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 $a_{\mathrm{theor}} \simeq 2.25$ 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

R. Nossal* and S. L. Brenner

Physical Sciences Laboratory, Division of Computer Research and Technology,
National Institutes of Health, Bethesda, Maryland 20014. *Received April 11, 1977*

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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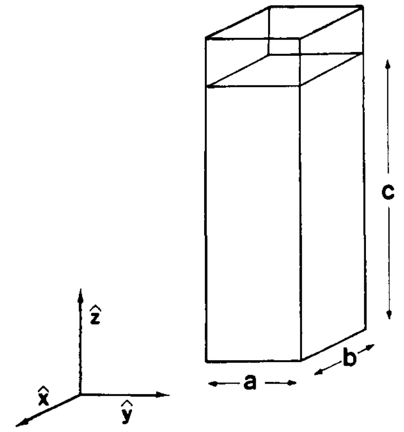

Figure 1. The gel is contained in a cuvette having rectangular cross section. We assume that the scattering plane lies perpendicular to the z axis.

mode is excited, the time dependence of the measured autocorrelation function should be independent of scattering angle. We find that, when the top surface of the gel is free, the *observable* mode frequencies are given by

$$\omega_{pq\gamma} = \pi C_{\mathrm{long}}\left[\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{\gamma^2}{c^2}\right]^{1/2} \tag{2}$$

where γ either is zero or a half-integer value ($n + \frac{1}{2}$), p, q, and n are arbitrary integers (except that p and q cannot both be zero), a, b, and c are the dimensions of the gel (see Figure 1), and C_{long} is the longitudinal sound velocity (see eq 18 and 27, below). However, if the cuvette is closed and if the top surface of the gel is constrained in the same way as are the bottom and sides, only the $\omega_{p,q,0}$ modes will be seen.

II. Intensity Autocorrelation of Scattered Light

At sufficiently low light levels the number of photons $n(t)$ detected by a photomultiplier tube during a short element of time $\Delta\tau$ is proportional to the intensity of the electromagnetic field impinging upon its surface, i.e.,

$$n(t) \propto \frac{1}{\Delta\tau}\int_{t-(\Delta\tau/2)}^{t+(\Delta\tau/2)} E^*(\tau)E(\tau)\,\mathrm{d}\tau \sim (E^*(t)E(t))$$

where $E(t)$ is the magnitude of the field at time t. Thus, the joint expectation of the number of photons detected at time t with those detected at a later time $t + t'$ may be expressed as $\langle n(t)n(t + t')\rangle \sim \langle E^*(t)E(t)E^*(t + t')E(t + t')\rangle$ which, for a stochastically stationary scattering process, is equivalent to $\langle n(0)n(t')\rangle \sim \langle E^*(0)E(0)E^*(t')E(t')\rangle$.

We consider the field at the detector to consist of a component whose intensity varies with time E_{sc} and a component E_0 whose intensity is essentially constant and uncorrelated with the first. When the strength of the constant component is much greater than that of the fluctuating component, one can write[4]

$$\langle E^*(0)E(0)E^*(t)E(t)\rangle \simeq I_0{}^2 + 2I_0(\langle E^*{}_{\mathrm{sc}}(0)E_{\mathrm{sc}}(0)\rangle + Re\langle E^*{}_{\mathrm{sc}}(0)E_{\mathrm{sc}}(t)\rangle)$$

where $I_0 \equiv \langle E^*{}_0E_0\rangle$ is the intensity of the constant component. Intensity variation of the component E_{sc} results from fluctuations in the local polarizability of the irradiated region of the sample. The important point is that the time autocorrelation of the pulses emitted by the photodetector contains a small time-varying signal resting upon a large time-independent background. The time-dependent part, which we henceforth designate as $I(\mathbf{Q},t)$, is proportional to the time autocorrelation of the scattered field, i.e., $I \sim Re\langle E^*{}_{\mathrm{sc}}(0)\cdot E_{\mathrm{sc}}(t)\rangle$.

