Brillouin light scattering from polymer gels[a)]

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This paper is devoted to the theory of laser light scattering from polymer gels. The principal purpose of the inquiry is the structure of the Brillouin peaks that arise from the damped sound modes that are supported by the polymer network–fluid system. Our analysis includes coupling between sound waves in the fluid and elastic waves in the polymer network that is present even in the absence of any dissipative mechanisms. Explicit expressions are given for the eigenmodes of the gel in the presence of viscous damping and strong friction between the fluid motion and the polymer network. A comparison is made between the theory and available experimental evidence. The main point is that the shift and width of the Brillouin light scattering peaks (and by analogy sound attenuation) may usefully be employed to study both the static and dynamical properties of polymer gels.

I. INTRODUCTION

Recently, there has been renewed interest in the study of gels and cross-linked polymer networks because of their importance in biology and chemistry. Efforts have been made to improve understanding of the dynamical properties of gels by use of modern laser light scattering techniques. In particular, in a pioneering study, Tanaka, Hocker, and Benedek[1] demonstrated how the spectrum of light scattered from a gel could be employed to characterize the viscoelastic properties of the gel. These authors focused attention on the broadening of the central or Rayleigh line around the exciting frequency that is observed in the polarized or unpolarized scattered light. The broadening arises from the overdamped motion of the polymer network.

The purpose of the present work is to inquire about information that may be obtained about the gel by considering the broadening of the Brillouin peaks that appear in the light scattering spectrum. One may anticipate that the density fluctuations that are propagating through the medium as sound waves will suffer additional scattering from the relatively fixed elastic polymer network. This scattering will lead to a shorter lifetime for the density fluctuations and, hence, to spectral broadening. This problem is closely related to the problem considered by Bacri *et al.*[2,3] on the use of ultrasonic wave attenuation as a tool for measuring gelation processes.

Our reason for studying this problem is partially motivated by noticing the similarity that might be expected between a cross-linked polymer gel and a concentrated, i.e., entangled or semidilute,[4] polymer solution in a good solvent. The properties of concentrated polymer solution, because of the relative immobility of individual chains, may be better modeled by an elastic network invaded by solvent, rather than the more customary binary fluid model which is employed for dilute polymer solutions. New methods that potentially may be employed to characterize concentrated polymer systems are of great interest.

The limiting case of the picture adopted here for a concentrated polymer solution is similar to flow in porous media. This lies at the base of the Debye–Bueche[4] model for the frictional properties of polymer solution. The microscopic basis of this model has been the subject of some recent investigation.[5] Because of this analogy, it is also not surprising to find that geophysicists who are interested in employing acoustic measurements to characterize fluid bearing porous media encounter similar hydrodynamic phenomena. An example of recent pertinent geophysical work is due to Johnson and collaborators[6] in their studies of so-called Biot waves[7] in porous media.

The outline of the paper is as follows. Section II presents a brief summary of pertinent light scattering theory. Section III is devoted to an analysis of the hydrodynamic equations. Section IV discusses the resulting dispersion equation in various limits. Section V derives the light scattering spectrum for one of the cases discussed in Sec. IV. Section VI includes a comparison of the predictions obtained in previous sections to related work and some concluding remarks.

II. LIGHT SCATTERING

The spectrum of light scattered from the gel[8] will be proportional to

$$I(\mathbf{k},\omega)=2\,\mathrm{Re}\int_0^\infty dt\exp(-i\omega t)\langle\delta\hat{\epsilon}(\mathbf{k},t)\delta\hat{\epsilon}(-\mathbf{k})\rangle\,, \qquad (2.1)$$

where ω is the frequency shift from the exciting laser line, k is the wave vector characterizing the fluctuation of the dielectric constant $\delta\epsilon$ that gives rise to the scattering

$$|\mathbf{k}|=\frac{4\pi}{\lambda}\,n\sin(\theta/2)\,, \qquad (2.2)$$

with θ the scattering angle, n the average index of refraction of the medium, and λ the incident wavelength.

The Fourier transform of the space and time dependent fluctuating dielectric constant $\delta\epsilon(\mathbf{r},t)$ is given by

$$\delta\hat{\epsilon}(\mathbf{k},t)=\int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})\delta\epsilon(\mathbf{r},t)\,. \qquad (2.3)$$

These dielectric fluctuations arise from equilibrium thermal fluctuations of the thermodynamic variables that

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characterize the system. The angular brackets in Eq. (2.1) denote an average over the equilibrium fluctuations; the time dependence of the fluctuations is computed from appropriate linearized hydrodynamic equations. Our attention will be limited here to polarized scattering.

