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# Elastodynamics of gels

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The mechanical properties of gels are analyzed in terms of models which treat the three-dimensional displacements of the solid and fluid parts separately and on an equal footing, with no assumptions regarding smallness of concentration or even weakness of the solid skeleton frame. Thus, a unified description of the normal modes in a gel is presented; parameters deduced from measurement on a given mode are shown to influence the properties of the others. It is still assumed, however, that the fluid and solid components can be described by their bulk densities, elastic moduli, etc. This picture is discussed in light of experimental results.

## I. INTRODUCTION

"A gel is a form of matter intermediate between a solid and a liquid. It consists of polymers, or long chain molecules, cross linked to create a tangled network and immersed in a liquid medium. The properties of the gel depend strongly on the interaction of these two components. The liquid prevents the polymer network from collapsing into a compact mass; the network prevents the liquid from flowing away. Depending on chemical composition and other factors, gels vary in consistency from viscous fluids to fairly rigid solids, but typically they are soft and resilient or, in a word, jellylike."<sup>1</sup>

There has been a substantial recent increase in the understanding of gels, both theoretically and experimentally. One of the most useful means of probing gel properties is via their mechanical normal modes of damped vibration. Tanaka *et al.*<sup>2,3</sup> have clearly observed a longitudinal mode which is diffusive and which corresponds roughly to the overdamped motion of the polymer network through the (stationary) fluid; in addition there is, of course, the usual acoustic longitudinal mode, which is propagatory. Although it is possible under some circumstances to describe a given mode independently of the other(s), it is clearly desirable to establish a unified formalism in which all normal modes are simultaneously (and correctly) described. It is obvious that the theory must keep track of the motions of the two components separately, and on equal footing, at least in some average sense. Such treatments of the gel problem have been presented but they are oversimplified in the sense that they are specialized to (i) one-dimensional (e.g., longitudinal) motion only (ii) small concentration of polymer, (iii) weak elastic moduli of the polymer skeletal frame, and (iv) incompressible polymer strands. It is the purpose of this paper to demonstrate that none of these simplifications is necessary. Indeed, many "plastics" consist of polymer networks in a liquid plasticizer; by varying the polymer concentration, one can continuously span the range from gels (small concentration) to plastics (large concentration). Thus it is useful to have results for an arbitrary concentration.

It will be presumed that the gel can be conceptualized as a porous medium consisting of two interpenetrating macroscopic substances (fluid and solid) which are characterized by their pertinent densities, elastic con-

stants, etc. Section II is devoted to a brief view of the Biot theory<sup>4-7</sup> of acoustics in porous media and it is then applied to the gel problem. This theory has been applied to a wide variety of acoustic problems in porous media including porous rocks,<sup>8</sup> ocean sediments,<sup>9</sup> loose and fused glass beads,<sup>10,11</sup> and fourth sound in superfluid/superleak systems.<sup>11,12</sup> Thus, in the larger context of acoustic propagation in porous media it is particularly instructive to examine the predictions of the theory as applied to gels. One of the drawbacks of the Biot theory is that attenuation is ascribed solely to the relative motion of fluid against solid; attenuation within fluid or solid components is neglected. Since most gels consist mainly of fluid, it may be supposed that attenuation due to rate of change of macroscopic deformation of the fluid is important; this is included in a model developed in Sec. III. Here "macroscopic" means on the size scale of a wavelength as opposed to the size of a pore. (A pore is a characteristic fluid volume entrained by the network.) Theoretical predictions are discussed in light of experimental results in Sec. IV; although the theory gives a good account of the data, there is some evidence that the elastodynamic properties of the gel cannot be modeled simply as two interpenetrating media each of which is characterized by its own frequency independent bulk properties.

