Self-diffusion of water in gelatin gels:
2. Quasi-elastic neutron scattering data

Yu. B. Mel'nichenko
The Institute of Macromolecular Chemistry, Academy of Sciences Ukraina, Khar'kov Road 48, 252 160 Kiev, USSR

and L. A. Bulavin
Physics Department, Kiev State University, Glushkov Street 6, 252127 Kiev, USSR

(Received 9 April 1990; revised 8 June 1990; accepted 28 August 1990)

The self-diffusion of water in gelatin gels of different concentrations was studied by quasi-elastic neutron scattering (QENS). The total self-diffusion coefficients and their components corresponding to the contributions from collective (Lagrange type) and single-particle (Frenckel type) mechanisms of molecular motions were determined. From the data obtained one can conclude that the self-diffusion of free water proceeds by a single-particle mechanism. The growth of a bound water fraction in the system with gelatin leads to the gradual pumping of single-particle diffuse modes into collective modes. Purely collective diffuse modes accompanied by complete retardation of macroscopic water diffusion are observed at relatively low gelatin volume fractions ($\varphi \sim 0.4$) compared to the expected volume fractions ($\varphi \sim 0.7$) at which water binding to polymer by hydrogen bonds would lead to the same effect. This is associated with the fact that gels show the microspace effect favourable for the existence of bound water.

(Keywords: self-diffusion; gelatin; gels)

INTRODUCTION

The fundamental theoretical and experimental investigations of physical properties of gels and in particular the transport of small particles through the gel, have recently acquired special significance. It has been established that gels are an analogue of a porous 'sponge' with pore sizes corresponding to the distance between neighbouring crosslinks of a polymer network[1,2]. The model of self-diffusion of Brownian particles through a system of randomly distributed stationary obstacles (scattering centres) was used to theoretically describe the mobility of small particles in a gel[3,4]. Using this model based on the concept of an effective medium, small concentrations of obstacles can limit the mobility of particles due to two physical effects. First, direct scattering can take place, and second, hydrodynamic self-interaction of particles can occur due to reflections of hydrodynamic perturbations from the scattering centres. With the growth of obstacle concentrations (volume fraction of monomers) the gel structure may exert considerable influence on the mobility of particles. A densely crosslinked network can result in 'caging' when particles move along paths limited by gel pore sizes (ξ) and a 'microspace effect' can occur[5]. This effect is shown as cooperative behaviour between particles over three dimensions of an order of ξ and complete retardation of diffusion. It should be noted that the existing theories cannot quantitatively describe the above effects.

In this work we investigate the self-diffusion of a solvent (water) in gelatin gels obtained from aqueous gelatin solutions when temperature falls below 30°C. Because of numerous polar and ionic groups present in gelatin macromolecules, some of the water molecules are bound to the polymer by hydrogen bonds[6]. In our previous work[7] we investigated the macroscopic self-diffusion of water molecules in gelatin gels of different concentrations. It was established that this process was determined by the effect of a hydrodynamic self-interaction. The relationship between the self-diffusion coefficient of a solvent and the volume fraction of a polymer is described by the root-mean-square law predicted by theory[3,4], with the activation energy being close to that of bulk water. The object of the present work is to study the self-diffusion of water in gelatin gels by the quasi-elastic neutron scattering (QENS) technique which enables the molecular motions to be followed at ultimately small observation times. In such an experiment the total self-diffusion coefficient of water, as well as its components corresponding to contributions from free and bound water, can be determined. The data obtained are compared with the results of earlier macroscopic measurements.

