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## An experimental measurement of the permeability of deformable porous media

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**Résumé.** — La perméabilité d'objets poreux fragiles tels que des gels ou des agrégats formés par flocculation ou sur la surface d'un filtre doit être mesurée en présence d'écoulements suffisamment faibles pour ne pas perturber la structure poreuse. Nous avons développé une méthode de mesure différentielle de perméabilité. Nous montrons une application de cette technique à la mesure de perméabilité d'un gel chimique au long de la réaction de gélification.

**Abstract.** — The permeability of tenuous porous objects such as gels or aggregates formed by flocculation or on a filter surface must be measured in the presence of sufficiently weak flows not to perturb the solid structure. We have developed of differential permeability technique which we apply to the study of the formation of a chemical gel in time.

### 1. Introduction.

The flow of a viscous fluid through a porous medium and, more generally, the study of the transport properties within these media is of considerable interest. On the fundamental side, these properties belong to the general class of problems of transport in random geometries which is the object of many present studies. On the applied one, porous media problems are met in various fields of science : hydrology (partially and fully saturated soils, spread of pollutants); assisted recovery in oil fields; chemical engineering (filters, chromatography on gels, heterogeneous catalysis); in biophysics (transport across membranes).

A first geometrical characteristic of a porous system is the porosity  $\phi$  which is the volume fraction of the voids. The specific area  $S$  (area/unit volume) is accessible from adsorption isotherms (both parameters can also be determined from stereological studies on random cuts if the medium is homogeneous and isotropic). However the parameters do not characterize fully the pore size and, in particular its connectivity.

The permeability  $k$  introduced by H. Darcy [1] more than one century ago is a geometrical coefficient (homogeneous to a (length)<sup>2</sup>) which relates the average flow rate per unit area in a permeable medium,  $Q$ , to an applied pressure gradient for a fluid of viscosity  $\eta$

$$Q = - (k/\eta) \nabla p. \quad (1)$$

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This linear relation is obtained from a complex averaging of the viscous flow, as described by the Stokes equation, through the medium; the average is taken on a representative elementary volume still large enough compared with the pore size [2]. The relation is only valid at low  $Re$  numbers ( $Re = \rho \sqrt{k} \cdot v / \eta < a$  few units) where  $v$  is a local velocity,  $\sqrt{k}$  is of order of a pore size. A number of empirical relations relate the permeability to geometrical characteristics of the porous medium. The most classical one is the Kozeny-Carman [3] formula which can be established for a random network tubes having a tortuosity,  $\gamma$ , along the average flow direction ( $\gamma$  is a ratio of lengths and can be estimated from the measurement of conductance of an insulating porous material filled with a conducting fluid).

$$k_{KC} = \phi^3 / [\alpha(1 - \phi)^2 S^2] \quad (2)$$

where  $\alpha = k_0 \gamma^2$  is the so-called « Kozeny constant »,  $k_0$  is a « shape factor ». For a packed bed  $\alpha \simeq 5$  and  $S = 6/D_p$ , where  $D_p$  is the particle diameter. The relation (2) applies well for a variety of regular porous media although it has no absolute validity. In a simple version,  $K \propto \phi^m$ , of Kozeny-Carman relation  $m$  can vary, depending on the porous material, between 1.2 and 3 !

The permeability can be easily deduced from the measurements of flow rate and applied pressure gradient across a sample large with respect to the representative elementary volume. However classical methods apply only to consolidated or at least rigid

porous media where the solid structure is not modified by the fluid flowing across it. In this article we consider the opposite case of tenuous porous structures (such as gels or weak aggregates formed by flocculation or on the surface of a filter) for which we have developed an original differential method on the principle above. The experimental techniques are presented in part 2 and illustrated by showing experimental results on calibrated millipore filters and, more extensively, on the permeability variation during a gelation transition. An extensive account and discussion of the sol-gel critical permeability is presented in a distinct publication [5]. Let us recall however some properties of the sol-gel transition which will be necessary to understand the result of this illustrative experiment.

