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Brillouin light-scattering from poly(vinyl alcohol) hydrogels

S. C. Ng, T. J. C. Hosea and L. M. Gan (*)

Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

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Résumé. — Le déplacement et la largeur Brillouin dans les hydrogels de l'alcool polyvinylique avec deux densités de réticulation différentes ont été obtenus en fonction du rapport volumétrique du réseau du gel par interféromètre Fabry-Pérot à cinq passages. Les résultats sont présentés à l'aide de la théorie de la diffusion Brillouin proposée récemment par MM. J. A. Marqusee et J. M. Deutch.

Abstract. — The Brillouin shift and width for poly(vinyl alcohol) hydrogels of two different cross-link densities have been obtained as a function of gel network volume fraction using a five-pass Fabry-Pérot interferometer. The results are discussed in the light of a theory for Brillouin light-scattering from gels proposed recently by J. A. Marqusee and J. M. Deutch.

1. Introduction.

Much information concerning the structure [1], the hypersonic propagation of waves [2, 3], mechanical relaxations [4], the sol-gel transition temperature and phase diagram [5, 6] of polymer gels has been obtained using the technique of Brillouin light-scattering. However detailed experimental data are still not available for comparison with a theory proposed recently by J. A. Marqusee and J. M. Deutch (MD) [7] for Brillouin light-scattering from gels. The purpose of the present work is to provide such data and make comparison with the theory.

2. Experimental.

In this study, we have chosen as an example of a typical polymer gel poly(vinyl alcohol) (PVA) cross-linked by ^{60}Co γ -radiation. Pure PVA powder with a number average degree of polymerization of 2 613 was obtained from Aldrich Chemical Co. Inc. USA. A solution of 13 weight percent PVA was obtained by dissolving the PVA powder in distilled water. Two identical samples of this PVA solution were irradiated in glass tubes with ^{60}Co γ -rays at a dose rate of 0.364 Mrad/h for 32 h (specimen A) and 64 h (specimen B). After the irradiation the gels formed were found to have expelled a small amount of water which was greater in the case of specimen B. This indicates that specimen B has a greater cross-link density. The exact content of PVA (mass = m_p) in the gels was determined after completion of the Brillouin light-scattering experiments by heating them at 75 °C in vacuum until completely dehydrated.

(*) Department of Chemistry, National University of Singapore, Singapore 0511.

The Brillouin spectrum of each sample was measured as a function of gel network volume fraction (ϕ) at room temperature. The volume fraction ϕ was varied by controlled evaporation of water from the gel. After being completely dehydrated specimen A was reswollen by immersion in distilled water for one week and the Brillouin spectra measured again as a function of ϕ . Assuming that the gel solution behaves like a two-phase porous medium, ϕ can be determined by the equation :

$$\phi = \left[\frac{\rho_n}{\rho_f} \left(\frac{m(\phi)}{m_n} - 1 \right) + 1 \right]^{-1}$$

where ρ_n and ρ_f are the density of PVA and water respectively and $m(\phi)$ is the total mass of the gel.

All Brillouin spectra were obtained by exciting the samples using a Spectra-Physics argon-ion laser operating at single mode 514.5 nm. The light scattered through 90° was analysed using a Burleigh DAS-1 five-pass Fabry-Pérot interferometer system. The true spectrum was obtained from the measured spectrum using the technique of Bayesian iterative deconvolution. The Brillouin shift ν_B and width Γ_B (FWHM) of the deconvoluted spectrum were then obtained by least-squares fitting of a Lorentzian line-shape. Details of light-scattering technique have been discussed in [6]. The refractive index n at wavelength 514.5 nm for the two samples was also measured as a function of ϕ by refraction and using Snell's law.

