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Diffusion constants in polyacrylamide gels

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The stimulated spin-echo method with pulsed magnetic field gradients was used to study the self-diffusion process of the fluid in swollen and collapsing polyacrylamide gels. Restricted-diffusion effects are evidenced by the dependence on the time of diffusion Δ of the diffusion constant D_f. The results are interpreted in terms of the diffusion process through permeable barriers. A changeover in the time behavior of D_f for the gel around the critical point is pointed out. The pseudodiffusion of the chains is investigated separately. Within the time scale of the experiment (≤ 100 ms) the squared dependence on the magnetic field gradient of the echo amplitude allows the definition of a local diffusion constant D_{ch} for the monomer units. D_{ch} depends on the measuring time in the form expected when restoring forces are active.

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I. INTRODUCTION

Polyacrylamide (PA) gels consist of polymer chains with crosslinks which trap fluid among them. A remarkable property of PA gels is the volume phase transition, with continuous and reversible changes in volume induced by temperature, electric field or *p*H variation in the medium [1]. The unusual transport and relaxation properties of gels have stimulated many studies. In particular, fluid and polymer chain diffusion processes are of strong interest. For the fluid the general aspects of the diffusion in porous and complex media (with the related concepts of conductivity, mobility, porosity, and topology) can be used for an analysis of the experimental findings. Furthermore, by extending descriptions mostly developed for long polymer molecules in solutions [2] and based on the correlation function for local velocity, a definition of diffusion constants for dilute chains in terms of the viscosity and Flory radius can be given. For interacting chains entangled in a solution, the extension is somewhat arbitrary. Two diffusion coefficients can be defined. A cooperative concentration-dependent diffusion constant D_{coop} (meaning that all chains participate and interact) controls the time dependence of the collective concentration fluctuations. D_{coop} is usually measured by quasielastic light scattering (QELS) and can be related to the elastic bulk and shear moduli and to the friction constant. A local diffusion constant D_{ch}, on the other hand, describes the diffusion of a small fraction of the chain, as measured for instance with dilute tracers or by nuclear magnetic resonance (NMR) techniques involving signals arising from the nuclei of the monomer units.

QELS experiments [3] provided D_{coop} in PA gels undergoing the collapse phase transition. The slowing down of the concentration fluctuations causes a decrease in the decay rate $\Gamma_q \simeq D_{\mathrm{coop}} \mathbf{q}^2$ of the scattered light, for the $\mathbf{q} \rightarrow 0$ Fourier modes. The dependence of D_{coop} on the concentration C_e of the network in swollen PA gels has also been studied [4], yielding $D_{\mathrm{coop}} \simeq C_e^{0.76}$ cm^2/s, in good agreement with scaling predictions [2].

NMR techniques provide a suitable approach for the study of microscopic dynamics and local diffusion processes. Early proton spin-lattice and spin-spin relaxation rates and diffusion constant measurements in PA gels [5] showed that the diffusion constant of the fluid D_f is close to the value in free water. Only indirect information about D_{ch} could be obtained [5]. The polymer chain dynamics was studied from deuteron quadrupole relaxation [6]. It was found that the local motions of the segmental units of the chain are isotropic and weakly coupled to the density fluctuations of the whole gel, and characterized by a correlation time $\tau_e \simeq 2 \times 10^{-10}$ s. τ_e is practically constant along the collapse, exhibiting a sizable increase only for marked shrinking.

High-resolution neutron scattering (NS) can be used, in principle, to study the dynamic response of the system for selected wave vectors $\mathbf{q}$, spanning from the region probed by QELS up to values corresponding to a few monomer units. The width Γ_q of the quasielastic NS peak for PA gels has recently been investigated with a high-resolution spectrometer [7], for wave vectors in the range from 0.3 to 3.5 Å^{-1}. This $\mathbf{q}$ range is well above the hydrodynamic regime where a cooperative diffusion constant from $\Gamma_q = Dq^2$ is defined. Correspondently, there is a $\mathbf{q}$ dependence of the form $\Gamma_q \propto \mathbf{q}^3$, and it was only possible to define a $\mathbf{q}$-dependent D_{ch} [7]. For $\mathbf{q} \simeq 1$ Å^{-1}, corresponding to a spatial scale of a few monomer units, an indicative value for D_{ch} of the order of 10^{-6} cm^2/s for swollen gels can be extracted, which decreases by a factor around 10 at the critical point.

