However, recent Monte Carlo studies[5,7] of asphericity in lattice model chains with excluded volume forces do not show such a behavior, as shown in Table I. In addition, Gobush, Šolc, and Stockmayer[3] considered this problem from a different point of view, based on a smooth density model. Although they obtained the larger asphericity for large z, that is, $\langle\lambda_1\rangle:\langle\lambda_2\rangle:\langle\lambda_3\rangle = 28.7:4.75:1.00$, it could not be found that only $\langle\lambda_1\rangle$ increases without limit. This discrepancy may be attributed not only to our selection of the major axis chosen to be parallel to the $\mathbf{q}_1$ vector in a Fourier space but also to the condition of $G_1 = 0$ in the present treatment. It is very difficult, however, to relax the above two conditions.

Summary

It seems very difficult to estimate analytically, under the presence of excluded volume forces, the eigenvalues of the symmetric tensor[8] which characterizes the instantanious shape of the chain. We therefore are forced to consider the model easy to handle. In particular, for the model introduced by Doi and Nakajima, we have shown in 1 and this paper that it is possible to introduce explicitly the effect of excluded volume forces to it. The results obtained, however, do not agree with those of computer experiments and other approaches. More precise theoretical and experimental studies are necessary for the discussion of the excluded volume forces on the principal components $\langle\lambda_i\rangle$.

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Laser Light Scattering from Soft Gels

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ABSTRACT: Photon correlation spectroscopy has been used to probe standing displacement waves set up in cuvettes exposed to mechanical vibrations. The dependence of mode frequencies on cuvette dimensions agrees with predictions of a simple theoretical model. Time behavior of the oscillating portion of the measured photon autocorrelation functions is found to be independent of $\mathbf{Q}$ (the Bragg wave vector), also in accord with theory. Values of longitudinal sound speed are obtained and corresponding values of elastic moduli are determined. Agarose and polyacrylamide gels of differing concentration have been investigated, establishing that materials whose elastic moduli fall within the range 10^2–10^5 dyn/cm^2 can be studied by this technique. Elastic moduli of agarose are found to vary with weight percentage of polymer ρ according to $E \sim \rho^m$, where $m \simeq 4.1$. Corroborative measurements have been made with instrumentation designed to analyze the frequency distribution of scattered light.

I. Introduction

Various materials of biological origin possess rheological properties characteristic of weakly cross-linked polymer networks. Examples are the lens and *vitreous humor* of the eye,[2] sputum,[3] and mucus,[4] constituents of connective tissue such as hyaluronic acid,[5] and the cytoplasm of motile cells.[6,7] In the present paper we describe a procedure involving laser inelastic light scattering which can be used to study the mechanical properties of such gel-like materials. The method differs from prior laser light scattering techniques[8–12] in that it probes low-frequency displacement waves which are selected by the mechanical resonant cavity defined by the gel boundaries, whereas other techniques detect short-lived thermally induced density fluctuations.

A theory for interpreting these light scattering measurements is presented in an accompanying paper.[13] We show that the material parameter which can be extracted from the data is the low-frequency longitudinal sound velocity, which can be related to elastic coefficients (the compressibility and shear moduli). Based on preliminary measurements, we envision that the technique can be used to probe materials whose elastic moduli fall within the range 10^2–10^5 dyn/cm^2. Illustrative data are given primarily for agarose gels, but similar observations have been made when measuring other materials such as specially prepared collagen gel networks, *vitreous humor* obtained from the eyes of fetal calves, and polyacrylamide gels of appropriate composition. The longitudinal sound velocity is determined from the frequencies of observed oscillatory components of photon autocorrelation functions. Oscillations previously were noted by Wun, Feke, and Prins[10] when they, too, used laser light scattering to investigate agarose gels.

Other rheological techniques which are used to study the properties of soft gels generally measure the response which the material shows to an imposed macroscopic mechanical disturbance.[14] Such methods have the disadvantage of causing significant perturbation of the gel structure and, therefore, are not suitable for studying pressure-dependent polymeric systems such as cytoplasmic extracts near a sol-gel transition.[15] Light scattering techniques, being noninvasive, do not suffer from such limitations. Furthermore, light scattering measurements oftentimes are extremely rapid (of the order of a minute or less) so that the kinetics of gelation can be studied and have the advantage that in principle only very small volumes of material are needed.