3. Results.

The results for the Brillouin shift ν_B at room temperature for both samples of the PVA hydrogel are displayed in figure 1. For increasing ϕ , ν_B increases slowly at first in a fairly linear fashion. Above $\phi \simeq 0.4$ however ν_B increases more rapidly but for large ϕ returns to a roughly linear behaviour. The error bars on the figure reflect the slight weight loss in the specimens during the measurement of the light-scattering spectrum. This weight loss has a maximum of a few percent for intermediate ϕ . The resulting error in ϕ is appreciable for ϕ in the range of $\sim 0.4 \rightarrow \sim 0.8$. For specimen A, the results for ν_B for both dehydration sequences are identical to within expe-

Fig. 1. — The Brillouin shift in PVA hydrogel as a function of volume fraction. ■ : Sample A, initial dehydration sequence. □ : Sample A, second dehydration sequence. ○ : Sample B. △ : datum for pure water [10]. Line 1 is a guide to the eye. Lines 2 and 3 are the theoretical curves for $\lambda = 0$ and $\lambda = 1$ (see text).

rimental error. This indicates that the system fully recovers its original form when reswollen even from a completely dehydrated state. The results for specimen B (with a greater density of cross-linking) appear to depend on ϕ in the same manner as for specimen A, indicating that v_B is also independent of cross-link density [2]. Since specimen B was irradiated for so long then it is unlikely that there are any free polymers left dissolved in the fluid. The fact that $v_B(\phi)$ is so similar for both specimens suggests that effectively all the dissolved polymer is taken up in the network structure. The measurements of refractive index n during the dehydration sequence indicated that n is also independent of cross-link density and varies smoothly from the value for pure water [8] at $\phi = 0$ to a value for completely dehydration, $\phi = 1$, close to that of the commercially quoted value of 1.50 for bulk PVA [9]. Furthermore measurements of the density of the fully-dried specimens were close to the commercial value of $1\,269\text{ kg m}^{-3}$ for bulk PVA [9] indicating that there are effectively no free spaces in the dehydrated network. That the network is preserved, albeit in a « collapsed form », is clear from the fact that the specimens can be reswollen to their original state. The measurements for $n(\phi)$ were parameterized in terms of a second order polynomial in ϕ :

$$n(\phi) = n_0 + n_1 \phi + n_2 \phi^2 . \tag{1}$$

The values obtained for n_0 , n_1 and n_2 are given in table I. These results together with the value for $v_B(\phi = 1)$ give the speed of sound in the dehydrated PVA as $C_n = 3\,783.6\text{ m s}^{-1}$. We know of no other measurements of C_n with which this result can be compared. Extrapolation of the results for v_B to $\phi = 0$ gives a value for the speed of sound in the fluid of $C_0 = 1\,478\text{ m s}^{-1}$ close to the accepted value for water at room temperature [8].

The measurements of the Brillouin width Γ_B are displayed in figure 2. Γ_B increases rapidly with increasing ϕ reaching a maximum near $\phi \simeq 0.65$ thereafter dropping rapidly as ϕ approaches 1. Again to within experimental accuracy Γ_B is independent of cross-link density and previous dehydration history. The appreciable errors in Γ_B for ϕ in the range $\sim 0.4 \rightarrow 0.8$ are a consequence of the uncertainties in ϕ for the v_B measurements in figure 1. Small changes in ϕ during the measurement of a spectrum will cause a small drift Δv_B in the Brillouin shift with a consequent slight broadening of the Brillouin profile roughly equal to Δv_B . The error bars in figure 2 indicate the estimated size of Δv_B as determined from the known changes in ϕ .

4. Comparison with theory.

MD consider two limiting cases appropriate to a coupled fluid and network system. They define a parameter $0 \leq \lambda < 1$ which is a measure of the degree of coupling between elastic waves in the network and fluid. The first case occurs for small frictional damping f and predicts essen-

Table I. — *The bulk physical properties of water, PVA and PVA hydrogel at room temperature.*

Parameter	Value	Reference
ρ_f	998 kg m^{-3}	[8]
ρ_n	$1\,269\text{ kg m}^{-3}$	[9]
C_0	$1\,475.5\text{ m s}^{-1}$	[10]
C_n	$3\,783.6\text{ m s}^{-1}$	This work
$\frac{4}{3} \eta_s + \eta_B$	$2.92 \times 10^{-3}\text{ kg m}^{-1}\text{ s}^{-1}$	[10]
n_0	1.3365	} This work see equation (1)
n_1	1.0648×10^{-1}	
n_2	6.6895×10^{-2}