In this paper the results of a study of the diffusion processes in PA gels, obtained by means of NMR stimulated echo with pulsed magnetic field gradients (PGSE) are reported, both for the fluid and for the monomer units of the chains. The measurements involve swollen gels, gels undergoing the collapse transition, and gels where the concentration of crosslinks in the polymer network was changed.

The paper is organized as follows. Section II is devoted to details on the samples and the experimental

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methods. In Sec. III the results for the fluid (III A) and for the chains (III B) are presented. In Sec. IV the experimental findings are analyzed and discussed.

II. EXPERIMENT

The diffusion process was studied at different polymer concentrations and crosslink densities and along the volume collapse phase transition. The PA gels, prepared according to standard procedures [1,3], were driven to the collapse by adding acetone to the fluid medium. Our gels can be considered zero hydrolized, with only a limited degree of spontaneous ionization, due to preparation and to thermal effects. Then the collapse transition should be of the second order, with the critical point for the acetone concentration occurring around 42% at room temperature. The polymer chain concentration C_e was varied from 5 to 30%. C_e was estimated using the dry and swollen gel weights, taking into account the different densities for water and for polyacrylamide. For gels at the acrylamide concentration of 5%, the bisacrylamide amount, which controls the crosslink density, was varied from $c_{\mathrm{bis}}=0$ up to $c_{\mathrm{bis}}\sim 25\%$ [c_{bis} =(bisacrylamide weight)/(acrylamide weight)]. For the chain diffusion measurements, gels with deuterated fluid were used (see below).

All measurements were carried out on protons, at room temperature, in a magnetic field $H_0\simeq 9$ kG, with a pulsed NMR spectrometer whose radio frequency (RF) field H_1 could be increased up to about 80 G. The pulsed field gradients were generated by a selective excitation unit equipped with power amplifiers. The gradient G could be increased up to 120 G/cm, with a region of uniform G of about 0.5 cm along the steady-field z direction. The gradient pulse rise or fall time was approximately 100 μs. Quadrupolar coils generating gradient along the z and y directions ($H_1 \| x$), up to values of 5 G/A cm were also used.

The diffusion was studied mostly by using the stimulated echo pulse sequence [8]. In order to minimize the effects due to the inhomogeneity of the external magnetic field (more effective at long times), the modified Carr-Purcell sequence was also used [9]. The measurements were carried out by varying the gradient strength G, the duration δ of the gradient pulse, and the time interval Δ between the two pulses, depending on the nuclear echo dephasing time. The effect of the diffusion was studied by means of the relation

$$y=y(\delta G,\Delta)=\ln\frac{A(G)}{A(0)}=-\gamma^2\delta^2\langle z^2\rangle_\Delta\frac{G^2}{2}\ . \qquad (1)$$

If the Einstein condition is obeyed, then the nuclear mean square displacement $\langle z^2\rangle_\Delta$ along the direction of the gradient in the time Δ is related to D by $\langle z^2\rangle_\Delta=2D\Delta$. More complex situations, where transport is not governed by the solution of Fick's second law, as in polymer systems [10], require special discussion (see Sec. IV). It can be observed that any Gaussian statistics for the proton presence probability [11] should allow one to use Eq. (1). The echo height A in the presence and absence of the gradient was measured as a function of G^2. When a straight line condition was observed, we assumed that Eq. (1) could be used to derive a diffusion constant D, even though D was found to be Δ dependent in gels. It is noted that under our experimental conditions of the field strength and relaxation times (δ must be shorter than T_1 and T_2), motions implying rms displacements less than about 2000 Å cannot be detected.

The signals due to the CH_2 and CH protons in the PA chains do not affect the measurements of the diffusion constant of the fluid D_f. In fact, the smallness of the amount of the polymer with respect to the whole gel and the difference in the relaxation times ($T_2\sim 3$ s for the fluid and $T_2\sim 3$ ms for the chains at the measuring frequency $\nu_L\simeq 38$ MHz) allows one to find experimental conditions such that no contribution to the echo signal comes from the protons belonging to the polymer chains.