For the isotropic systems of current interest, refractive index fluctuations can be taken as being proportional to local deviations in material density. Thus, the scattered field can be shown[5] to be proportional to $\delta\rho(\mathbf{Q},t) = \int \mathrm{d}^3\mathbf{r}\, e^{-i\mathbf{Q}\cdot\mathbf{r}}\delta\rho(\mathbf{r},t)$, i.e., to that Fourier component of the density which has wave vector $\mathbf{Q} \equiv \mathbf{k}_{\mathrm{i}} - \mathbf{k}_{\mathrm{s}}$ where $\mathbf{k}_{\mathrm{i}}$ and $\mathbf{k}_{\mathrm{s}}$ are the wave vectors of the incident and detected fields. [The magnitude of $\mathbf{Q}$ is a function of scattering angle θ, $|\mathbf{Q}| = (4\pi n/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident light and n is the mean value of the index of refraction of the medium; we note that $\mathbf{Q}$ lies in the plane defined by $(\mathbf{k}_{\mathrm{i}},\mathbf{k}_{\mathrm{s}})$.] Consequently, $I(t)$ may be expressed as

$$I(\mathbf{Q},t) \sim Re\langle\delta\rho^*(\mathbf{Q},0)\delta\rho(\mathbf{Q},t)\rangle \tag{3}$$

In a continuum, the deviation of the density ρ from local equilibrium is given by the continuity equation[3] (conservation of mass)

$$\delta\rho = -\rho\nabla\cdot\mathbf{u} \tag{4}$$

where $\mathbf{u}(x,y,z) = (u_x(x,y,z),u_y(x,y,z),u_z(x,y,z))$ is the displacement vector. The latter indicates the displacement of a differential volume element whose equilibrium position is at (x,y,z). Thus, for small fluctuations in density one has

$$\delta\rho(\mathbf{Q},t) \simeq -\mathrm{i}\rho_0\mathbf{Q}\cdot\mathbf{u}(\mathbf{Q},t) \tag{5}$$

where ρ_0 is the equilibrium density and, for example, $u_x(\mathbf{Q},t)$ is defined by

$$u_x(\mathbf{Q},t) = \int_V \mathrm{d}\mathbf{r}\, e^{\mathrm{i}\mathbf{Q}\cdot\mathbf{r}}u_x(\mathbf{r},t) \tag{6}$$

where the integration is over the volume of material.

We assume that $\mathbf{Q}$ lies in the (x,y) plane so that its components are $\mathbf{Q} = (Q_x,Q_y,0)$ (see Figure 1). It then follows from eq 3 and 5 that $I(\mathbf{Q},t)$ can be expressed as

$$I(\mathbf{Q},t) \sim Re\{Q_x{}^2\langle u_x^*(\mathbf{Q},0)u_x(\mathbf{Q},t)\rangle + Q_xQ_y[\langle u_x^*(\mathbf{Q},0)u_y(\mathbf{Q},t)\rangle + \langle u_y^*(\mathbf{Q},0)u_x(\mathbf{Q},t)\rangle] + Q_y{}^2\langle u_y^*(\mathbf{Q},0)u_y(\mathbf{Q},t)\rangle\} \tag{7}$$

In the next section we modify an argument previously outlined by Sommerfeld (ref 2, p 315 ff) regarding solutions of the elasticity equations and thereby derive expressions for the displacements.

III. Solution of the Elasticity Equations

We recall that the classical elasticity equations are derived from Newton's second law. In the absence of external forces, the latter can be written in terms of the displacement vector $\mathbf{u} = \{u_x(r,t),u_y(r,t),u_z(r,t)\}$ as[2]

$$\rho\frac{\partial^2\mathbf{u}}{\partial t^2} = \nabla\cdot\tilde{\sigma} \tag{8a}$$

where ρ is the mass density and $\tilde{\sigma}$ is the stress tensor. The components of the stress tensor σ_{ij} signify the force along the j axis (x, y, or z) on a unit plane perpendicular to the i axis so that the net force on a unit cube of the material (i.e., the difference of the stresses on opposite walls of the cube) is given by the divergence of the stress tensor. When the displacements are small, so that stress is proportional to strain, the stress tensor can be written in terms of the displacement vector as

$$\sigma_{ij} = \mu\left(\frac{\partial u_i}{\partial j} + \frac{\partial u_j}{\partial i}\right) + \lambda\delta^{\mathrm{kr}}{}_{ij}\nabla\cdot\mathbf{u} \tag{8b}$$

where μ and λ are the Lamé coefficients[17] and $\delta^{\mathrm{kr}}{}_{ij}$ is the Kronecker delta ($\delta^{\mathrm{kr}}{}_{ij} = 1$ if $i = j$, $\delta^{\mathrm{kr}}{}_{ij} = 0$ if $i \neq j$).

Fluctuations of refractive index largely result from motions of the fibrous constituents of the gel. Thus, the material parameters which appear in eq 8 fundamentally pertain to the polymer lattice. Several investigators have indicated that kinetic equations for lattice displacements also contain dissipative terms.[6,7,10,13,14] However, our intention here is to study how macroscopic boundaries affect the displacements and, in their present form, eq 8 are mathematically tractable yet seem to provide good approximations to the observable excitations. In Appendix B we discuss the consequences of including dissipative terms and argue that they affect the amplitudes of displacements without changing the frequencies (see, also, discussion in section V).