Gels form a particular class of porous media [6, 7]. They appear in many living systems (the crystalline of the eye) but their broadest range of occurrence is clearly food structures where they combine the advantage of a weak, easily deformable, mechanical structure together with a strong holding power for the liquid substances held into it. It is thus of interest to study both the mechanical properties and permeability (the holding power) of such materials. Quite generally [4], polymeric gels are formed from tridimensional reticulation of polymeric chains (branched polymers). For low concentrations, only finite size polymeric clusters appear in solution (the sol phase). Above a critical degree of reticulation (or time  $t_c$  in chemical gels) a gel forms. The critical properties of the sol-gel transition around  $t_c$  have been described using percolation statistics [4] (and more recently of cluster aggregation). Using an original magnetic sphere rheometer equipment [8], we have studied the divergence of  $\eta(t)$  as  $t_c$  is approached from below and the progressive onset of elasticity above  $t_c$ . It turns out that, quite generally (this is also true for the electrical resistance of a solid), the viscosity and elasticity, despite the simplicity of their measurements, are not simple quantities to characterize in relation with the microscopic structures. On the other hand, the permeability provides a deep insight in the structure of the branching of polymers taking place during gelation.

In weakly connected gels, there is a large correlation length  $\xi$  ( $\xi$  should diverge at  $t_c$ ) which gives the mesh size of the gel structure holding the polymeric solution. We can expect it to relate to  $k$  by  $k \sim \xi^2$ . The porosity should be of the order of 1 if we consider that the amount of polymer is only a few percents of the total solution. Similarly a tortuosity  $\gamma \sim 1$  is expected. A simple generalization of relation (1) would give :

$$|Q/\nabla p| \propto \xi^2(t)/\eta(t) \quad (3)$$

where  $\eta(t)$  is the critical viscosity due to the large finite clusters.

However it is expected from percolation models that the divergence of  $\xi^2$  should be larger than that

of  $\eta$  and consequently that the permeability of a gel should approach zero at  $t_c$ .

However the discussion can be extended beyond the sol-gel transition problem. In well formed gels, Weiss *et al.* [6] have shown that the permeability was a good way to explore the heterogeneity of the pore structure (in Stokes flow, the pressure head ratio for two tubes of same length with radii differing by a factor of 2 is of 16). Thus the heterogeneity of the pore sizes should reveal itself in the permeability [9]. This is particularly important for weak structures which have heterogeneous and some time fractal pore structures.

## 2. Experimental method.

**2.1 AIM OF THE EXPERIMENT.** — The measurement of the permeability of a non deformable porous medium is fairly simple and can be obtained from a variation of flow rate *versus* applied pressure gradient for one or a series of liquids of known Newtonian viscosity. However deformable porous structures cannot support the shear stresses coming from the applied  $\nabla p$  without deformation. Gels are one example of such structures. In deformable porous membranes,  $k$  can also depend on the applied pressure. In addition we want to limit the amount of fluid passing through the medium during the measurement to avoid introducing external fluids which can modify chemically the nature of the branched polymer structure (effects of swelling) or to empty partially the medium, which would lead to the formation of meniscus in the system and to additional forces. Most of all, the introduction of an external liquid in the gel during its formation would modify the reaction rate. A differential method satisfies best the above requirements.

**2.2 SET UP.** — The figure 1 gives a schematic description of the experiment. A gel sample of height  $H = 2$  cm is contained within the upper part of a leak proof cell E made of two superimposed cylinders of

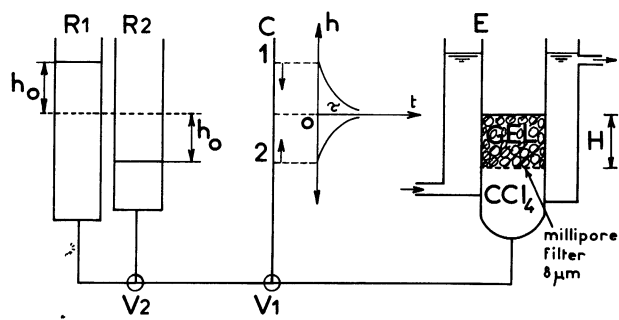


Fig. 1. — Schematic of the experimental technique discussed in chapter 2; E cell containing the gel in the upper part (above the filter) and surrounded by a thermal regulating bath. The level of the solvent can be modified using  $\text{CCl}_4$  which fills the rest of the cell and the tube assemblies. Connections of the reservoirs  $R_1$ ,  $R_2$  and capillary tube are made using the valves  $V_1$ ,  $V_2$ .