As can be seen in Sec. III, the results obtained for the diffusion of the fluid show a non-Brownian behavior at short times. Since several artifacts can arise in the PGSE NMR measurements (due to eddy current effects, gradient pulse mismatches, or sample movements), the diffusion constant in pure water and in a solution of water and glycerol was measured, in order to test the reliability of our apparatus, by choosing values of Δ and G for which a departure from the behavior expected for conventional molecular diffusion was observed in PA gels. The results are reported in Fig. 1, as a function of the gradient pulse spacing Δ [Fig. 1(a)] and of $k=\gamma^2G^2\delta^2(\Delta-\delta/3)$ [Fig. 1(b)]. The k values result from the parameters $G=45$, 60, and 90 G/cm, $\delta=0.5$, 1, and 2 ms, and $\Delta=12$, 18, 25, 65, and 105 ms. It appears from the data in Fig. 1 that no artifact yielding an apparent Δ dependence of D is present in these cases.

As far as concerns the measurements of the diffusion constant of the monomer units, the signal arising from

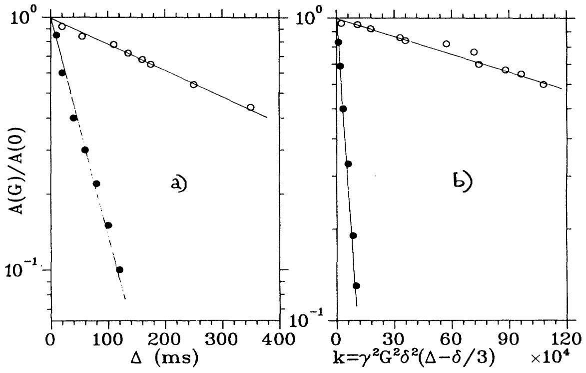

FIG. 1. Test of the experimental procedure on pure water (●) and on water-glycerol solution (○) having diffusion constants in the same range of the ones in gels. In part (a) the echo decays for water ($\delta=500$ μs; $G=70$ G/cm) and for the water-glycerol solution ($\delta=2$ ms; $G=45$ G/cm) are reported as functions of the diffusion time Δ. In part (b) the echo decays for the same systems as a function of $k=\gamma^2G^2\delta^2(\Delta-\delta/3)$ for k given from combinations of the parameter values $\delta=0.5$, 1, and 2 ms; $\Delta=12$, 18, 25, 65, and 105 ms; and $G=45$, 60, and 90 G/cm are shown. Δ is the time interval between the two field gradient pulses of intensity G; δ is the gradient pulse duration.

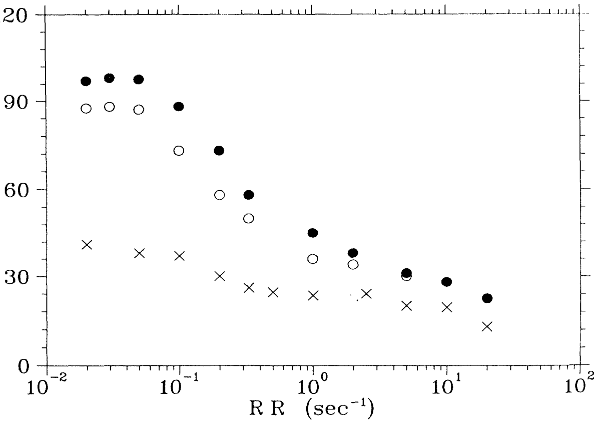

FIG. 2. Representative plots of the amplitudes of echo signals $h(2\tau)$ for $\tau \simeq 700$ μs, obtained under successive dilutions in D_2O (deuteration degree 100%) for different repetition rates RR [(●) after the first dilution, the second (○), and the third one (×)]. The saturation of any residual signal from protons which do not belong to the polymer chain is clearly shown. The typical experimental condition for the measurements of D_{ch} was RR $\simeq 5$ s^{-1}.

protons into the fluid had to be removed through a careful procedure. The gels, although prepared in D_2O, could still release protons from the NH_2 group [12]. Therefore they were left in a bath of D_2O at a deuteration degree of 100% (provided by Sigma Company), then the liquid was removed, and another equilibrium was allowed in another bath of D_2O and the process of progressive dilution was repeated several times. The removal of protons from the fluid medium was checked by collecting the NMR echo signals with different repetition rates for the pulse sequence (see Fig. 2). Furthermore, in the measurements for D_{ch} a repetition rate of five sequences per second was used: as seen in Fig. 2 any remaining contribution from protons in the fluid is thus wiped out by saturation. Details of the apparatus and the experimental procedures are given elsewhere [13].

