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DYNAMIC LIGHT SCATTERING FROM POLYACRYLAMIDE-WATER GELS

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Résumé. — On détermine par des mesures de diffusion Rayleigh de lumière, le module d’élasticité $G_1$ et le coefficient de diffusion des mouvements collectifs $D_c$ dans un système polyacrylamide-eau, en fonction de la concentration. Les gels sont copolymérisés avec du bisacrylamide qui agit comme agent réticulant. Tandis que $G_1$ ne varie que légèrement en fonction du taux de réticulation (dans la région où la diffusion multiple est négligeable), le module d’élasticité $G_m$ mesuré mécaniquement croît fortement avec ce taux, atteint à peu près $G_1$, puis chute quand les gels deviennent opalescents et inhomogènes. Pour des concentrations entre 0,025 et 0,12 g cm$^{-3}$, $G_1$ varie comme $c^{2.35\pm0.06}$ à la température ambiante. Pour la densité de réticulation utilisée dans les mesures mécaniques, $G_m$ est généralement plus petit que $G_1$ d’un facteur 2, mais aux concentrations de polymère les plus basses, la différence croît du fait des chaînes pendent.

On trouve que $D_c$ varie comme $c^{0.65\pm0.03}$ en accord avec les observations sur d’autres systèmes de polymères. La différence entre cet exposant et celui prévu pour l’inverse de la longueur d’écran est compatible avec une loi de volume libre pour la variation de la viscosité du solvant en fonction de la concentration.

Abstract. — Rayleigh light scattering measurements are reported of the elastic modulus $G_1$ and collective motion diffusion constant $D_c$ of a series of polyacrylamide-water gels as a function of concentration. The gels were copolymerized with N,N'-methylene bisacrylamide which acts as a cross-linking agent. While $G_1$ varies only slightly with cross-linking density at constant polymer concentration $c$ (in the region where multiple scattering is negligible), the mechanically measured elastic modulus $G_m$ increases strongly with increasing cross-linking, almost attaining the value of $G_1$, then falls as the gels become opalescent and inhomogeneous. For concentrations between 0.025 and 0.12 g cm$^{-3}$, $G_1$ varies as $c^{2.35\pm0.06}$ at room temperature. At the cross-linking densities used for the mechanical measurements, $G_m$ is generally smaller than $G_1$ by a factor of 2, but at lower polymer concentrations the difference increases as the effects of loose chains become pronounced. $D_c$ is found to vary as $c^{0.65\pm0.03}$, in agreement with observations on other polymer systems. The difference between this exponent and that expected for the inverse screening length is consistent with a free volume behaviour of the solvent viscosity.

1. Introduction. — A number of authors have used photon correlation spectroscopy to investigate the light scattering properties of gels [1-8]. Tanaka, Hocker and Benedek [2], hereafter referred to as THB, applied this technique to measure the diffusion coefficient $D_c$ of the collective concentration fluctuation motions in polyacrylamide (PA)-water gels, and observed that the correlation function of the light scattered by these motions is a single exponential, of decay rate

$$\Gamma = D_c K^2$$

where $K$ is the scattering wave vector of the light. These authors also made mechanical measurements

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of the elastic moduli $G_m$ of their samples, and thereby could estimate the frictional constant $f = G_m/D_c$. Although measurements were reported for only two concentrations, their results indicate that $G_m$ is a strongly varying function of the polymer concentration.

More recently Munch et al. [8] published measurements on polystyrene (PS) gels, using accurately calibrated chain masses between cross-linking points. For the solvents benzene and ethyl acetate their results obey a scaling law behaviour for $D_c$ as a function of polymer concentration in the semidilute concentration range. Moreover, they show that the elastic modulus measurements of Belkebir-Mrani [9, 10] on the system PS-benzene are also consistent with a scaling law behaviour, i.e.

$$G_m = G_0 e^a$$

where $G_0$ is a constant and $a$ is equal to 2.25 as predicted for good solvents [11, 12]. For comparison, the two measurements of the elastic moduli quoted by THB for PA-water gels at room temperature lead on interpolation to a value of $a$ close to 7. For polymers in semidilute solution, such a large value of the exponent is surprising: in theta solution [13, 21] the exponent is predicted theoretically to be 3, and anything larger suggests strong collapse of the polymer coils. PA gels, however, are rather stable systems, as witnessed by their widespread use for the separation of biological molecules. Above 0 °C, there is no visible sign of a transition.