In general, one assumes that the system is in local equilibrium and that the dielectric fluctuations may be expressed in terms of linear deviations of a pertinent subset of the thermodynamic variables $\{\delta\psi_j(\mathbf{r},t)\}$ from equilibrium:

$$\delta\hat{\epsilon}(\mathbf{k},t)=\sum_j\left(\frac{\partial\epsilon}{\partial\psi_j}\right)\delta\hat{\psi}_j(\mathbf{k},t)\,, \tag{2.4}$$

where the dielectric constant derivatives are evaluated at equilibrium. Accordingly, from Eq. (2.1) the spectrum is

$$I(\mathbf{k},\omega)=2\sum_{j,l}\left(\frac{\partial\epsilon}{\partial\psi_j}\right)\left(\frac{\partial\epsilon}{\partial\psi_l}\right)\times\mathrm{Re}\int_0^\infty dt\exp(-i\omega t)\langle\delta\hat{\psi}_j(\mathbf{k},t)\delta\hat{\psi}_l(-\mathbf{k})\rangle\,. \tag{2.5}$$

We shall assume that there are two pertinent variables that couple to the dielectric constant. These are the network density ρ_n and the solvent density ρ; thus $\partial\epsilon/\partial\psi_j$ will vanish except for these two variables. For the sake of concreteness, one may, at optical frequencies envision that ϵ depends upon these densities according to

$$\epsilon-1=4\pi(\alpha_n\rho_n+\alpha\rho)\,, \tag{2.6}$$

where α_n and α are the polarizability of the network and the solvent, respectively. Thus we neglect other potential thermodynamic fluctuation mechanisms, e.g., temperature, that may influence the light scattering.

In general, the linearized hydrodynamic equations for the thermodynamic variables will take the form, in vector notation,

$$\frac{\partial\delta\hat{\psi}}{\partial t}(\mathbf{k},t)=-\mathbf{M}(\mathbf{k})\cdot\delta\hat{\psi}(\mathbf{k},t)\,. \tag{2.7}$$

The one-sided time Fourier transform may be formally performed to obtain

$$\delta\tilde{\hat{\psi}}(\mathbf{k},\omega)=\int_0^\infty dt\exp(-i\omega t)\delta\hat{\psi}(\mathbf{k},t)=(i\omega\mathbf{I}+\mathbf{M})^{-1}\cdot\delta\hat{\psi}(\mathbf{k})\,. \tag{2.8}$$

This expression may be substituted into Eq. (2.5) to reach the result

$$I(\mathbf{k},\omega)=2\sum_{j,l,r}\left(\frac{\partial\epsilon}{\partial\psi_j}\right)\left(\frac{\partial\epsilon}{\partial\psi_l}\right)\times\mathrm{Re}(i\omega\mathbf{I}+\mathbf{M})^{-1}_{jr}\langle\delta\hat{\psi}_r(\mathbf{k})\delta\hat{\psi}_l(-\mathbf{k})\rangle\,. \tag{2.9}$$

We shall assume, although this assumption is open to attack, that the equilibrium fluctuations of the thermodynamic variables that shall be selected to describe the system under consideration are uncorrelated. Thus, we have

$$\langle\delta\hat{\psi}_r(\mathbf{k})\delta\hat{\psi}_l(-\mathbf{k})\rangle=\delta_{rl}\langle|\delta\hat{\psi}_l(\mathbf{k})|^2\rangle\,. \tag{2.10}$$

Relaxing this assumption would require an analysis of equilibrium thermodynamic fluctuation theory for elastic media. Potential modification to Eq. (2.10) could be included in the analysis, at the expense, however, of simplicity.

With Eq. (2.10), the result for the light scattering spectrum is

$$I(\mathbf{k},\omega)=2\sum_{j,l}\left(\frac{\partial\epsilon}{\partial\psi_j}\right)\left(\frac{\partial\epsilon}{\partial\psi_l}\right)\mathrm{Re}[i\omega\mathbf{I}+\mathbf{M}(\mathbf{k})]^{-1}_{jl}\langle|\delta\hat{\psi}_l(\mathbf{k})|^2\rangle\,. \tag{2.11}$$

Evaluation of this expression from an appropriate set of linearized hydrodynamic equations is undertaken in the next section. The sums in Eq. (2.11) are understood to extend over the two variables solvent density ρ and network density ρ_n.

III. LINEARIZED HYDRODYNAMIC EQUATIONS

The linearized hydrodynamic equations that we adopt to describe the gel system are as follows:

(1) The continuity equation for the solvent density

$$\frac{\partial\delta\rho}{\partial t}+\rho^0\nabla\cdot\mathbf{v}=0\,, \tag{3.1}$$

where v is the solvent fluid velocity.