II. Materials and Methods

Agarose gels were prepared by heating aqueous suspensions of undissolved polymer to the point where clear solutions were observed (usually just below boiling). The hot solutions were poured into glass cuvettes and allowed to cool. Measurements were made directly on the cuvettes in which the gels had hardened, generally no earlier than 18 h after preparation. Two samples of agarose polymer were employed, both having been obtained from Kallestad Laboratories, Chaska, Minn. Sample A1 (lot No. J011, prepared by Marine Colloids, Rockland, Maine) had a gel strength break force of 977 g/cm^2 at 1% gel concentration; sample A2 (lot No. G011, prepared by L'Industrie Biologique Française S. A., Gannevilliers, France) had an unknown but lower gel strength at the same concentration. Cuvettes of differing size were used in order to ascertain the manner in which sample dimensions affect the standing wave frequencies; in any given experiment cuvettes were filled with the same hot solution. In studies involving the effect of varying the polymer concentration, different amounts of concentrated hot solution were mixed with appropriate amounts of hot solvent, using cuvettes of identical dimensions.

Collagen gel networks were prepared from rat tail tendon collagen by heat precipitation in a NaCl–TES buffer[27] at neutral pH.[16] Collagen concentrations of 0.1 mg of protein/mL of buffer formed gels which were soft enough to sustain weakly damped mechanical vibrations. Polyacrylamide gels were formed by polymerization of acrylamide and *N,N'*-methylenebis(acrylamide), using ammonium persulfate as an initiator and *N,N,N',N'*-tetramethylethylenediamine as catalyst (Biorad Laboratories, Richmond, Calif.).

Two spectrometer systems were used. One incorporates a specially designed 128 channel hard-wired single-clipped digital autocorrelator and is similar to an instrument which has been discussed elsewhere.[17] In this case a He–Ne laser (Spectra-Physics Model 125) is employed as the source and an ITT F-4085 phototube is used to detect the scattered light. The laser, sample platform, and detector rest on a 1.25 in. thick marble slab, raised above the floor by a lattice of 6 in. × 8 in. cinderblock lintels separated by 1 in. thick cork spacers. Occasionally, various mechanical vibrators (e.g., a small motor or an audio speaker connected to a sine-wave generator) were placed on the table at positions which were empirically determined as being appropriate for adding mechanical energy to the sample without causing the gel to vibrate at the externally imposed frequencies (see below). The second spectrometer, which rests on a 3 in. thick concrete slab raised above the floor by concrete pylons, utilizes a Coherent Radiation CR-2 Argon-ion laser, an EMI 9840 phototube, and a Nicolet UA500B real-time spectrum analyzer.

III. Results and Discussion

The theoretical interpretation of the present measurements is based on the notion that the gel scatters light as a consequence of refractive index inhomogeneities which result from fluctuations in material density within the scattering volume. As in other laser light scattering studies[8] of such materials, density fluctuations are assumed to be calculable from macroscopic elasticity equations, although in our case it is essential to take finite boundaries into account.

In the accompanying paper[13] we derive expressions for the time autocorrelation function of detected photons for an isotropic gel contained in a cuvette having rectangular cross section. The theoretical model predicts that this quantity should consist of a flat background term plus time-varying components of the form[13]

$$I(\mathbf{Q},t) \sim f(\mathbf{Q}) \cos(\omega t) \tag{1}$$

where $f(\mathbf{Q})$ is dependent upon scattering angle ($\mathbf{Q}$ is the Bragg wave vector). The mode frequencies $\{\omega\}$ do not depend upon $\mathbf{Q}$ but are related to the dimensions of the cuvette and the density and elastic moduli of the material being studied. Two cases are considered: (i) a gel which is completely enclosed so that all six sides are in contact with an immobile surface, and (ii) a gel contained in an open cuvette, so that the top surface is free to move in any direction. The observable frequencies $\{\omega\}$ are shown to be given as

$$\omega = \pi C_{\text{long}} \left(\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{\gamma^2}{c^2} \right)^{1/2} \tag{2}$$

where a, b, and c are the dimensions of the cuvette (c being the dimension of an axis which is assumed to lie perpendicular to the scattering plane), C_{long} is the longitudinal sound velocity, and p and q are arbitrary integers which cannot simultaneously be zero. When the gel is completely enclosed γ is zero. However, when the top surface of the gel is not constrained γ either can be zero or any arbitrary half-integer value ($n + 1/2$). In order to derive such results, we assume that a gel does not detach from the walls of the cuvette but, as a first approximation, we consider the shear stresses at the walls to be negligible.[13]

a. Qualitative Features. Examples of measured autocorrelation functions $\langle n(0)n(t) \rangle$ are shown in Figure 1. A constant background has been electronically subtracted in this representation in order to highlight the time-varying term of interest. (The amplitude of the time-varying portion is but a few percent of that of the background.)