It is arguable whether it is appropriate to apply the mechanically measured elastic modulus $G_m$ to light scattering. $G_m$ is obtained from the measured bulk shear modulus of the gel, and converted to a longitudinal modulus on the assumption that on a local scale the poisson ratio of the gel is zero [2]. This conversion is made necessary by the longitudinal nature of the modes scattering the light. The longitudinal modulus $G_l$ pertinent to light scattering, on the other hand, describes a high frequency response of the system. In uncross-linked concentrated polymer solutions, the low frequency mechanical modulus tends to zero. In the case of PA gels, however, THB obtained remarkable agreement between the ratio $G_m/D_c$ and independent mechanical measurements of the friction constant $f$, thereby lending support to the use of the mechanical value $G_m$. It seems, nonetheless, legitimate to doubt the validity of their friction constant measurements, since the strain imposed on one of their samples by the hydrostatic pressure head was an order of magnitude greater than the elastic modulus of the gel, making it likely that the flow rate of water through the gel was measured in a non-linear regime.

Since one can measure not only the time constant of the correlation function, but also the intensity of the light scattered by the concentration fluctuations [14], it is possible to calculate the elastic module $G_l$ relevant to the collective fluctuations in the gel. It is of interest to compare this value with that obtained by mechanical means, and also with the predictions of scaling theories, which have had much success in describing the properties of semidilute solutions of polymers.

In this paper we present measurements of the elasticity and collective diffusion coefficient, obtained by photon correlation spectroscopy, in a series of PA-water gels of different concentrations. These gels are easy to prepare, scatter light strongly and give rise to simple exponential correlation functions for polymer weight fractions greater than about 0.03. The values obtained for the elasticity of the gels $G_l$ by light scattering are compared with the $G_m$ obtained mechanically.

2. Experimental technique. — The principle of photon correlation spectroscopy has been amply described in the literature [15]. In the case of the PA-water gels described here, light is scattered overwhelmingly by trapped dust particles, microscopic bubbles and other inhomogeneities in the samples, and to a much smaller extent by the concentration fluctuations of interest in the experiment. In the gel the inhomogeneities are static or quasi-static, and the light they scatter mixes with that scattered by the concentration fluctuations to give a heterodyne signal which is accumulated in a correlator.

If coherent light of intensity $I_0$ at fixed wavelength $\lambda$ is incident on a gel of dielectric constant $\varepsilon$ and polymer weight fraction $w$ at temperature $T$, the time dependent part of the correlation function of the heterodyned light scattered perpendicular to the plane of polarization by the concentration fluctuations is

$$S(t) = C \frac{I_0 NT \Delta w^2}{G_1 \left( \frac{\partial \varepsilon}{\partial w} \right)^2} \exp(-D_c K^2 t)$$

where $C$ is a constant which depends on $\lambda$, the geometry used, the quantum efficiency of the photomultiplier, and the duty factor of the correlator. $N$ is the number of light pulses generated by the reference signal during the accumulation period (i.e. approximately the total number of pulses received), and $\Delta$ is the clock period of the correlator. The incident intensity $I_0$ is monitored by removing a small fraction of the light with a beam splitter to a photocell. Although the proportionality factor $C$ may be measured directly [14], the error involved is quite large (ca. 30%), and in practice it is more convenient to calibrate the system with a standard concentrated polymer solution of polystyrene in cyclohexane, for which the values of $G_l$ are available in the literature [16].