diameters  $D = 3.5$  cm separated by a fine screen (a metallic teflon coated grid plus a millipore filter). The screen supports the porous medium. The lower part of E is filled with a denser fluid (support liquid) in contact with the gel. The liquid ( $\text{CCl}_4$  for the gel experiment with polyacrylamide) is non miscible with the polymer solution. The cell is temperature controlled by an outer water circulation to adjust the reaction rate and solvent viscosity which both vary appreciably with temperature. The lower part of E is connected to a vertical calibrated capillary tube C by a teflon line and a three way valve  $V_1$ . The tube C is also connected to two wide reservoirs  $R_1$  and  $R_2$  which can be connected separately with the capillary using a second three way valve  $V_2$ . The level of the support liquid practically does not vary in each reservoir when they are put in contact with the narrow capillary tube C (diameter  $d = 0.5, 1.0$  or  $2.0$  mm). Still,  $d$  is large enough in order that, when C is connected with the cell E, the relaxation of the hydrostatic unbalance (measured initially by  $h_0$ ) is controlled by the permeability of the porous material and not by the viscous stresses in the capillary. The procedure is as follows :

- a) initially  $R_1, R_2, C$  and E are in communication. The level of the support liquid is adjusted to be just at the lowest level of the porous medium ;
- b) the communications between  $R_1$  and  $R_2$  and C and E are suppressed. The reservoirs  $R_1$  and  $R_2$  are respectively displaced by a small height  $h_0$  above and below the equilibrium level ( $h_0$  is chosen to avoid any further appreciable hydrostatic stress on the gel) ;
- c) C is put in contact with  $R_1$  (or  $R_2$ ) ;
- d) finally C is isolated from  $R_1$  and  $R_2$  and connected with E. The level of the support liquid in the capillary relaxes practically to the initial equilibrium level as the ratio of the diameter  $D$  of E to  $d$  is large ;
- e) the measurements are made in a sequence  $R_1, R_2, R_1, \dots$  to keep the level of the liquid in the gel fixed and to avoid chemical or interfacial effects with air or with the support liquid.

**2.3 PERMEABILITY MEASUREMENT.** — The dynamics of the relaxation of the level of the capillary during step can be easily obtained, when it is controlled uniquely by the permeability of the porous medium  $k$ , by expressing the conservation of the flow rate and applying Darcy relation. One gets

$$h(t) = \pm h_0 \exp(-t/\tau) \tag{4}$$

where

$$\tau^{-1} = (\rho g / \Delta H) (D/d)^2 (k/\eta) \tag{5}$$

$\rho$  is the density of the support liquid which gives the restoring bulk hydrostatic force  $\nabla p$ ;  $\eta$  is the viscosity of the liquid within the gel.

**2.4 OPTICAL DETECTION.** — The crucial feature in the experiment is the continuous measurement of the height  $h(t)$  of the liquid in the capillary. The 10 times magnified image of the meniscus between support

fluid and air is formed on the sensitive element of a spot follower device (Sefram Graphispot). As the displacement of this spot follower is horizontal, a couple of plane mirrors transforms the vertical displacement of the meniscus in an horizontal one. Using a light black particle floating on the top surface of the meniscus provides a more contrasted image for the spot follower device. The mechanical displacement is coupled with a precision potentiometer. The resulting voltage signal proportional to  $h(t)$  is digitized and stored in a micro-computer before being processed. The processing technique of the exponential decay law with an unknown base line makes use of an algorithm which we describe in part 4. A simpler experiment just uses the analog recording function of the spot follower to obtain the exponential variation.