EXPERIMENTAL

Samples

For gel preparation, gelation of a photographic grade was used. The viscosity of a 10% aqueous solution at 40°C is 2×10^{-2} N m^{-2} s, with pH 6.2, and an isoelectric point of 4.7. The molecular weight distribution of this gelatin determined on a Du Pont 88000 liquid chromatograph is given in *Figure 1*. It can be seen that gelatin possesses a multimodal molecular weight distribution, the main peak of which corresponds to the so-called α-gelatin with $M_w \sim 10^5$. The peaks corresponding to β-gelatin with $M_w \sim 2 \times 10^5$ and to microgels with $M_w \sim 10^6$ are also clear. The samples were prepared in the following way. Gelatin was first swollen in the appropriate amount of distilled water (with 11% residual water in the gelatin)

0032-3861/91/183295-04

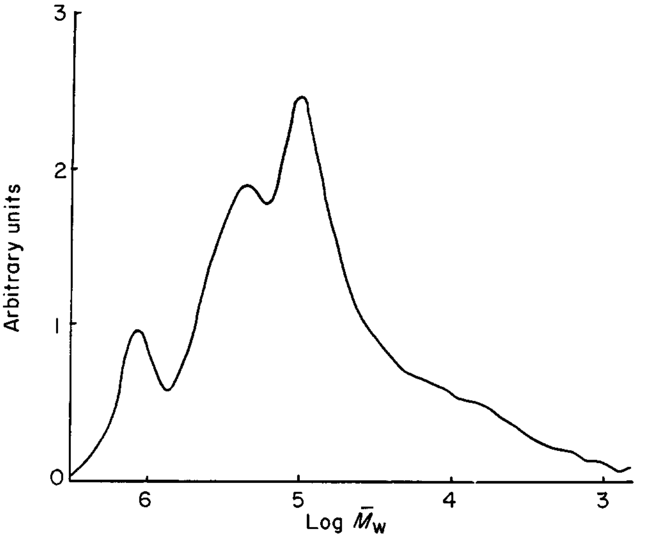

Figure 1 Molecular weight distribution of gelatin

for 2 h. Then the mixture was heated to 45°C and stirred thoroughly until dissolution was complete. The volume fraction of the polymer was calculated assuming the additivity of water and gelatin volumes, the density of the latter was taken as 1.465 g cm^{-3}. The solution was poured into a flat aluminium cell (160 mm diameter), with the temperature being maintained at 16 ± 0.1°C. Before measurement the gel obtained was aged for 12 h. The gelatin and gel preparation conditions were the same as those used in our previous work[7].

Procedure

QENS measurements were performed using a multidetector time-of-flight spectrometer on a research WWR reactor at the Nuclear Research Institute, Academy of Sciences, Kiev. A schematic diagram of the experimental unit and its detailed description are given elsewhere[8]. In the experiment a monochromatic neutron beam with energy $E_0 = 12.97$ meV was used. The absolute energy resolution of the spectrometer was 0.66 meV. The neutron spectra were recorded over a range of scattering angles ($\theta = 9.5$–$101.3°$) and analysed with a multichannel time-delay analyser. Due to the small thickness of gel samples (0.8 mm) in the cell, correlations for multiple scattering could be neglected, since the fraction of scattered neutrons did not exceed 20% of the incident beam intensity. All the measurements were performed at 16°C.

RESULTS AND THEORETICAL INTERPRETATION

Typical QENS spectra for a gelatin gel with $\varphi = 0.129$ at different scattering angles are given in *Figure 2*. Similar spectra were recorded for gels with $\varphi = 0.031$, 0.063, 0.199, 0.274 and 0.353. The information on relatively low-energy diffuse motions of water molecules is contained in the energy broadening (ΔE) of quasi-elastic peaks measured at different values of wave vector transfer:

$$|\kappa| = 4\pi\lambda^{-1}\sin(\theta/2)$$

where λ is the neutron wavelength. The contribution to ΔE from the scattering on gelatin macromolecules can be neglected, since the self-diffusion coefficient is several orders lower than that of the solvent[9]. To find ΔE from the experimental data, taking into account the influence of the spectrum corresponding to inelastic scattering, we used the procedure given elsewhere[10]. The plots of ΔE as a function of κ^2 for several samples are given in *Figure 3*. The behaviour of $\Delta E(\kappa^2)$ is greatly dependent on the volume fraction of gelatin in a gel. When $\varphi \ll 1$, the linear section of the plot is observed only at small κ^2. (The plot $\Delta E(\kappa^2)$ for the smallest investigated gel concentration $\varphi = 0.031$ is very similar to that of pure water given in reference 10.) The linear section becomes considerably extended with growing φ, and at high gelatin concentrations $\Delta E(\kappa^2)$ is linear practically over the entire range of κ^2.

