Notes

Diffusing-Wave Spectroscopy Study of the Motion of Magnetic Particles in Chemically Cross-Linked Gels under External Magnetic Fields

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Various types of stimuli-responsive hydrogels that may swell or deswell dramatically with relatively small changes in environmental conditions have been studied in the past few years for possible applications as sensors, processors, and actuators.[1−4] The stimuli include temperature, pH, solvent composition, electric field, and light intensity. However, the attempts at developing such environmental sensitive gels are often complicated by the fact that the structural changes are kinetically restricted by the diffusion of liquid molecules into or out of the polymer matrix. The swelling or deswelling rate is rather small and strongly depends on the geometry and the size of the gel sample. Furthermore, the formation of a collapsed skin layer on the surface of the gel blocks the outflow of entrapped water.[1,5,6]

On the other hand, magnetic field sensitive gels, ferrogels, could undergo size changes with quite fast response, independent of the geometrical characteristics of the sample.[7,8] These gels contain magnetic particles dispersed homogeneously and confined in a polymer network. Under a nonuniform magnetic field, the particles undergo motion which in turn induces elongation, contraction, or bending of the gels with short response time. The highest working frequency of these materials was found to be ∼40 Hz. A phenomenological model based on retarded elasticity and lumped inertia describes satisfactorily the dynamical behavior.[7]

The magnetic particles motion under external magnetic field has not been studied at a microscopic scale, up to now. Diffusing-wave spectroscopy (DWS) could be a suitable method to analyze the microscopic behavior of the particles in gels because this method can be easily adapted to various experimental setups. Without any external force, DWS provides the mean-square displacement of particles undergoing a Brownian motion in viscoelastic media. These past years, many researches have been reported on DWS of entangled synthetic/biological polymer solutions and concentrated colloidal suspensions.[9−12] DWS can also be applied to nonergodic systems such as gels.[13,14]

In this note, we report on a DWS study of the dynamics of magnetic particles confined in chemically cross-linked gels under external oscillating magnetic fields. We observed an enhancement of the particle fluctuations and the occurrence of a relaxation mode due to the coupling between the field gradient and the magnetic particles, superimposed on the thermal motion. The characteristic time of this additional mode is dependent on both the frequency of the magnetic field and the geometry of the magnets arrangement.

The investigated samples are chemically cross-linked poly(vinyl alcohol) (PVA) gels in which polystyrene microgel particles containing magnetite are dispersed. The particles are slightly colored and can be well dispersed in water and PVA solutions. The average radius of the particles is 1.3 μm. The preparation of the particles is described in ref 15. The polymer concentration and cross-linking ratio of the PVA gels are respectively 5% and 0.005. A detailed procedure of the preparation of the gels is written elsewhere.[14] The particles were homogeneously dispersed (1%) in PVA solutions prior to cross-linking reaction.

The experiments were performed with three different setups. Schematic illustrations of the positions and motions of the components are drawn in Figure 1. At the studied conditions, the magnetic field intensity B ($\leq$100 mT) is not large enough to saturate the magnetization. Note that the same gel containing polystyrene particles without magnetite does not show any magnetic field effect under the conditions of this study (data not shown), indicating that a possible influence of the field on the light migration such as Faraday effect does not affect the results.

First, we have used a geometry in which the gel is fixed in between two permanent magnets translated in the x direction by means of a piezoelectric actuator at various frequencies (Figure 1b,1). The gradient of the magnetic field in the x direction is shown in Figure 2. The gradients in the y and z directions, measured at the center of the sample, are much smaller than that in the x direction. Observed from the detection fiber, the particles undergo a motion through the gel due to the alternating magnetic force. To perform an ensemble averaging of the correlation function of the multiply scattered intensity, the sample was scanned periodically at a frequency of 10^{-4} Hz over a displacement of 1 mm in the y direction by means of an optical fiber. Figure 3 shows the dynamical structure factors obtained in both the absence and the presence of magnetic field with a magnetic field of intensity $B = 25$ mT (at the center of the gel) at various frequencies. The displacement of the magnets is $\pm$250 μm, which correspond approximately to a relative variation of the magnetic force of 20%. In the absence of magnetic field the dynamical structure

