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New method of viscosity measurement near the gelatin sol-gel transition

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Résumé. — La mesure d'un temps caractéristique de relaxation de rotation de petites particules ferromagnétiques dispersées dans une solution à 7 % de gélatine, permet l'observation de la viscosité au voisinage de la transition sol-gel.

L'exposant critique de la viscosité $s = 0,95 \pm 0,10$, valable sur 3 décades en température, est en accord avec des calculs numériques effectués dans le cadre d'une approximation de champ effectif en théorie de la percolation.

Abstract. — The viscosity of a 7 % gelatin solution has been measured in the very close vicinity of the gelation transition, by rotational relaxation of ferromagnetic particles imbedded in the mixture.

The viscosity critical exponent $s = 0.95 \pm 0.10$ which is obtained over 3 decades in temperature, is well accounted for by numerical calculations in the effective field treatment of percolation theory.

Gelatin is the water-soluble product of the dissolution, disorganization or degradation of water-insoluble collagen fibers [1]. The resulting peptide chains take up random configurations and at sufficiently high temperature the mixture is a blend of monomers in a form of coils, and solvent. As the temperature is decreased, polymerization and reorganization of some helical structure occur with the formation of n -mers and subsequent growing of the gyration radius of the macromolecular clusters. An infinite polymer appears in the bath, at the temperature T_g of the reversible liquid-gel transition, but there are still a non-negligible amount of small n -mers in the system. For $T < T_g$, the gel fraction S_∞ — the infinite polymer — grows by linkage of the residual n -mers. When the gel fraction is completed by all monomers incorporation, curing of the gel occurs by the linkage of pending chains to form an unique infinite cross-linked network at $T \ll T_g$.

The macroscopic viscosity $\bar{\eta}$ of the sol-phase depends of the size of the polymer clusters : $\bar{\eta}$ grows when the temperature is lowered to attain an infinite value when $T = T_g$.

In this letter, we present a very simple method for observing the growing of the macroscopic viscosity in the sol-phase when T_g is approached and for measuring the corresponding critical exponent.

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1. Experimental method. — The method of measurement is based on the study of rotational relaxation time of small aggregates of magnetic particles imbedded in the gelatin solution.

In a uniform magnetic field the particles experience a torque and line up with the field : the solution shows a linear birefringence [2]. We observe the decreasing birefringence signal when the field is turned off.

We use a commercially available product, AO5 ferrofluid (from Ferrofluidic Corporation, U.S.A.) which is a colloidal suspension of monodomain ferromagnetic Fe_3O_4 particles, roughly spherically shaped, of dimension around 125 Å, coated with a monomolecular layer that acts as an elastic cushion preventing agglomeration.

In fact when the solution is submitted once to a small magnetic field (≈ 20 G), the ferrofluid particles in water-base suspension form needle-shaped agglomerates which are very difficult to destroy [3].

The size distribution of these needles is not known, but observations from electronic microscope pictures [4] suggests that the number of individual grain is very low, the main structure being composed of chains ranging from 0.1 μ to more than 10 μ .

1.1 SAMPLES PREPARATION. — A gelatin solution in water was prepared with the following composition : 7 g of gelatin powder (from Prolabo, Paris) are dissolved in 100 cm³ of hot water and kept at 70 °C during 15 min.

A drop of water-based ferrofluid is introduced in the gelatin solution to obtain a mixture with 10^{13} magnetic particles/cm³. Reference solutions of the same concentration of ferrofluid in pure water have also been made to measure the size distribution of the magnetic agglomerates in a liquid of known viscosity.

The liquid mixture is introduced in a (10 × 3 × 3) mm brass tank in which optical windows allows a laser beam to go through the sample. A platinum sensor is immersed directly in the liquid to measure the temperature.

The tank is fixed on a Peltier effect temperature regulation system giving a stabilization of the tank temperature of 5×10^{-3} K.

1.2 BIREFRINGENCE MEASUREMENTS. — Figure 1 shows the sensitive set-up used in these measurements. The principle of operation is described elsewhere [5]. The voltage obtained at the output of the lock-in detector is directly proportional to the birefringence of the sample. In our system, we cannot observe any decay rate of the birefringence signal which is more rapid than 0.5 ms.