**3. Experimental results.**

We first checked the technique using commercially available filters of graded permeability. In particular we used two millipore filters when permeability  $k_{ca}$  was given (millipore catalog 1982 ; p. 33). The table gives the catalog characteristics and the results of the present experiment : characteristic decay time constant as given from the data of figure 2 and experimental permeability  $k_{ex}$

	$k_{ca}$	$\tau$	$k_{ex}$
Filter 0.6 $\mu\text{m}$	$1.34 \times 10^{-10} \text{ cm}^2$	2.9 s	$1.3 \times 10^{-10} \text{ cm}^2$
Filter 8 $\mu\text{m}$	$2 \times 10^{-9} \text{ cm}^2$	0.4 s	$7 \times 10^{-10} \text{ cm}^2$

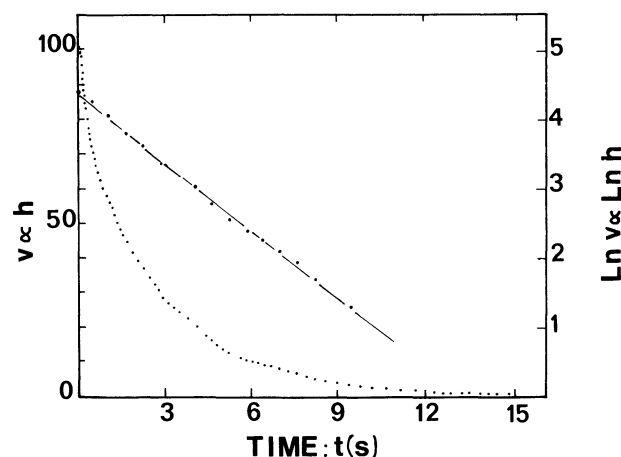


Fig. 2. — Signal recording in linear and logarithmic plot giving the relaxation of the capillary level (see the schematic of the  $h(t)$  curve in Fig. 1) obtained for a 0.6  $\mu\text{m}$  millipore filter ( $\tau = 2.9$  s).

The agreement for small permeability filters is excellent. On the other hand for larger permeabilities the agreement is poorer. On one hand, the accuracy on the mean pore size dimension as given by the

furnisher is poorer on the larger filter  $8 \mu\text{m} \pm 1.8 \mu\text{m}$  than for the small one. More importantly, there are experimental limitations in the study of short time constants  $\tau$ . A first one is the limitation of the time constant of the present graphispot follower which could however be replaced by an other optical detection. In addition the capillary time constant is found to be equal to  $\tau_c = (32 \eta_0 L)/(\rho g d^2) \sim 0.3 \text{ s}$ ; where  $L \sim 10 \text{ cm}$  is the length of the supporting liquid ( $\text{CCl}_4$ ) in the capillary,  $\eta_0$  and  $\rho$  are respectively the viscosity and the density of this liquid. The use of larger diameter capillaries would reduce this unaccuracy for samples of larger permeabilities.

As a second example of application of the technique, we present measurements on the critical permeability of gels. A more detailed description of the experiment and discussion of the critical effects of gelation can be found in reference [5].

In the study of gels we used the ratio  $K = k/\eta$  to characterize the permeability as this is a ratio characteristics of the material which enters equations (1) and (5) (in fact the quantity  $K$  was used as a definition of permeability in Darcy's work).

We have followed the variation of  $K$  occurring during the radical copolymerization of acrylamide with N-N'-methylene bis-acrylamide in aqueous solution. The total concentration of the monomers (acrylamide + bis-acrylamide) is 3% w/w and the ratio of bis-acrylamide to acrylamide is 2.7%. The initiator is ammonium persulphate ( $c = 0.3\%$  w/w). At the beginning of the experiment all the components, previously prepared in separated solutions, are mixed in the cell E which had been previously filled by a packed bed of solid grains (diameter = 0.3 mm) of permeability (estimated to  $\sim k_b = 10^{-6} \text{ cm}^2$ ) much larger than that of the  $8 \mu\text{m}$  millipore filter used as a lower support (see table above). This bed is used to