The observed effects may be explained in terms of time scales of molecular motions in a fluid (rapid single-particle and slower collective motions)[11]. The total

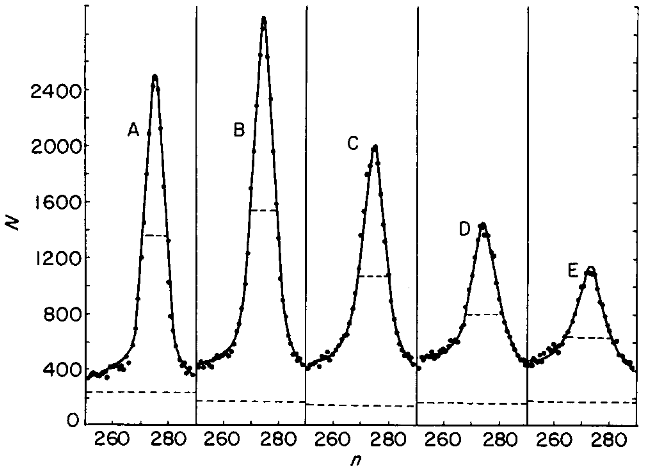

Figure 2 QENS spectra for the gelatin gel with $\varphi = 0.129$ at different scattering angles: (A) 25.1°; (B) 40.1°; (C) 54.7°; (D) 70.2°; (E) 86.1°. The number of time-delay analyser channels (8 μs in width) corresponding to the energy of scattered neutrons is n; N is the number of neutrons recorded in an nth channel

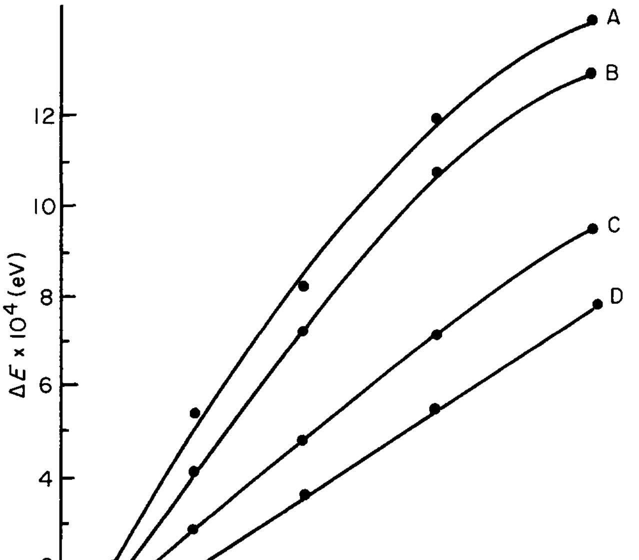

Figure 3 Energy broadening of a quasi-elastic peak as a function of κ^2 at different gelatin concentrations: (A) 0.031; (B) 0.063; (C) 0.129; (D) 0.353