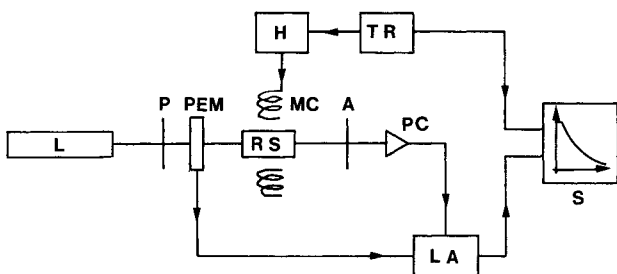


Fig. 1. — Experimental set-up. Laser L, analyser and polarizer A and P, photoelastic phase modulator PEM, magnetic coils MC and pulsed alimentation H, temperature regulated sample RS, photocell PC, lock-in amplifier LA, trigger TR and scope S.

1.3 MAGNETIC COILS. — The sample tank is surrounded by two magnetic Helmholtz coils. The alimentation of the coils delivers adjustable current pulses of 5 A, 4 s long and 100 μs fall time. The magnetic field available at the tank location was near 100 G. The current pulse is triggered manually or at a very slow rate (10^{-2} Hz) to prevent parasitic heating of the tank.

1.4 EXPERIMENT METHOD. — The temperature of the sample is maintained stable within 10^{-3} K and a current pulse is applied on the magnetic coils : the birefringence signal grows, shows a constant value during the main duration of the pulse and decreases after the cut-off of the field. This decrease is recorded as a function of time on an oscilloscope and then photographed. In this preliminary experiment the analysis has been done on the photograph serie.

The measurement begins in the sol-phase of the

gelatin solution just after the sample preparation, near 38 °C. Then for any temperature stabilized during the cooling, the relaxing birefringence signal is recorded. The thermodynamic equilibrium is expected to be attained in less than 5 min. for a 1 K variation as can be deduced from quenching experiments on gelatin of closed composition (6.5 %) [6].

1.5 EXPERIMENTAL RESULTS.

• The main observed feature is the increase of the total time needed for the birefringence signal to relax $g(t)$ when the temperature decreases in the sol-phase : it varies in a ratio 10^3 between 34 °C and the gel transition temperature $T_g = 23.8$ °C.

• The relaxing signal does not follow an exponential variation as function of time : the best fit is obtained with

$$\frac{g(t_0) - g(t)}{g(t_0)} = \frac{1}{\log\left(\frac{t_m}{t_0}\right)} \log\left(\frac{t}{t_0}\right)$$

as is shown by the semi-log drawing on figure 2. The time t_0 corresponds to the beginning of the experiment. In fact, t_0 cannot be taken smaller than 0.5 ms due to the bandwidth of the lock-in amplifier out-put. t_m is the time needed by g to attain practically the noise level.

Figure 2 shows only the analysis of the relaxing signal near 29 °C. The logarithmic variation is observed in the whole range of temperature attained.

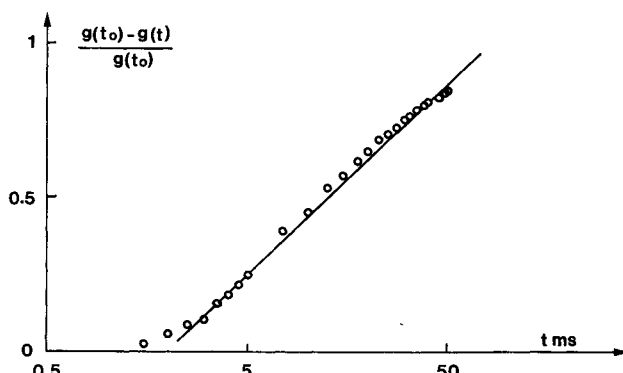


Fig. 2. — Analysis of the birefringence relaxation at 29 °C as a function of time on a linear-log plot ;

$$\frac{g(t_0) - g(t)}{g(t_0)} = \frac{1}{\log\left(\frac{t_m}{t_0}\right)} \log\left(\frac{t}{t_0}\right)$$

The meaning of t_0 and t_m is explained in the text.