The experimental arrangement consists of a laser (He Ne SP 124, delivering 15 mW) the beam of which is suitably attenuated and focused into the sample cell, inside a thermostat jacket. Scattered light from one or two coherence areas in the sample, as defined by fixed...
circular apertures, is collected by a photomultiplier tube of low dark current. In the present experiment 90°
scattering was generally used. A fast discriminator shapes the pulses arriving at the anode of the photo-
multiplier, and sends them to a pulse scaler and a
digital correlator. The pulse scaler measures \( N \), the
number of pulses, to be corrected for dark current, in the experimental accumulation period,
while the correlator generates the function \( S(t) \) of
eq. (3). A HP 5302A counter was used for the pulse
scaler; this permits the pulse count rate \( p \) to be set at
the start of each run by adjustment of the incident
light intensity \( I_0 \), in order to satisfy the condition for
square law response of the correlator, namely

\[
p A \ll 1 .
\]

(4)

Attenuation of the beam is not trivial, since most
attenuators deviate the beam, resulting in serious
misalignments as the intensity is varied. A convenient
solution is to use a single linear graded attenuator, the
deviation of which is independent of the attenuation
chosen.

Although we were not able to use split beam geo-
metry to prove that the observations were made in the
heterodyne mode, there is nevertheless strong evidence that this is the case. For fixed \( I_0 \), the observed signal
intensity is proportional, above a certain limit, to the
oscillator strength chosen; when, however, the sample
is displaced, so that a region of unusually low scattering
intensity is observed, the signal intensity drops,
and the observed decay time becomes notably shorter.

To obtain the values of \( G_1 \) from eq. (3) it is essential
to know \( \partial E / \partial w \) both for the reference sample and the
PA-water system under study at the wavelength of
light used, i.e. 632.8 nm. A set of samples of polystyrene
(Pressure Chemical, \( M_w = 2 \times 10^6 \)) in cyclohexane
was prepared in sealed fluorescence cells and allowed
to come to equilibrium for a month at 50 °C. The
refractive index measurements were made with an
Abbe refractometer at 45 °C, using the laser beam
(diffused by a thin sheet of teflon), the light being
refracted by the interface of the solution and the
optically polished bases of the cells. To correct for
deviations from parallelism of the glass base, averages
were taken for the light entering from each of the four
faces of the cells. Eight samples of polymer weight
fraction \( w \) ranging from 0 to 0.5 gave an excellent fit to
the polynomial of order three for the refractive index
of polystyrene-cyclohexane at 45 °C for 632.8 nm:

\[
n(w) = 1.411 26 + 0.123 29 w +
+ 0.036 22 w^2 + 0.047 79 w^3 .
\]

(5)

The PA-water gels were prepared using standard
recipes [17], starting from synthesis grade acrylamide
and N, N’ methylenebisacrylamide (bis) from Merck.
However, apart from 0.07 % ammonium persulphate
and 0.03 % N-N-N’-N’ tetramethylethylene diamine,
used as initiators in all the gels, no salt or buffer was
added to the solutions, so that the ionic strength was
zero throughout. In this way the composition of the
solution resembled as closely as possible a binary
solution. Although the gels could be cooled below 0 °C,
the lowest temperature of supercooling observed
was \(- 7.5 °C\), at which point the samples switched to
an opaque frozen state and the thermocouple placed
inside the gel recorded an abrupt temperature jump
to \( 0.0 \pm 0.01 °C \). In a 2.5%, sample the gel became
permanently damaged by this irreversible transition.
These observations are at variance with the results
quoted in reference [7] for a 2.5% gel, for which a
second order transition was noted at \(- 17 °C \).
Although these authors do not describe the prepara-
tion of their sample, the difference in behaviour may
have been caused by the presence of a salt in their
solutions: the freezing point of the water would
thereby be lowered and the temperature of phase
separation of the gel raised. In the usual preparation of
the gel, a buffer is added composed of hydrochloric
acid and an organic base, tris (hydroxymethyl) aminomethane; the use of these substances was
avoided in the present experiment, as they may give
rise to a ternary or higher order solution, whose modes
of concentration fluctuation are complex and in
general statistically inseparable.

The solutions were degassed briefly in a syringe to
remove dissolved oxygen, and transferred to the
rectangular fluorescence cells where they were care-
fully capped with a layer of distilled water to reduce
oxygen absorption at the surface. Heating effects were
minimized by placing the cells in water at room tem-
perature. Polymerization took place within half an
hour.