When eq 8b is inserted into eq 8a, the following coupled equations are obtained for the components of the displacement vector

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \mu \nabla^2 u_i + (\lambda + \mu) \frac{\partial}{\partial i} (\nabla \cdot \mathbf{u}) \qquad i = x, y, z \tag{9}$$

We consider the gel to be contained in a cuvette of rectangular cross section and solve eq 9 subject to the boundary conditions (see Figure 1)

$$u_x = 0, \quad \sigma_{xy} = \sigma_{xz} = 0, \quad x = 0, a \tag{10a}$$

$$u_y = 0, \quad \sigma_{yx} = \sigma_{yz} = 0, \quad y = 0, b \tag{10b}$$

$$u_z = 0, \quad \sigma_{zx} = \sigma_{zy} = 0, \quad z = 0 \tag{10c}$$

$$\int_0^a \int_0^b [\sigma_{zx} u_x + \sigma_{zy} u_y + \sigma_{zz} u_z]\, dx\, dy = 0, \quad z = c \tag{10d}$$

The first three of these conditions (eq 10a–c) specify that the gel does not detach from the walls of the cuvette although (as a first approximation) there is no resistance to lateral movement. The condition given in eq 10d asserts that the total work performed in displacements of the top (free) surface of the gel is zero.[2] The conditions given in eq 10a–c also imply that energy is not exchanged with the surroundings as a consequence of gel displacements, but they are more restrictive than the one given in eq 10d.

The top surface here is considered to be free, but we later consider the top of the gel to adjoin a closed cuvette face and show that for many applications it is unnecessary to specify boundary forces along the *z* surfaces with precision. Although it is difficult to quantify the degree to which the approximation of zero stress at the cuvette faces actually satisfies the true physics of the boundary interactions, the results shown in the preceding paper (see, especially, Figures 4 and 5) are consistent with the conditions given in eq 10. We envision applying results of our analysis to experimental situations where the gel slips easily along the surfaces of its container.

Using the relationship between stress and displacement vector (eq 8b), the conditions given by eq 10a–c may be written in the equivalent form

$$u_x = 0, \quad \partial u_y/\partial x = \partial u_z/\partial x = 0, \quad x = 0, a \tag{11a}$$

$$u_y = 0, \quad \partial u_x/\partial y = \partial u_z/\partial y = 0, \quad y = 0, b \tag{11b}$$

$$u_z = 0, \quad \partial u_x/\partial z = \partial u_y/\partial z = 0, \quad z = 0 \tag{11c}$$

Equations 8 and 11 can be solved by a scheme which is similar to that used by Sommerfeld.[2] [In most respects the method is identical with that given in ref 2 but, since the boundary conditions are different, details differ somewhat.] It is easily verified that eq 8 are satisfied by functions of the form

$$\begin{aligned} u_x &= A \sin \frac{\alpha\pi x}{a} \cos \frac{\beta\pi y}{b} \cos \frac{\gamma\pi z}{c}\, e^{-\mathrm{i}\omega_{\alpha\beta\gamma} t} \\ u_y &= B \cos \frac{\alpha\pi x}{a} \sin \frac{\beta\pi y}{b} \cos \frac{\gamma\pi z}{c}\, e^{-\mathrm{i}\omega_{\alpha\beta\gamma} t} \\ u_z &= C \cos \frac{\alpha\pi x}{a} \cos \frac{\beta\pi y}{b} \sin \frac{\gamma\pi z}{c}\, e^{-\mathrm{i}\omega_{\alpha\beta\gamma} t} \end{aligned} \tag{12}$$

and that the boundary conditions (eq 11a–c) imply that α and β are integers,

$$\alpha = p, \beta = q \qquad p, q = 0, 1, 2, \ldots \tag{13}$$

We also find, when the conditions given in eq 10d and 8 are applied to eq 12,

$$\begin{aligned} 0 = \frac{\pi ab}{4} \Bigg\{ -\mu \left(\frac{\gamma}{c} \{A^2(1 - \delta^{\mathrm{kr}}{}_{\alpha,0}) + B^2(1 - \delta^{\mathrm{kr}}{}_{\beta,0})\} \right) \\ + \left\{ \frac{\alpha A}{a} + \frac{\beta B}{b} \right\} C + C \left([2\mu + \lambda] \frac{\gamma C}{c} + \lambda \left\{ \frac{\alpha A}{a} + \frac{\beta B}{b} \right\} \right) \Bigg\} \\ \times \cos \gamma\pi \sin \gamma\pi\, e^{-2\mathrm{i}\omega t} \end{aligned} \tag{14}$$

Thus, γ takes the value $\gamma = n$ or $\gamma = (n + 1/2)$, n being any arbitrary integer, since in that case the factor appearing in eq 14, $\sin \gamma\pi \cos \gamma\pi$, is zero. However, we show below that only certain of the allowed modes are pervious to the light scattering probe and that those modes for which γ is a nonzero integer do not contribute to $I(\mathbf{Q},t)$. [In the appendix we show that any values of γ which might satisfy eq 14, other than $\gamma = 0$ or $\gamma = n + 1/2$, also are unlikely to be of significance.]

