Collective diffusion of gels in a theta solvent
A.-M. Hecht, E. Geissler

To cite this version:

HAL Id: jpa-00209757
https://hal.archives-ouvertes.fr/jpa-00209757
Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Collective diffusion of gels in a theta solvent (*)

A.-M. Hecht and E. Geissler

Laboratoire de Spectrométrie Physique (**) Université de Grenoble I, B.P. 68, 38402 St Martin d'Hères Cedex, France

(Reçu le 12 juillet 1983, accepté le 20 octobre 1983)

Résumé. — On applique une pression extérieure à des gels de polyacrylamide dans la condition thêta, par l'intermédiaire d'une membrane semi-perméable, pour produire leur dégonflement. L'analyse du profil du gradient de concentration permet la mesure en fonction de la concentration, d'une part de la pression osmotique, d'autre part du coefficient de diffusion collectif $D$. Pour obtenir $D$, on suppose que le coefficient de friction $f$ entre le polymère et le solvant varie comme $c^m$ où $m$ est un paramètre ajustable. On montre que le meilleur accord est obtenu avec $m = 2$, comme le prévoit la théorie des lois d'échelle pour les solutions semidiluées de polymère en solvant thêta.

Abstract. — Experimental measurements are reported of the deswelling process in presence of an external applied pressure of polyacrylamide gels at theta conditions. Analysis of the profile of the concentration gradient enables the swelling pressure as a function of concentration to be deduced as well as the collective diffusion coefficient $D$. To obtain an explicit expression for $D$, the polymer-solvent friction constant $f$ is assumed to vary with the concentration as $c^m$, where $m$ is an adjustable parameter. It is found that the best fit is obtained for $m = 2.0$, in accordance with scaling theory for semi-dilute theta solutions.

Scaling theories have been successful in predicting the thermodynamic and hydrodynamic properties of semidilute solutions of polymers in good solvents. In theta solvents, the situation is more complicated: photon correlation spectra become non exponential [1] and therefore less amenable to unambiguous analysis. For small transfer wave vectors $k$, scaling theory predicts that the collective diffusion coefficient $D$ varies linearly with $c$, the polymer concentration [2]. While this behaviour has not so far been observed at the transfer wave vectors used in photon correlation spectroscopy, it has been shown to hold, for a limited concentration range, at much larger length scales [3].

Several years ago we attempted to remove the centre of mass motions, which are an inherent complication in these systems, by making photon correlation observations of cross-linked gels in the theta condition [4]. The resulting correlation functions were sufficiently close to exponentiality to allow the extraction of a single relaxation rate, which was found to be proportional to $K^2$. In contrast, the proportionality constant $D$ varied approximately as $c^{0.5}$ instead of as $c$ as expected.

In an attempt to elucidate this behaviour, we have applied a technique that we employed recently to investigate the friction coefficient $f$ in gels in presence of a good solvent [5, 6]. Here, we report measurements of the deswelling properties of polyacrylamide gels with methanol-water (25\%:75\% by volume) in the poor solvent region. As before, the analysis is based on the observation [7] that in the diffusion coefficient $D$ varied approximately as $c^{0.5}$ instead of as $c$ as expected.

$$D = (K_{osm} + \frac{3}{5} G)/f,$$

where $K_{osm}$ the osmotic modulus, and $G$, the shear modulus, have different scaling behaviours on deswelling.

The experiment consists of applying an external pressure via a piston and a porous membrane to the surface of a gel, thus causing uniaxial deswelling. The effect of the hydrostatic pressure on the thermodynamic properties is very small [8], and can be discounted. The resulting concentration gradient is accompanied by a refractive index gradient in the sample, and is observed by illuminating the sample with a set of diffraction fringes generated by a laser and a variable slit [5]. The profile of the concentration gradient (Fig. 1), measured as a function of time $t$ and...
Fig. 1. — Refractive index gradient \( \frac{dn}{dx} \) as a function of the distance \( x \) from the initial position of the piston, for time \( t = 1.518 \times 10^{-4} \) s. The conversion to \( \frac{dc}{dx} \) is made using \( \frac{dn}{dc} = 0.176 \) cm\(^3\) g\(^{-1}\). Each point on the graph represents one dark fringe in the diffraction pattern generated by the laser and the slit. The abnormally high value of the first point, which is a systematic feature of these profiles, is of uncertain origin, but may be associated with the deviations from flatness of the piston surface; results from this region were not used in the calculation of \( D \).

The applied pressure, yields three important pieces of information:

1) It is found experimentally that \( c \) is a function of \( z = x/\sqrt{t} \), where \( x \) is the distance of a given point in the gel from the position of the membrane at time \( t = 0 \). This observation allows the deswelling process to be written in the form of an ordinary differential equation, corresponding to the one dimensional motion of the system.