III. RESULTS

A. Diffusion of the fluid

Water diffusion measurements in PA gels at 5% of monomer, with different crosslink densities as a function of Δ, are reported in Fig. 3. For comparison, the results for free water and for a polymer solution ($c_{bis}=0$) are also given. When no crosslinks are present, a small time dependence of D_f for $\Delta \leq 10$ ms is observed (this point will be discussed in Sec. IV). The Brownian regime is present for $10 \leq t \leq 400$ ms with a time-independent diffusion constant $D \simeq 2 \times 10^{-5}$ cm^2/s, close to the one in pure water for which we obtained $D = 2.3 \pm 0.05 \times 10^{-5}$ cm^2/s, at $T = 296$ K. Conversely, even for a concentration of crosslinks of a few percents, a marked Δ dependence is observed for $\Delta \leq 100$ ms, and a t-independent value $D_f \simeq 1 \times 10^{-5}$ cm^2/s is obtained only at long times.

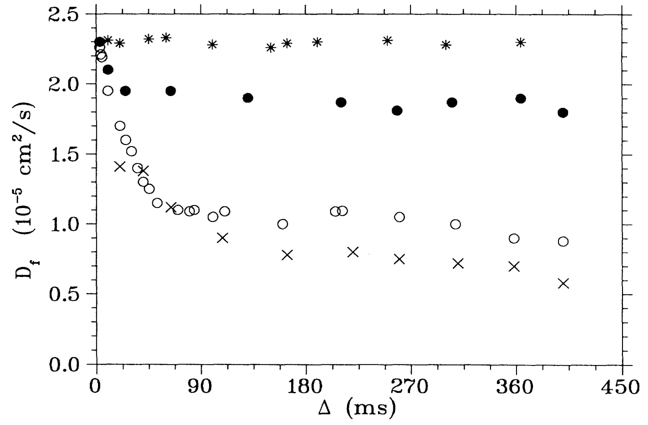

FIG. 3. Diffusion constant D_f of the fluid (water) in PA gels vs the diffusion time Δ for two different crosslink densities: (○) $c_{bis}=2.6\%$ and (×) $c_{bis}=25\%$ (c_{bis} is the percent of bysacrylamide with respect to the monomer) as obtained from the slope of y vs G^2 [see Eq. (1) in the text]. The data are compared with the diffusion constant of free water (∗) and of a polyacrylamide solution with no crosslink: ($c_{bis}=0$) at the same monomer concentration (5%) (●).

It is to be noted that the asymptotic value of D_f is only slightly reduced by increasing the number of crosslinks by a factor of almost 10, for a given C_e.

In Fig. 4 the ratio $D(t)/D(0)$, where $t \equiv \Delta$ and $D(0)$ is the extrapolated value for $\Delta \rightarrow 0$, for gels at different polymer concentrations C_e is reported. Gels at $C_e = 30\%$ show an analogous behavior (data are not reported in the figure). However, in this latter case no flattening of D_f is

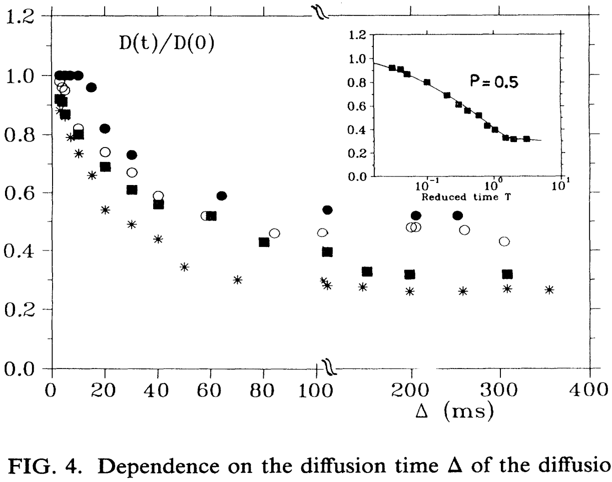

FIG. 4. Dependence on the diffusion time Δ of the diffusion constant D_f for water in PA gels (swollen, $c_{bis}=2.6\%$) at various polymer concentrations C_e (g/cc), as measured from the plot $y \propto G^2$ [see Eq. (1) in the text]; $C_e = 0.025$ (●), 0.05 (○), 0.1 (■), and 0.2 (∗). $D(0)$ is the value for $\Delta \rightarrow 0$ (see Fig. 3). In the inset the data for $C_e = 0.1$ are plotted vs the reduced time $T \equiv D(0)t/a^2$. The solid line is the plot of Eq. (1) of Ref. [18] in the case of permeable barriers, for reduced permeability $P = 0.5$ (see text).