Expressions for the frequencies are obtained by inserting eq 12 in eq 8 and cancelling common factors. One finds[2]

$$\begin{aligned} A \left(\Omega + \frac{\alpha^2}{a^2} \right) + B \frac{\alpha\beta}{ab} + C \frac{\alpha\gamma}{ac} &= 0 \\ A \frac{\beta\alpha}{ba} + B \left(\Omega + \frac{\beta^2}{b^2} \right) + C \frac{\beta\gamma}{bc} &= 0 \\ A \frac{\gamma\alpha}{ca} + B \frac{\gamma\beta}{cb} + C \left(\Omega + \frac{\gamma^2}{c^2} \right) &= 0 \end{aligned} \tag{15}$$

with Ω defined by

$$(\lambda + \mu)\Omega = \mu \left(\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right) - \frac{\rho\omega^2}{\pi^2} \tag{16}$$

In order that eq 15 have a nontrivial solution, Ω must take on either of the two values $\Omega = 0$ or

$$\Omega = -\left[\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right]$$

which follow from setting the determinant of the coefficients of A, B, and C equal to zero.[2] The corresponding frequencies are given according to eq 16 as

$$\omega_{\alpha\beta\gamma} = \pi C_{\mathrm{tr}} \left(\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right)^{1/2} \tag{17a}$$

$$(\text{if } \Omega = 0)$$

$$\omega_{\alpha\beta\gamma} = \pi C_{\mathrm{long}} \left(\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right)^{1/2} \tag{17b}$$

$$\left(\text{if } \Omega = -\left[\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right] \right)$$

where the coefficients C_{tr} and C_{long} are usually identified as the transverse and longitudinal sound velocities.[2,3]

$$C_{\mathrm{tr}} = \left(\frac{2\mu}{\rho} \right)^{1/2}, \quad C_{\mathrm{long}} = \left(\frac{\lambda + 2\mu}{\rho} \right)^{1/2} \tag{18}$$

We also find relationships between the coefficients A, B, and C by inserting the two permissible values of Ω into eq 15 to obtain

$$A \frac{\alpha}{a} + B \frac{\beta}{b} + C \frac{\gamma}{c} = 0 \qquad (\text{if } \Omega = 0) \tag{19a}$$

$$\frac{\beta A}{b} = \frac{\alpha}{a} B, \quad \frac{\beta}{b} C = \frac{\gamma}{c} B \qquad \left(\text{if } \Omega = -\left[\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} \right] \right) \tag{19b}$$

As shall be shown below, the conditions given in eq 19a imply that frequencies associated with transverse modes (eq 17a) are unlikely to be observed, since their corresponding photon autocorrelation functions have very small amplitudes in comparison with those of longitudinal excitations which are similarly excited (see section IV and the appendix).

IV. Photon Autocorrelation Function $I(\mathbf{Q},t)$

In order to complete the derivation of $I(\mathbf{Q},t)$ according to eq 7, one next needs to take Fourier transforms of the displacements and then form appropriate autocorrelations. From eq 6 one finds, for example, that $u_x(\mathbf{Q},t)$ is given as

$$u_x(\mathbf{Q},t) = \frac{\alpha Q_y A c \sin \gamma\pi}{\mathrm{i} a \gamma} \times \left[\frac{1 - (-)^{\alpha} e^{\mathrm{i} Q_x a}}{\dfrac{\alpha^2\pi^2}{a^2} - Q_x{}^2}\right]\left[\frac{1 - (-)^{\beta} e^{\mathrm{i} Q_y b}}{\dfrac{\beta^2\pi^2}{b^2} - Q_y{}^2}\right] e^{-\mathrm{i}\omega_{\alpha\beta\gamma} t} \tag{20}$$