Throughout the article, I have imagined that the normal modes are driven at some known frequency  $\omega$  which is real valued, and I have solved for the complex-valued wave vector  $q(\omega)$ . This is particularly useful for most acoustics applications but there are situations in which  $q$  is known and is real valued (e.g., Brillouin scattering) and  $\omega$  is complex. It is, of course, possible to solve the differential equations either way but I have chosen to present the results using the first method. The application of this model to inelastic light scattering is discussed in another article.<sup>13</sup>

## II. THEORY

In a series of papers,<sup>4-7</sup> Biot proposed a simple phenomenological theory of acoustic propagation in porous, fluid filled, macroscopically homogeneous and isotropic media. It is assumed that there exist volumes large compared to pore/grain sizes but small compared to a wavelength and that each volume element is describable by the average displacement of the fluid  $\mathbf{U}(\mathbf{r}, t)$  and of the solid  $\mathbf{u}(\mathbf{r}, t)$ . The equations of motion are

$$\rho_{11} \frac{\partial^2 \mathbf{u}}{\partial t^2} + \rho_{12} \frac{\partial^2 \mathbf{U}}{\partial t^2} = P \nabla (\nabla \cdot \mathbf{u}) + Q \nabla (\nabla \cdot \mathbf{U}) - N \nabla \times \nabla \times \mathbf{u} + bF(\omega) \left( \frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right), \quad (2.1a)$$

$$\rho_{22} \frac{\partial^2 \mathbf{U}}{\partial t^2} + \rho_{12} \frac{\partial^2 \mathbf{u}}{\partial t^2} = R \nabla (\nabla \cdot \mathbf{U}) + Q \nabla (\nabla \cdot \mathbf{u}) - bF(\omega) \left( \frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right). \quad (2.1b)$$

Here I have used the notation of Ref. 4 as it is simpler than (although equivalent to) that of the later articles. The motions of the solid and of the fluid parts are treated on an equal footing except that the fluid neither creates nor experiences a shear restoring force. Equations (2.1a) and (2.1b) represent a significant departure from the work of DeGennes<sup>14</sup> and of Bacri and Rajaonarison<sup>15</sup> (BR) who assumed one-dimensional motion only for a dilute concentration of polymer. They also differ from the model of Tanaka *et al.*<sup>2</sup> (THB) for the diffusive motion of the polymer network through the fluid, which is presumed to be stationary. The quantities  $P$ ,  $Q$ , and  $R$  are generalized elastic coefficients which can be related,<sup>5</sup> via gedanken experiments, to the bulk modulus of fluid  $K_f$ , the bulk modulus of solid  $K_s$ , the bulk modulus  $K_b$  of the skeletal frame, and to  $N$  which is the shear modulus of both the skeletal frame and of the composite:

$$P = \frac{(1-\phi)[1-\phi-(K_b/K_s)]K_s + \phi(K_s/K_f)K_b}{1-\phi-(K_b/K_s) + \phi(K_s/K_f)} + \frac{4}{3}N, \quad (2.2a)$$

$$Q = \frac{[1-\phi-(K_b/K_s)]\phi K_s}{1-\phi-(K_b/K_s) + \phi(K_s/K_f)}, \quad (2.2b)$$

$$R = \frac{\phi^2 K_s}{1-\phi-(K_b/K_s) + \phi(K_s/K_f)}. \quad (2.2c)$$

$\phi$  is the porosity (fluid volume fraction); it is related to the gel concentration  $C_0$  by  $C_0 = 1 - \phi$ . For many gels,  $C_0 \ll 1$  but Eqs. (2.1) and (2.2) are equally applicable for arbitrary  $\phi$ . In the so-called "jacketed and drained" gedanken experiments<sup>5</sup> the solid component is stressed by a permeable jacket surrounding the sample but the fluid in the pores is allowed to escape (through the jacket) as needed in order to remain at ambient pressure. Therefore,  $K_b$  and  $N$  are the elastic constants of the skeletal frame;  $K_b$  (sometimes called the "osmotic modulus of compression"  $K_{os}$  or simply "the bulk modulus of the skeletal network") describes the response of the solid skeleton when it is uniformly compressed externally, and  $N$  the shear modulus (sometimes denoted by " $\mu$ " or " $G$ ") describes the shear response. The quantities  $K_b$ ,  $N$  can therefore be measured independently by static means.<sup>2</sup> For gels, these frame moduli are intimately dependent upon various electrochemical interactions with the host fluid as well as the "rubber elasticity" of the cross-linked, long chain molecules which is highly temperature dependent.<sup>1-3</sup> Therefore it is *not* true that  $K_b$ ,  $N$  are independent of pore fluid as is frequently the case in more commonly encountered porous media having larger pore dimensions (e.g., fused glass beads). Indeed, Patterson<sup>16-18</sup> has argued that  $K_b$  (in the band width accessed