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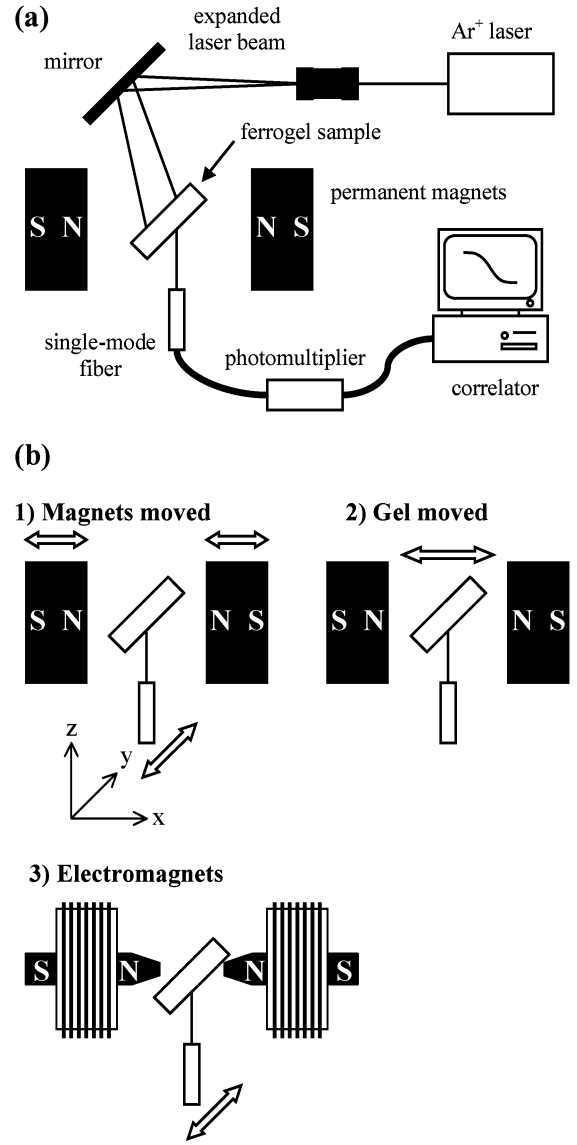

Figure 1. Schematic illustrations of the experimental setups for DWS measurements under magnetic field. (a) Spatial arrangement of the components. (b) Motions of components to create the alternating magnetic field. (1) A pair of permanent magnets is translated in the *x* direction. The ensemble averaging over speckles is performed by translating the optical fiber in the *y* direction. (2) The ferrogel sample is translated between the fixed magnets. (3) A pair of electromagnets is used. The ensemble averaging over speckles is performed by translating the optical fiber in the *y* direction.

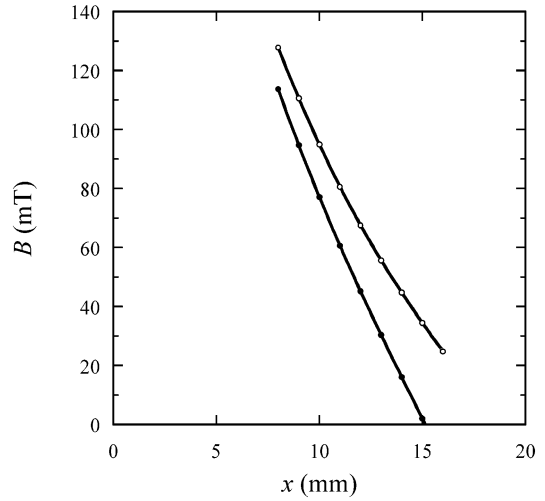

Figure 2. Magntic field intensity between the pair of the permanent magnets as a function of the distance from the surface of one of them. The distance between the two magnets, *d*, is 30 mm (closed circles) or 37 mm (open circles).

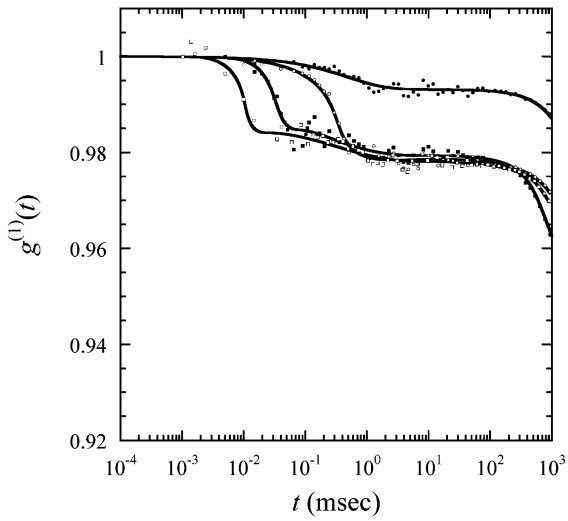

Figure 3. Normalized field correlation function of a ferrogel under oscillatory magnetic field of various frequencies. The oscillatory magnetic field is created by translating a pair of permanent magnets (sinusoidal wave with amplitude 500 μm). The distance between the two magnets, *d*, is 37 mm. The intensity of the magnetic field is 25 mT. The frequencies are 3 Hz (open squares), 1 Hz (closed squares), and 0.1 Hz (open circles). Results without magnetic field: closed circles. The translation of detection fiber to measure the ensemble average leads to a cutoff of the correlation function at about 10^3 ms.

factor exhibits only one relaxation mode which is best fitted by a stretched exponential with an exponent $\beta = 0.7$ and an average relaxation time $\tau_0 \cong 1$ ms. This relaxation corresponds to the Brownian diffusion of the particles.