The refractive index measurements on the PA-water
system at 632.8 nm gave a linear dependence on the
concentration between \( w = 0 \) and 0.5 at 23 °C

\[
n(w) = 1.329 2 + 0.182 6 w
\]

and at 2 °C

\[
n(w) = 1.329 7 + 0.192 6 w .
\]

(6)

The concentrations were measured subsequently by
removing the gel from the optical cell and baking to
dryness for three weeks in an oven at 50 °C, thus
giving the dry weight. The polymer weight fraction \( w \)
was defined as the ratio of the dry weight to the total
sample weight. In samples with carefully controlled
initial ingredients, the concentrations calculated by
the drying method were about 7% greater than that
expected from the weights of acrylamide and bis
present. We attribute this difference to the residual
water clinging to the hydrophilic amide groups; as this
is a constant factor it has no effect on the slope of the
log-log plots used in the scaling law representations.
Unpolymerized acrylamide amounted to about 3%.
This was determined by preparing two identical
samples, one of which was dried in the usual way,
and the other was washed for a week in distilled water
before drying.
The conversion from polymer weight fraction \( w \) to polymer concentration in \( \text{g cm}^{-3} \) \( (c) \) was obtained by measuring the density \( \rho \) of a series of gels. Within experimental error \( \rho \) was found to be linearly dependent on \( w \)

\[
\rho = 1.000 + 0.346 \ w
\]  

with

\[
c = \rho w .
\]

The mechanical measurements of the elastic moduli of the gels were performed at room temperature (23 °C) by using two equal portions of the sample as a support for a glass microscope slide. The slide was loaded so that it remained always horizontal, and the displacements were measured with a cathetometer. THB show that for small compressions \( \Delta l \), the elastic modulus is

\[
G_m = \frac{2 \, \Delta P}{3} \left( \frac{l_0}{\Delta l} \right)
\]

where \( l_0 \) is the unloaded length of the gel column and \( \Delta P \) is the applied pressure. For finite compressions this relation must be replaced by

\[
G_m = \frac{2 \, \Delta P}{(x - 1/x^2)}
\]

where \( x = l/l_0 \) and \( l \) is the loaded length of the column.

To avoid ageing effects [18] the mechanical measurements were performed within 24 hours of sample preparation.

3. Results and discussion. — One of the essential parameters in the preparation of polyacrylamide gels is the cross-linking density [19] as determined by the ratio \( \text{bis/acylamide} \) (B/A). A set of samples with total polymer concentration \( c = 0.066 \) was prepared, having different B/A ratios, and their elastic moduli measured both mechanically and by light scattering. The results, plotted in figure 1, show that the zero frequency mechanical modulus \( G_m \) is a strong function of the cross-linking density, while the high frequency light scattering modulus \( G_l \) is practically independent of this parameter. For B/A < 10^{-2}, however, the light scattering spectra become non exponential, resembling in this respect other polymers in semidilute solution with poor solvents [8, 14]. Figure 1 indicates that the mechanical modulus is determined by the permanent cross-links, while the light scattering modulus is governed by the density of entanglements, which in turn depends only on the polymer concentration. For fixed total polymer concentration, an increase of the cross-linking density causes the mechanical modulus to increase rapidly until the light scattering value is nearly attained. At higher B/A ratios the increase in cross-linking density produces a partial phase separation [19]: the samples become opaque and the mechanical modulus drops. At lower total concentration \( c \), the onset of opalescence occurs at higher values of B/A. For the samples of figure 1 (\( c = 0.066 \) g cm^{-3}) opalescence became so marked that the intensity of the scattered light could not be reliably measured with the heterodyne technique for values of B/A greater than \( 3.3 \times 10^{-2} \).