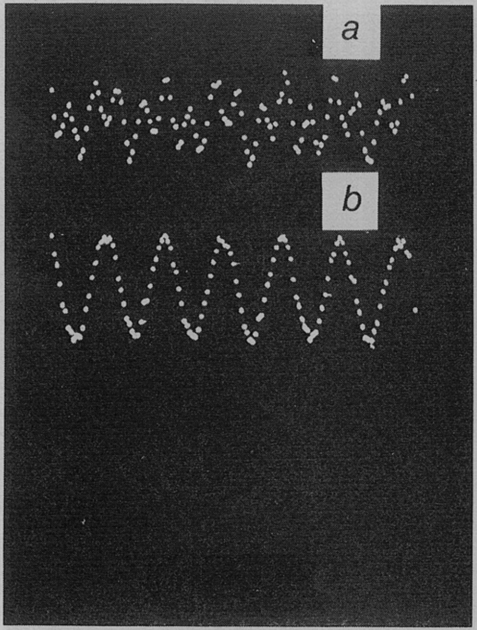

Figure 1. Photon autocorrelation function $\langle n(0)n(t) \rangle$ for 0.35% agarose gel (sample A2) formed in a 1 × 2 × 4 cm glass cuvette. Scattering angle = 52°, $\Delta\tau = 1000$ μs/channel. (a) Autocorrelation function showing the superposition of several standing waves. Measurements were made before external mechanical vibrations were supplied. (b) Autocorrelation function for the same sample but after activation of a vibrator which had been placed on the table near the spectrometer. In both cases a flat background has been subtracted electronically, so that essentially only the time-dependent portion of $\langle n(0)n(t) \rangle$ is observed.

The correlation function shown in Figure 1a appears to consist of several oscillating terms, indicated by the appearance of amplitude "beats". When working with agarose, a perplexing variability in such autocorrelation functions initially was observed. However, we subsequently discovered that the reproducibility of measurements could be enhanced by certain experimental manipulations. For example, a flat (i.e., essentially constant) autocorrelation function frequently would be measured if a gel had been standing on the light

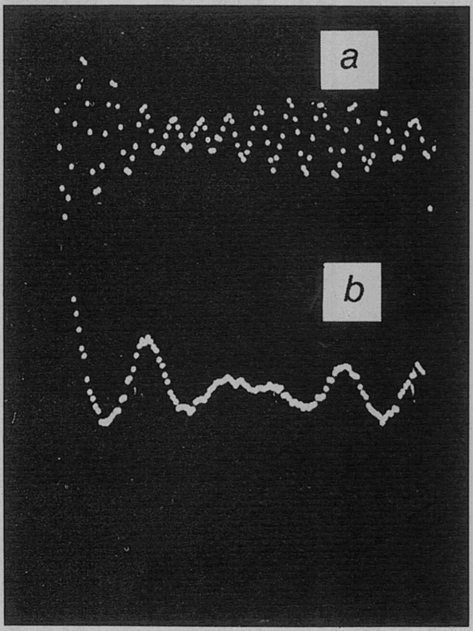

Figure 2. Examples of photon autocorrelation functions which show "beating" of several normal mode frequencies: (a) 0.20% agarose gel (sample A1) in a 1 × 1 × 4 cm cuvette, $\theta = 61°$, $\Delta\tau = 2000$ μs/channel; (b) 1.0% collagen gel, 2 × 4 × 4 cm cuvette, $\theta = 67°$, $\Delta\tau = 4000$ μs/channel.