by photon correlation spectroscopy, 0-10<sup>6</sup> Hz) is largely independent of whether the polymers are cross linked to each other or not, at least for his gels. For purposes of this article, it is assumed that  $K_b$ ,  $N$ ,  $K_f$ , and  $K_s$  are all frequency independent (but see Sec. IV). It is also assumed that the solid material is isotropic.<sup>19</sup> The combination  $K_b + (4/3)N$  is the longitudinal modulus of the frame and is equal to quantities introduced by others for the gel problem:  $K_b + (4/3)N = K + (4/3)\mu$  (THB<sup>2</sup>) =  $E$  (DeGennes<sup>14</sup>) =  $E_r$  (BR<sup>15</sup>) =  $K_{os} + (4/3)G$  (Patterson).<sup>17,18</sup> I will show that  $K_b$  and  $N$  appear separately in an important result (the speed of sound) and not simply in this one combination. Equations (2.2) are equivalent to those given in e.g., Stoll,<sup>9</sup> or Geertsma and Smit.<sup>20</sup> The power of this formalism derives from the existence of the gedanken experiments that lead to Eqs. (2.2). In particular, I will be able to derive results for an arbitrary gel concentration, and not just the dilute limit considered by others.

The density terms  $\rho_{ij}$  are related to the density of solid  $\rho_s$  and fluid  $\rho_f$  by

$$\rho_{11} + \rho_{12} = (1 - \phi)\rho_s, \quad (2.3a)$$

$$\rho_{22} + \rho_{12} = \phi\rho_f. \quad (2.3b)$$

the total density is  $\rho_T = \phi\rho_f + (1 - \phi)\rho_s$ . It is worth pointing out that  $\rho_f$  and  $\rho_s$  may not equal their bulk values  $\rho_f^0$ ,  $\rho_s^0$ ; if, e.g., the polymer molecules "fit into" the spaces between the solvent molecules, so that the total density is  $\rho_T = \rho_f^0 + (1 - \phi)\rho_s^0$ , then obviously  $\rho_f > \rho_f^0$ . We return to this point in the discussion following Eqs. (2.14), where it is shown to account for some of the differences between my results and those of others. The term  $\rho_{12}$  describes the inertial (as opposed to viscous) drag that the fluid exerts on the solid as the latter is accelerated relative to the former and vice versa.<sup>21</sup> The equation of motion of the solid part, e.g., Eq. (2.1a), may be rewritten using Eq. (2.3a):

$$(1 - \phi)\rho_s \frac{\partial^2 \mathbf{u}}{\partial t^2} = -\rho_{12} \left( \frac{\partial^2 \mathbf{U}}{\partial t^2} - \frac{\partial^2 \mathbf{u}}{\partial t^2} \right) + bF(\omega) \left( \frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right) + (\text{spatial derivative terms}). \quad (2.1a')$$

