polymer reports

Dynamics of stretched swollen networks

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Concentration fluctuations in swollen gels are controlled by a collective diffusion coefficient D_c. Two experimental observations are described in which a swollen gel is mechanically deformed from its equilibrium configuration. In the first, the anisotropy of D_c in a uniaxially deswollen polyacrylamide–water gel is investigated using dynamic light scattering. No anisotropy is detected. In the second, D_c is measured by the neutron spin echo technique in a stretched poly(dimethylsiloxane) gel swollen in toluene. The measured anisotropy is small and at the limit of the experimental error.

(**Keywords: dynamics; swollen networks; diffusion coefficient**)

INTRODUCTION

Some time ago, in the context of neutron scattering from anisotropically swollen gels[1], we referred to unpublished dynamic light scattering observations for polyacrylamide gels, in which it was found that strong uniaxial deswelling produced no measurable anisotropy of the collective diffusion coefficient D_c. The gel was deswollen in a rectangular light scattering cell in such a way that the sample cross-section perpendicular to the principal stress axis remained constant (*Figure 1*). Under heterodyne conditions, the decays of the correlation functions with the stress axis perpendicular to and at 45° to the transfer wave vector Q were found to be indistinguishable within experimental error.

More recently, the osmotic properties of uniaxially deswelling poly(vinyl acetate) gels have been investigated, in which the perpendicular cross-section was allowed to vary freely[2]. Once again, the osmotic parameters in the uniaxially deswollen state exhibited no measurable anisotropy.

In contrast to these observations, Takeba *et al.*[3], using photon correlation spectroscopy, have reported that when swollen polyacrylamide gels are stretched, strong anisotropy of D_c develops. They found that $D_{c\parallel}/D_{c\perp}$ varies approximately linearly with the elongation ratio Λ, in such a way that for $\Lambda = 2$, $D_{c\parallel}/D_{c\perp} \sim 2$.

These observations, though surprising, are not necessarily mutually irreconcilable. It is conceivable that in the deswollen state, since the elastic contribution to the network free energy is much smaller than the osmotic contribution, any anisotropy is correspondingly small. In the stretched state, however, these energies become comparable, and the relative contribution of the elasticity is larger: this would favour the appearance of anisotropy.

The present experiment was designed to investigate anisotropy in the relaxation rate of concentration fluctuations in stretched swollen PDMS gels, using the technique of neutron spin echo[4–6]. One advantage of this technique compared with photon correlation spectroscopy is that it is free from ambiguities as to the detection mode, i.e. heterodyne or homodyne. The relevance of this remark is that large scale macromolecular

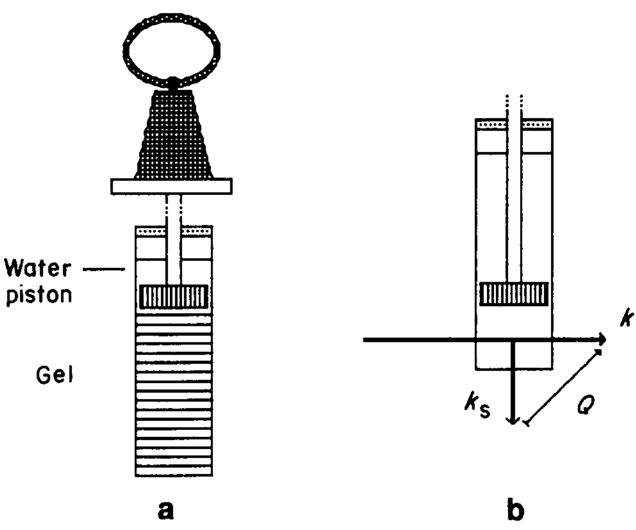

Figure 1 Experimental arrangement for measuring D_c in a uniaxially deswollen gel. (a) Gel in rectangular light scattering cell with applied weight. (b) Light scattering geometry when deswelling is complete. $\mathbf{k}_i$ and $\mathbf{k}_s$ are the incident and scattered wave vectors. The transfer wave vector ($\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_s$) is either perpendicular to the symmetry axis (cell upright), or at 45° (cell laid on its side, with the observation being made through the cell bottom)

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superstructures, which are a common feature of gels, are often the cause of unrecognized heterodyning of the signal, and can lead to misinterpretation of the correlation spectra. Any uncertainty can usually be lifted by using split beam interferometry[7], or by moving either the sample or detector[8].