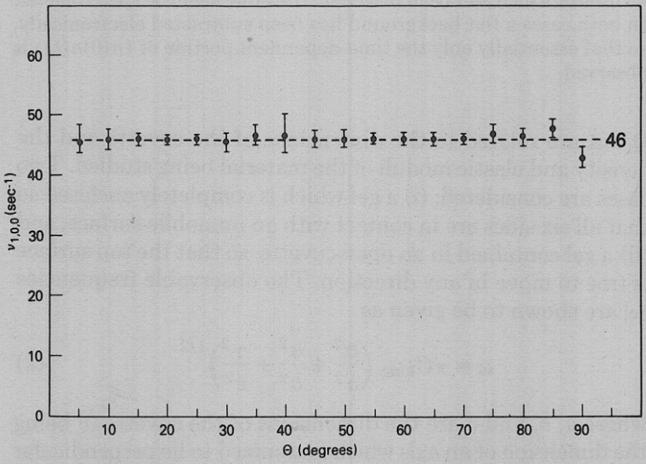

Figure 3. Angle dependence of the photon autocorrelation function. Shown here are the lowest frequencies of $I(\mathbf{Q},t)$ ($\nu = \omega/2\pi$, see eq 2) which are observed at different scattering angles (0.20% agarose (A1), 1 × 1 × 4 cm cuvette). Each point was determined from a single measurement, and error bars indicate possible uncertainties in locating positions of the peaks of the oscillating autocorrelation functions.

scattering table undisturbed for several hours; in this instance a gentle movement of the cuvette usually restored an oscillation to the correlation function which could be measured after such stimulation had ceased. When a complex function such as that shown in Figure 1a was observed, a slight touch given to the cuvette oftentimes resulted in an autocorrelation function which appeared as a pure cosine function. Simple autocorrelation functions likewise were discerned when a low-frequency vibrator was placed near the mount upon which the light scattering cuvette rests. The correlation function shown in Figure 1b was obtained by such a scheme, in which the source of the mechanical disturbance was a small electric motor connected to a variable power supply.

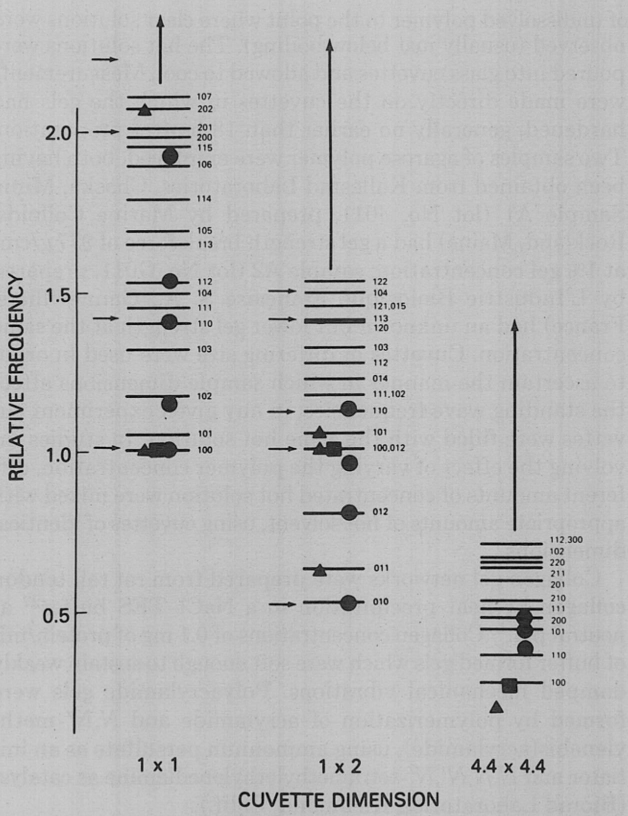

Figure 4. Comparison of predicted mode frequencies with those of experimentally observed photon autocorrelation functions. Cuvettes of different cross section were used, but all were filled to a height of 4 cm. Data and theoretical values have been normalized to the value of the lowest frequency observed when measurements are made with a 1 × 1 × 4 cm cuvette (which is assumed to be $\omega_{1,0,0}$ for that cuvette). The horizontal lines are mode frequencies given by eq 2 for half-integer values of γ; arrows pertain to mode frequencies for which γ is taken to be zero. Data from several experiments, employing various agarose samples, appear on this graph: (▲) 0.2% (sample A1); (●) 0.35% (sample A1); (■) 0.35% (sample A2).

Certain of the standing displacement waves which can be sustained in the cuvette are selectively excited when an external vibrator is used. The example shown in Figure 1b is the lowest frequency mode appearing in a 1 × 1 cm rectangular cuvette filled to a height of 4 cm with a 0.35% agarose gel (sample A2). Provided that a critical oscillator frequency is not surpassed, the frequency of the external oscillation can be changed without affecting the frequency of the photon-autocorrelation function. Depending on the particular material being used, once the relatively pure cosine oscillation seen in (b) is excited, the external oscillator can be turned off and the autocorrelation function will remain as such for several minutes or, in some cases, for hours before reverting to (a).