(2) The continuity equation for the elastic gel network

$$\frac{\partial\delta\rho_n}{\partial t}+\rho_n^0\nabla\cdot\mathbf{u}=0\,, \tag{3.2}$$

where u is the velocity of the network from equilibrium.[9] Note that the network velocity u is related to the network displacement s according to

$$\frac{\partial\mathbf{s}}{\partial t}=\mathbf{u}\,.$$

Similarly, the fluid velocity v is related to the fluid displacement d according to

$$\frac{\partial\mathbf{d}}{\partial t}=\mathbf{v}\,.$$

Thus we have the relations

$$\delta\rho=-\rho^0\nabla\cdot\mathbf{d}\,,\qquad\delta\rho_n=-\rho_n^0\nabla\cdot\mathbf{s}\,. \tag{3.3}$$

(3) The linearized equation for the network displacement

$$\rho_n^0\frac{\partial^2\mathbf{s}}{\partial t^2}=\rho_n^0\frac{\partial\mathbf{u}}{\partial t}=\mu\nabla^2\mathbf{s}+(\kappa+\mu/3)\nabla(\nabla\cdot\mathbf{s})+\beta\nabla(\nabla\cdot\mathbf{d})-f(\mathbf{u}-\mathbf{v})\,. \tag{3.4}$$

In this expression the coefficients κ and μ are the network bulk and shear modulus terms, respectively. The last term on the right-hand side of Eq. (3.4) denotes the frictional damping on the elastic network resulting from the fluid moving relative to the network. The next to last term on the right-hand side of Eq. (3.4) contains the coupling effect of elastic waves in this two-phase system. Displacements of the fluid influence the networks and vice versa. Since Tanaka *et al.*[1] did not include the influence of the fluid on the network, the last two terms on the right-hand side of Eq. (3.4) do not appear in their analysis.

(4) The linearized Navier–Stokes equation for the velocity of the fluid

$$\rho^0 \frac{\partial \mathbf{v}}{\partial t} = -c_0^2 \nabla \delta\rho + \eta_s \nabla^2 \mathbf{v} + (\eta_v + \eta_{s/3}) \nabla(\nabla \cdot \mathbf{v}) + \beta \nabla(\nabla \cdot \mathbf{s}) - f(\mathbf{v} - \mathbf{u}) , \quad (3.5)$$

where c_0 is the speed of sound η_s and η_v, the shear and bulk fluid viscosity, respectively. The next to last term on the right-hand side of Eq. (3.5) includes the coupling of the elastic waves of the network with the fluid motion. Note that the coefficients β and f that appear in Eqs. (3.4) and (3.5) are identical as required by symmetry.[6,7] The final term on the right-hand side of Eq. (3.5) reflects the additional fluid damping due to the frictional loss in the network. In these equations the superscript zero on ρ^0 and ρ_n^0 denote the equilibrium fluid and gel density, respectively.

This hydrodynamic equation is not equivalent to the one introduced by Bacri and Rajaonarison[2] in their study of ultrasonic attenuation in gels. Bacri *et al.* do not include the coupling of the elastic waves described by the term involving β. For $\beta = 0$, the hydrodynamic description we have adopted reduces to that of Bacri *et al.*

It should be noted that other hydrodynamic equations, consistent with the symmetry and physics of the assumed physical situation, could be proposed. The virtue of the dynamical set adopted here is that the essential physics is contained (a) in the simple frictional damping term proportional to f that describes the exchange of momentum between the fluid and the network and (b) the coupling β of the elastic waves in the fluid and in the network. To our knowledge, the implications of this coupling for sound absorption or light scattering from polymer gels has not yet been explored.

When $f = 0$, one has the limiting case of a coupled elastic medium without damping. If $\mathbf{d} = 0$ (and hence $\mathbf{v} = 0$) in Eq. (3.4), one has the limiting case, considered by Tanaka *et al.*,[1] of the gel dissipating energy into the surrounding quiescent fluid. For our purposes, the critical terms are the elastic coupling term β and the frictional damping term f. It is these terms that carry information about the polymer network into the width of the Brillouin peaks.

The set of hydrodynamic equations may be most simply solved in terms of the Fourier–Laplace ($iw = z$) transform of the densities $\delta\rho$ and $\delta\rho_n$, the longitudinal part of the fluid velocity $\nabla \cdot \mathbf{v}$, and the longitudinal part of the network velocity $\nabla \cdot \mathbf{u}$. Thus we take

$$\delta\hat{\boldsymbol{\psi}}(\mathbf{k}, t) = \text{column}[\delta\hat{\rho}(\mathbf{k}, t), \delta\hat{\rho}_n(\mathbf{k}, t), -i\mathbf{k} \cdot \hat{\mathbf{v}}(\mathbf{k}, t), -i\mathbf{k} \cdot \hat{\mathbf{u}}(\mathbf{k}, t)] . \quad (3.6)$$