EXPERIMENTAL

As described elsewhere[9,10], gels were prepared from a melt of α,ω-dihydroxy terminated poly(dimethylsiloxane) (PDMS) chains (Rhône-Poulenc). The viscosity average molecular weight of the precursor chains was 40 000. The crosslinking agent, ethyl triacetoxy silane, was mixed in a dry nitrogen atmosphere to produce a precursor mixture that develops crosslinks when exposed to atmospheric water. The mixture was poured into a polytetrafluoroethylene mould and left for 2 months in contact with the atmosphere.

At the end of the curing process, the samples were stripped from their moulds and washed in octane, and the diluent was replaced by toluene, which is also a good solvent for PDMS at 25°C. The extractable material, removed by successive solvent exchange, did not exceed 4–5% by weight. The swelling equilibrium concentration of the samples in excess toluene was measured to be 0.16 g cm^{-3}.

A sheet of PDMS elastomer, glued at its extremities with silica-filled PDMS to glass slides, was placed in a stretching frame (*Figure 2*), then swollen in deuterated toluene in a large cell with glass windows. With the fully swollen gel, a maximum stretching ratio $\Lambda = 1.40$ could be attained. At larger values of Λ, the gel tended to tear.

The quasielastic neutron scattering measurements were made on the IN11 instrument at the Institut Laue Langevin, Grenoble, at an incident wavelength of 8.9 Å, with a wavelength spread ($\Delta\lambda/\lambda$) of 21%. This wavelength spans the time delay window 0–16 ns. Three different scattering angles θ were chosen to give scattering vectors $Q = 0.025$, 0.031 and 0.043 Å^{-1}. This choice was made so as to be in the region $Q\xi \leqslant 1$, where the relaxation rate of the collective mode is $\Gamma = D_c Q^2$, ξ (~ 16 Å) being the polymer-polymer correlation length in the swollen gel. The stretching frame, immersed in excess toluene, could be placed with the extension axis horizontal (i.e. parallel to the scattering plane) or vertical in a thermostatically controlled enclosure held at 25°C.

The polyacrylamide–water gels were made from a solution of acrylamide and bisacrylamide (BDH) in a weight ratio of 37.5/1, according to a standard recipe[11]. The parent mixture was poured into a 1 × 1 × 4 cm glass light scattering cell (Hellma) and allowed to gel at room temperature. The samples were left in their cells after completion of gelation.

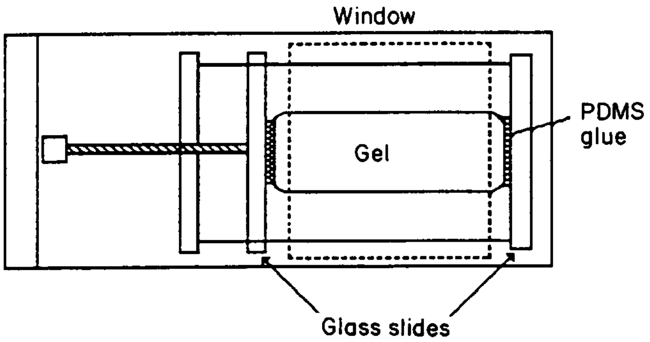

Figure 2 Stretching frame and sample holder for anisotropic neutron scattering measurements

RESULTS

Dynamic light scattering

First the results of earlier dynamic light scattering measurements are described, in which polyacrylamide–water gels were prepared in rectangular scattering cells[12]. A piston with a semipermeable membrane was placed in contact with the confined gel, then loaded with a suitable weight until equilibrium was established (*Figure 1a*). This process took several months. For an initial polymer concentration of 0.033 g cm^{-3} and a piston load of 208 g, the final gel concentration was 0.108 g cm^{-3}, i.e. a compression ratio $\Lambda = 0.306$. The light scattering measurements were performed with an argon ion laser working at 4880 Å, and the scattering angle was 90°. *Figure 1b* shows the scattering geometry employed. Heterodyning was ensured by selecting a bright spot in the diffraction pattern. The temperature was 17.5°C.