2) Integration of the curve \( \frac{dc}{dz} (z) \) gives the increment \( dz \) in concentration generated by the applied pressure. This is equivalent to a measurement of the swelling pressure as a function of concentration.

3) The diffusion coefficient is obtained from the equation of motion [6]

\[
- \frac{1}{2} \frac{d\phi}{dz} = \frac{d}{dz} \left\{ (1 - \phi) D(\phi) \frac{d\phi}{dz} \right\}
\]

which gives

\[
D = \frac{-z(\frac{dc}{dz})}{2 \left[ \frac{d^2c}{dz^2} \left( 1 - \frac{c}{\rho} \right) - \frac{1}{\rho} \left( 1 - (\rho - c) \frac{1}{D} \frac{dc}{dz} \right) \left( \frac{dc}{dz} \right)^2 \right]}
\]

(1)

where \( \phi = c/\rho \) represents the volume fraction of the polymer in the gel. Analysis of the shape of the curve, combined with an adjustable model for \( D(c) \), enables a self-consistent expression for \( D(c) \) to be found.

1. Experimental section.

The samples used here were prepared in the same way as in reference 4, except that, following the procedure of François and coworkers [9], 0.1 M NaCl was added to the solvent in order to minimize preferential absorption effects. The only observed result of this addition was to cause a slight deterioration in the quality of the solvent, and for this reason the experiments were carried out at 14 °C rather than 11.5 °C as in reference 4. This precaution is probably excessive : the effective theta region, as defined in the Daoud and Jannink scheme [10], extends, for the concentration used, by more than 10\(^{\circ}\) above and below the dilute solution definition of the theta temperature. The gels used here were all prepared at the concentration \( c_0 = 0.072 \) g cm\(^{-3}\). At no time was any phase separation observed.

In contrast with the previous deswelling experiments with good solvents [5, 6], two difficulties were encountered here which required extra precautions in the sample preparation. The first was the appearance of pronounced optical defects, caused by convection currents generated during the gelation process, which tended to blur the fringes, thus making measurements difficult. It was found that these defects could be greatly reduced by preparing the gels at 25 °C rather than at 18-20 °C. To obtain a clear smooth surface in contact with the membrane, the gels were extracted from their cells and reversed; in this way the irregularly polymerized free upper surface was removed from the crucial region of the imposed concentration gradient.

The second difficulty encountered was caused by the extreme tackiness of the gels prepared in the poor solvent : the gels tend to stick to the walls of the glass fluorescence cells, giving rise to spurious local concentration gradients and anomalous apparent values of \( D \). A palliative for this problem was found in using the methanol-water mixture without salt as the wetting liquid between gel and piston, but this was not sufficient to remove all doubt. The solution finally adopted for this problem consisted of using disposable polystyrene spectrophotometric cells to which the polyacrylamide does not adhere [11]; however, since these cells are of inferior optical quality, a refractive index matching method had to be used in order to reduce spurious deviations in the fringes.

To achieve the conversion from the refractive index gradient to the concentration gradient, the value of \( \frac{dn}{dc} \) was taken to be [4] 0.176 cm\(^3\) g\(^{-1}\).

The shear modulus of the gel \( G_0 \) was measured in three separate ways.

1) By observation of the fundamental torsional mode in a gel held in a cylindrical glass former [12]: using a laser source and a small sliver of gold-plated
glass cover-slide embedded vertically into the top surface of the gel, the sample was fixed concentrically on the axis of a small DC electric motor driven by a variable frequency oscillator. At the resonance condition (ca. 100 Hz), the reflection of the laser beam by the mirror expanded into a straight line that defines the displacement of the gel (Fig. 2).

2) A similar observation of the quasi-longitudinal fundamental mode that occurs in a gel held in a rectangular cell of square cross-section, when only the top surface is free [13]. In this case the small mirror is placed flat on the free surface of the gel, to which it adheres.

3) By direct observation of the deformation of the gel, extracted from its mould, when a uniform pressure is applied to its upper surface.