The hydrodynamic equations may now be written in the form stated in Eq. (2.7), were the hydrodynamic matrix is

$$\mathbf{M}(\mathbf{k}) = \begin{bmatrix} 0 & 0 & \rho^0 & 0 \\ 0 & 0 & 0 & \rho_n^0 \\ -\omega_0^2/\rho^0 & -\beta k^2/\rho_n^0\rho^0 & bk^2 + f/\rho^0 & -f/\rho^0 \\ -\beta k^2/\rho_n^0\rho^0 & -\omega_n^2/\rho_n^0 & -f/\rho_n^0 & f/\rho_n^0 \end{bmatrix} . \quad (3.7)$$

We have introduced

$$b = (\eta_v + \tfrac{4}{3}\eta_s)/\rho^0 , \quad (3.8)$$

$$\omega_0^2 = c_0^2 k^2 , \quad (3.9)$$

and

$$\omega_n^2 = c_n^2 k^2 = k^2(\kappa + \tfrac{4}{3}\mu)/\rho_n^0 , \quad (3.10)$$

where c_n is the velocity of sound in the network.

The solution of the hydrodynamic equations in Fourier–Laplace space is obtained by inverting the matrix $\{i\omega\mathbf{T} + \mathbf{M}\}$. The general structure of the solution, formally presented in Eq. (2.8), is

$$\delta\hat{\tilde{\psi}}_i(\mathbf{k}, \omega) = [\det(i\omega\mathbf{T} + \mathbf{M})]^{-1} \sum_j P_{ij}(\mathbf{k}, \omega)\delta\hat{\psi}_j(\mathbf{k}) , \quad (3.11)$$

where P_{ij} is the cofactor of the matrix element $[i\omega\delta_{ij} + M_{ji}]$. The correlation functions are simply obtained from Eq. (3.11):

$$\langle \delta\hat{\tilde{\psi}}_i(\mathbf{k}, \omega)\delta\hat{\psi}_j(-\mathbf{k}) \rangle = [P_{ij}(\mathbf{k}, \omega)/\det(i\omega\mathbf{T} + \mathbf{M})] \times \langle |\delta\hat{\psi}_j(\mathbf{k})|^2 \rangle , \quad (3.12)$$

where we have used the assumption of statistical independence of the equilibrium fluctuations Eq. (2.10).

In order to calculate the inverse Laplace transform of Eq. (3.12) or to obtain simple expressions for the spectrum, we need to determine the roots of the determinant. Approximate solutions of this dispersion equation are discussed in the next section.

IV. THE DISPERSION EQUATION

According to Eq. (2.11), the behavior of the hydrodynamic modes will be governed by roots of the determinant of the hydrodynamic matrix $[i\omega\mathbf{I} + \mathbf{M}(\mathbf{k})]$. From Eq. (3.7) one finds this dispersion equation

$$[\omega^2 - \omega_0^2 - i\omega(bk^2 + f/\rho^0)](\omega^2 - \omega_n^2 - i\omega f/\rho_n^0) - (i\omega f/\rho_n^0 - \beta k^2/\rho_n^0)(i\omega f/\rho^0 - \beta k^2/\rho^0) = 0 . \quad (4.1)$$

For light scattering, $\mathbf{k}$ is fixed and one solves for the four roots of Eq. (4.1) that describe the dynamics of the hydrodynamic modes. This dispersion equation differs from the one given by Bacri *et al.*

In general, we will be interested in physical situations that correspond to various limiting cases of the parameters that appear in Eq. (4.1). We shall examine some of the more important cases below. Each of the cases yields roots found by a perturbation analysis that are identified with hydrodynamic modes.

Before proceeding, it is helpful to note that if coupling between the network and the solvent has not been included in the hydrodynamic description Eq. (3.7) then one would have arrived at the dispersion equation

$$[\omega^2 - \omega_0^2 - i\omega(bk^2 + f/\rho^0)](\omega^2 - \omega_n^2 - i\omega f/\rho_n^0) = 0 . \quad (4.2)$$

This dispersion relation yields two roots corresponding to propagating modes in the solvent. In the limit, where the damping in the solvent is small $(bk^2 + f/\rho^0)/\omega_0^2 \ll 1$, one obtains the expressions familiar from ordinary Brillouin scattering from sound waves with the addition

of angle independent frictional damping:

$$\omega_{1,2} = \pm\omega_0 + \tfrac{1}{2}i(bk^2 + f/\rho^0) \ . \tag{4.3}$$

Similarly, the network supports two modes with frequencies

$$\omega_{3,4} = \frac{if}{2\rho_n^0}\left[1 \pm \sqrt{1 - \frac{4\omega_n^2}{(f/\rho_n^0)^2}}\ \right] \ . \tag{4.4}$$