That is, even for a nonviscous pore fluid [ $bF(\omega) \equiv 0$ ], there is a reactive force per unit volume on the solid [whose mass is  $(1 - \phi)\rho_s$ ] whenever one component is accelerated relative to the other. The proportionality constant  $\rho_{12}$  represents the induced mass tensor<sup>21</sup> per unit volume, assumed to be diagonal in the coordinate indices for a homogeneous isotropic system; it is always proportional to the fluid density and, because of Newton's Third Law, it is always negative:

$$\rho_{12} = -(\alpha - 1)\phi\rho_f, \quad (2.3c)$$

where  $\alpha > 1$  is a purely geometrical quantity independent of solid or fluid densities. Berryman<sup>22</sup> has considered the case of isolated spherical solid particles in the fluid to derive  $\alpha = \frac{1}{2}[\phi^{-1} + 1]$ , for example. The remaining parameter governs attenuation:  $b = \eta\phi^2/k$ , where  $\eta$  is the fluid viscosity and  $k$  is the fluid per-

meability.<sup>4</sup> law which  $\text{cm}^3 \text{s}^{-1}$  through static pres

$$Q = -(\dots)$$

The permeability to be independent of pore fluid pressure is measured by the gradient of the solid concentration. The straight line through the origin is  $k = \phi r^2/8$ , similar to the problem: the laws for the porous medium when the porosity is normal to the presented relative motion in Sec. II. always appear in  $\omega$ ]. That

$$(1 - \phi)\rho_s$$

where

$$\tilde{\rho}_{12}(\omega)$$

and similar to (2.3a) and  $-\phi\rho_s - \tilde{\rho}_{12}$

Although the solution of  $F$  describes the displacement it is not yet done.<sup>25,26</sup> analogy with Therefore

$$\tilde{\alpha}(\omega) =$$

The plane and (2.1b) is complete. It is conventional the usual have two are two wave and given by

$$\tilde{v}^2(\text{fast}, s)$$

where

$$\Delta = P$$

meability.<sup>4</sup> The permeability is defined through Darcy's law which relates the volume flow rate of fluid  $Q$  (in  $\text{cm}^3\text{s}^{-1}$ ) through a sample of area  $A$  due to an applied static pressure gradient  $\nabla P$ ,

$$Q = -(k/\eta) A \nabla P.$$

The permeability  $k$  is a geometrical quantity presumed to be independent of fluid viscosity; obviously, it can be measured by monitoring the static flow due to a pressure gradient.<sup>2</sup> It has the dimension of area and is indicative of the flow channel sizes; for a permeable solid consisting of cylindrical pores of radius  $r$  drilled straight through the sample, the permeability is simply  $k = \phi r^2/8$ , for example.<sup>23</sup> The quantity  $b$  is equal to similar quantities introduced by others for the gel problem:  $b = f(\text{THB or BR}) = \Phi$  (DeGennes).  $F(\omega)$  allows for the fact that the effective damping changes when the viscous skin depth ( $\sqrt{2\eta/\rho_t \omega}$ ) becomes smaller than the pore size as the frequency  $\omega$  increases.<sup>24</sup> It is normalized by  $F(0) = 1$ . Note that, in the model presented so far, attenuation is ascribed solely to the relative motion of fluid and solid; we return to this point in Sec. III. It is also worth noting that  $\rho_{12}$  and  $bF(\omega)$  always appear together in the combination  $\rho_{12} - [ibF(\omega)/\omega]$ . That is, Eq. (2.1a') can be rewritten as

$$(1 - \phi) \rho_s \frac{\partial^2 \mathbf{u}}{\partial t^2} = -\bar{\rho}_{12}(\omega) \left( \frac{\partial^2 \mathbf{U}}{\partial t^2} - \frac{\partial^2 \mathbf{u}}{\partial t^2} \right) + (\text{spatial derivative terms}), \quad (2.1a'')$$

where

$$\bar{\rho}_{12}(\omega) = \rho_{12} - \frac{ibF(\omega)}{\omega},$$

and similarly for Eq. (2.1b). By analogy with Eqs. (2.3a) and (2.3b), it is convenient to define  $\bar{\rho}_{11}(\omega) = (1 - \phi)\rho_s - \bar{\rho}_{12}(\omega)$  and  $\bar{\rho}_{22}(\omega) = \phi\rho_t - \bar{\rho}_{12}(\omega)$ .