As might be expected for small deformations at low frequency, these three measurements gave consistent values of $G_0$, the shear modulus of the gel at its preparation concentration, $c_0 = 0.072$ g cm$^{-3}$, namely,

$$G_0 = (1.26 \pm 0.07) \times 10^4 \text{ dynes cm}^{-2}. \quad (2)$$

2. Static properties.

We adopt as a first step the theory of gel swelling described by Flory [14], extended to a theta system (interaction parameter $\chi = \frac{1}{2}$). Three concentrations are defined, namely $c$, the current average gel concentration, $c_0$, the reference concentration at which the gel is prepared, and $c_e$, the concentration of isotropic swelling equilibrium with the solvent. This last condition is met when the swelling pressure of the gel, $\Pi$, is zero, i.e. when

$$\Pi = \frac{RT}{3 v_1} \left( \frac{c^3}{\rho} \right) - G_0 \left[ \left( \frac{c}{c_0} \right)^{1/3} - \frac{c_e}{c_0} \right]$$

$$= 0. \quad (3)$$

In this expression, $v_1$ is the molar volume of the solvent, $\rho$ the density of the pure polymer, and $G_0$ the shear modulus of the gel in the unperturbed state ($c_0$). Equation 3 is of unusual interest, since all the quantities are measurable and no adjustable parameter is involved.

The experimental procedure consists of preparing the gel samples at concentration $c_0$ in an optical cell of square cross-section. Deswelling takes place subsequently in the same cell in such a way that the gel dimension perpendicular to the motion is constant. If the direction of motion is designated by the $x$-axis, then the expansion factors of the gel along each of the three directions are

$$\alpha_x = c_0/c, \quad \alpha_y = \alpha_z = 1, \quad (4)$$

and the equilibrium swelling pressure exerted on the piston in contact with the gel can be written still in the Flory formalism as

$$\Pi = G_0 \left\{ \left[ \left( \frac{c}{c_0} \right)^{1/3} \right] - \frac{c_e}{c_0} \right\} \left( \frac{c}{c_0} \right)^3 - \frac{c_0}{c} + \frac{c}{2c_0} \right\}. \quad (5)$$

On account of the one-dimensional geometry defined by equation 4, the exponent of the third term in equation 5 is unity, instead of the more familiar form $(c/c_0)^{1/3}$ which applies to isotropic swelling.

Comparison of the measured values of $G_0$, $c_e$, $c_0$ and $\Pi(c)$ for our samples at 14°C permits an estimate of the validity of equation 5. The value of $c_e$ is determined by measuring the weight of a sample allowed to come to equilibrium with the solvent at the working temperature with the dry weight of the same sample, found to be 0.055 g cm$^{-3}$. On the basis of equation 5, using three applied pressures (58, 108 and 208 g cm$^{-2}$), and the corresponding values of $c$ obtained from integration of the concentration gradient curves (0.095, 0.111 and 0.142 g cm$^{-3}$, respectively), one obtains

(Flory) $G_0 = (2.15 \pm 0.20) \times 10^4$ dynes cm$^{-2}$. \quad (6)

The terms $c_i/c_0$ and $c_e/c_0$ appearing in equations 3 and 5 arise from the well known logarithmic term in Flory's expression for the entropy of a gel [14]. If, alternatively, we adopt the procedure advocated by certain authors [15] which consists of ignoring this term, then expressions 3 and 5 simplify, and the value of $G_0$ becomes

$$G_0 = (1.41 \pm 0.14) \times 10^4 \text{ dynes cm}^{-2}. \quad (7)$$

In view of the better agreement between the result 7
and the direct experimental measurement of $G_0$ given in equation 2, we shall base our calculations on the simplified formula without the logarithmic term, namely

$$II = G_0 \left( \frac{c}{c_0} \right)^{1/3} \left( \frac{c}{c_0} \right)^3 - \frac{c_0}{c} \right].$$

(8)

It is important to emphasize that the above agreement is not sufficient to prove that the logarithmic term does not exist, because the rôle played by the inhomogeneities in the gel remains undetermined. The existence of such inhomogeneities can be ascertained by comparing the supposedly equal terms on the right hand side of equation 3: the first term, taking for the molar volume of the methanol-water saline solution $v_1 \approx 24 \text{ cm}^3$, is $2.2 \times 10^4 \text{ dynes cm}^{-2}$, while the second is equal to $1.3 \times 10^4 \text{ dynes cm}^{-2}$. For the equilibrium condition of equation 3 to hold, the osmotic pressure term must clearly be smaller than its theoretical value. Such a discrepancy is to be expected when inhomogeneities are present [16].