In the limit of large damping, $f/\rho_n^0 \gg \omega_n$, one obtains the modes of the gel identified by Tanaka *et al.*; there is a very rapidly decaying mode

$$\omega_3 \simeq if/\rho_n^0 \tag{4.5}$$

and a diffusive mode

$$\omega_4 \simeq i\omega_n^2\rho_n^0/f \ . \tag{4.6}$$

In general, of course, there will be coupling between the elastic waves of the fluid and the network $\beta \neq 0$ even in the absence of damping. For the case $b = f = 0$ one finds the dispersion equation

$$(\omega^2 - \omega_0^2)(\omega^2 - \omega_n^2) - \beta^2 k^4/\rho_n^0\rho^0 = 0 \ . \tag{4.7}$$

The resulting roots of ω^2 describe the new eigenfrequencies of the *coupled* elastic media. The result for these new frequencies $\omega_\pm^2$ is

$$\omega_\pm^2 = \tfrac{1}{2}\left\{(\omega_0^2 + \omega_n^2) \pm \left[(\omega_0^2 - \omega_n^2)^2 + \frac{4\beta^2k^4}{\rho^0\rho_n^0}\right]^{1/2}\right\} . \tag{4.8}$$

Evidently, for sufficiently large β, the frequency ω_-^2 will be negative and thus ω_- will become complex. However, as is well known from the theory of harmonic lattices, one may expect a limit on the magnitude of β. In analogy to what is found for coupled binary harmonic crystals,[10] we shall assert that

$$\frac{\beta^2}{\rho^0\rho_n^0} = \lambda c_0^2 c_n^2 \ , \tag{4.9}$$

with $0 \leq \lambda < 1$. Note that the limit $\beta \to 0$ ($\lambda \to 0$), the eigenfrequencies approach the unperturbed fluid and network frequencies $\omega_+^2 \to \omega_0^2$ and $\omega_-^2 \to \omega_n^2$.

In addition, there is dissipative coupling between the network and the solvent. In the limit of small damping in both the solvent $(bk^2 + f/\rho^0)/\omega_0 \ll 1$ and the network $f/\rho_n^0\omega_n \ll 1$, one finds damping of the four eigenfrequencies, Eq. (4.8). The resulting modes are of the form

$$\omega_{1,2} = \pm\omega_+ + i\Gamma_+ \ , \tag{4.10}$$

where

$$\Gamma_+ = \frac{\tfrac{1}{2}[(\omega_+^2 - \omega_n^2)(f/\rho^0 + bk^2) + (\omega_+^2 - \omega_0^2)(f/\rho_n^0) - f\omega_0\omega_n(\lambda/\rho_n^0\rho^0)^{1/2}]}{[\omega_+^2 - \omega_-^2]} \tag{4.11}$$

and

$$\omega_{3,4} = \pm\omega_- + i\Gamma_- \ , \tag{4.12}$$

where

$$\Gamma_- = \frac{\tfrac{1}{2}[(\omega_-^2 - \omega_n^2)(f/\rho^0 + bk^2) + (\omega_-^2 - \omega_0^2)(f/\rho_n^0) - f\omega_0\omega_n(\lambda/\rho_n^0\rho^0)^{1/2}]}{[\omega_-^2 - \omega_+^2]} \ . \tag{4.13}$$

Note that in the limit of no coupling between the elastic waves $\beta = 0$, one finds Eq. (4.10) approaches Eq. (4.3) and Eq. (4.13) approaches the small friction limiting form of Eq. (4.4):

$$\omega_{3,4} = \pm\omega_n + \tfrac{1}{2}if/\rho_n^0 \ . \tag{4.14}$$

In this limit of small coupling, only linear terms in f are retained.

A more interesting limiting case is *strong friction* in both the fluid

$$(f/\rho^0) \gg bk^2 \ , \ \omega_0, \ \beta k^2/\rho^0 \tag{4.15}$$

and the network

$$(f/\rho_n^0) \gg \omega_n \ , \ \beta k^2/\rho_n^0 \ . \tag{4.16}$$

For this case there are two propagating modes that correspond to sound waves in the *average* coupled elastic medium of network and fluid. These propagating frequencies may easily be identified by setting $s = d$ in the hydrodynamic equation. Not surprisingly, one finds that strong frictional damping between the network and the fluid provides relaxation to a medium of density.

$$\rho_T = \rho^0 + \rho_n^0 \tag{4.17}$$

that supports a dampened sound wave. One finds

$$\omega_{1,2} = \pm\bar{\omega} + i\Gamma k^2 \ , \tag{4.18}$$

where $\bar{\omega} = \bar{c}k$ and the average sound speed is given by

$$\rho_T\bar{c}^2 = (c_0\sqrt{\rho^0} + c_n\sqrt{\rho_n^0})^2 + 2c_0c_n(\sqrt{\lambda} - 1)\sqrt{\rho_n^0\rho^0} \ . \tag{4.19}$$

The damping of these modes is found to be

$$\Gamma = \tfrac{1}{2}\left\{b\rho^0/\rho_T + \frac{\rho_T}{f}\left(\frac{\rho^0\rho_n^0}{\rho_T^2}\right)^2 \times [c_0^2 - c_n^2 - c_0c_n(\rho^0 - \rho_n^0)(\lambda/\rho_n^0\rho^0)^{1/2}]^2/\bar{c}^2\right\} . \tag{4.20}$$

In the limit $\lambda = 0$, one obtains a slightly more general expression than found by Bacri *et al.* in their discussion of sound attenuation in gels; their result is reproduced in the limit $c_0^2 \gg c_n^2$ and $\rho^0 \gg \rho_n^0$, with $\beta = 0$.

