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Classification

Physics Abstracts

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Translational and collective Diffusion in semi-dilute gels

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Résumé. — Les coefficients de diffusion translationnels et collectifs sont comparés dans des gels aqueux de polyacrylamide. Nous concluons que :

- a) la viscosité du solvant ne dépend pas de la concentration du polymère ;
- b) les mesures dynamiques de diffusion de lumière ne donnent les exposants des lois d'échelle qu'après avoir tenu compte de l'écoulement du solvant et des interactions hydrodynamiques résiduelles.

Abstract. — A comparison is made between measurements of the translational and collective diffusion constants in polyacrylamide-water gels. We conclude that :

- a) the solvent viscosity does not depend on polymer concentration, and
- b) scaling exponents can be deduced from dynamic light scattering measurements only after correction for solvent displacement and residual hydrodynamic interactions.

The properties of polymer solutions in the concentration range where the polymer molecules overlap (the semi-dilute regime) are described by a screening or correlation length ξ [1, 2]. Using scaling arguments de Gennes [3] has shown that the static and dynamic behaviour of ξ are the same, and in particular, in a good solvent ξ^{-1} should vary as $c^{3/4}$, where c is the weight of polymer dissolved in one cubic centimetre of solution. Neutron elastic scattering measurements of the concentration dependence of ξ [1], as well as measurements of the longitudinal elastic modulus

$$E \propto k_B T / \xi^3 \quad (1)$$

(where k_B is Boltzmann's constant and T the absolute temperature) by mechanical [4, 5] and inelastic light scattering methods [6] confirm that within experimental error this scaling relation is valid for the static case. In contrast, observations by inelastic light

scattering [5, 6, 7] and, more recently, inelastic neutron scattering [8], of the collective motion diffusion constant

$$D_c = \frac{k_B T}{6 \pi \eta \xi} \quad (2)$$

(where η is the solvent viscosity) yield exponents which are consistently smaller than 0.75.

We have previously attempted to explain this discrepancy in terms of a concentration dependent solvent viscosity [6], presumably caused by the slowing of solvent molecular motions at an adsorbing surface [9, 10]. Other authors call into question the equivalence between the dynamic and the static behaviour [11, 12], and connect the phenomenon with similar discrepancies in the dilute and the individual chain regimes [13, 14].

In this letter we describe measurements to compare the translational diffusion constant D_t of the solvent with the collective diffusion constant D_c in the same gel. If the solvent viscosity is affected by the presence

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of the polymer it should induce a corresponding change in the translational diffusion constant

$$D_t = \frac{k_B T}{6 \pi \eta a} \quad (3)$$

where a , the radius of the diffusing water molecule, may be expected not to depend on concentration. It is well known that D_t/D_0 , where D_0 is the diffusion constant of the pure solvent, is concentration dependent [15, 16] as well as temperature dependent [17].

Firstly however, it should be mentioned that there is an important difference between translational and collective diffusion in a gel : in the former the solvent alone diffuses while the polymer remains, on average, stationary and there is therefore no relative displacement ; in the latter the motion of a polymer segment induces a counter-motion in the solvent, since the process occurs at constant volume :

$$\phi \dot{\mathbf{r}} + (1 - \phi) \mathbf{u} = 0 \quad (4)$$

where ϕ is the volume fraction of polymer, \mathbf{r} the position of the polymer segment and \mathbf{u} the solvent displacement velocity. The equation of motion of the polymer segment in the gel is [3]

$$\Phi(\dot{\mathbf{r}} - \mathbf{u}) = -EK^2 \mathbf{r} \quad (5)$$

where Φ is the friction constant and \mathbf{K} the wave-vector. Thus writing

$$D_c = \frac{E}{\Phi} \quad (6)$$

one obtains an observed collective diffusion constant

$$\begin{aligned} D_c^{\text{obs}} &= D_c(1 - \phi) \\ &= D_c \left(1 - \frac{c}{\rho_p}\right) \end{aligned} \quad (7)$$

where ρ_p is the density of the polymer in the dissolved state and D_c is as in eq. (2). Neglect of the factor $(1 - \phi)$ can cause a serious discrepancy in the apparent value of the scaling exponent for D_c . For example, for a polymer with $\rho_p = 1$ in a good solvent ($D_c \propto c^{0.75}$) the apparent collective diffusion constant in the range $0.01 < c < 0.1$ gives a reasonable approximation to a straight line in a log-log plot but has an average slope of about 0.71.