For magnetic fields with frequencies in the range ≤ 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 clearly sees two modes. The fast mode corresponds to the motion of the magnetic particle induced by the magnetic field. The amplitude of the relaxation was found to be independent to the first order of the frequency of the magnetic field. Under magnetic field, the slow mode has approximately the same amplitude and relaxation time τ_0 as the Brownian diffusion mode observed in the absence of the magnetic field. This suggests that the particle aggregation or chain formation due to the polarization of the particle under the magnetic field is negligible and that presumably the particles confined in the gel cannot associate to each other at low particle concentration.

As for the fast mode, it is characterized by a decay sharper than a single relaxation process. The sharpness of this mode increases upon increasing the frequency of the magnetic field. It has been previously reported that the sharpness of decay for a translational motion due to shear is faster than that of the thermal motion.[18] This mode that results from the coupling between the field gradient and the magnetic particles is likely associated with the unidimensional motion of the particles along the field gradient in the *x* direction.

We have analyzed in more detail the nature of this unidimensional particle motion induced by the inhomo-

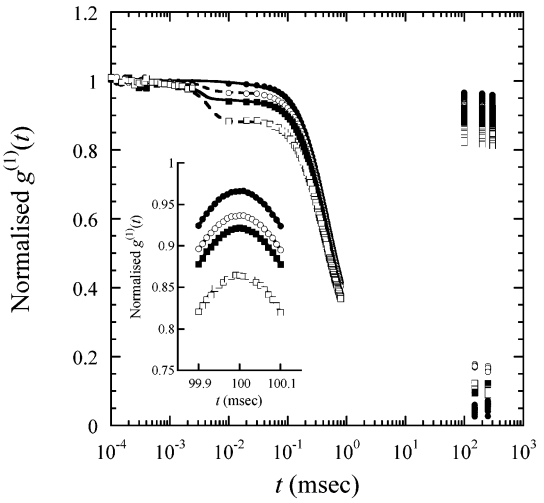

Figure 4. Normalized field correlation function of a ferrogel under oscillatory motion (10 Hz) in static magnetic fields of various intensities. The initial decay, the first (100 ms), second (200 ms), and third (300 ms) echoes are shown. The autocorrelation function at 150 and 250 ms are decorrelated. Inset: the expanded view of the first echo. The distance between the two magnets, d, is 30 mm. The intensity was varied by adjusting the position of the ferrogel sample. $B = 0$ mT (filled circles), 34 (open circles), 66 (filled squares), and 100 (open squares). Data points are missing in certain time ranges for a technical reason (a limited number of calculating points being consumed to increase the precision of echoes).

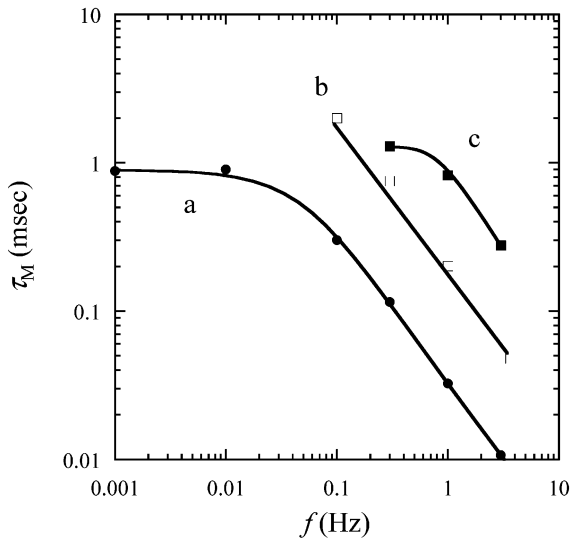

Figure 5. Characteristic time τ_M of magnetic particles motion in PVA gels as a function of frequency of the alternating magnetic field. Curve a: 1.3 μm particles, permanent magnets. Curve b: 0.25 μm particles, electromagnets. Curve c: 1.3 μm particles, electromagnets.

geneous magnetic field with respect to the following three aspects: reversibility, rate, and displacement.