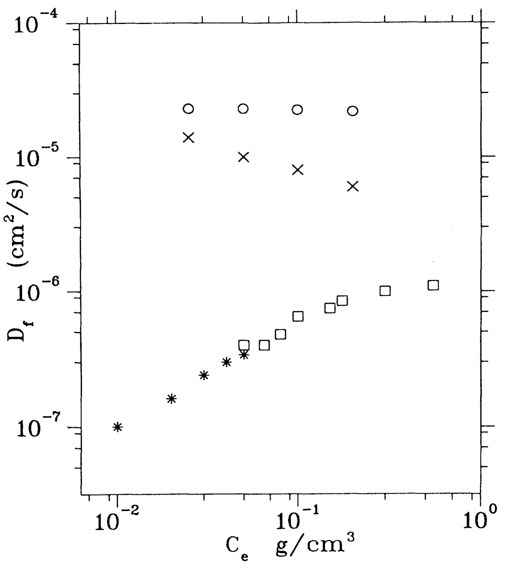

FIG. 5. Diffusion constants D_f for water in swollen PA gels, at the ordinary concentration of crosslinks, as a function of C_e for measuring time $\Delta \rightarrow 0$ (○), and $\Delta \geq 100$ ms (×), where D_f is no longer Δ dependent (see Fig. 4). The results for the cooperative diffusion constants $D_{\rm coop}$ of the PA gels, as obtained by quasielastic light scattering QELS are reported (stars from Ref. [4]; open squares from Ref. [14]).

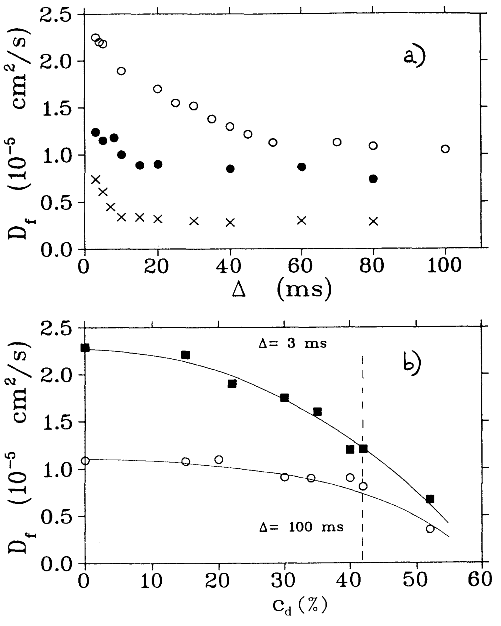

FIG. 6. Diffusion constants D_f of the gel fluid as a function of Δ, for the swollen gel at zero acetone concentration (○, $c_d = 0$), for the gel close to the critical point (●, $c_d \simeq 42\%$), and for the collapsed gel (×, $c_d \geq 50\%$) [(part (a)]. In part (b) of the figure the dependence of D_f on the acetone concentration c_d along the collapse curve is reported for two values of the measuring time Δ. The solid lines in part (b) are an aid for the eye.

present for Δ up to 360 ms. We noted that the condition of a straight line for y vs G^2 [Eq. (1)], as well as the independence of δ, was well verified.

In Fig. 5 the values of $D_f(0)$ and $D_f(\Delta \gg 100$ ms) for the gels at different C_e are reported, together with the results for $D_{\rm coop}$ as measured from QELS [4,14]. The results for D_f as a function of Δ along the collapse curve are shown in Fig. 6(a). In Fig. 6(b) the results for D_f at two measuring times are reported as a function of the acetone concentration c_d.