An analogous expression is found for $u_y(\mathbf{Q},t)$. It thus follows from eq 7 that $I(\mathbf{Q},t)$ is given as

$$I(\mathbf{Q},t) = 4Q_x{}^2 Q_y{}^2 (abc)^2 (A\alpha b + B\beta a)^2 \left(\frac{\sin \gamma\pi}{\gamma}\right)^2 \times \left[\frac{1 - (-)^{\alpha} \cos (aQ_x)}{(\alpha^2\pi^2 - a^2 Q_x{}^2)^2}\right]\left[\frac{1 - (-)^{\beta} \cos bQ_y}{(\beta^2\pi^2 - b^2 Q_y{}^2)^2}\right] \times \cos (\omega_{\alpha\beta\gamma} t) \tag{21a}$$

Equation 21a has the form $I = f(\mathbf{Q},\mathbf{k}) \cos \omega_k t$, where $\mathbf{k}$ is a wave vector whose components are $k_x = \pi\alpha/a$, $k_y = \pi\beta/b$, $k_z = \pi\gamma/c$. The dispersion relation which relates $\omega_{\alpha,\beta,\gamma}$ to k is given by eq 17 and, since only discrete values of $\mathbf{k}$ are allowed due to finite boundaries, only discrete values of $\omega_{\alpha,\beta,\gamma}$ are permissible. In the more familiar case that a scattering ensemble is taken to be infinite in extent,[10] ω becomes a continuous function of k. Also, for an infinite ensemble $f(\mathbf{Q},\mathbf{k})$ is proportional to[5] $\delta(\mathbf{Q} - \mathbf{k})$ and ω becomes a functional of Q, i.e., $\omega_k \rightarrow \omega(Q)$.

Note that since Q^2 is of the order of 10^{10} cm^{-2} whereas a^2 and b^2 are of the order of cm^2, eq 21a is well approximated by the somewhat simpler form

$$I(\mathbf{Q},t) \simeq 4(abc)^2 \left(\frac{\sin \gamma\pi}{\gamma}\right)^2 \left(\frac{A\alpha}{a} + \frac{B\beta}{b}\right)^2 \times \left[\frac{1 - (-)^{\alpha} \cos aQ_x}{(aQ_x)^2}\right]\left[\frac{1 - (-)^{\beta} \cos bQ_y}{(bQ_y)^2}\right] \times \cos (\omega_{\alpha\beta\gamma} t) \tag{21b}$$

The multiplicative factors in the above expression limit the modes which can be seen by light scattering. First, note that $(\sin \gamma\pi)/\gamma$ vanishes when γ is a nonzero integer, so that modes of integral γ values other than 0 will not contribute to $I(\mathbf{Q},t)$. Second, we deduce that transverse modes are much more difficult to see than are corresponding longitudinal modes. This point is unambiguously demonstrated for the $\gamma = 0$ modes since, in that case, eq 19a implies that the factor $(A(\alpha/a) + B(\beta/b))^2$ pertaining to transverse modes is zero for all α and β and, by eq 21b, $I(\mathbf{Q},t)$ vanishes. In contrast, upon using eq 19b we see that for longitudinal modes the same factor takes the form

$$\left(\frac{\alpha A}{a} + \frac{\beta B}{b}\right)^2 = \left(\frac{c}{\gamma}\left[\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2}\right] C\right)^2 > 0 \tag{22}$$

(longitudinal modes)

Although the amplitudes for the transverse *half-integer* modes are not strictly zero, we can demonstrate that, at least for low values of γ, they are small when compared with the longitudinal modes of the same order. When $\Omega = 0$ but $\gamma \neq 0$ we have from eq 19a

$$\left(\frac{\alpha A}{a} + \frac{\beta B}{b}\right)^2 = \left(\frac{\gamma C}{c}\right)^2 \tag{23}$$

(transverse modes)

Comparing the latter with the expression given in eq 22 and assuming that the coefficients C are identical, we find that the ratio of the two expressions is

$$R \equiv \frac{[I(\mathbf{Q},t)]_{\mathrm{long}}}{[I(\mathbf{Q},t)]_{\mathrm{tr}}} = \frac{1}{\gamma^4}\left[\left(\frac{\alpha c}{a}\right)^2 + \left(\frac{\beta c}{b}\right)^2\right]^2 \tag{24}$$

Taking as an example the values $c/a = c/b = 4$, $\alpha = 1$, $\beta = 0$, $\gamma = 5/2$, we find that the amplitude of $I(\mathbf{Q},t)$ relating to the longitudinal excitation is 6.5 times that of the autocorrelation function associated with the transverse mode; for the lowest lying $\gamma = 1/2$ mode this ratio is approximately 4000. However, if the gel geometry is cubelike, so that $c/a \sim 1$, we find that the value of R associated with the lowest lying modes is only 10.5. In the latter instance it might be possible to observe transverse modes if external vibration is used to enhance their amplitudes.