This observation is relevant to the light scattering experiments of Wun and Carlson on PA gels [5]. These authors quote B/A ratios in excess of \( 6 \times 10^{-2} \) for samples of 5% nominal concentration. Multiple scattering in such gels is intense, and could be the cause of the non-exponential spectra observed by these authors, who also noted a strong angular dependence of the signal intensity. To check this latter point, a 6% gel was prepared with B/A = \( 2.67 \times 10^{-2} \) (i.e. with negligible multiple scattering) using a cylindrical cell to eliminate the need for the transmission and refraction corrections. The observed intensities must be multiplied by a factor sin \( \theta \) to account for the variation of the scattering volume with the scattering angle \( \theta \). In the observed range, between 116° and 60°, the signal intensity per unit scattering volume was found to be a constant within the experimental uncertainty.

The B/A ratios of the gels used in this experiment were chosen with regard to homogeneity and absence of opalescence, generally following the instructions given in the literature [17, 19]. The mechanical measurements were made on samples all with B/A ratio \( 2.67 \times 10^{-2} \). The elastic moduli \( G_m \) are shown on figure 2 on a log-log plot to reveal possible scaling law behaviour. Above \( c = 0.04 \) g cm^{-3}, the measured values fall within experimental error on a straight line with slope \( 2.55 \pm 0.17 \). The measurement of THB for their 5% sample is in good agreement with the present values, although this may be coincidental since these authors do not give details of their B/A
Fig. 2. — Logarithm of the elastic modulus $G$ (dyne cm$^{-2}$) vs logarithm of polymer concentration (g cm$^{-3}$). Light scattering results. ○ Mechanical measurements. * Mechanical measurements of reference [2]. The slope of $a$ is $2.35 \pm 0.06$; that of $b$ is $2.55 \pm 0.17$.

The error quoted is the standard deviation due to the scatter in the experimental points, each being weighted by the spread in the individual measurements making up a data point. Generally each point was an average of four individual measurements taken in different parts of the same sample. The principal source of error in $\eta_0$ comes from the measurement of the intensity, and is about 10%. Other sources of error, arising from ratio, nor is their definition of the concentration necessarily identical with our own. Their 2.5% sample, however, is more than ten times softer than suggested by extrapolation of this line; although we were unable to perform measurements at such a low concentration because of the extreme softness of the samples, our qualitative observations are in agreement with theirs. On account of the proximity of this elastic collapse at low concentrations, the point corresponding to the sample with $c = 0.0339$ was not used in the computation of the above scaling law line.

In contrast, the values of the elastic modulus measured by light scattering, $G_l$, also plotted on figure 2, show no sign of collapse at low concentrations. The B/A ratios used are shown in table I. Only the data from the samples giving exponential correlation spectra were used in the computation of the upper straight line of figure 2; the data points from the three highest concentrations were likewise neglected for this line, as there appears to be a systematic upwards deviation at high concentrations. The mean slope of the resulting curve is

$$a = 2.35 \pm 0.04.$$  

TABLE I

Polyacrylamide-water gels used for light scattering

<table>
<thead>
<tr>
<th>Sample</th>
<th>$w$ (g cm$^{-3}$)</th>
<th>$c$ (g cm$^{-3}$)</th>
<th>$B/A$</th>
<th>$D_e$ (cm$^2$ s$^{-1}$)</th>
<th>$G_l$ (dyne cm$^{-2}$)</th>
<th>$\eta_0$ (cP)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.174</td>
<td>0.183</td>
<td>6.7 $\times$ 10$^{-2}$</td>
<td>7.90</td>
<td>0.237</td>
<td>1.71</td>
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<tr>
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<td>0.116</td>
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<td>0.074</td>
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<td>0.072</td>
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<tr>
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<td>0.093</td>
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<td>0.036</td>
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<tr>
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<td>0.045</td>
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<td>3.81</td>
<td>0.0017</td>
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<tr>
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<td>8.93</td>
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<tr>
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<td>5.36</td>
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<tr>
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<tr>
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<td>4.66</td>
<td>0.0085</td>
<td>1.10</td>
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<td>3.48</td>
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<td>5.31</td>
<td>0.024</td>
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<td>0.0448</td>
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<td>0.0597</td>
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<td>4.62</td>
<td>0.015</td>
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<td>0.0807</td>
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<td>5.25</td>
<td>0.028</td>
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</tr>
<tr>
<td>24</td>
<td>0.1052</td>
<td>0.1090</td>
<td>2.7 $\times$ 10$^{-2}$</td>
<td>6.19</td>
<td>0.061</td>
<td>1.39</td>
<td></td>
</tr>
</tbody>
</table>