The third mode is rapidly decaying, similar to Eq. (4.5), which it approaches for $\rho^0 \gg \rho_n^0$:

$$\omega_3 = if(\rho_T/\rho^0\rho_n^0) \ . \tag{4.21}$$

The final mode is the diffusive mode similar to the one identified by Tanaka *et al.* [Eq. (4.6)]:

$$\omega_4 = i\left(\frac{\rho_n^0\rho^0}{\rho_T}\right)\frac{k^2}{f}\,\frac{c_0^2c_n^2}{\bar{c}^2}\,(1 - \lambda) \ . \tag{4.22}$$

For $\lambda = 0$ and $\rho^0 \gg \rho_n^0$, this reduces to the expression

found by Tanaka *et al.*

These approximate expressions for the four modes of the coupled network–fluid gel system are the principal results of this section. We find that the modes exhibit coupling both in their elastic properties for $\lambda \neq 0$ and in their dissipative behavior.

V. THE LIGHT SCATTERING SPECTRUM

The light scattering spectrum may be obtained numerically once the values of the transport coefficients are specified. Alternatively, analytic expressions for the spectrum may be obtained in limiting cases, such as those discussed in the prior section, when approximate roots to dispersion equation may justifiably be adopted. In this section we present explicit results for the spectrum for one of the limiting cases considered in Sec. IV. The spectrum may be obtained in a similar manner.

The case we consider is the strong friction case where the four approximate roots are given by Eqs. (4.18), (4.21), and (4.22). For this case one can invert the Laplace transform to obtain the time dependence of the correlation functions. To lowest order in the designated small quantities, one finds

$$\frac{\langle \delta\hat{\rho}(\mathbf{k},t)\delta\hat{\rho}(-\mathbf{k})\rangle}{\langle|\delta\hat{\rho}(\mathbf{k})|^2\rangle} = \frac{(\rho_n^0 c_n^2+\beta)}{\rho_T \bar{c}^2}\exp(-D_g k^2 t) + \frac{(\rho^0 c_0^2+\beta)}{\rho_T \bar{c}^2}\exp(-\Gamma k^2 t)\cos\bar{\omega}t\,, \tag{5.1}$$

$$\frac{\langle \delta\hat{\rho}_n(\mathbf{k},t)\delta\hat{\rho}_n(-\mathbf{k})\rangle}{\langle|\delta\hat{\rho}_n(k)|^2\rangle} = \frac{(\rho^0 c_0^2+\beta)}{\rho_T \bar{c}^2}\exp(-D_g k^2 t) + \frac{(\rho_n^0 c_n^2+\beta)}{\rho_T \bar{c}^2}\exp(-\Gamma k^2 t)\cos\bar{\omega}t\,, \tag{5.2}$$

$$\frac{\langle \delta\hat{\rho}(\mathbf{k},t)\delta\hat{\rho}_n(-\mathbf{k})\rangle}{\langle|\delta\hat{\rho}_n(\mathbf{k})|^2\rangle} = \frac{(\rho_n^0 c_0^2+\beta\rho_n^0/\rho^0)}{(\rho^0 c_n^2+\beta\rho^0/\rho_n^0)}\frac{\langle \delta\hat{\rho}_n(\mathbf{k},t)\delta\hat{\rho}(-\mathbf{k})\rangle}{\langle|\delta\hat{\rho}(\mathbf{k})|^2\rangle} = \frac{(\rho^0 c_n^2+\beta\rho^0/\rho_n^0)}{\rho_T\bar{c}^2}[\exp(-\Gamma k^2 t)\cos\bar{\omega}t - \exp(-D_g k^2 t)]\,, \tag{5.3}$$

where we have defined a "diffusion" coefficient [Eq. (4.22)]:

$$D_g = \left(\frac{\rho_n^0\rho^0}{\rho_T}\right)\frac{c_0^2 c_n^2}{f\bar{c}^2}(1-\lambda)\,. \tag{5.4}$$

Due to the frictional and elastic coupling, both the fluid and network densities manifest two propagating modes and a diffusive mode. In the limit $c_n \ll c_0$ and $\rho_n^0 \ll \rho^0$, the time dependence of the fluid fluctuations are primarily governed by the propagating mode, while in this limit the network fluctuations are predominantly diffusive.