Although the linear term in the Taylor's series expansion of  $F(\omega)$  mimics the effects of  $\rho_{12}$  (i.e., both terms describe an  $\omega^2$  dependence of the force on the relative displacement), they are of different physical origin and it is not valid to put  $\alpha = 1$  (i.e.,  $\rho_{12} = 0$ ) as has been done.<sup>25,26</sup> Equivalently, one could define  $\bar{\alpha}(\omega)$  by analogy with Eq. (2.3c), viz:  $\bar{\rho}_{12}(\omega) = -[\bar{\alpha}(\omega) - 1]\phi\rho_t$ . Therefore,

$$\bar{\alpha}(\omega) = \alpha + \frac{ibF(\omega)}{\omega\phi\rho_t}. \quad (2.3c')$$

The plane wave normal mode solutions to Eqs. (2.1a) and (2.1b) are describable by a wave vector  $q(\omega)$  which is complex valued because of the attenuation mechanism. It is convenient to define a complex phase velocity by the usual:  $\bar{V}(\omega) = \omega/q(\omega)$ . Equations (2.1a) and (2.1b) have two independent longitudinal modes (because there are two degrees of freedom) which are called the "fast" wave and the "slow" wave; their phase velocities are given by

$$\bar{V}^2(\text{fast, slow}) = \frac{\Delta \pm [\Delta^2 - 4(\bar{\rho}_{11}\bar{\rho}_{22} - \bar{\rho}_{12}^2)(PR - Q^2)]^{1/2}}{2(\bar{\rho}_{11}\bar{\rho}_{22} - \bar{\rho}_{12}^2)}, \quad (2.4)$$

where

$$\Delta = P\bar{\rho}_{22} + R\bar{\rho}_{11} - 2\bar{\rho}_{12}Q.$$

The fast wave is the usual acoustic compressional mode and it corresponds to fluid and solid moving in phase with respect to each other whereas the slow wave corresponds to out of phase relative motion of the two. On the other hand, there is only one nontrivial transverse mode whose phase velocity is

$$\bar{V}^2(\text{shear}) = \frac{N}{(1 - \phi)\rho_s + (1 - \bar{\alpha}^{-1})\phi\rho_t}. \quad (2.5)$$

The other shear mode is the trivial mode  $\omega = 0$  for all wave vectors. These two transverse modes will be altered by the inclusion of an additional absorption mechanism considered in the next section, the compressional modes less so. It will prove instructive to analyze the results of the theory presented thus far.

The nature of the normal modes predicted by the theory depends upon whether one is in the high frequency or low frequency limit of the theory.<sup>4</sup> The crossover between the two occurs when the viscous skin depth,  $\delta = \sqrt{2\eta/(\rho_t \omega)}$ , is equal to an effective flow channel size,  $a$  which is indicative of the pore sizes):

$$\omega_c = (2\eta)/(\rho_t a^2).$$

### A. High frequency limit

If  $\omega \gg \omega_c$ , the attenuation mechanism has little effect on the velocities of the normal modes which are derived from Eqs. (1); according to Biot,<sup>4</sup> one has  $\lim_{\omega \rightarrow \infty} F(\omega) \propto \omega^{1/2}$  and, therefore  $\lim_{\omega \rightarrow \infty} \bar{\alpha}(\omega) = \alpha$  (a constant not<sup>25,26</sup> equal to 1). Thus, each  $\bar{\rho}_{ij}$  is real valued and frequency independent and so all three velocities are real and non-dispersive. Although the slow wave, in this high frequency regime, was first observed by Plona,<sup>10</sup> it was subsequently shown that 4th sound<sup>27</sup> in a superfluid/superleak system is the paradigm of the acoustic slow-wave.<sup>12</sup> In 4th sound, the superfluid component has identically zero viscosity ( $\omega_c = 0$ ) and one is always in the high frequency limit of the theory. If, in addition, the skeletal frame is much stiffer than the pore fluid ( $K_b, N \gg K_t$ ), the two modes decouple; the fast wave corresponds to motion of the solid part and the slow wave corresponds to motion of the fluid. The velocities in this limit (high frequency, stiff frame) are