The results of the light scattering measurements are shown in *Figure 3*. It can be seen that the decays of the correlation functions of the deswollen gel with the stress axis perpendicular to and at 45° to the transfer wave vector Q are indistinguishable within experimental error.

Neutron spin echo

The neutron spin echo measurements of the PDMS gel swollen in deuterated toluene in the stretched geometry are displayed in *Figures 4* and *5*. These data have been corrected for static scattering from non-uniformities in the polymer concentration[13]. In the logarithmic scale of *Figure 4* the curves have been

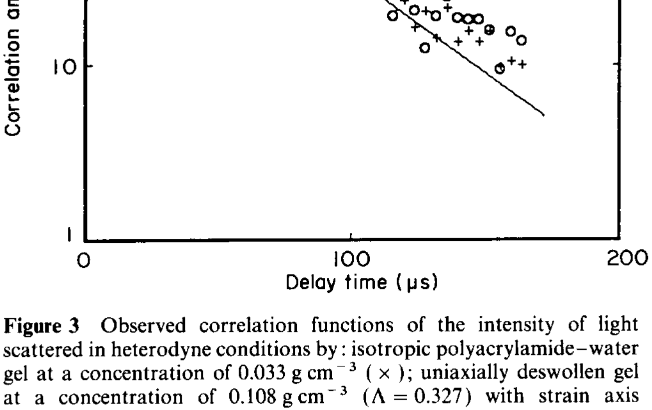

Figure 3 Observed correlation functions of the intensity of light scattered in heterodyne conditions by: isotropic polyacrylamide–water gel at a concentration of 0.033 g cm^{-3} (×); uniaxially deswollen gel at a concentration of 0.108 g cm^{-3} ($\Lambda = 0.327$) with strain axis perpendicular (+) and at 45° (○) to the scattering vector. The apparent diffusion coefficients are $4.0 \pm 0.1 \times 10^{-7}$ and $4.2 \pm 0.2 \times 10^{-7}$ cm^2 s^{-1}, respectively. The measurements were made using an argon ion laser with incident wavelength 4880 Å and scattering angle 90°

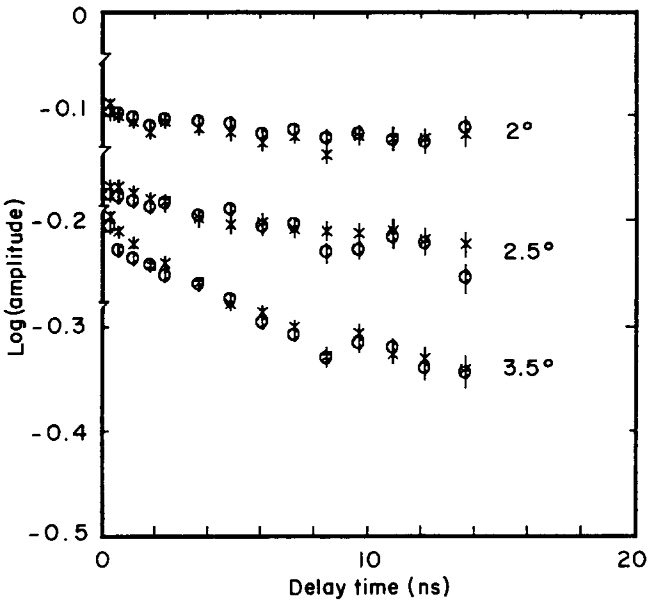

Figure 4 Corrected neutron spin echo decays from PDMS gel swollen in deuterated toluene and stretched to $\Lambda = 1.25$: (○) stretch axis in scattering plane; (×) stretch axis perpendicular to scattering plane