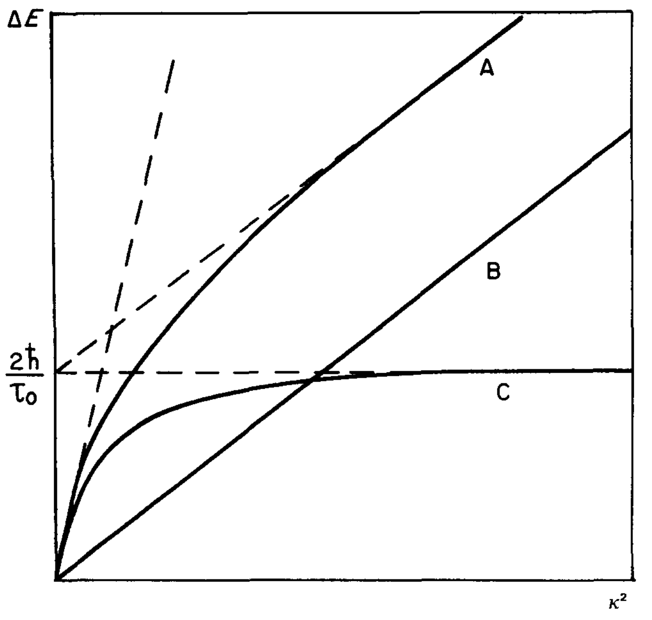

Figure 4 Qualitative patterns of $\Delta E(\kappa^2)$: (A) $\Delta E = \Delta E_{\text{coll}} + \Delta E_{\text{s-p}}$; (B) ΔE_{coll}; (C) $\Delta E_{\text{s-p}}$. Asymptotics are designated by broken lines

broadening of a quasi-elastic peak can be presented as:

$$\Delta E = \Delta E_{\text{coll}} + \Delta E_{\text{s-p}} \tag{1}$$

where ΔE_{coll} and $\Delta E_{\text{s-p}}$ are the contributions to the broadening from collective (Lagrange) and single-particle (Frenckel) components of diffuse molecular motions, respectively. Taking both contributions into consideration, the observed broadening of the quasi-elastic peak can be presented as[12,13]:

$$\Delta E = 2\hbar D_{\text{coll}}\kappa^2 + \frac{2\hbar}{\tau_0}\left[1 - \frac{\exp(-2W)}{1 + D_{\text{s-p}}\kappa^2\tau_0}\right] \tag{2}$$

where the first term is linear with respect to κ^2 and the second term corresponds to collective and single-particle mechanisms of molecular motions characterized by the corresponding self-diffusion coefficients D_{coll} and $D_{\text{s-p}}$, respectively. The term $\exp(-2W) \approx 1$ is the Debye–Waller factor[14], and τ_0 is the time of molecule equilibrium between two jumps (residence time).

The qualitative patterns of $\Delta E(\kappa^2)$ described by equation (2) and its components (the first and second terms on the right-hand side of equation (2)) are given in *Figure 4*. As shown in *Figure 4*, $\Delta E(\kappa^2)$ consists of the sum of a function linear for all κ^2 which corresponds to the collective contribution and a more complex function corresponding to the single-particle motions, which are described by the first and the second terms in equation (2), respectively. The latter possesses two asymptotics: $\Delta E_{\text{s-p}} \sim \kappa^2$ for small κ and $\Delta E_{\text{s-p}} = 2\hbar/\tau_0 = \text{constant}$ for large κ. The corresponding asymptotics of ΔE are: $\Delta E \approx 2\hbar(D_{\text{coll}} + D_{\text{s-p}})\kappa^2$ for small κ and $\Delta E = \Delta E_{\text{coll}} +$ constant for large κ. If the contribution from single-particle motions is small, the deviation of $\Delta E(\kappa^2)$ from linearity is also small for all κ. Thus, it follows that the linear section in the observed experimental $\Delta E(\kappa^2)$ (*Figure 3*) and the deviation from linearity characterize the relative contributions from collective and single-particle diffuse modes of a solvent in the system.