B. Pseudodiffusion constant for the polymer chains

The diffusion process of the monomer units belonging to the polymer chains was studied from the slope of y vs G^2 at different measuring times Δ, according to the method outlined in Sec. II. We would like to point out that a limited range of y [see Eq. (1)], typically down to 0.5, could be explored since the gradient power $G\delta$ could not be further increased, owing to the limitations of the experimental setup and because of the shortness of the proton transverse relaxation time T_2. On the other hand, Δ cannot be increased above ~ 100 ms, even by using the stimulated echo sequence, since T_1 is about this value at $\nu_L = 38$ MHz [12]. The results for $D_{\rm ch}$ as a function of Δ, for a swollen gel and for a gel close to the critical point, are shown in Fig. 7. One can observe that the slowing down of the density fluctuations of the network, which causes a decrease in $D_{\rm coop}$ [4,14], is also indirectly reflected in $D_{\rm ch}$, local diffusion being, however, a function of the measuring time.

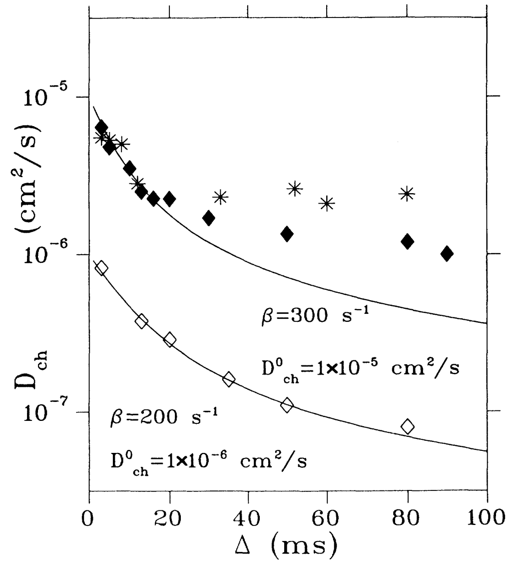

FIG. 7. Pseudodiffusion constant of the polymer chains as a function of the measuring time Δ, for PA chains in solution with no crosslinks (∗), for the swollen gel ($c_d = 0$) (◆), and for the gel close to the critical point (◇). The solid lines represent the best fit behaviors according to Eq. (3) in the text.

IV. DISCUSSION AND SUMMARIZING REMARKS

Let us first discuss the results for D_f. From Figs. 3 and 4 it can be seen that D_f is a function of Δ even for $C_e \leq 0.05$, for $\Delta \lesssim 100$ ms. This means that $\langle z^2 \rangle_\Delta$ is not a linear function of the measuring time [see Eq. (1)]. A plot of $\langle z^2 \rangle_\Delta$ vs Δ shows that only for times larger than about 100 ms is the Gaussian diffusion regime, yielding a straight line extrapolating to the origin, actually reached.

We would like to emphasize that a mismatch in the area of the two pulses [15] is not responsible, in our case, of the behavior of D_f at short times. It would also be present for free water, which is not the case, as appears in Fig. 3. A short time alteration of D has been claimed [16] to result from the presence of a distribution of internal field gradients, due, for instance, to a variation in the susceptibility on a microscopic scale. Such an effect affects D only when the variance of the distribution σ is much larger than G^2. However, in our experimental conditions, y is $\propto G^2$. It can be observed that in Ref. [16] even in the control PA gel (where no superparamagnetic particles were added and no internal field gradients should have been present), D is reduced to 1.7×10^{-5} cm^2/s for $\Delta \geq 30$ ms, consistent with our findings.

A possible interpretation of the behavior of D_f vs Δ can be given by extending a picture of permeability in membranes or porous media walls. It has been found, by quasielastic light scattering measurements [17], that when a particle has to move in the presence of dense polymer networks, a first time interval of abnormal diffusion occurs, with $\langle z^2 \rangle \propto \sqrt{t}$. For larger times the diffusion becomes Fickian, and one can expect a linear relationship of $\langle z^2 \rangle$ with t. Such a situation may be analogous, in some way, to that expected for the movements of a particle of the fluid medium in the gel, and a semiquantitative interpretation of the time behavior of D_f can be attempted in terms of diffusion through permeable membranes. It has been shown, by means of numerical solution based on the stochastic Liouville equation and for barriers of finite permeability p [18], that with the pulsed gradient spin-echo method a time-dependent diffusion constant is measured for a time interval related to p. The actual intrabarrier diffusion constant D_0 is given by extrapolating for $t \to 0$ the function $D(t)$ vs Δ, while the long time diffusion constant $D_\infty \equiv D(t\to\infty)$ decreases with decreasing P, where P is the reduced permeability $P=pa/D_0$, with a constraints spacing. In particular, the ratio D_∞/D_0 is given by $A=P/(1+P)$, and the time t^* at which the diffusivity takes its long-term behavior is $t^* \simeq a^2/D_0$. The inset in Fig. 4 shows the typical behavior of $D(t)/D_0$ as a function of the reduced time $T=D_0 t^*/a^2$ for a reduced permeability $P=0.5$ (solid line).