We address first the issue concerning the reversibility of the unidimensional particle displacement under external alternating magnetic field. Reversible motions can be distinguished from irreversible ones by the so-called "echo technique", used for the study of the droplets rearrangements in concentrated emulsions under oscillatory shear.[16] When elastic bodies containing scatterers are subjected to a straining motion, the autocorrelation function decays rapidly. However, if the motion is reversed and the scatterers return to their initial positions, the autocorrelation function recovers its value without strain. A series of echoes appear at times corresponding to integer multiples of the reciprocal of the frequency as echoes. On the contrary, if the scatterers do not return to their initial position (because of yielding, for example), the height of the echoes is diminished.

In the experiments of Figure 3, we do not observe echoes. This indicates that the particles rearrange in the course of the unidimensional motion induced by the periodically oscillating magnetic field. To study more accurately this effect, we used the second geometry inspired by the echo technique (Figure 1b,2). The ferrogel sample is mounted on a piezoelectric actuator and translated under sinusoidal motion in a static nonuniform magnetic field created by a pair of stationary permanent magnets.[17] This geometry should allow to detect not only the two particle motions (Brownian motion and the motion induced by the magnetic field) but also the periodic translational motion of the sample.

Figure 4 shows normalized dynamic structure factors for a sample submitted to a translational motion under magnetic field at various magnetic field intensities. The comparison between these results and those of Figure 3 reveals two differences. First, the correlation function drops sharply in the vicinity of 0.1 ms, and at 1 ms it is totally decorrelated. Second, the autocorrelation function exhibits a series of echoes at 100, 200, 300 ms, etc. These are due to the collective motion of the translated sample. It is found that the height of the different echoes is the same up to the tenth (data not shown). We do not see the relaxation due to Brownian motion because its characteristic time is almost the same as that of the decorrelation of the translation. At very short time ($t \leq 10^{-3}-10^{-2}$ ms) one observes the relaxation of the particle concentration fluctuation followed by a plateau. As this decorrelation is not observed without the field, it originates from the magnetic field and is consistent with that obtained with the first experimental setup: from curve a of Figure 3 we expect $\tau_M = 0.003$ ms for 10 Hz, which is in good agreement with the result of Figure 4.

The inset of Figure 4 shows an expanded view of the first echo at various magnetic field intensities. It is seen that the height of the echo under magnetic field is lower than that without field and decreases upon increasing the magnetic field intensity. The fact that the height of the echoes did not fully recover indicates that the displacement due to the magnetic force is not totally reversible although the displacement-controlled translation of the sample is periodic.

The origin of this effect which indicates a rearrangement of the particles as they move through the gel is not clear. One possibility is that the magnetic particles are polarized under external magnetic field and the interparticle magnetic forces might not be negligible and might induce an additional displacement of the particles out of the periodic trajectory due to the periodic external force. Also, some particles can be trapped in the inhomogeneities of the gel, thus modifying the average interparticular distances.

The characteristic time τ_M of the relaxation due to the magnetic field is the directly related to the rate of the particle motion. The characteristic time τ_M (taken as the time at half decay) is inversely proportional to the frequency of the oscillatory magnetic force as shown in Figure 5 (curve a). At frequencies lower than 0.01 Hz, τ_M levels off at about 1 ms, which is the same value as that of the Brownian motion. This suggests that the

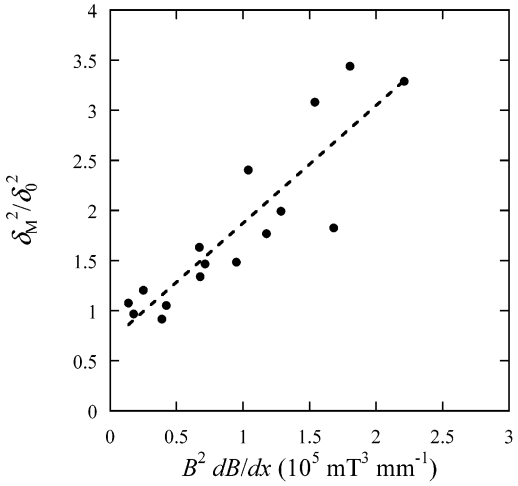

Figure 6. Normalized mean-square characteristic spatial length δ_M^2 as a function of $B^2\ dB/dx$.