V. Discussion

We have shown that various oscillating photon autocorrelation functions can be observed when laser inelastic light scattering is used to probe the mechanical properties of soft gels. Although the relative intensities of the various components of $I(\mathbf{Q},t)$ will depend upon $\mathbf{Q}$, the oscillation frequencies are angle independent. Measurable frequencies are in two sets, namely,

$$\left.\begin{aligned} \omega_{pq} &= \pi C_{\mathrm{long}} \left[\frac{p^2}{a^2} + \frac{q^2}{b^2}\right]^{1/2} \\ \omega_{pqn} &= \pi C_{\mathrm{long}} \left[\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{(n + 1/2)^2}{c^2}\right]^{1/2} \end{aligned}\right\} \text{(open cell)} \tag{25}$$

where p, q, and n are arbitrary integers, except that p and q cannot both be zero. Examples of the mode structure given in eq 25 are shown in Figure 4 of ref 1.

For comparison we also investigated the form of $I(\mathbf{Q},t)$ obtained when a gel is *fully* enclosed in a cuvette. We considered the top surface to be in contact with a wall so that, instead of the boundary condition given by eq 11d, we used $[u_z = 0;\ \partial u_x/\partial z = \partial u_y/\partial z = 0]$ at $z = c$ (cf. eq 11c). The derivation is similar to that which led to eq 20 and 21, resulting in an equation which, as before, is of the form given in eq 1. However, the frequencies in this case are given as

$$\omega_{pq} = \pi C_{\mathrm{long}} \left[\frac{p^2}{a^2} + \frac{q^2}{b^2}\right]^{1/2} \quad \text{(closed cell)} \tag{26}$$

where p and q are integers, not both zero.[18]

Of course, the quantities of real interest are the elastic moduli which determine the longitudinal sound velocity. C_{long} can be expressed in terms of the elasticity coefficients,

$$C_{\mathrm{long}} = \left(\frac{K + 4/3 G}{\rho}\right)^{1/2} \tag{27}$$

where K is the "compressibility modulus" (whose inverse K^{-1} relates volume changes to applied pressure when a body is subject to pure hydrostatic compression) and G is the "rigidity modulus" (whose inverse G^{-1} pertains to shape changes occurring in response to applied shear stresses). Alternatively, C_{long} can be expressed as[3]

$$C_{\mathrm{long}} = \left[\frac{E(1 - \sigma)}{\rho(1 + \sigma)(1 - 2\sigma)}\right]^{1/2} \tag{27'}$$

where E is Young's modulus (relating the extension or compression of an unconstrained material to forces which are applied parallel to the deformation; for example, $u_{zz} = p/E$, where p is a uniform pressure applied at the ends of a rod) and σ is Poisson's ratio (the ratio of transverse compression to longitudinal extension). We recall that ρ, appearing in eq 27, signifies material density (mass/volume). The coefficients which appear in eq 18 and 27 are isothermal moduli, since the frequencies given in eq 25 and 26 are much lower than those associated with typical molecular relaxation processes.

The refractive index inhomogeneities which cause detectable light scattering derive from the presence of polymer strands in the gel. Thus, the measured compressibility moduli are, to first order, essentially those of the polymer matrix *alone*. The properties of the solvent influence the measurement only indirectly, which explains why the frequencies $\{\omega_{\alpha,\beta,\gamma}\}$ tend to zero as the polymer concentration is decreased (see Figure 7 of ref 1). In principle the elastic moduli can be related to the detailed mechanical structure of a gel.[6-8] In highly cross-linked structures such as rubber the magnitude of the compressibility modulus is much greater than that of the rigidity modulus,[9] i.e., $K \gg G$, so that $C_{\text{long}} = (K/\rho)^{1/2}$. If the gel structure is loose (spongelike) one expects little lateral motion when the gel matrix is compressed,[10] in which case $\sigma \approx 0$ and, as seen from eq 27′, the longitudinal sound speed essentially depends on the Young's modulus.

We emphasize that in contrast to thermal motions which have been probed in previous light scattering studies,[10-13] the gel excitations now of concern are of mechanical origin.[1] The idealized model described by eq 8–11 suggests that, once excited, the various standing modes persist with constant amplitude. Equations 8 and 10 presumably should contain additional terms to account for damping of lattice vibrations and, also, to describe external forces which couple to the gel through the walls of the cuvette. A simplified model which encompasses such effects is examined below, in Appendix B. However, a more general theory incorporating these aspects needs to be developed, perhaps in the form of a modification of Szu's recent work on the Brownian motion of elastically deformable bodies.[14] Nonetheless, for the materials which we have heretofore studied, neglecting such factors does not seem to lead to inconsistencies when experimental results are analyzed.[1]