In Figure 2 we show other examples of beat phenomena. Note that had these measurements been made on faster time scales (shorter time intervals $\Delta\tau$), the photon autocorrelation functions might have seemed, simply, to be damped cosine oscillations.

b. Angle Dependence. Equation 1 implies that the frequencies of $I(\mathbf{Q},t)$ should be independent of scattering angle. In Figure 3 we show the results of an investigation undertaken in order to test this prediction. Here the lowest frequency mode of a 1 × 1 × 4 cm cuvette containing a 0.20% gel (sample A1) was excited and the scattering angle changed by 5° intervals (Snell's law was used to correct for refraction). No significant angle dependence was observed.

We also investigated the possibility that the observed autocorrelation function might change if the position of the light beam was varied. $I(\mathbf{Q},t)$ was found to be insensitive to the height of the beam above the bottom of the cuvette or its relation to the cuvette walls, which tends to rule out the possibility that we were observing some sort of unanticipated convection phenomenon. Various modifications of experimental conditions, such as surrounding the cuvette with a temperature controlled vessel, were effected to further test this point, all of which yielded the same conclusion.

c. Dependence of Mode Structure upon Cuvette Dimensions. Equation 2 implies that the frequencies of the observed autocorrelation function should decrease when the dimensions of the cuvette are increased. For example, if the cuvette is doubled in size, the lowest lying mode frequency should be halved. This prediction is confirmed by data which are shown in Figure 4. There, we compare the anticipated mode frequencies with those actually observed when gels have been poured into several different cuvettes. The solid lines are the frequencies $\omega_{p,q,\gamma}$ given by eq 2, and the symbols (see figure caption) are the data. In all cases the frequencies are normalized to the value of $\omega_{1,0,0}$ calculated for the $1 \times 1 \times 4$ cm cuvette (in this way we eliminate the dependence of the $\{\omega\}$ on the material parameters of the gel (see eq 2)). Results of several experiments are included in Figure 4.

The basic dependence upon cuvette size seems to be well substantiated. We also explored the higher order modes by increasing the frequency of the external oscillation. Although the external oscillation was tuned through a continuous range of frequencies, *discrete* changes in the frequency of the autocorrelation function were noted. We see, in Figure 4, that observed frequencies lie close to those predicted by eq 2; the slight deviations could reflect the approximate nature of the idealized boundary conditions which have been used to describe the interaction of a gel with the walls of a cuvette.

d. Spectral Analysis of Scattered Light. Using an instrument which one of us (R.A.G.) recently constructed, we have confirmed some of the above-mentioned observations by analyzing the frequency components of the fluctuating light intensity. Typical results are shown in Figure 5, where the ordinate is the amplified intensity of the voltage appearing at the output of the phototube (in arbitrary units) and the abscissa can be interpreted as the frequency shift of the components of the scattered light field.[18] The vertical lines which have been drawn along the x axis are positioned at frequencies which would be predicted by eq 2 if the lowest occurring (in frequency) prominent peaks are taken to lie at $\omega_{1,0,0}$. [These lines are analogues of the excitation level diagram shown in Figure 4.] The correspondence between predicted and measured spectra seems to be satisfactory, given the many approximations arising in the related theoretical analysis[13] including those previously mentioned concerning interactions of the gels with the walls of the cuvettes. Because of the complicated Q dependence of the form factor $f(\mathbf{Q})$ (see eq 1 and eq 21 of ref 13), we have not tried here to predict the amplitudes of the peaks. In accordance with theory, however, changes in relative intensity of the spectral peaks have been seen to occur when either the scattering angle or wavelength of the incident light is varied, whereas the positions of peaks remained constant.