In figure 1 are shown the measured values of D_t/D_0 for water in polyacrylamide gels as a function of polymer concentration at 300 K. The gels were prepared at various concentrations as described in reference [6] and the measurements made with a nuclear spin echo technique [18] in the presence of a steady magnetic field gradient of about 0.5 G/cm. The resonance frequency was 32 MHz. Because the observations were all made at long times (> 10 ms) after the initial $\pi/2$, pulse, the residual dipolar interactions between protons on the polymer chains cancel out

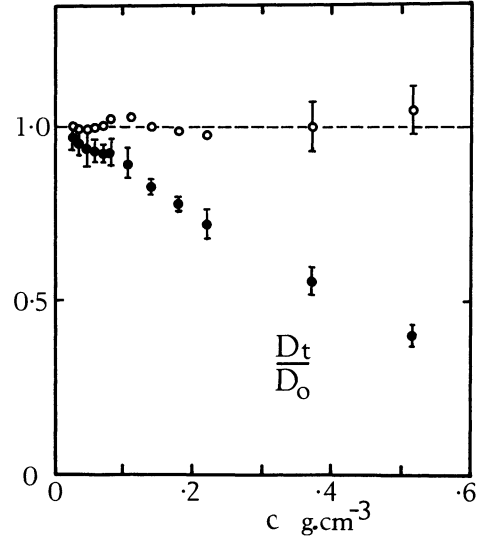


Fig. 1. — Relative translational diffusion constant D_t/D_0 of water in polyacrylamide gels as a function of polymer concentration at 300 K (filled circles) ;

$$\text{open circles : } \frac{D_t}{D_0(1 - 1.6 \phi)}.$$

The measurements were made using pulsed magnetic resonance at 32 MHz in a magnetic field gradient. The density ρ_p of polyacrylamide is taken as 1.345 g.cm^{-3} in the relation $\phi = c/\rho_p$.

their contribution to the nuclear magnetic resonance signal, leaving only the signal from the protons of the diffusing water.

The experimental points of figure 1 fit a curve of the form

$$\frac{D_t}{D_0} = 1 - f\phi \quad (8)$$

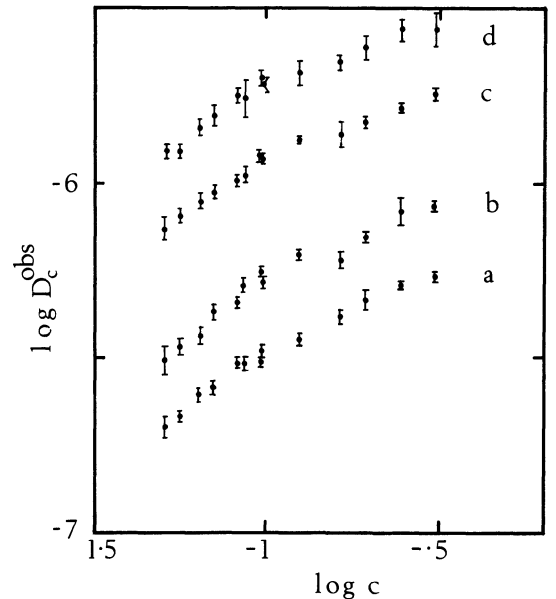


Fig. 2. — Logarithm of measured collective diffusion coefficient D_c^{obs} obtained by light scattering versus $\log c$, where c is in g.cm^{-3} and D_c^{obs} in $\text{cm}^2.\text{s}^{-1}$; a 284.5 K; b 294.5 K; c 324 K; d 351 K. The error bars shown are standard deviations, each point being an average of four measurements.