Fig. 2. — The Brillouin width in PVA hydrogel as a function of volume fraction. The symbols are as in the key to figure 1. Line I is a guide to the eye. Lines II and III are theoretical curves (see text).

tially a « two-mode » type of behaviour for the Brillouin spectrum. In this case two pairs of peaks should be observable, which for weak coupling $\lambda \simeq 0$, are close to the Brillouin angular frequencies $\pm \omega_0$ and $\pm \omega_n$. Here $\omega_0 = C_0 k$, $\omega_n = C_n k$ and C_0 , C_n are respectively the speed of sound in the fluid and network and k is the sound wavevector. The other limiting case is for strong frictional damping :

$$f \gg \left(\frac{4}{3} \eta_s + \eta_B \right) k^2, \quad 2 \pi \Gamma_B \rho_f (1 - \phi) \quad (2)$$

where η_s and η_B are respectively the shear and bulk viscosities in the fluid (see table I). This corresponds essentially to a « one-mode » type of behaviour which predicts a single pair of Brillouin peaks at $\pm \bar{\omega}$. Here $\bar{\omega} = \bar{C}k$, $\bar{C}$ is the average speed of sound in the medium. $\bar{C}(\phi=0) = C_0$ and $\bar{C}(\phi=1) = C_n$.

The present measurements of the Brillouin spectra of PVA hydrogel showed the presence of only a single pair of modes. It therefore seems appropriate to compare our results with the theory for the limit of strong friction. MD give two equations for the ϕ -dependence of $v_B (= \bar{C}k/2 \pi$ of Ref. [7]) and $\Gamma_B (= \Gamma k^2/\pi$ of Ref. [7]) which in terms of ϕ are :

$$\begin{aligned} \bar{C}^2 &= \frac{C_0^2 \rho_f + \phi(C_n^2 \rho_n - C_0^2 \rho_f) + 2 C_0 C_n \sqrt{\lambda \rho_n \rho_f (\phi - \phi^2)}}{\rho_f + \phi(\rho_n - \rho_f)} \\ 2 \Gamma &= \frac{\frac{4}{3} \eta_s + \eta_B}{\rho_f + \phi(\rho_n - \rho_f)} + \frac{\rho_f^2 \rho_n^2 (\phi - \phi^2)^2}{[\rho_f + \phi(\rho_n - \rho_f)]^3} \frac{1}{f \bar{C}^2} \times \\ &\quad \times \left\{ C_0^2 - C_n^2 - C_0 C_n [\rho_f - \phi(\rho_n + \rho_f)] \sqrt{\frac{\lambda}{\rho_n \rho_f (\phi - \phi^2)}} \right\}^2. \end{aligned}$$

It should be noted however that the range of ϕ for which these expressions are applicable is not precisely defined and, although perhaps questionable, in the absence of such guidance we make a comparison with our results over the complete range of ϕ . The relevant values for the physical constants required are listed in table I. The resulting predictions for v_B have been displayed in

figure 1 for the limiting cases of no coupling $\lambda = 0$ and maximum coupling $\lambda = 1$. Although an initial linear increase with ϕ is predicted, in comparison with experiment the curvature is incorrect. The prediction for small λ seems somewhat better than for larger λ . It was found that no permissible variation of λ with ϕ would permit the theory to describe the full set of experimental data. Further pursuit of a better description requires consideration of a possible ϕ -dependence of ρ_f , ρ_n , C_0 and C_n . Measurements of the specimen density over the full range of ϕ indicate that, as might be expected, ρ_f and ρ_n are not detectably dependent on ϕ and it is safe to use those values appropriate to the bulk materials. C_0 is quite small in comparison with C_n and it may easily be demonstrated that even if C_0 were to drop to zero this would improve matters only marginally. The only remaining quantity is C_n « the speed of sound in the network ». Treating this merely as an adjustable parameter it is found that in order to describe the experimental measurements C_n must decrease rapidly from its bulk value of $\sim 3\,784\text{ m s}^{-1}$ at $\phi = 1$ to much smaller values for low ϕ . Figure 3 shows the required variation of $C_n(\phi)$ for the two limiting possibilities $\lambda = 0$ and $\lambda = 1$. We know of no reason why C_n should vary thus. Although C_n is expected to depend on cross-link density [7], this is not observed to be the case for our two different specimens A and B. Furthermore the cross-linking is not thought to vary with ϕ for the present specimens since the cross-linking is radiation induced. For these reasons the required dependence of $C_n(\phi)$ should be regarded at this stage merely as a parametrization of our experimental results, without any physical justification.