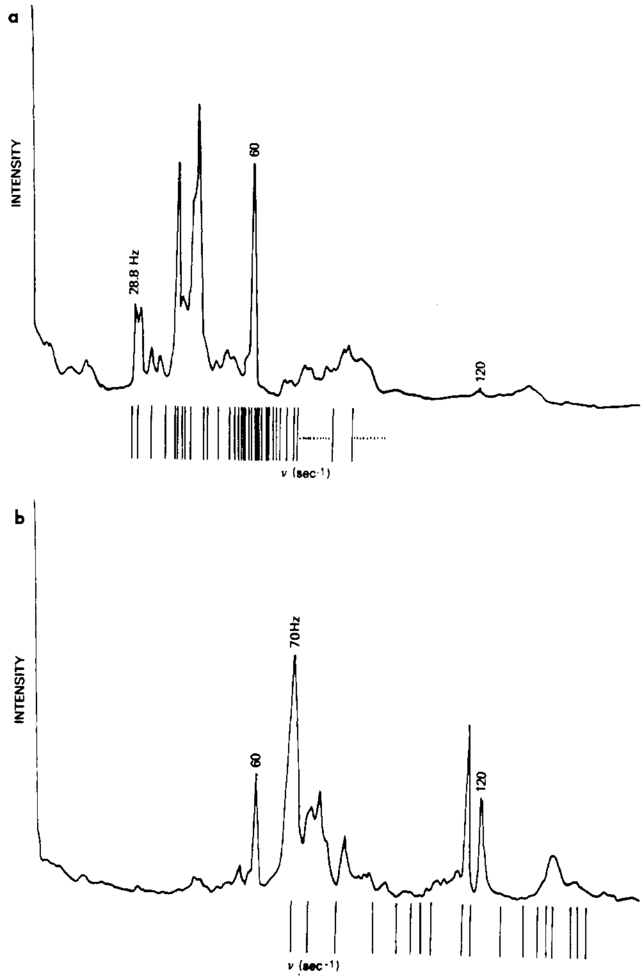

Figure 5. Typical light beating spectra. The vertical lines indicate frequencies determined from eq 2, assuming that the line farthest at the left corresponds to $\nu_{1,0,0}$. Results pertain to two different polymer preparations: (a) agarose gel of 0.15% concentration (sample A1, $1 \times 1 \times 4$ cuvette); (b) similar sample, containing 0.25% polymer. These measurements also were used to obtain some of the results shown in Figure 6 (dashed line) and are consistent with other data taken for the purpose of determining the concentration dependence of elastic moduli.

The results shown in Figure 5 were obtained in the absence of any applied source of mechanical excitation.[28] By employing well-defined mechanical oscillators, some interesting experiments can be undertaken with the spectral-analysis instrumentation which are not easily performed with a correlator-based system. For example, we used the amplified output of a sine-wave generator to drive an audio speaker coupled to the light scattering table by a block of styrofoam. The frequency of the oscillator was gradually increased while the amplitude was kept fixed. Essentially no effect on the measured spectrum was noted until the oscillator frequency coincided with one of the peaks, in which case the amplitude of that peak was greatly enhanced. Such observations confirm the notion that the cuvette acts as a mechanical resonant cavity. In addition, smaller changes were noted in the amplitudes of certain other peaks, suggesting that modifications of this technique could be used to examine coupling between the various modes of mechanical excitation arising from nonlinear terms not currently accounted for in the theoretical treatment of this problem.

e. Concentration Dependence of Elastic Moduli. Values of elastic moduli can be obtained from eq 2 upon recognizing that the longitudinal sound speed is given in terms of the compressibility modulus K and shear modulus G as

$$C_{\text{long}} = [(K + \tfrac{4}{3}G)/\rho]^{1/2} \qquad (3)$$

Here, ρ is the material density, that is, the weight of polymer per unit volume of the gel. Alternatively, C_{long} can be expressed in terms of Young's modulus E and Poisson's ratio σ as

$$C_{\text{long}} = [E(1 - \sigma)/\rho(1 + \sigma)(1 - 2\sigma)]^{1/2} \qquad (3')$$

The manner in which elastic moduli depend upon polymer concentration is of concern to theorists who are interested in developing statistical-mechanical models to explain how macroscopic response relates to the microscopic structure of soft gels.[19-23] Consequently, we determined the longitudinal sound speed of agarose and certain cross-linked polyacryl-

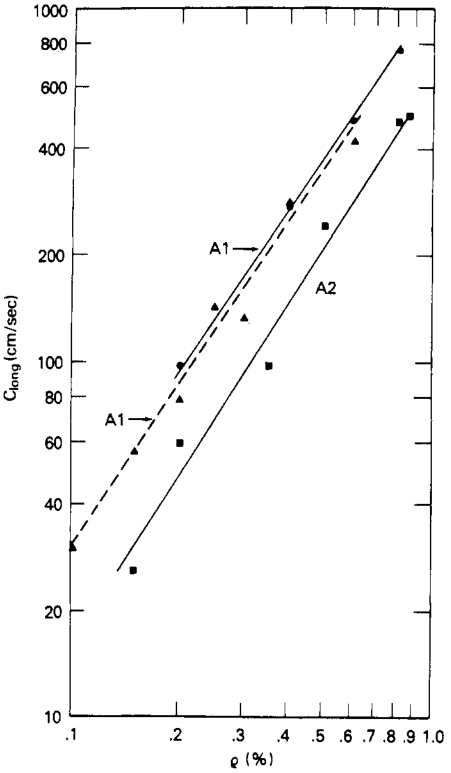

Figure 6. Logarithmic plots of the concentration dependence of the longitudinal sound speed $C_{long} = [(K + \frac{4}{3}G)/\rho]^{1/2}$ for agarose gels. The dashed line has been obtained from spectral analysis and the solid lines have been determined by photon autocorrelation measurements. Note that although different agarose samples might yield gels of differing strengths at identical polymer concentrations, the moduli obey the same empirical power law relationship relating elastic moduli to the density ρ.

amide gels for several polymer concentrations (wgt/vol).