The light scattering spectrum for this case may be constructed:

$$\begin{aligned} I(\mathbf{k},\omega) = {} & \left(\frac{\partial\epsilon}{\partial\rho}\right)^2 k_B T\frac{\rho^0}{c_0^2}\left\{\frac{\rho^0 c_0^2+\beta}{\rho_T\bar{c}^2}\left[\frac{\Gamma k^2}{(\omega-\bar{\omega})^2+\Gamma^2k^4}+\frac{\Gamma k^2}{(\omega+\bar{\omega})^2+\Gamma^2k^4}\right]+\frac{2(\rho_n c_n^2+\beta)}{\rho_T\bar{c}^2}\frac{D_g k^2}{\omega^2+D_g^2k^4}\right\} \\ & +\left(\frac{\partial\epsilon}{\partial\rho_n}\right)^2\frac{k_B T\rho_n^0}{c_n^2}\left\{\frac{2(\rho^0 c_0^2+\beta)}{\rho_T\bar{c}^2}\frac{D_g k^2}{\omega^2+D_g^2k^4}+\frac{\rho_n^0 c_n^2+\beta}{\rho_T\bar{c}^2}\left[\frac{\Gamma k^2}{(\omega-\bar{\omega})^2+\Gamma^2k^4}+\frac{\Gamma k^2}{(\omega+\bar{\omega})^2+\Gamma^2k^4}\right]\right\} \\ & +\left(\frac{\partial\epsilon}{\partial\rho_n}\right)\left(\frac{\partial\epsilon}{\partial\rho}\right)\frac{k_B T\rho^0\rho_n^0}{\bar{c}^2\rho_T}\left[2+\frac{\beta(\rho^0 c_0^2+c_n^2\rho_n^0)}{c_n^2 c_0^2}\right]\left\{\frac{\Gamma k^2}{(\omega-\bar{\omega})^2+\Gamma^2k^4}+\frac{\Gamma k^2}{(\omega+\bar{\omega})^2+\Gamma^2k^4}-\frac{2D_g k^2}{\omega^2+D_g^2k^4}\right\}\,, \end{aligned} \tag{5.5}$$

where we have replaced the equal time correlation functions by their $\mathbf{k}\to 0$ limit, and we have taken them to be

$$\langle|\delta\hat{\rho}(\mathbf{k})|^2\rangle = k_B T\frac{\rho^0}{c_0^2}$$

and

$$\langle|\delta\hat{\rho}_n(\mathbf{k})|^2\rangle = k_B T\frac{\rho_n^0}{c_n^2}\,. \tag{5.6}$$

It should be noted that, for simplicity, we have not displayed the non-Lorentzian contributions to the light scattering spectrum. These terms are expected to be small.

The above spectrum describes two Brillouin peaks and a central diffusive peak. Both the network and fluid fluctuations contribute to the amplitude of the three features in the spectrum. Their widths and positions have been described in the previous sections. The fast frictional damping ω_3 [Eq. (4.21)] contribution to the spectrum is of higher order in the designated small quantities and thus is not expected to be observable.

VI. COMPARISON WITH EXPERIMENT AND CONCLUDING REMARKS

In this paper we have presented a theory for light scattering from a gel or polymer network that includes Brillouin scattering. Two different limiting cases were examined in Sec. III: (a) small friction in both the solvent and the network and (b) strong friction in both the solvent and the network. At sufficiently low concentrations all gels would follow case (a). However, concentrations that correspond to ordinary laboratory conditions normally will correspond to case (b). If the theory is to be successful, it must simultaneously predict the width of the diffusive central peak ω_4 [Eq. (4.22)], the splitting $\bar{c}(\mathbf{k})$ [Eq. (4.19)], and width [Eq. (4.20)] of the two Brillouin peaks. Experiments may be undertaken at variable temperature and/or variable

network concentration ρ_n, the former usually[2,3] directed toward study of the sol–gel transition.

We are aware of only a single Brillouin light scattering study of gels. Bedborough and Jackson[11] determined that the Brillouin *shift* versus gel concentration increased linearly at relatively low concentration. The data presented by Bedborough and Jackson for the *linewidth* as a function of gel concentration are more ambiguous but appear to predict a linear increase of linewidth at low gel concentrations.

