lower modulus and higher viscosity indicating that the gel surface region has a loosely crosslinked network structure with dangling chains.

We also outlined the possibilities offered by the DWS technique to investigate the motion of magnetic particles confined in a gel, under an inhomogeneous magnetic field. It was shown that the application of a periodic magnetic field to a ferrogel induces a sharp decay in the autocorrelation function with a characteristic time that is a decreasing function of the frequency of the magnetic field. This decay can be assessed to a uni-dimensional motion of the magnetic particles along the gradient field.

[1] F.C.MacKintosh, C.F. Schmidt, *Curr. Opin. Colloid Interface Sci.*, **1999**, *4*, 300

[2] J.L. Harden, V. Viasnoff, *Curr. Opin. Colloid Interface Sci.*, **2001**, *6*, 438

[3] T.G. Mason, D.A. Weitz, *Phys. Rev. Lett.*, **1995**, *74*, 1250

[4] A. Palmer, T.G. Mason, J. Xu, S.C. Kuo, D. Wirtz, *Biophys. J.*, **1999**, *76*, 1063

[5] T. Gisler, D.A. Weitz, *Phys. Rev. Lett.*, **1999**, *82*, 1606

[6] P. Hébraud, F. Lequeux, J.P. Munch, D.J. Pine, *Phys. Rev. Lett.*, **1997**, *78*, 4657

[7] J.G.H. Joosten, E.T.F. Gelladé, P.N. Pusey, *Phys. Rev. A*, **1990**, *42*, 2161.

[8] G. Nisato, P. Hébraud, J.-P. Munch, S.J. Candau, *Phys. Rev. E,* **2000**, *61*, 2879.

[9] T. Narita, A. Knaebel, J.-P. Munch, S.J. Candau, *Macromolecules*, **2001**, 34, 8224.

[10] D.A. Weitz, D.J. Pine, In *Dynamic Light Scattering: The Method and Some Applications*, W. Brown, Ed., Clarendon, Oxford, **1993**, pp652.

[11] A. Palmer, T.G. Mason, J. XU, S.C. Kuo, D. Wirtz, *Biophys. J.*, **1999**, 76, 1603

[12] P.N. Pusey, W. Van Megen, *Physica A*, **1989**, 157, 705

[13] B. Schnurr, F. Gittes, F.C. MacKintosh, C.F. Schmidt, *Macromolecules*, **1997**, 30, 7781

[14] A. Silberberg, In *Polyelectrolyte Gels*, R.S. Harland, R.K. Prod'homme, Eds., American Chemical Society, Washington DC, **1992**, pp146 and 150.

[15] J.P. Gong, T. Narita, T. Kurokawa, G. Kagata, Y. Osada, G. Nishimura, M. Kinjo, *J. Am. Chem. Soc.* **2001**, *123*, 5582.

[16] T. Narita, A. Hirai, J. Xu, J.P. Gong, Y. Osada, *Biomacromolecules* **2000**, *1*, 162.

[17] X.M. Zhang, J. Xu, K. Okawa, Y. Katsuyama, J.P. Gong, Y. Osada, K.S. Chen, *J. Phys. Chem. B* **1999**, *103*, 2888.

[18] A. Kii, J. Xu, J.P. Gong, Y. Osada, X.M. Zhang, *J. Phys. Chem. B 2001, 105*, 4565.

[19] M. Zrínyi, D. Szabó, and H.-G. Kilian, *Polymer Gels Networks* **1998**, *6*, 441.

[20] M. Zrínyi, L. Barsi, and A. Büki, *Polymer Gels Networks* **1997**, *5*, 415.

[21] E.M. Furst and A.P. Gast, *Phys. Rev. E,* **1998**, *58*, 3372.