Proceeding from the above approach, the experimental data were processed in the following way. From the linear asymptotics of $\Delta E(\kappa^2)$ for small κ the total self-diffusion coefficient $D = D_{\text{coll}} + D_{\text{s-p}}$ was found by the equation $\Delta E = 2\hbar D\kappa^2$. The contribution to D corresponding to the collective motions (D_{coll}) was found from the asymptotics of $\Delta E(\kappa^2)$ for large κ. For such κ, as follows from equation (2), $\Delta E \approx 2\hbar D_{\text{coll}}\kappa^2 + (2\hbar/\tau_0)$ which enables the residence time for a given φ to be simultaneously determined. With known D and D_{coll}, the self-diffusion coefficient corresponding to the single-particle motions was found by subtraction: $D_{\text{s-p}} = D - D_{\text{coll}}$. The D, D_{coll} and $D_{\text{s-p}}$ for different volume fractions of gelatin in a gel are given in *Figure 5*. The absolute values of self-diffusion coefficients, the relative value of D_{coll}/D and the residence times of water molecules are summarized in *Table 1*.

DISCUSSION

The self-diffusion coefficient of fluid molecules in a polymer gel can be determined by the tracer technique, nuclear magnetic resonance (n.m.r.) and QENS. It should be noted that these methods are basically different, since the self-diffusion coefficients studied in the experiments are formed within different observation times t_{obs}. In the tracer technique, n.m.r. and QENS, the t_{obs} values are $\sim 10^{2\text{–}4}$, $\sim 10^{-(4\text{–}6)}$ and $\sim 10^{-(10\text{–}13)}$ s, respectively. (Using back-scattering and spin-echo spectrometers one can succeed in reducing the lower limit of t_{obs} probed by QENS to $\sim 10^{-9}$ and $\sim 10^{-7}$ s, respectively[15].) In our previous study[7], we determined the self-diffusion coefficient of water in gelatin gels of different concentrations using macroscopic measurements by the slow neutron transmission technique which is an analogue of the tracer technique. The H_2O molecules which diffused from the reservoir into a D_2O-saturated gel were used as tracers. The data obtained are given in *Figure 5* (curve B). As is seen, $D(\varphi)$ obtained by the tracer technique is in good agreement with that of $D_{\text{s-p}}$. (Comparing curves B and C in *Figure 5*, one should take into account that curve B corresponds to the interdiffusion coefficient of H_2O and D_2O molecules in the gel, while curve C corresponds to the single-particle self-diffusion of pure H_2O in the gel.) Since the tracer technique measures the mass transfer of water which is naturally identified with the self-diffusion of free water in the gel, the observed agreement makes it possible to conclude that the self-diffusion of free water in gelatin gel pores proceeds by a single-particle mechanism.

It is known from the literature (ref. 6 and references cited therein) that the quantity of bound water in the gelatin gel is ~ 0.5 g water g^{-1} gelatin. A higher content of gelatin per unit volume of the system leads to a corresponding growth in the fraction of bound water making slow collective diffuse motions together with the macromolecules of a polymer matrix about equilibrium

Table 1 Variation of self-diffusion coefficients and residence time at different gelatin concentrations

	φ					
Parameter	0.031	0.063	0.129	0.199	0.274	0.353
D ($\times 10^6$, cm^2 s^{-1})	13.6	10.1	7.1	6.1	5.3	4.9
D_{coll} ($\times 10^6$, cm^2 s^{-1})	4.8	5.2	5.2	5.4	5.1	4.8
$D_{\text{s-p}}$ ($\times 10^6$, cm^2 s^{-1})	8.8	4.9	1.9	0.7	0.2	0.1
D_{coll}/D (%)	35	51	73	89	96	98
τ_0 ($\times 10^{12}$, s)	2.0	2.7	9.8	22	66	165