« arm » the gel as it forms, and to prevent its deformation in the first stage of gelation which would strongly perturb the critical measurements. The time of this operation is taken as the origin of the time scale  $t$ . A typical record of the fluid level  $h(t)$  in the capillary obtained at  $t = 19\,000 \text{ s}$  (a little above the critical time  $t_c$ ) for the sol-gel transition is drawn in figure 3. Notice that  $h(t) \propto V(t)$  where  $V(t)$  is the voltage obtained on the precision potentiometer described in paragraph 2.4. The fit of the variation by an exponential decay law gives a relaxation time equal to  $\tau = 4.8 \text{ s}$ . From this value, the permeability  $K$  is found to be about  $3 \times 10^{-7} \text{ cm}^4 \text{ s}^{-1} \text{ dyn}^{-1}$ . Let us notice that the prefactors involved in relation (5) between  $K$  and  $\tau$  do not vary with time so that the evolution of  $\tau$  is the same as that of  $K^{-1}$ . On the other hand, as there is a ratio of 500 between the surface of the capillary and the flow cell, and the initial difference of level  $h_0$  is taking equal to 5 mm, the displacement of liquid level in the polymeric medium is about  $10 \mu\text{m}$ . This very low value allows us to investigate the permeability during the crosslink formation of the gel avoiding just the destruction of the medium as well as keeping the level of the solvent always above the gel. The filter thickness is equal to  $150 \mu\text{m}$  and the lower front between the polymer solution and  $\text{CCl}_4$  always remains within the filter.

On figure 4, the decay time  $\tau \propto K^{-1}$  is plotted versus the time  $t$ . The relaxation time is quite constant during the first stage of the copolymerization. It measures the ratio  $K$  of the permeability of the suspending bed of particles + that of the millipore filter to the viscosity of the sol (solution + polymeric clusters). The ratio remains constant up to a few percent of the gelation time. As we approach the sol-gel transition we observe a strong increase of  $\tau$  due to a critical increase of the viscosity of the sol flowing

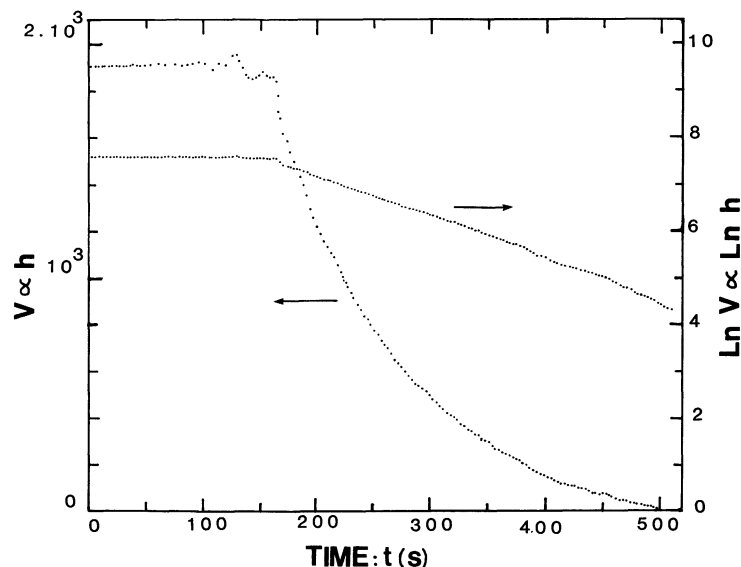


Fig. 3. — Same as figure 2 for a gel just above the gel part at  $t = 19\,000 \text{ s}$  ( $\tau = 4.8 \text{ s}$ ).