thermal motion randomizes the slower motion induced by the magnetic field. In Figure 5 are reported the frequencies dependencies of τ_M for two types of magnetic particles (1.3 and 0.25 μm in radius) and two different geometries. In the third setup, the ferrogel was fixed between two electromagnets that could be turned on and off, one by one at various frequencies.[20] The results obtained are quite similar to those obtained with the permanent magnets: τ_M decreases upon increasing frequency. The effect of the geometry of the magnetic field is illustrated by the comparison between the curves a and c obtained for the same system but using the permanent magnets and the electromagnets, respectively. The different values of τ_m resulting from different distributions of forces and displacements in the direction of the sample thickness suggest that the particle velocity is the relevant parameter rather than the frequency. The comparison between curves b and c shows the effect of the nature of the particles. The observed difference likely results from differences in the scattering mean free path l^* and in the interparticle interactions.

The mean-square displacement of particle is calculated from the amplitude of the relaxation. From the curves of Figure 3, one can also determine the intermediate value g_{int} of the structure factor at $\tau_M < t < \tau_0$. 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 δ_M explored by the particles:

$$g_{int} = \exp\left(-\sqrt{\frac{\delta_M^2 L^2}{6l^{*2}}}\frac{2\pi}{\lambda}\right) \qquad (1)$$

where L is the thickness of the gel (2 mm), l^* is the scattering mean free path (570 μm), which is determined as explained in the literature,[19] and λ is wavelength of the laser.

From the dynamical structure factors given in Figure 3, we have calculated the values of δ_M^2 as a function of the magnetic force F, which at low field intensity B can be written as

$$F \propto B^2\ dB/dx \qquad (2)$$

Figure 6 shows the normalized mean-square characteristic spatial length, δ_M^2/δ_0^2, as a function of $B^2\ dB/dx$, where δ_0^2 is the value corresponding to measurements in the absence of magnetic field (3 nm^2). The value of B is taken at the center of the sample. It is found that within the experimental accuracy the mean-square length explored by the particles increases with the magnetic force.

In conclusion, this paper outlines the possibilities offered by the DWS technique to investigate the motion of magnetic particles confined in a gel, under an inhomogeneous magnetic field.

It is shown that the application of a periodic magnetic field to a ferrogel induces a sharp decay in the autocorrelation function with a characteristic time which is a decreasing function of the frequency of the magnetic field. This decay can be assessed to a unidimensional motion of the magnetic particles along the gradient field. At low frequencies, this motion is randomized by the thermal motion. The excursion of the magnetic particles within the gels is enhanced with respect to that due to the sole thermal motion, and the mean-square characteristic length is in the first approximation proportional to the magnetic force exerted on the particles. We found reproducibly the same behavior for different experimental geometries. It is hoped that these results will provide an incentive for the development of models describing the flow of magnetic particles trapped in a gel, induced by the application of an inhomogeneous magnetic field, and explaining the connection between the microscopic behavior and the macroscopic response of the samples.

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(15) Magnetic particles were prepared by emulsion polymerisation 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 mol % 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 dihexylsodium sulfosuccinate, 0.25 g of potassium

hydrogen carbonate, and 5 g of the magnetite sol under gentle stirring for 2 h 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.

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(17) Neodium iron boron magnets (2.5 cm in diameter) were purchased from Edmund Industrial Optics (Barrington, NJ). Two magnets were placed facing the same pole. The distance between them was changed to modify the field gradient. Magnetic field intensity was measured with a teslameter equipped with a Hall effect probe (model 5080, F.W. Bell, Orlando, FL). The sample ferrogels prepared in a glass cell (diameter 21 mm, thickness 2 mm) were mounted on a piezoelectric actuator and translated sinusoidally between the two magnets in the direction of the field gradient. The frequency and displacement of the gel motion are 10 Hz and 500 μm, respectively. DWS measurements were made as follows. A laser beam expanded to 1 cm in diameter was used as an incident beam. Multiply scattered light from the sample ferrogels was collected by a single-mode optical fiber at the transmission geometry. The intensity autocorrelation function was calculated using a BI9000 correlator (Brookhaven Instruments Corp., Holtsville, NY). Because of the translation of the gels, ensemble averaging is carried out without further treatment.

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(20) The electromagnets consist of a coil (2000 turns of copper wire) and an iron core. The poles of the two magnets are placed face to face. Potentiostatic square wave are applied to the coils, and the electromagnets are turned on and off one by one using a laboratory made switcher so as to alternate the direction of applied magnetic forces. The ensemble average of the correlation function was obtained by a scanning via the optical fiber. At frequency higher than 5 Hz, induced current and heat production are not negligible, and the DWS measurements were not reproducible.

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