$$V(\text{fast}) \doteq \left[ \frac{K_b + \frac{4}{3}N}{(1 - \phi)\rho_s + (1 - \alpha^{-1})\phi\rho_t} \right]^{1/2}, \quad (2.6a)$$

$$V(\text{slow}) \doteq V_t / \sqrt{\alpha}. \quad (2.6b)$$

Since  $V_t = \sqrt{K_t/\rho_t}$  is the speed of sound in the bulk fluid, the quantity  $\sqrt{\alpha}$  is a kind of index of refraction of this mode (since it is the ratio of two speeds) and is due to the tortuous nature of the pore space. See Refs. 11, 12, and 28 and references within for a more complete discussion of these points.

### B. Low frequency limit

For sufficiently low frequencies  $\omega \ll \omega_c$  the viscous skin depth is much larger than a characteristic pore size. Therefore, the quantity  $\bar{\alpha}$  is large and imaginary  $\bar{\alpha}(\omega) \approx i\eta\phi/(\omega k\rho_t)$  from Eq. (2.3c'). The fast compressional and the shear modes are propagatory with small attenuation; in this low frequency limit their wave vec-

tors can be shown, from Eqs. (2.4) and (2.5), to be of the form

$$q(\omega) = \omega/V + i\gamma \quad [\equiv \omega/\tilde{V}(\omega)], \quad (2.7)$$

where  $V$ , the phase velocity, is constant and the attenuation  $\gamma$  is proportional to  $\omega^2$ . Basically, the viscosity of the fluid locks it onto the skeletal frame so that fluid and solid oscillate together, with equal amplitudes, and there is little dissipation because there is little relative motion. In this low frequency limit the slow compressional wave is diffusive, rather than propagatory, and its motion is described by a diffusion equation,<sup>29</sup>

$$C_D \nabla^2 \xi = \frac{\partial \xi}{\partial t}, \quad (2.8a)$$

where  $\xi$  is a normal mode coordinate and  $C_D$  is given by

$$C_D \equiv \frac{kK_t}{\eta\phi} \left( 1 + \frac{K_t}{\phi(K_b + \frac{1}{3}N)} \right) \times \left\{ 1 + \frac{1}{K_s} \left[ \frac{4}{3}N \left( 1 - \frac{K_b}{K_s} \right) - K_b - \phi(K_b + \frac{1}{3}N) \right] \right\}^{-1}. \quad (2.8b)$$

Equivalently, the phase velocity is complex valued as can be seen in a straightforward manner from Eq. (2.4):

$$\lim_{\omega \rightarrow 0} \tilde{V}^2(\text{slow}) = -i\omega C_D. \quad (2.9)$$

A commonly observed example of this low frequency diffusive slow wave occurs in media having a very stiff frame ( $K_b, N \gg K_t$ ) such as a porous sedimentary rock saturated with water.<sup>30</sup> The diffusivity, Eq. (2.8b), simplifies greatly:

$$\lim_{K_b, N \gg K_t} C_D = \frac{kK_t}{\eta\phi}. \quad (2.10)$$

In this limit the mode consists of a fluid pressure pulse diffusing through a rigid matrix.<sup>30</sup>

**C. The gel limit**

We now consider the application of the theory to the gel problem. Because the pores in a gel are so small (typically  $\sim 100 \text{ \AA}$ ) the crossover frequency is very high ( $\omega_c \sim 10^{10} \text{ s}^{-1}$ ) and one is essentially always in the low frequency limit of the theory  $\omega \ll \omega_c$ . Thus, the real parameter  $\alpha$ , Eq. (2.3c'), drops out of all the relevant expressions. Equivalently, one could set have  $\rho_{12} \equiv 0$  in Eqs. (2.1). (Indeed, the pores are so small that the low frequency limit of the theory applies up to frequencies where incoherent scattering of the elastic waves dominates. See Ref. 11 for details.) Furthermore, the skeletal frame is generally very much more deformable than the pore fluid ( $K_b, N \ll K_t$ ) and this simplifies the results greatly. It is obviously not at all necessary to make this assumption but it is particularly informative to do so. First, the diffusivity of the slow wave, Eq. (2.8b) becomes