A typical B/A ratio

non exponential

non exponential

non exponential
the estimations of the concentration, \((\varepsilon'/\varepsilon)\);\(V/2\), and the
temperature are not greater than 5 \%, and the total
error in the relative measurement of the elasticity \(G_1\)
does not exceed 13 \%; this leads to a probable error in
the slope of 0.06. Our resultant estimate of the slope is therefore

\[ a = 2.35 \pm 0.06 \, . \]  

(11)

Although this slope is somewhat larger than indicated
by the scaling theory for good solvents (2.25)\([11, 12]\),
it should be pointed out that water is not a very good
solvent of polyacrylamide: specific viscosity measure-
ments \([22]\) yield a significantly weaker molecular
weight dependence than for polystyrene in benzene; furthermore, uncross-linked polyacrylamide, poly-
merized without the presence of bis generates a non-
exponential correlation function, which is charac-
teristic of a poor solvent \([8, 14]\).

Tricritical expansion theory \([13]\) predicts \(a = 3\) for
polymers in semidilute solutions with poor solvents.
One might conclude that the present observations
were made at a temperature intermediate between a
good solution and a theta solution. In figure 3 is shown

![Graph showing the temperature dependence of \(G_1/w^2\) for two samples, with \(w \cong 0.025\) and \(w \cong 0.30\); within experimental error the two sets of measurements are described by

\[ G_1/w^2 = f(w) \left( T - 170 \right) \]  

(12)

where \(T\) is expressed in K.

It was not possible to explore this relation to very
low temperatures since the range of supercooling was
limited to about \(-7^\circ\)C. The form of eq. (12) indicates
that the scaling exponent does not change notably
with temperature. Few data were found in the literature
with which to compare eq. (12). Measurements, of the
firmness (a quantity akin to the elastic limit) of a 12 \%
polyacrylamide gel have been reported \([23]\) indicating
a positive temperature dependence, but with a tem-
perature intercept of about 120 K. The results of refe-
rence \([7]\) show a spinodal temperature at 256 K, but
as noted above the position of the spinodal is sensitive
to the presence of salt in the solution.

Although the uncertainty associated with the slope
of the line through the measurements of \(G_m\) is larger
than that of \(G_1\) on account of the smaller number of
samples measured, the difference in slope is probably
real and reflects a change in the gel structure as the
concentration decreases. One expects the 4-functional
bis to be preempted soon after the start of the poly-
merization process, while the bifunctional acrylamide
polymerization proceeds more slowly. In dilute solu-
tions this will lead to many loose coils, with entan-
glements slipping easily and a consequent distribution
of relaxation times; by increasing the density of cross-
linking agent at low concentration the loose chains are
tied into the structure and the light scattering spectra
become exponential again. At high concentrations,
on the other hand, the congestion of entanglements
slows the rate of slipping to such an extent that the
entanglements are virtually permanent tie points. Such
a picture would explain the catastrophic fall in mecha-
nical modulus at low concentrations where the pro-
bability for two overlapping coils to be bridged by a
bis molecule becomes small.

Measurements were also made of the decay rates \(\Gamma\)
of the correlation functions. In agreement with THB,
\(\Gamma\) was found to be proportional to \(K^2\), \(K\) being the
light scattering vector, giving the collective motion
diffusion constant \(D_c = \Gamma/K^2\). The results are shown
in figure 4, again in a log-log plot as a function of
concentration. The values for the two samples
from THB are also plotted, on the assumption that
their spectra were obtained in the heterodyne rather
than the homodyne mode as the authors presumed.
For the non-exponential curves, which once again were
not used for the least squares fit, the points plotted on
the graph correspond to the first cumulant of the
correlation function. The least squares forced fit to
the data up to \(c = 0.12\) g cm\(^{-3}\) gives

\[ D_c = 2.8 \times 10^{-6} \, e^{0.65 \pm 0.03} \, \text{cm}^2 \, \text{s}^{-1} \]  

(13)

The exponent in eq. (13) is in agreement with the results
of Munch \textit{et al.} \([8]\) for the system ethyl acetate-
polystyrene in the semidilute range.