In spite of the fact that the variation is non-exponential, the time Δt needed to divide the birefringence signal g by a factor e , has been measured and is given *versus* $(T - T_g)$ on a linear (Fig. 3) and log-log plots (Fig. 4). The experimental points are correctly

aligned for 3 decades of variation in $\Delta T = T - T_g$ and defined a slope (Fig. 4)

$$s = 0.95 \pm 0.10.$$

• The sol-gel transition is determined very sharply ($\approx 10^{-2}$ K) as the temperature at which the birefringence signal begins decreasing as a consequence of the locking of the ferrofluid chains by the infinite network. The absolute value of s , measured over 10 K, is practically not affected by this uncertainty.

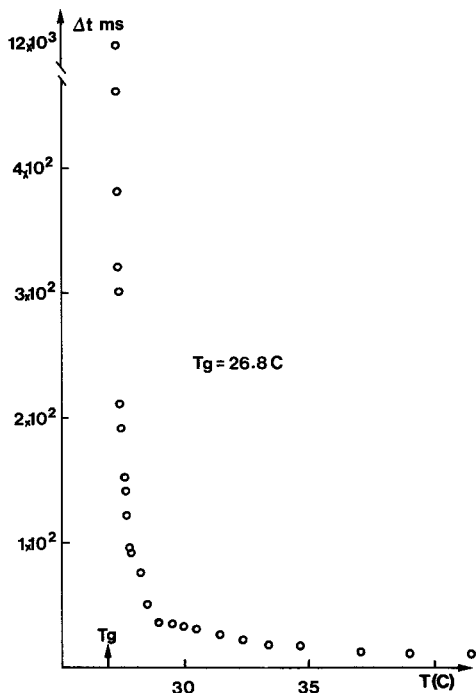


Fig. 3. — Characteristic time Δt of birefringence relaxation as a function of the temperature. It is shown in the text that Δt is proportional to the macroscopic viscosity $\bar{\eta}$.

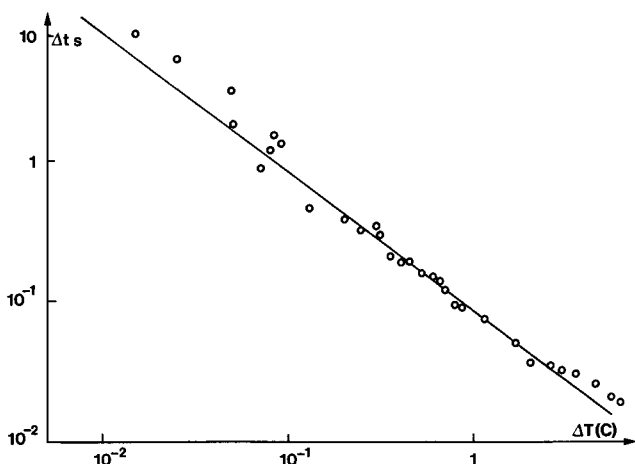


Fig. 4. — Log-log plot of the characteristic time Δt of the birefringence as a function of the temperature difference $\Delta T = T - T_g$ where $T_g = 26.8$ °C, is the gelation point. The slope $s = 0.95 \pm 0.10$ is the critical exponent of the macroscopic viscosity $\bar{\eta}$.

2. **Theory.** — The relaxing birefringence signal $g(t)$ is proportional to the number of optically anisotropic ferrofluid particles :

$$g(t) = G \int_1^F \varphi_f e^{-D_f t} df$$

where G is a constant depending on the birefringence of all the particles, D_f the rotation diffusion constant of a chain of f magnetic particles, and φ_f the number concentration of chains formed by f particles. F is the number of magnetic grains belonging to the longest chain.

In the case of long prolate ellipsoids the rotation-diffusion constant D_f is related mainly to the length a of the elongated particles and shows very little dependence on any other dimensions b of the ellipsoid [7] :

$$D_f = \frac{kT}{16 \pi \eta a^3} 3 \left[2 \ln \left(\frac{2a}{b} \right) - 1 \right].$$

We then take the coefficient D_f corresponding to an equivalent sphere of radius $r_f \sim a$ which takes into account all important parameters :

$$D_f \approx \frac{kT}{8 \pi \eta r_f^3}.$$

We suppose $r_f = a_1 f^\delta$ where δ is an unknown parameter and a_1 the ferrofluid one-particle radius.