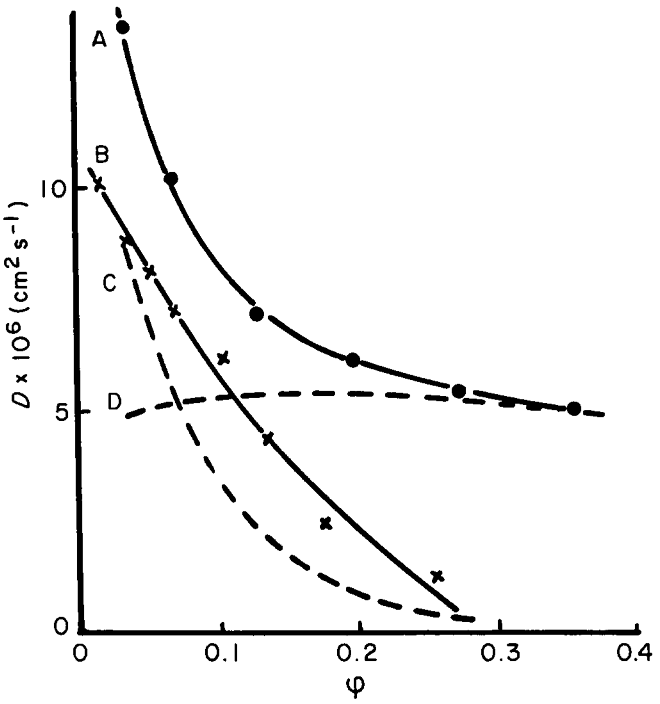

Figure 5 Self-diffusion coefficient of water as a function of φ: (A) total self-diffusion coefficient; (B) data obtained by the tracer technique[7]; (C) $D_{s\text{-}p}$; (D) D_{coll}

centres remaining stationary on average. As follows from the data obtained, a growing fraction of bound water in the gel results in considerable retardation of mass transfer revealed by the tracer technique as well as in the pumping of single-particle diffuse modes into collective ones probed by QENS. This leads to a considerable increase in the ratio D_{coll}/D, and starting from $\varphi \sim 0.4$ the self-diffusion of water proceeds exclusively by a collective mechanism (*Table 1*). Using the above, one can show that all water in the gel should become bound at much higher volume fractions of gelatin (close to 0.7). The observed discrepancy may be explained by a microspace effect which appears as active cooperative behaviour of water molecules within microscopic ranges corresponding to the pore sizes (ξ) of the gelatin gel, when the values of the latter are small enough. To estimate the value of ξ at which the microspace effect starts, we may use the following information: a major fraction of gelatin macromolecules is α-gelatin with $M_w \sim 10^5$ (*Figure 1*); the concentration of gelatin coil overlapping[9], $C^* = 0.045$ g cm^{-3}; and up to a gel concentration $C = 0.3$ g cm^{-3} the Flory–Huggins parameter[16] is practically constant and equal to 0.5. Let us assume that: the concentration C^* corresponds to the threshold of coil overlapping in α-gelatin and is the smallest concentration at which gelation is possible; the spacing of the lattice of entanglement in aqueous gelatin solutions of different concentrations corresponds to the distance between two neighbouring crosslinks of formed gels, i.e. any noticeable aggregation of chains during gelation is absent; and water remains a θ-solvent up to $C = 0.586$ g cm^{-3} which corresponds to $\varphi = 0.4$. Identifying the radius of gyration (R_g) of α-gelatin coils with the spacing of the lattice of entanglement ξ of the solution at $C = C^*$, we have[17] for the θ-temperature $R_g \sim \xi \sim M_w^{0.5} \sim 300$ Å. Since for θ-solvents ξ varies with inverse concentration[18], the increase of gelatin concentration in the solution from $C^* = 0.045$ to 0.586 g cm^{-3} results in a decrease in ξ from 300 to ~23 Å. Within the above assumptions the latter value can be taken as a rough estimate of gelatin gel pore sizes at which the microspace effect appears.