Scaling theory for good solutions predicts that the
screening length \(\xi\) of the collective motions varies
as \(\sim e^{-0.75}\), it being generally assumed that the solvent
viscosity \(\eta_0\) is a constant in the expression for \(D_c\):

\[ D_c = k_B T/6 \pi \eta_0 r \]  

(14)
The radius of the Stokes sphere, \( r \), in eq. (14) is related to the elementary fluctuating volume \( \xi^3 \) through

\[
\frac{4\pi}{3} r^3 = \xi^3. \tag{15}
\]

Thus \( D_e \) may be expected to scale as \( c^{0.75} \). Investigations of the translational diffusion coefficient \( D_t \) of water in similar gels [24, 25], however, indicate that \( \eta_0 \) may vary appreciably with gel concentration. Mohamed et al. [26] observe that the translational diffusion constant for sufficiently small molecules varies approximately as \( \frac{1}{3} \) in polyacrylamide gels; if this factor is used to account for the variation of \( \eta_0 \) with concentration, then combining eqs. (14) and (15) with the experimental data points for \( D_e \), one obtains

\[
\xi \propto c^{-0.80}. \tag{16}
\]

Although the above exponent should not be interpreted as a precise experimental result on account of the uncertainty in the correction factor for \( \eta_0 \), it is clear that this factor can significantly alter the value of the exponent describing the dependence of \( \xi \) obtained from light scattering measurements [8, 20].

Figure 4 also shows at concentrations higher than about 15% an abrupt departure from the initial linear dependence, concomitant with the excess stiffness observed in \( G_e \). In distinction to solutions of polystyrene [14, 27], no evidence was seen for a maximum in \( D_e(c) \). If it is assumed that this change in behaviour in \( D_e \) is also a result of changes in the solvent viscosity in eq. (14), one can determine \( \eta_0 \) by means of the equation suggested by de Gennes [12]

\[
G_i = A \xi^3 c^3 \tag{17}
\]

where \( A \), a number close to unity, has been set equal to one. Expression (18) is plotted in figure 5 as a function of concentration in a semilogarithmic plot. The fact that a straight line is observed, within experimental error, suggests that the knee observed in figure 4 is primarily a result of the free volume behaviour of \( \eta_0 \). The coincidence of this value with the macroscopic viscosity of water at 22 °C is probably not entirely fortuitous: it strongly suggests that not only does the screening parameter \( \xi \) possess scaling properties but also that its magnitude is physically significant.

4. Conclusions. — The observations presented here show that measurements of the elastic modulus of gels by light scattering \( (G_e) \) and by uniaxial compression \( (G_m) \) do not necessarily yield the same result. \( G_i \) depends principally on the polymer concentration, and, for the range of scattering vectors used here, is practically independent of the density of cross-linking in the gel. The near agreement with the scaling theory prediction for the concentration dependence confirms that the light scattering response is governed by the density of entanglements. The residual discrepancy between the predicted value of 2.25 for the concentration exponent and the measured value of 2.35 \( \pm 0.06 \), however, is probably real, and may result from the fact that water is not a good solvent. At high polymer concentrations the gels become stiffer than indicated by the scaling law.

The mechanical modulus, on the other hand, corresponds to a measurement over many seconds, and is governed by the density of permanent ties or...
cross-links. Increasing the cross-linking density at constant total polymer concentration causes $G_m$ to increase until its value nearly reaches $G_b$, at which point phase separation sets in.

The measurements of the collective motion diffusion coefficient $D_e$ yield a dependence on concentration with an exponent $0.65 \pm 0.03$, in agreement with the results of Munch et al. for another polymer system with an intermediate quality solvent. The knee observed in the plot of log $D_e$ vs log $c$, occurring for concentrations above 0.12 g cm$^{-3}$ can be accounted for by a variation of the solvent viscosity according to a free volume relation.

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