The most important terms in the integral correspond to values of f and t for which the exponential argument :

$$D_f t \leq 1$$

this expression defining the lower limit of integration.

$$f^* = \left(\frac{kT}{8 \pi a_1^3 \eta} t \right)^{1/3\delta}.$$

We expect that for a given value of t/η the birefringence signal is mainly due to particles ranging from f^* to F . A rough calculation of r_{f^*} , taking the exact value of D_f , with $a/b \sim 50$ and $\delta = 1$, gives a value of 0.1μ : it is probable that all birefringent particles are taken into account in this approximation.

As is pointed in [8] the value of the viscosity measured depends on the probe dimension r_f , and the macroscopic viscosity $\bar{\eta}$ is obtained only for $r_f \geq \xi = r_{N^*}$, with ξ the characteristic length of the largest clusters of gelatine : with a monomer coil radius 100 \AA , the correlation length of 10μ is obtained for $\Delta p \approx 10^{-3}$. Thus a viscosity correction should have perhaps been made for the last decade in our measurement.

The experimental variation $g(t)$ is logarithmic (Fig. 2) and this suggests that the size distribution φ_f of the ferrofluid chains is :

$$\varphi_f \approx \frac{1}{f^2}.$$

Then, the birefringence relaxing signal is :

$$g(t) \simeq G \left[\log F - \frac{1}{3\delta} \log \left(\frac{kT}{6\pi a_1^3 \eta} t \right) \right].$$

We measure a certain interval of time Δt on the relaxing signal defined by :

$$\frac{1}{e} g(t_0) = g(t_0 + \Delta t).$$

In our case we take $t_0 \simeq 0.5$ ms and, as Δt varies from 8 ms to 12 s, $t_0 \ll t$ is a very good approximation. In these conditions, we find that Δt is proportional to the macroscopic viscosity $\bar{\eta} : \bar{\eta} \sim \Delta t$ noticing that t_0/η has a constant value, which is a consequence of the experimentally observed constant level of $g(t_0)$. The viscosity critical exponent s is defined by :

$$\bar{\eta} = \eta_0 |\Delta p|^{-s}$$

in which $\Delta p = p - p_c$, where p is the fraction of reacted bonds and p_c the gelation threshold. η_0 is the viscosity of the original solution of monomers at high temperature. Supposing a linear relation between Δp and $\Delta T = T - T_g$ in the vicinity of T_g , the slope of the log-log drawing of $\Delta t(T)$ (Fig. 4) gives the critical exponent s .

It can be remarked that the result $\Delta t \sim \bar{\eta}$ would have been found for any distribution $\varphi_F \simeq 1/f^\varepsilon$, $\varepsilon > 1$: this approximation is not critical in the calculation.

3. Discussion. — In spite of the fact that the classical theory of gelation [9] does not attempt to predict the viscosity behaviour, three values of the

critical exponent s are available in the literature [10, 11, 12]. Among them, the effective medium approximation of the percolation theory [12] gives a value $s = 1$, which is very well verified in our experiment. This exponent has already been found experimentally in styrene divinylbenzene gelating system [13] and governs the viscosity behaviour far from the transition point, whereas $s \simeq 0.78$ very close to the transition ; this last value has been numerically calculated and found for the electrical conductance in random mixtures of normal and superconducting elements [11] which as certain arguments suggest [10] follow the same behaviour as the gelating system viscosity.

We do not find any indications of such a crossover in the gelatin system.

Some remarks can be made at this stage.

— The effective medium approximation is a mean field treatment and applies only outside a *critical region*, which is difficult to appreciate in the gelatin case as the connection is not known between p and T , in spite of certain theoretical arguments [14]. We can only claim that Δp is proportional to ΔT in the immediate vicinity of T_g , and this approximation is used here.

— The calculations and theories that we just mentioned are concerned with chemical gelation which supposes strong and not reversible crosslinking between polymers. It is not obvious that the same kind of theoretical treatment can be applied to the gelatin system.

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