Damping might derive from various mechanisms, including friction between polymer network and the solvent,[10] statistical dissipation of excitation due to spatial defects in the lattice structure of the gel,[7] or scattering of density waves by imperfections located at the boundaries. Energy which initially is contained in a particular excitation becomes redistributed over a broad set of different excitation modes. However, the latter give rise via phonon–phonon interactions to yet other phonons, some having the wavelength of the original excitations. Thus, a dynamic equilibrium of mechanical excitations could be established throughout a random polymer matrix. The cuvette essentially acts as a resonant cavity, sustaining those density fluctuations whose spatial structure is consistent with eq 2, whereas other excitations are rapidly damped. Weak external vibrations compensate for energy lost from the gel by frictional damping of excitations at the walls of the cuvette.

The physics encompassed in this model obviously needs further elaboration. However, we note that each element of the "chaotic" band of lattice vibrations would contribute its own component to the intensity autocorrelation function $\langle n(0)n(t)\rangle$. The sum of these components might constitute a significant portion of the anomolously high constant background which frequently is observed when quasielastic light scattering is used to probe gel excitations.[1,15]

Other factors which need to be considered include interference arising from spatially correlated scattering centers and possible multiple scattering. However, we have found it possible to rationalize available data while neglecting such considerations.[1]

VI. Appendix. Other Roots of Equation 14

Equation 14 in principle also can be satisfied if the term Ξ, defined as

$$\Xi = -\mu\left(\frac{\gamma}{c}\left[A^2(1-\delta^{\text{kr}}{}_{\alpha,0}) + B^2(1-\delta^{\text{kr}}{}_{\beta,0})\right] + C\left[\frac{\alpha A}{a} + \frac{\beta B}{b}\right]\right) + C\left[(2\mu+\lambda)\frac{\gamma C}{c} + \lambda\left(\frac{\alpha A}{a} + \frac{\beta B}{b}\right)\right] \qquad \text{(A1)}$$

is zero. Are there any values of γ for which such is the case?

Let us first consider the situation when

$$\Omega = -\left(\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{2}\right)$$

(see eq 15–19). Upon using the relationships given in eq 19b, Ξ is found to be

$$\Xi_{\text{long}} = (\lambda - 2\mu)\left[\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2}\right] + 4\mu\frac{\gamma^2}{c^2} \qquad \text{(A2)}$$

In general, only rather special combinations of α, β, γ can satisfy $\Xi_{\text{long}} = 0$. This small subset of "extra" standing waves would occur at frequencies well above the lowest lying mode. If the Lamé coefficient λ were greater than twice the shear modulus, Ξ_{long} could not be zero under any circumstances and there would be no longitudinal excitations having frequencies other than those given in eq 25.

To consider transverse excitations we first recognize that eq 19a, when used in eq A1, yields

$$\Xi_{\text{tr}} = -\frac{\mu\gamma}{c}\left[A^2(1-\delta^{\text{kr}}{}_{\alpha,0}) + B^2(1-\delta^{\text{kr}}{}_{\beta,0}) - 3C^2\right] \qquad \text{(A3)}$$

Therefore, there might be cases where Ξ_{tr} is zero. However, we know that the amplitude of the correlation function for transverse modes usually is dwarfed by that for longitudinal modes so that such modes, even if they did occur, probably would not be discernible.

VII. Appendix B. Effects of Dissipative Terms and External Forces

We now illustrate how energy transferred to the polymer lattice by mechanical excitation can compensate for the frictional energy dissipated as a result of the interaction of polymer chains with surrounding fluid. For didactic purposes it suffices to use a somewhat simplified model, obtained by modifying eq 9 to include friction (in which case the equations become those employed by Tanaka et al.[10]) and extrinsic forces.

To simplify the analysis, the one-dimensional analogue of the resulting equations is considered, viz. (cf. eq 9 and 18)

$$\frac{\partial^2 u_x}{\partial t^2} - C_{\text{long}}{}^2\frac{\partial^2 u_x}{\partial x^2} + \beta\frac{\partial u_x}{\partial t} = F(x,t) \qquad \text{(B1)}$$

where $\rho\beta$ is the friction coefficient[10] and ρF represents an extrinsic force acting upon the lattice. The latter could arise from several sources, but we here assume that $F(x,t)$ derives from vibrations which are transmitted to the polymer by the surrounding fluid. The displacement u_x is subject to the boundary conditions given in eq 11a, as is the force; i.e., $u_x(0,t) = u_x(a,t) = 0$, $F(0,t) = F(a,t) = 0$.