Comparison of the theory presented here with this data requires a number of assumptions about the behavior of the various physical quantities that enter into the theory. We shall assume that the gel solution behaves much like a two-phase porous medium with the gel network present at volume fraction (or porosity) ϕ, as a "solid" phase of density ρ_n^*, and the solvent present at volume fraction $(1-\phi)$ with density ρ_f^*. Thus,

$$\rho_n^0 = \phi\rho_n^* \quad , \quad \rho^0 = (1-\phi)\rho_f^* \quad . \tag{6.1}$$

We further assume that the speed of sound in the solvent, c_0, and in the network, c_n, are primarily functions of ρ_f^* and ρ_n^* and only weakly dependent on ϕ. Such an assumption is questionable, especially for the network, since higher concentration usually means increased cross linking that tends to increase c_n. Evidently, the theory we have employed assumes that the wavelength of light is large compared to the mean distance separating network regions. This translates into the condition that the wavelength of light be large compared to pore sizes in the porous medium analogy. With these assumptions, the prediction of the theory presented above in the strong friction limit at low concentrations for the shift Eq. (4.19) is

$$\bar{c}k = c_0 k\left[1 + \phi^{1/2}\left(\frac{\lambda\rho_n^*}{\rho_f^*}\right)^{1/2}\left(\frac{c_n}{c_0}\right) + \tfrac{1}{2}\phi\,\frac{\rho_n^*}{\rho_f^*}\left(\frac{c_n^2 - c_0^2}{c_0^2}\right)\right]. \tag{6.2}$$

The lowest order terms for the width Eq. (4.20) ($\lambda \neq 0$) are

$$\Gamma = \frac{1}{2}\left\{b^*\left[1 + \phi\,\frac{(\rho_f^* - \rho_n^*)}{\rho_f^*}\right] + \lambda\phi\,\frac{\rho_n^* c_n^2}{f}\right\} \quad , \tag{6.3}$$

and for $\lambda = 0$

$$\Gamma = \frac{1}{2}\left\{b^*\left[1 + \phi\,\frac{(\rho_f^* - \rho_n^*)}{\rho_f^*}\right] + \phi^2(\rho_n^*)^2\,\frac{(c_0^2 - c_n^2)^2}{c_0^2}\right\}, \tag{6.4}$$

where

$$b^* = (\eta_v + \tfrac{4}{3}\eta_s)/\rho_f^* \quad . \tag{6.5}$$

The friction coefficient f should be expected to be a sensitive function of ϕ. In particular, for small ϕ it may well be assumed to behave linearily with ϕ, $f = f_0\phi + \cdots$. The result would be a prediction for a linear increase width with ϕ provided $\lambda = 0$.

Of course, at very low values of ϕ one would expect a transition to the case of small friction Eq. (4.14), with a prediction of the width as

$$\text{width} = \left[b^* k^2(1+\phi) + \frac{f_0\phi}{\rho_f^*}\right] \quad . \tag{6.6}$$

The transition from the regime described by Eq. (6.3) to that described by Eq. (6.6) is best studied, in principle, by angle dependent measurements that, unfortunately, are not available.

We conclude that *qualitative* agreement with the trend found in the available data is possible. However, on a quantitative level further difficulties arise. Namely, if one attempts to reconcile the Brillouin measurements[11] with the Rayleigh measurements,[1,12,13] despite the fact that different gels are involved, one finds a major discrepancy in the elasticity of the gel. For the Brillouin measurements, with the assumption $\lambda = 0$ one must have $\omega_n > \omega_0 \sim 10^{10}$ Hz. But the Rayleigh measurements suggest $\omega_n \sim 10^8$ Hz. Similarly, the friction coefficient inferred from the Brillouin measurements is an order of magnitude less than that found in some of the Rayleigh measurements.[12,13] Similar discrepancies were found in the sound absorption measurements of Bacri *et al.*, who suggest that the hydrodynamic scheme must be modified to permit *dispersion* in both the elasticity of the network $c_n(\omega)$ and the friction coefficients $f(\omega)$. Development of a systematic hydrodynamic treatment of this gel system with an internal degree of freedom which gives rise to such dispersion is underway and will be reported elsewhere. In this regard, it is important to note that the hydrodynamic description we have adopted is not unique. Indeed, other hydrodynamic descriptions which are consistent with both the symmetry and physics of gels can be constructed. One such example is presented by the work of Biot[7] and of Johnson *et al.*,[6] where there is additional inertial coupling of the form $\rho_{12}(\partial u/\partial t)$ and $\rho_{12}(\partial v/\partial t)$ in Eqs. (3.4) and (3.5), respectively.

It should also be noted that expressions for the sound attenuation in a gel described by the hydrodynamic equations included in Sec. III may easily be determined through an analysis similar to that undertaken in Sec. IV. The sound attenuation is found by determining the complex part of the wave vector **k**, for real frequencies ω, in contrast to the light scattering calculation where the complex frequencies ω are determined for real values of k.

The main point is that combined Brillouin and Rayleigh light scattering measurements have the potential of elucidating the dynamical behavior of gels. The central quantity of interest is the friction coefficient $f(\phi, \omega)$ that is likely to be a complicated, nonanalytic function of both the volume fraction of the gel in the solution and the frequency of the mechanical disturbance. This friction coefficient combined with the elastic properties of the system will provide a description of the gel adequate for most purposes.

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