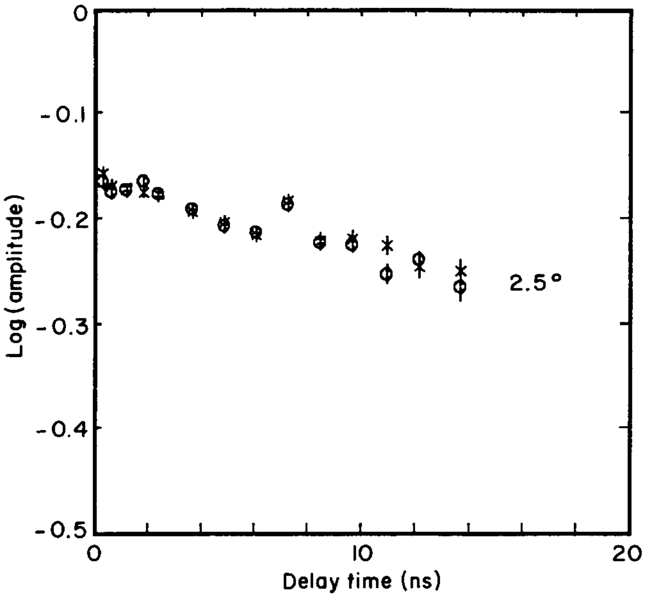

Figure 5 Corrected spin echo decays from PDMS gel swollen in deuterated toluene and stretched to $\Lambda = 1.40$: (○) stretch axis in scattering plane; (×) stretch axis perpendicular to scattering plane

artificially separated to avoid confusion. The spin echo decays from the perpendicular and parallel orientations are hardly distinguishable, for both stretching ratios of the gel ($\Lambda = 1.25$ and 1.40). *Table 1* gives the ratios of the apparent collective diffusion coefficient $D_{c\parallel}/D_{c\perp}$ deduced from these curves, using single exponential fits to the data. The error quoted in *Table 1* is from the statistical scatter in the experimental points. The scatter in the absolute values of $D_{c\parallel}$ and $D_{c\perp}$ is of course larger than that of their ratio $D_{c\parallel}/D_{c\perp}$, since the relative measurement eliminates several sources of systematic error.

In reference 3, the observations on stretched polyacrylamide gels yielded an approximately linear relation of the form:

$$D_{c\parallel}/D_{c\perp} \propto \Lambda^n$$

Table 1 Ratio of D_c measured by neutron spin echo in the directions parallel and perpendicular to the stretch axis in a swollen PDMS gel

θ (deg)	Λ	$D_{c\parallel}/D_{c\perp}$
2.0	1.25	0.92 ± 0.13
2.5	1.25	1.10 ± 0.07
3.5	1.25	1.00 ± 0.04
2.5	1.40	1.11 ± 0.07

with $n \sim 11/12$. Applied to the present gel, this would imply $D_{c\parallel}/D_{c\perp} = 1.23$ at $\Lambda = 1.25$ and $D_{c\parallel}/D_{c\perp} = 1.36$ at $\Lambda = 1.40$. The neutron spin echo observations of the PDMS gels investigated here indicate that anisotropy in D_c is comparable with the statistical noise. If any anisotropy is present, it is small. The average ratios found for our sample are:

$$\Lambda = 1.25 \qquad D_{c\parallel}/D_{c\perp} = 1.02 \pm 0.04$$

$$\Lambda = 1.40 \qquad D_{c\parallel}/D_{c\perp} = 1.11 \pm 0.06$$

CONCLUSIONS

The effects of stretching on D_c of the gel are very small. The present observations on stretched PDMS gels swollen in toluene are consistent with our earlier observations on deswollen gels. These results imply that in measurements of local parameters (e.g. correlation lengths and radii of gyration) at low deformations, the macroscopic stress in a gel is strongly screened at small distances.

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