If the forcing term is decomposed into Fourier components as $F(x,t) = \sum_{n=-\infty}^{\infty} f_n(t)\sin(n\pi x/a)$, $u_x(x,t)$ is given as

$$u_x(x,t) = \sum_{n=-\infty}^{\infty} a_n(t)\sin\frac{n\pi x}{a} \qquad \text{(B2)}$$

The coefficient $a_n(t)$ is obtained by solving

$$\frac{d^2a_n}{dt^2} + \omega_n{}^2 a_n + \beta\frac{da_n}{dt} = f_n(t) \qquad (B3)$$

where ω_n is defined as (cf. eq 17)

$$\omega_n{}^2 = \frac{\pi^2 n^2 C_{\mathrm{long}}{}^2}{a^2} \qquad (B4)$$

Equation B3 can be solved by variation of parameters, which yields (see, e.g., Chandrasekhar's review article,[16] eq 194)

$$a_n = \frac{1}{\mu_1 - \mu_2}\left\{e^{\mu_1 t}\int_0^t e^{-\mu_1 \xi} f_n(\xi)\,d\xi - e^{\mu_2 t}\int_0^t e^{-\mu_2 \xi} f_n(\xi)\,d\xi\right\} + a_{10}e^{\mu_1 t} + a_{20}e^{\mu_2 t} \qquad (B5)$$

where

$$\mu_1 = -\frac{\beta}{2} + \left(\frac{\beta^2}{4} - \omega_n{}^2\right)^{1/2}, \quad \mu_2 = -\frac{\beta}{2} - \left(\frac{\beta^2}{4} - \omega_n{}^2\right)^{1/2} \qquad (B6)$$

and a_{10} and a_{20} are constants (which implicity depend on n). The terms $a_{10}e^{\mu_1 t}$, $a_{20}e^{\mu_2 t}$ decay rather rapidly, so that we need focus only on the integrals which contain the forces. Expressing the components of force in terms of Fourier integrals as

$$f_n(t) \sim \int f_n(\nu) \sin \nu t \, d\nu \qquad (B7)$$

we thus need consider (cf. eq B5)

$$\mathrm{i}_n(\nu) = \frac{1}{\mu_1 - \mu_2}\left\{e^{\mu_1 t}\int_0^t e^{-\mu_1 \xi} \sin \nu\xi \, d\xi - e^{\mu_2 t}\int_0^t e^{-\mu_2 \xi} \sin \nu\xi \, d\xi\right\} \qquad (B8)$$

where $a_n = \int f_n(\nu)\mathrm{i}_n(\nu)\,d\nu$.

Suppose $\beta > 2\omega_n$. Then, upon performing the integrals and some simple algebra, one finds

$$\mathrm{i}_n(\nu) = \frac{\nu\beta \cos \nu t + (\omega_n{}^2 - \nu^2) \sin \nu t}{(\omega_n{}^2 - \nu^2)^2 + \nu^2\beta^2} + \text{terms } \mathcal{O}(e^{\mu_1 t}, e^{\mu_2 t}) \qquad (B9)$$

Similar expressions are obtained if $f_n(t)$ contains cosine terms (see eq B7) or if $\beta < 2\omega_n$.

The expression for u_x influences the light scattering signal via eq 7. Thus, these results would imply that the photon autocorrelation function consists of a series of oscillating terms, the amplitudes of which are determined by the amplitudes of the components of the transmitted force field. If the forcing field contained only components whose frequencies were close to a particular ω_n, we could observe a single cosine component in the autocorrelation function due to the resonant structure of the denominator of eq B9. In the absence of strong external vibrations the $\{f_n\}$ (see eq B7) have such properties, since lattice excitations whose wavelengths are appropriate to the cavity dimensions experience constructive interference due to reflections from the cavity boundaries and thus increase in amplitude relative to these excitations which are not in resonance. Thus, even were "friction" to be present, the frequencies observed in the resulting autocorrelation function would be those given in eq 17. When the dissipative forces are very strong (i.e., large β), the amplitudes of the oscillating modes are attenuated.

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(17) The Lame coefficients are related to the compressibility and shear moduli by $K = \lambda + \frac{2}{3}\mu$ and $G = \mu$, respectively.

(18) Fully enclosing the gel ensures that the measured frequencies pertain to longitudinal excitations since the amplitudes of $I(\mathbf{Q},t)$ associated with transverse modes are zero when γ is zero (cf. eq 23 and the discussion following eq 24). On several occasions we performed measurements on samples which were completely enclosed. The measured lowest frequencies of $I(\mathbf{Q},t)$ were found to be identical with those obtained when using open cuvettes, thus reinforcing the notion that the excitations which can be probed by this technique are longitudinal modes.