The importance of pore sizes (or molecular void space) for the dynamics of solvent or solute molecules was noted by other authors. In reference 19 the specific effect of crosslink density on the molecular motions in the solvent channels of polystyrene matrices was observed. Similar cooperative phenomena appeared in the form of an anomalous growth of a bound water fraction in polyelectrolyte polyacrylamide gels[20] as well as in the form of clusters of copper ions in poly(vinyl alcohol) gels[21] with a decrease in their pore sizes to 20–30 Å. The latter values are in good agreement with our estimation of ξ corresponding to the microspace effect appearing in gelatin gels. Therefore, the observed interruption of mass transfer of water at relatively small volume fractions of a polymer as compared to the expected values (and the corresponding disappearance of single-particle diffuse modes) is associated with the fact that the investigated gels possess the three-dimensional effect favourable for the existence of bound water. It promotes the 'clustering' of water molecules at ξ of ~20–25 Å and corresponding complete retardation of their macroscopic diffusion.

In conclusion, it should be noted that the microspace effect also results in a considerable increase in residence time as compared to that of pure water. As follows from the data given in *Table 1*, τ_0 increases by about 80 times which corresponds to a six- to seven-fold increase in the bond energy of water molecules[22] becoming comparable with that of the formation of ion-molecular complexes[23]. The detailed analysis of $\tau_0(\varphi)$ will be given elsewhere[22].

REFERENCES

1 De Gennes, P. G. *Macromolecules* 1976, **9**, 594
2 Nystrom, B. and Root, J. *J. Macromol. Sci., Rev. Macromol. Chem.* 1980, **C19**, 35
3 Altenberger, A. R. and Tirrell, M. V. *J. Chem. Phys.* 1984, **80**, 2208
4 Cukier, R. I. *Macromolecules* 1984, **17**, 252
5 Katayama, S. *J. Pharm. Soc. Jpn.* 1986, **106**, 1069
6 Maquet, J., Theveneau, H., Djabourov, M., Leblond, J. and Papon, P. *Polymer* 1986, **27**, 1103
7 Mel'nichenko, Yu. B., Klepko, V. V. and Shilov, V. V. *Europhys. Lett.* 1990, **13**, 505
8 Bulavin, L. A., Vasilkevich, A., Ivanitsky, P., Kzotenko, V., Maistzenko, A., Mel'nichenko, Yu. B. and Slisenko, V. *Phys. Liquids (USSR)* 1984, **12**, 103
9 Chang, T. and Yu, H. *Macromolecules* 1984, **17**, 115
10 Bulavin, L. A., Vasilkevich, A., Dozosh, A., Ivanitsky, P., Kzotenkov, V. and Slisenko, V. *Ukrainian Phys. J. (USSR)* 1986, **31**, 1703
11 Bogolyubov, N. N. 'Problems of Dynamic Theory in Statistical Physics', Nauka, Moscow, 1964
12 Oskotsky, V. S. *Phys. Solids (USSR)* 1963, **5**, 1082
13 Ivanov, T. J. *J. Exp. Theor. Phys. (USSR)* 1966, **46**, 1120
14 Lovesey, S. W. in 'Dynamics of Solids and Liquids by Neutron Scattering', Springer-Verlag, Berlin, 1977
15 Higgins, J. S. 'Proc. NATO Adv. Study', Glasgow, 1988, p. 349
16 Lewicki, P. P., Busk, G. C. and Labuza, T. P. *J. Colloid Interface Sci.* 1978, **64**, 501
17 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1982
18 Daoud, M. and Jannink, G. *J. Phys. (Fr.)* 1976, **37**, 973
19 Regen, S. L. *Macromolecules* 1975, **8**, 689
20 Katayama, S., Hirokawa, Y. and Tanaka, T. *Macromolecules* 1984, **17**, 2641
21 Fujiwara, S., Katsumata, S. and Seki, T. *J. Phys. Chem.* 1967, **71**, 115
22 Mel'nichenko, Yu. B. and Bulavin, L. A. to be published
23 Antonchenko, V. D. 'Microscopic Theory of Water in Membrane Pores', Naukova Dumka, Kiev, 1983