Figure 6 pertains to measurement made on agarose gels of various compositions. When using the autocorrelator-based instrument, interpretation of the data is facilitated by exciting the samples in their lowest order modes. Such excitation can be accomplished by applying external vibration at a frequency below that of the standing wave whose indices are $[p = 1, q = 0, \gamma = 0]$. The data illustrated by solid curves in Figure 6 were obtained in this manner. For comparison, we also show results observed by spectral analysis (indicated by dashed lines), which were obtained without an extraneous oscillator.

Agarose is believed to form a dynamic lattice of multiply entwined, double helical hydrogen-bonded strands,[24] but the structure of the lattice is not yet well characterized. Furthermore, commercial agarose is derived from seaweed, and its physical and chemical properties differ according to its source and the specific processes used in its isolation.[25] Thus, this material probably is not a good subject for extensive investigation. (Our major interest here has been to illustrate the ease with which measurements can be made.) Nonetheless, it is perhaps interesting that our results indicate that elastic moduli of agarose can be written in the form

$$E \sim \rho^m \tag{4}$$

where $m \simeq 4.1$. Although there is some contention concerning the precise value of the exponent m, several theories predict a strong dependence upon polymer concentration.[29] The fact that the mode frequencies tend to zero at vanishing polymer concentration (see, e.g., Figure 7) indicates that the moduli which we are measuring primarily are properties of the polymer lattice and not of the solvent.

The exponent m seems to vary for different materials. In a recent light scattering study on concentrated solutions of polysterene, Hecht and Geissler[26] found m to have the value $m \simeq 3$. By comparison, pseudoequilibrium moduli determined by mechanical viscometry for poly(vinyl chloride) gels formed in various solvents provided values of m lying between 3 and 4.[14] Our own preliminary light scattering studies of cross-linked polyacrylamide gels (cross-link to monomer ratio 1:75) indicate a value of m close to 3.9.

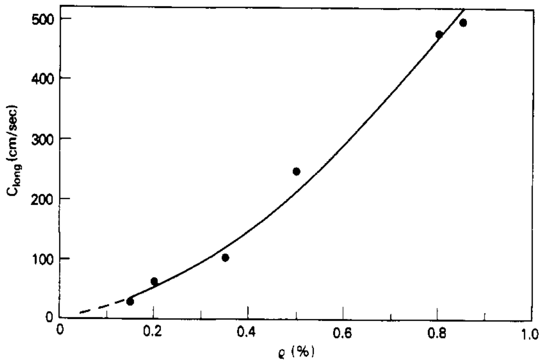

Figure 7. Longitudinal sound speed vs. density ρ for agarose A2 sample. (Linear plot of the data shown in Figure 6.)

IV. Further Remarks

Use of the technique described in this paper is restricted to studies of spatially isotropic gels which are capable of sustaining weakly damped mechanical oscillations. Polymer concentrations must fall within a fairly narrow range, since gelation will not occur if the amount of polymer is too low whereas gels become stiff above a certain concentration. The data presented in Figure 6 correspond to values of elastic moduli lying between 10^2 and 5×10^5 dyn/cm^2 (see eq 2).

Unlike the observations reported upon in this paper, when stiff gels are studied by light scattering, photon autocorrelation functions are found to decay rapidly with an approximately exponential time course. Tanaka et al.[8] have shown that in such case the autocorrelation function scales with scattering angle as a functional of Q^2t, with a decay constant which varies as the ratio of $(K + \frac{4}{3}G)/f$. Here, f is a friction coefficient relating to motions of the polymer lattice relative to the surrounding solvent, and K and G are the elastic moduli which appear in eq 3. In contrast, the technique which we have just described measures the quantity $(K + \frac{4}{3}G)$ directly. Certain moderately stiff gels should be amenable to both sorts of analysis. Accordingly, values of friction coefficient and elastic moduli could be individually determined, although slight modification of the theoretical analysis of the experiments first might be required since we have failed to include dissipation in the macroscopic equations used to derive eq 2 and 3.[30]