where f is about 1.6 at this temperature (taking $\rho_p = 1.345$ for polyacrylamide). At lower temperatures the straight line becomes steeper, corresponding to larger f values. If the observed variation of D_i/D_0 were solely the result of a change in solvent viscosity, the total correction factor to be applied to the collective diffusion coefficient (eq. (2)) would become

$$(1 - \varphi)(1 - f\varphi) \simeq 1 - (1 + f)\varphi. \quad (9)$$

Figure 2 shows the experimental values of $\log D_c^{\text{obs}}$ versus $\log c$ for four different temperatures, each set of data displaying marked departure from linearity (negative curvature). If however the correction factor 9 is applied to these data, with $f \simeq 1.6$, positive curvature is generated. Acceptable linearity is obtained in the whole concentration range with a total correction factor $(1 - \alpha\varphi)$ only if α lies close to 1.7. The values of $D_c^{\text{obs}}/(1 - \alpha\varphi)$ with $\alpha = 1.67$ are shown in figure 3 in a double logarithmic representation.

Comparison of expression (9) with D_i and D_c^{obs} shows that these results are not compatible with a solvent viscosity varying more strongly than by a factor $(1 - 0.67\varphi)^{-1}$. A more severe limit may be placed on the possible viscosity variation by compar-

ing the dependence of $D_i(c)$ with the calculations of Wang [15] for an analogous case, self-diffusion of a liquid in the presence of large slowly moving obstacles : unscreened hydrodynamic interactions give rise to a reduction factor $(1 - f'\varphi)$ for the diffusion coefficient, where f' , which depends on the geometry, has a minimum value of 1.5. Application of this result to the present case limits the possible fractional change in viscosity to about $\varphi/10$.

Our conclusions are as follows :

1. The observed variation of D_i/D_0 is not caused by concentration dependence of the solvent viscosity, and is therefore hydrodynamic in origin. The observed variation at 300 K is in reasonable agreement with the calculations of Wang [15].

2. The presence of the solvent displacement factor $(1 - \varphi)$ in light scattering measurements makes it necessary to work with very low polymer concentrations, and hence large molecular weights, in order to obtain dynamic scaling exponents in the semi-dilute regime that are comparable with the theory of de Gennes.

However, the factor $(1 - \varphi)$ alone is not sufficient in the present case to account for all of the observed deviation of D_c^{obs} from linearity in a double logarithmic plot. The data suggest a total correction factor $(1 - \alpha\varphi)$ with $\alpha \simeq 1.67$. This residual difference may come from incomplete screening of the backflow interactions [3], and would therefore be expected to vanish at high polymer concentrations.

It should be remarked that similar considerations apply also to the high frequency individual chain modes. As the hydrodynamic interactions are less screened at high wave vectors, dynamic scaling exponents will be affected.

3. The slopes of the straight line fits of $\log D_c^{\text{obs}}/(1 - \alpha\varphi)$ vs. $\log c$ shown in figure 3, with $\alpha = 1.67$ are

T K	Slope
284.5	0.751 ± 0.013
294.5	0.755 ± 0.035
324	0.685 ± 0.019
351	0.666 ± 0.026

While the slopes corresponding to the lower temperatures are in reasonable agreement with the expected exponent 0.75, there is a significant departure at the two higher temperatures. We cannot exclude the possibility of appreciable ionization of the water [19] or polyelectrolyte-like behaviour [20] at elevated temperatures due to partial hydrolysis of the acrylamide. To avoid this complication it would clearly be desirable to make similar observations in a non-polar system.