The prediction of the theory for Γ_B is shown in figure 2 for the case of $\lambda = 0$ using the physical constants in table I. A constant value for the frictional damping of $f \simeq 4 \times 10^{13}\text{ kg m}^{-3}\text{ s}^{-1}$ has been chosen. Even with such simplistic assumptions the theory successfully predicts the essential qualitative features of Γ_B , in particular the presence of a maximum at intermediate ϕ . In the spirit of the approach taken for v_B we may adopt a value for C_n which depends on ϕ . Choosing the curve for $C_n(\phi)$ from figure 3 for $\lambda = 0$ and with a constant value for $f \simeq 9 \times 10^{12}\text{ kg m}^{-3}\text{ s}^{-1}$, the theory predicts a peak in Γ_B as shown in figure 2 which almost exactly coincides with that of the measurements. A better agreement may be obtained by treating f as a function of ϕ and such a dependence is shown in figure 3. Unfortunately such values for f

Fig. 3. — Lines i and ii : the dependence of $C_n(\phi)$ required to reproduce curve 1 in figure 1, for $\lambda = 0$ and $\lambda = 1$. Line iii : the dependence of $f(\phi)$ required to reproduce curve I in figure 2, with $C_n(\phi)$ as given by curve i here (see text).

are too small to satisfy the inequality (2), the right-hand side of which has an upper limit of $\sim 7 \times 10^{12} \text{ kg m}^{-3} \text{ s}^{-1}$.

It should be noted that the parametrizations $C_n(\phi)$, λ and $f(\phi)$ are by no means unique and that $C_n(\phi)$ may be chosen to vary in any desired way in the region bound by curves (i) and (ii) in figure 3 with an appropriate variation for $\lambda(\phi)$. However if λ is allowed to become larger than about 0.01 then it is found that $f(\phi)$ is required to take even smaller values, a feature clearly undesirable in the light of the failure of the inequality (2) already noted.

It is appropriate here to point out a weakness in the theory for the limit $\phi \rightarrow 1$. The resulting Brillouin width Γ_B is predicted to equal $\frac{k^2}{2\pi} \frac{1}{\rho_n} \left(\frac{4}{3} \eta_s + \eta_B \right)$ with no contribution from the sound attenuation in the network. We believe a more complete theory should account for this contribution. It may then be possible that such small values for f would not be necessary.

5. Conclusion.

Our measurements of the dependence of the Brillouin shift ν_B and Brillouin width Γ_B on volume fraction ϕ for specimens of irradiated PVA hydrogel have been compared with the theory of Marqusee and Deutch for Brillouin light-scattering from longitudinal modes in gels [7]. It is found that the measurements are roughly consistent with the essential features of the predictions of the theory for the case of strong frictional damping f .

However in order to obtain a complete description of the experimental data in terms of this theory it is found that the « speed of sound in the network » C_n must be forced to depend strongly on ϕ in contradiction with expectations. Furthermore the theory can only fit the experimental data for Γ_B if the frictional damping parameter f is forced to take values which are too small to satisfy the criteria of the model. It is possible that the present system is not appropriate for close comparison with the theory because it may correspond to a case of « intermediate » frictional damping for which the theory becomes much more complicated. However it has been noted that the model does not take account of the absorption of elastic waves propagating in the network. D. L. Johnson [11] has also examined the elastodynamics of gels and arrives at similar equations to those of Marqusee and Deutch [7]. However his expressions for sound velocity and attenuation in the gel case are given for frequency regimes which are either much lower or much higher than the frequencies in our Brillouin light-scattering experiments.

J. M. Deutch and D. L. Johnson [12] have extended this theory to the case of Brillouin light-scattering from transverse modes in gels. We have tried to observe these modes in PVA system but without success. We are currently investigating the possibility of studying other systems for which the existing theories may be more appropriate.

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