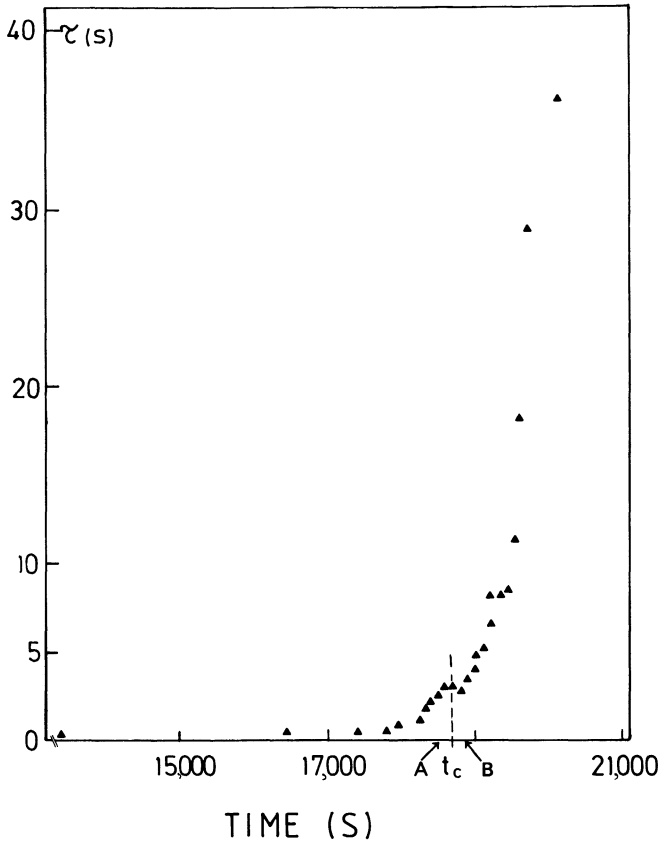


Fig. 4. — Variation of the relaxation time  $\tau$  during gelation. One observes schematically three different regimes : the increase of  $\tau$  observed up to the immediate vicinity of  $t_c$  (point A) in the figure is due to that of the viscosity of the sol. Above point B it is due to the strong decrease of the gel permeability. Finite size effects are seen in the intermediate time scale (when the correlation length of the polymer system is larger than the sustaining grain size).

in the porous medium ending around a time  $t_c = 18\,700$  s (defined from the rounded maximum in Fig. 4).

Above this time we observe an anomaly followed by a second even more rapid increase of  $\tau$ . The range of the anomaly around  $t_c$  can be tentatively associated with the fact that, when the size of the largest clusters measured by the correlation length  $\xi$  becomes larger than the average pore size of the granular suspending material, we expect a « cross over » to a new regime where the permeability of the cluster starts to control the permeability  $k$ . The sharp increase observed a little above  $t_c$  corresponds to a regime where the mesh size of the gel becomes smaller than that of the suspending medium and where its decrease as gelation proceeds controls the very fast decrease of permeability (or increase of  $\tau$  values). We have not addressed the problem of viscoelasticity which could manifest itself by a dependence of the flow rate *versus* pressure head and could be due to deformation of the finite clusters or of the gel lattice under shear. Experiments using a sphere vibrating at finite frequency in the sol

phase indicate a critical time constant variation and the relaxation time of the gel which is of order of 0.1 s at 1 % of  $t_c$  [10]. The shear rate is  $v/\xi \sim 1.s^{-1}$ ; consequently we expect a weak viscoelastic behaviour near the sol-gel transition.

#### 4. Computation of $\tau$ .

We must calculate the time constant  $\tau$  and the amplitude  $a$  of the function

$$y = a \exp(-t/\tau) + b. \quad (6)$$

The classical method using a linear regression on the logarithm of the function does not work because the value of the base line  $b$  is unknown.

The statistical solution (least squares type method) has serious shortcomings :

- the convergence of the calculus is too long, principally if the baseline is unknown ;
- the accuracy of the result is not easy to evaluate ; the quality factor is not a sufficient test to insure that the fit is good.

We propose in this paper a new method which avoids the previous problems and is easy to adapt to any microcomputer.

Consider the two quantities  $I_c, I_s$  defined by

$$I_s(\tau, T) = \int_0^T (a e^{-t/\tau} + b) \times \sin(2\pi t/T) dt \quad (7)$$

$$I_c(\tau, T) = \int_0^T (a e^{-t/\tau} + b) \times \cos(2\pi t/T) dt \quad (8)$$

the calculation gives

$$I_c(\tau, T) = \frac{2\pi a/T}{4\pi^2/T^2 + 1/\tau^2} (1 - e^{-T/\tau}) \quad (9)$$

$$I_s(\tau, T) = \frac{a/\tau}{4\pi^2/T^2 + 1/\tau^2} (1 - e^{-T/\tau}) \quad (10)$$

and the ratio  $I_c/I_s$  is directly related to the time  $\tau$

$$I_c/I_s = 2\pi\tau/T \quad (11)$$

$T$  is a fixed value of the time which corresponds, for example, to the last experimental point of the measure. The time constant  $\tau$  is deduced from the ratio of the two integrals  $I_c, I_s$ . The amplitude value  $a$  is calculated from one of the two equations (9) and (10).