Observations similar to those which have just been discussed were reported previously by Wun, Feke, and Prins.[10] However, those investigators noted that the oscillations seemed to be transient, believing the phenomenon to be related to convection which might occur upon cooling and "curing" of their agarose samples. In contrast, we find that the magnitudes of the oscillations might decrease after the gels have rested for several hours but that they can be restored by moving and slightly agitating the cuvettes; furthermore, the time dependence of the measured autocorrelation functions is quantitatively reproducible over many days if care is taken to ensure that the gels do not lose water by evaporation.

Correlation functions which truly change with time can be observed as a gel form from a hot solution. Since data can be acquired quite rapidly, it seems feasible to use laser light scattering to follow the kinetics of gel formation. In several instances we monitored the autocorrelation function as it changed from an exponential decay, characteristic of the hot polymer solution, to an oscillation whose frequency increased as the gel hardened.

Finally, we note that the measured correlation function does not seem to be particularly sensitive to changes in temperature once a stationary state of gelation has occurred. Although we have not yet investigated this point very carefully, such observation seems to be in accordance with theoretical studies which predict that elastic moduli of entangled polymer networks should vary linearly with absolute temperature.[22,23]

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(27) TES = *N*-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid.
(28) No external oscillation was present other than possible background vibration. The fact that similar results are obtained with the autocorrelation spectrometer, which is located elsewhere on the NIH campus, suggests that such vibrations are not directly manifest in the measurements.
(29) Such theories generally pertain to polymer solutions of lower concentrations than those which have been studied here. A model which partially accounts for chain entanglements recently has been studied by de Gennes,[23] for which the value $a_{\text{theor}} \simeq 2.25$ is predicted.
(30) In addition to frictional interactions between the polymer lattice and the surrounding fluid, dissipation presumably also derives from structural properties of the gel. For example, entrapped inclusions or segregated domains of gelation could cause damping of mechanical excitatory waves by mechanisms similar to those whereby lattice dislocations and other imperfections lead to phonon damping in solids. Appendix 3 of ref 13 includes discussion of a simplified gel continuum model in which both dissipation and extrinsic mechanical forces are taken into account.

Correlation Functions for Light Scattering from Soft Gels

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ABSTRACT: A theory of laser inelastic light scattering from soft polymer gels is developed. The scattering process probes density fluctuations in the gel, which here are assumed to result from standing displacement waves. The gel is modeled as a continuum and allowable displacement waves are found by solving the elasticity equations subject to boundary conditions appropriate to an open oblong cuvette. Only a subset of the resulting frequencies is sampled by the light scattering experiment. The derived photon correlation function can be expressed as a product of an oscillatory time-dependent part, which is independent of scattering angle, and an angle-dependent form factor, i.e., $I(\mathbf{Q},t) = \mathrm{f}(\mathbf{Q}) \cos \omega t$. The observable frequencies $\{\omega\}$ are proportional to the longitudinal sound velocity in the gel multiplied by a geometrical factor which depends on the sample dimensions.

I. Introduction

Under certain conditions moderately dense entangled polymer networks can support seemingly long-lived mechanical oscillations. We recently demonstrated that such excitations can be detected by laser inelastic light scattering.[1] The present note contains a derivation of mathematical expressions necessary for extracting values of elastic moduli from such measurements.

We analyze an elastic continuum constrained by the walls of a rectangular cuvette. Fluctuations in dielectric constant are presumed to be proportional in magnitude to density fluctuations in the gel, the latter being related to the local displacement of the gel through the continuity equation. Heterodyne conditions are assumed, and the pertinent photon autocorrelation function is expressible in terms of joint two-time expectations of certain Fourier components of the gel displacement functions. The displacements are determined by solving isotropic elasticity equations[2,3] subject to appropriate boundary equations, using a method due to Sommerfeld.[2]

The resulting time-dependent photon autocorrelation function $I(\mathbf{Q},t)$ is found to be of the form

$$I(\mathbf{Q},t) = f(\mathbf{Q}) \cos (\omega_{pq\gamma} t) \qquad (1)$$

where the frequency ω and amplitude $f(\mathbf{Q})$ take different values depending upon the particular standing displacement waves which are excited in the gel. The frequencies $\{\omega\}$ are not functions of $\mathbf{Q}$ (the Bragg wavevector). Thus, if only a single

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