If the walls of the pores trapping the fluid are considered as partially permeable membranes, the above mentioned results can be used for the interpretation of our data. From Fig. 4 it appears that the extrapolated D_0 is almost independent of the concentration C_e of PA chains, with $D_0 \sim 2.3\times 10^{-5}$ cm^2/s, close to that in free water. Therefore we conclude that the intrapore diffusion constant is related to free displacements of the fluid particles, as is expected. Conversely, D_∞ decreases with increasing C_e, thus indicating a permeability which decreases with increasing number of chains per unit volume. By taking into account that the ratio D_∞/D_0 is around 0.3 (see Fig. 4, typical for the gel at $C_e=0.1$), an effective permeability p for the barriers related to the polymer network can be extracted. From $pa/D_0=(\sqrt{t^*/D_0})p \simeq 0.5$, with $t^* \simeq 10^{-1}$ s, one derives $p \simeq 10^{-2}$ cm/s, which is of the order of that estimated in other organic systems [18]. It should be remarked that for $P \geq 0.5$ the echo decay vs t is still given by an exponential function [18], as we actually observed in the experiment.

An interesting conclusion can be drawn for the behavior of D_f along the collapse curve. The data in Fig. 6 indicate that the intrapore diffusion is only slightly dependent on the acetone concentration. Only for marked shrinking, well above the collapse ($c_d \geq 50\%$), and where the permeability is reduced by the resulting increase in the effective C_e, does a significant reduction in D_0 seem to occur (the G^2 dependence cannot not be studied for $\Delta \leq 3$ ms; see Sec. II).

We would like to emphasize, however, that the model of permeable barriers for the pores defined by the PA network is probably too crude to allow quantitative estimates. One should observe that for $t^* \simeq 10^{-1}$ s one would derive a value around $a \simeq 10$ μm for the equivalent pore radius. This is much larger than the average distance between adjacent crosslinks, which is several hundred Å. Even though pore sizes much larger than the mean value can be expected, the marked departure points out the oversimplification of the model.

Now we discuss results obtained for the pseudodiffusion process of the polymer chains (Sec. III B). We will tentatively apply a model of molecular diffusion in the presence of an attractive center, by assuming that the elastic terms associated with the network play the role of a restoring force pulling a given chain segment toward its original position $\mathbf{r}_0$ at the time t_0. The probability that a monomer is found at the position $\mathbf{r}$ after a time t is given by the equation

$$\frac{\partial P_{\rm ch}}{\partial t}=\beta(\nabla\cdot\mathbf{r})P_{\rm ch}+D\nabla^2 P_{\rm ch} , \tag{2}$$

where the restoring force is $\mathbf{F}=-\beta f\mathbf{r}$, with f the friction coefficient and β also defined through $\mathbf{v}=-\beta\mathbf{r}$ ($\mathbf{v}$ is the monomer velocity). Equation (2) leads to a Gaussian probability $P_{\rm ch}$ [11] which gives an echo decay of the form as in Eq. (1). The effective diffusion constant derived from the G^2 dependence of y is then written

$$D_{\rm ch}=D_{\rm ch}^0\frac{1-e^{-\beta\Delta}}{\beta\Delta} . \tag{3}$$

In Fig. 7 the data for $D_{\rm ch}$ are fitted according to Eq. (3). For the swollen gel $D_{\rm ch}^0$ (for the limit $\Delta\to 0$) is $\simeq 10^{-5}$ cm^2/s, smaller than D_f by only a factor of 2. After a diffusion time of the order of 50 ms, $D_{\rm ch}$ appears significantly reduced with respect to D_f. The fit according to Eq. (3) is rather poor at large Δ for the swollen gel. The best fit value for β turns out to be $\beta \simeq 300$ s^{-1}.