This method has many advantages :

- the result is independent from the baseline because the two following quantities are null

$$\int_0^T b \cos(2\pi t/T) dt = \int_0^T b \sin(2\pi t/T) dt = 0$$

- the result is relatively independent of noise : this method uses the principle of synchronous detection.

We have tested this method with a computer (commodore 8032). The experimental signal  $y(i)$  is simulated with  $n$  points of the exponential function  $y(i) = 2\,000 \times \exp(-i/30) + 500$ ; the integrals are evaluated by the trapezoidale rule. The calculus requires 19 s for a signal of 100 points, and gives amplitude and time relaxation with an accuracy of 0.1 %; then we have add random noise to the signal and the accuracy of the result is equal to 2 % with a noise equal of 10 % of the amplitude of the signal.

### 5. Conclusion.

We have presented an original differential permeability technique applicable to weak porous objects. We demonstrated its use on the example of the sol-gel transition of a chemical gel as reticulation of the polymeric network proceeded. The technique by itself cannot give a detailed geometrical information on the gel structure because it mixes up properties of the gel and of the solute (solution of clusters of finite size). However it can be coupled with direct elastic measurements on the gel, viscous one on the sol phase below  $t_c$  as well as with direct experiments using calibrated microscopic particles within the gel which can probe its correlation length (mesh size). On the other hand,

the experiments give a direct measurement of a property of direct interest for food industry as  $k/\eta$  measures the holding property of gel under an applied pressure (yoghurt, gellies, ...).

There are many other possible applications of the present system to practical systems. One of the most fascinating ones is the study of the permeability of tenuous granular structures as can be formed in the sedimentation of flocculating particles or in « cakes » formed at the surface of a filter. The structures formed by aggregation are often fractals (such are gels near  $t_c$ ) and can be easily destroyed under weak stresses; in particular their mechanical strength decreases as their size increase because, due to their fractal nature, their density decreases with size [11]. It is thus of large interest to study their permeability property using a weakly perturbing method such as described here.

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### References

- [1] DARCY, H., *Les fontaines publiques de la Ville de Dijon* (Dolmont, Paris) 1856.  
In this original work, the ratio ( $k/\eta$ ) was considered as the permeability - the Darcy permeability. The permeability  $k$  should be called *specific permeability*.
- [2] SLATTERY, J. C., *Momentum, Energy and Mass transfer in continua* (Mc Graw-Hill) 1972.
- [3] DULLIEN, F. A. L., *Porous Media : Fluid transport and pore structure* (Academic Press) 1979, p. 170.
- [4] DE GENNES, P.-G., *Scaling concepts in polymer physics* (Ithaca, NY, Cornell University Press) 1979.
- [5] GAUTHIER-MANUEL, B., AMBARI, A., ALLAIN, C., AMIEL, C., *Polymer Comm.*, **26** (1985) 210.
- [6] WEISS, N., VAN VLIET, T. and SILBERBERG, A., *J. Polym. Sci.* **17** (1979) 2229.
- WEISS, N. and SILBERBERG, A., in *Hydrogels for medical and related applications, ACS Symposium Series* **31** (1976) 69.
- [7] TANAKA, T., MOCKER, L. D. and BENEDEK, B. G., *J. Chem. Phys.* **59** (1973) 151.
- [8] GAUTHIER-MANUEL, B., GUYON, E., *J. Physique Lett.* **41** (1980) L-503.
- [9] Groupe Poreux P.C., *Scaling concepts in porous media*, ed. R. Pynn (Plenum, London) 1985.
- [10] GAUTHIER-MANUEL, B., ALLAIN, C. and GUYON, E., *C.R. Hebd. Séan. Acad. Sci. Série II* **296** (1983) 217.
- [11] CATES, M. E., *Phys. Rev. Lett.* **53** (1984) 926.  
KANTOR, Y. and WITTEN, T. A., *J. Physique Lett.* **45** (1984) L-675.