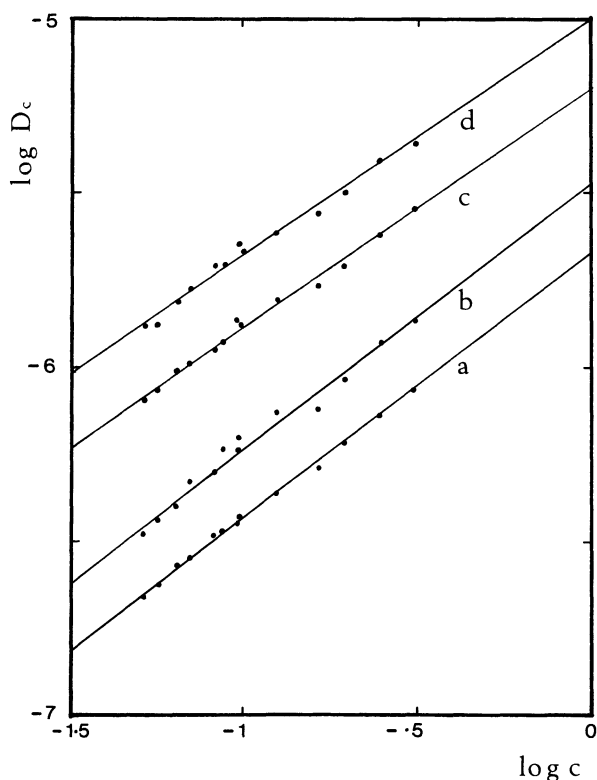


Fig. 3. — Logarithm of $D_c = D_c^{\text{obs}}/(1 - 1.67\varphi)$ ($\text{cm}^2 \cdot \text{s}^{-1}$) vs. $\log c$ ($\text{g} \cdot \text{cm}^{-3}$) at four temperatures. The straight lines shown are the least square fits to all the data points at each temperature.

a 284.5 K	$\log D_c = -5.676 + 0.75 \log c$
b 294.5 K	$\log D_c = -5.475 + 0.755 \log c$
c 324 K	$\log D_c = -5.200 + 0.685 \log c$
d 351 K	$\log D_c = -5.007 + 0.666 \log c$

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References

- [1] DAUD, M., COTTON, J. P., FARNOUX, B., JANNINK, G., SARMA, G., BENOIT, H., DUPLESSIX, R., PICOT, C. and DE GENNES, P. G., *Macromolecules* **8** (1975) 804.
 - [2] DAUD, M. and JANNINK, G., *J. Physique* **37** (1976) 973.
 - [3] DE GENNES, P. G., *Macromolecules* **9** (1976) 587 and 594.
 - [4] BELKEBIR-MRANI, A., Thesis, Strasbourg (1976).
 - [5] MUNCH, J. P., CANDAU, S., HERZ, J. and HILD, G., *J. Physique* **38** (1977) 971.
 - [6] HECHT, A. M. and GESSLER, E., *J. Physique* **39** (1978) 631.
 - [7] ADAM, M., DELSANTI, M. and JANNINK, G., *J. Physique Lett.* **37** (1976) L-53.
 - [8] RICHTER, D., HAYTER, J. B., MEZEI, F. and EWEN, B., *Phys. Rev. Lett.* **41** (1978) 1484.
 - [9] ZIMMERMAN, J. R. and BRITTIN, W. E., *J. Phys. Chem.* **61** (1957) 1328.
 - [10] WOESSNER, D. E. and ZIMMERMAN, J. R., *J. Phys. Chem.* **67** (1963) 1590.
 - [11] JASNOW, D. and MOORE, M. A., *J. Physique Lett.* **38** (1977) L-467.
 - [12] DAUD, M. and JANNINK, G., *J. Physique* **39** (1978) 331.
 - [13] ADAM, M. and DELSANTI, M., *Macromolecules* **10** (1977) 1229.
 - [14] MUNCH, J. P., LEMARÉCHAL, P., CANDAU, S. and HERZ, J., *J. Physique* **38** (1977) 1499.
 - [15] WANG, J. H., *J. Amer. Chem. Soc.* **76** (1954) 4755.
 - [16] DERBYSHIRE, W. and DUFF, I. D., *Faraday Discuss. Chem. Soc.* **57** (1974) 243.
 - [17] VOGIN, R., Thèse de troisième Cycle, Grenoble (1974).
 - [18] ABRAGAM, A., *The Principles of Nuclear Magnetism* (Oxford University Press) 1961, Ch. 8.
 - [19] WANG, J. H., *J. Phys. Chem.* **58** (1954) 686.
 - [20] DE GENNES, P. G., PINCUS, P., VELASCO, R. M. and BROCHARD, F., *J. Physique* **37** (1976) 1461.
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