For the gel close to the critical point, a good fit is obtained, which yields $D^0_{\rm ch} \simeq 10^{-6}$ cm^2/s and $\beta \simeq 200$ s^{-1}. One can note that $D^0_{\rm ch}$ decreases, as occurs for $D(t=0)$ for the fluid (see Fig. 6), but to a more sizable extent, on approaching the collapse. The β decrease is consistent with the slowing-down process: in fact, the local elastic constant βf is expected to decrease faster than the friction coefficient f, in qualitative agreement with the behavior of the cooperative diffusion constant, measured by QELS, which is related to the network macroscopic elastic moduli [19].

Finally we would like to call attention to a striking result implicit in the data for $D_{\rm ch}$ discussed above. Taking into account our experimental conditions and the constraints due to the relaxation times T_1 and T_2, one has to conclude that during a measuring time, typically around 50 ms, the rms displacements of the monomer unit are as large as several thousand Å. This conclusion appears to disagree with a picture of polymer chains somehow bounded by mutual crosslinks, or to indicate that a sizable fraction of the chains can diffuse almost freely, leaving unaltered the standard macroscopic properties of the gel.

To summarize, in this paper we have reported the results of a study of the local diffusion processes in polyacrylamide gels as obtained from the NMR pulse field gradient technique. The diffusion of the fluid medium and the polymer chain segments have been measured separately. The data show a time dependence of the diffusion process of the fluid with a Fickian diffusion regime occurring for $t \gtrsim 100$ ms, while at short times an effective time-dependent D_f is measured. For $t \rightarrow 0$ one has $D_f \simeq 2\times 10^{-5}$ cm^2/s, close to the diffusion constant of free water. At the critical point of the collapse transition, a changeover in the global behavior of D_f vs Δ is found. The results have been interpreted in the framework of a model of permeable barriers, and semiquantitative information about the effective permeability of the polymer network has been extracted.

The process of local diffusion of the polymer chains does not appear to be Fickian. A pseudodiffusion coefficient $D_{\rm ch}$ from the G^2 dependence of the echo attenuation can still be defined. $D_{\rm ch}$ depends on the measuring time. The data are tentatively interpreted in terms of diffusion in the presence of a restoring force. An effective local elastic constant is thus derived, which decreases on approaching the collapse. Unexpected large displacements of the polymer chains appear to occur.

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[1] See T. Tanaka, Physica A **140**, 261 (1986), and references therein.

[2] See P. G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell, University Press, Ithaca, NY, 1979).

[3] T. Tanaka, D. Fillmore, S. T. Sun, I. Nishino, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 636 (1980); T. Tanaka, S. Ishiwata, and C. Ishimoto, *ibid.* **38**, 771 (1977).

[4] T. Takebe, K. Nawa, S. Suehiro, and T. Hashimoto, J. Chem. Phys. **91**, 4360 (1989).

[5] F. Tabak, M. Corti, L. Pavesi, and A. Rigamonti, J. Phys. C **20**, 5691 (1987).

[6] M. Corti, L. Pavesi, A. Rigamonti, and F. Tabak, Phys. Rev. A **43**, 6887 (1991).

[7] L. Pavesi, A. Rigamonti, A. Deriu, F. Cavatorta, and H. D. Middendorf, Physica B **180**, 773 (1992).

[8] J. E. Tanner J. Chem. Phys. **52**, 2523 (1970).

[9] W. D. Williams, E. F. W. Seymour, and R. M. Cotts, J. Magn. Res. **31**, 271 (1978).

[10] G. Fleisher, D. Geschke, J. Karger, and W. Heink, J. Magn. Res. **65**, 429 (1985).

[11] E. O. Stejskal, J. Chem. Phys. **43**, 3597 (1965).

[12] L. Pavesi and T. H. Mareci, Ist. Lombardo (Rend. Sc.) B **126**, 139 (1992).

[13] L. Pavesi, Ph.D. thesis, University of Pavia, 1994.

[14] A. M. Hecht and E. Geissler, J. Phys. (Paris) **39**, 631 (1978).

[15] M. I. Hrovat and C. G. Wade, J. Magn. Res. **45**, 67 (1981).

[16] J. Zhong, R. P. Kennan, and J. C. Gore, J. Magn. Res. **95**, 267 (1991).

[17] Y. Suzuchi and I. Nishio, Phys. Rev. B **45**, 4614 (1992).

[18] E. von Meerwall and R. D. Ferguson, J. Chem. Phys. **74**, 6956 (1981).

[19] T. Tanaka, L. O. Hocker, and G. Benedek, J. Chem. Phys. **59**, 5151 (1973).