In figure 3 is shown the theoretical fit of equation 8 to the experimental observations of the swelling pressure, plotted on a double logarithmic scale. This curve allows a comparison with some earlier results on a similar system [4, 17], in which the longitudinal osmotic modulus $M_{os} (= K_{os} + \frac{4}{3} G)$ was measured using dynamic light scattering. $M_{os}$ is the elastic modulus encountered by a plane osmotic wave, corresponding to a movement whose geometry is defined by equation 4. Thus, from equation 8, at the reference concentration $c = c_0$, one obtains from the uniaxial swelling pressure $II$

$$M_{os} = c \frac{dII}{dc}$$

$$= G_0 \left[ 3 \left( \frac{c}{c_0} \right)^{4/3} + 1 \right].$$

(9)

In the present case this gives

$$M_{os}/G_0 = 7.15.$$  

(10)

The above value is in marked disagreement with the measurements of reference 17, for which the ratio $M_{os}/G_0$ was found to be roughly 2. It should be recalled for comparison that in the good solvent case [6], satisfactory agreement was obtained between the values of $M_{os}$ derived from analogous swelling pressure measurements and the value of $M_{os}$ directly observed by light scattering. The discrepancy between these two measurements for the poor solvent case thus lies well outside experimental error; in the next section we discuss a possible explanation for this effect.

In conclusion of this section, in view of the simplifications of the Flory theory adopted here, the shear modulus of the gels measured by osmotic swelling agrees tolerably well with the direct measurement.

In other words, the system behaves as if it were homogeneous. However, the theoretical contribution of the osmotic pressure is too high for equation 3 to balance. Such behaviour can be expected if inhomogeneities are present in a form which reduces the effective concentration of the gel, but does not contribute elastically or osmotically to the overall gel properties.

3. Dynamic properties.

Analysis of the deswelling profile gives information on the dynamic process. In reference 5 it was shown that the reduced first moment of the concentration gradient

$$\frac{M_i}{c_0} = \frac{1}{c_0} \int_0^\infty (z - z_0) \frac{dc}{dz} dz$$

(11)

was equal to the experimentally observed rate of advance of the piston, $z_0$, where, as before, $c_0$ is the concentration of the unperturbed gel. Within experimental error, the same equality was found to hold for the present samples.

To extract the diffusion coefficient from the concentration gradient curves, one must return to equation 1. Since this equation is not in an explicit form, some kind of self-consistency condition must be applied to obtain a solution. Following reference 6 we write the diffusion coefficient $D$ in the form

$$D = M_{os} f$$

(12)

where $f$, the polymer-solvent friction coefficient, is assumed to have the form

$$f = f_0 \left( \frac{c}{c_0} \right)^m.$$  

(13)
In a theta solvent, the scaling theoretical value [2] of $m$ is 2. The fitting procedure consists of using a trial value of $m$ and $f_0$ and inserting the appropriate values of $c$, $dc/dz$, and $d^2c/dz^2$ from various points along the concentration profile, such as shown in figure 1. Figure 4 shows the results obtained from two different concentration profiles obtained at separate times (open and filled circles), using $m = 2$. The continuous line was calculated from equations 12 and 13 taking $m = 2.0$, and selecting the vertical shift factor $f_0$ to obtain coincidence with the median of the experimental points. Changing the value of $m$ from 2.0 causes the sequence of points and the theoretical line to diverge over this concentration range, and the fit becomes markedly poorer.

For comparison with the above results, the value of $D$ measured by photon correlation spectroscopy in the unperturbed sample at the same temperature is shown in figure 4 as an asterisk, with an error bar corresponding to the experimental uncertainty. The agreement between the directly observed value and that obtained using the above fitting procedure is satisfactory.

It is relevant to note that the properties of these gels appear to depend on their preparation temperature. At lower temperatures convection currents during gelation cause weak but highly visible refractive index gradients in different parts of the sample. This effect, which is probably a result of the relatively poor thermal conductivity of the mixed solvent used here, is associated with rather small concentration differences, and is not therefore expected to affect measurably the thermodynamic parameters of the gel. On the other hand, there does seem to be a marked relation between the temperature of preparation and the elastic moduli of the gels: both $M_\infty$ and $D$ were smaller (by a factor of about 2) in the samples of reference 4 than reported here; the former were prepared much closer to the theta temperature. It follows that the quantitative comparison made by the authors elsewhere [17] between $M_\infty$ in the gels of reference 4 and the shear modulus of similar gels made at a higher temperature is unwarranted.

The fact that the exponent $m$ in equation 13 is found to coincide with the scaling value of 2 can be interpreted as supporting the conclusion of the previous section, namely that the microscopic inhomogeneities present in this system are apparently inert, playing little active part in the linear-response thermodynamic and hydrodynamic characteristics of the gel.

In conclusion, the gels in the theta region investigated here display a concentration dependence of the diffusion coefficient which is consistent with the predicted scaling behaviour for theta solutions at small transfer wave vectors [2], provided that in addition, account is taken of the variation upon deswelling of the shear elasticity associated with the permanent cross-links.

References