$$\lim_{K_b, N \ll K_t} C_D = \frac{k(K_b + \frac{1}{3}N)}{\eta}. \quad (2.11)$$

It is straightforward to show that this mode corresponds to the diffusion of the compressed matrix through the fluid, which remains essentially stationary in this

low frequency limit. Equation (2.11) is to be compared with a result derived independently by THB<sup>2</sup> and by DeGennes<sup>14</sup> using several *ad hoc* simplifying assumptions. Their result, in the present notation, is

$$C_D = \frac{k(K_b + \frac{1}{3}N)}{\eta\phi^2}. \quad (2.12)$$

(In the original notation,  $C_D = [K + \frac{1}{3}\mu]/f(\text{THB}) = E/\phi(\text{DeGennes})$ .) Equation (2.12) is essentially correct because it was assumed in both derivations that the gel concentration was small,  $\phi \approx 1$ , but Eq. (2.11) is applicable regardless of the concentration as long as the frame moduli are small. It is presumably applicable to the case of loose beads ( $\phi \approx 0.38$ ) saturated with fluid and subjected to a confining pressure. (See Ref. 11.) Both Tanaka and DeGennes assumed that, for the motion of the gel networks, one could consider the fluid as stationary, which is true but which need not be assumed at the beginning.

One powerful consequence of treating the displacements of the fluid and of the solid on an equal footing through this unified theory is that all modes are described by the same set of parameters. Gels are formed by dissolving the polymer molecules in an appropriate solvent, usually with some reagent that induces polymer cross linking; it not infrequently happens that the growth of the matrix forms slowly enough as time progresses that the values of  $k/\eta$  and  $K_b, N$  can be monitored throughout gelation, e.g., by light scattering of the diffusive mode, Eq. (2.8a) ff. As  $K_b, N$  grow from their initial value of zero in the "sol" phase (appropriate to a suspension), presumably the velocities of the fast compressional and shear modes also change. Similarly, the attenuation changes as  $k$  changes, upon gelation. (It is less widely recognized that the solvent properties also change; see Sec. IV.)

Consider, first, the fast compressional mode. By expanding Eq. (2.4) as a function of  $\omega, K_b$ , and  $N$  all considered as small parameters, it is straightforward, if tedious, to show that the dispersion relation is of the form of Eq. (2.7) with a velocity given by;

$$\lim_{\substack{K_b, N \ll K_t \\ \omega \ll \omega_c}} V(\text{fast}) = V_0 [1 + (\xi_1 K_b + \xi_2 N)/(2K_t)], \quad (2.13a)$$

where  $V_0$  is given by Wood's formula,<sup>31</sup> an exact result for the velocity of a suspension ( $K_b = N = 0$ ) in the low frequency limit:

$$V_0 = \sqrt{\frac{K^*}{\rho_T}}, \quad (2.13b)$$

where  $K^*$  is the bulk modulus of the suspension,

$$\frac{1}{K^*} = \frac{\phi}{K_t} + \frac{1-\phi}{K_s}, \quad (2.13c)$$

and  $\rho_T$  is the total density

$$\rho_T = \phi\rho_f + (1-\phi)\rho_s. \quad (2.13d)$$

Deviations from Wood's formula due to the finite stiffness of the frame are described by  $\{\xi_i\}$ :

$$\xi_1 = \phi^2 (K^* K_t) (K_t^{-1} - K_s^{-1})^2, \quad (2.13e)$$

$$\xi_2 = \frac{4}{3} K_t / K^*. \quad (2.13f)$$

The attenuation  $\gamma$  is obtained by expanding the complex valued phase velocity, Eq. (2.4) to first order in frequency and using Eq. (2.7):

$$\gamma(\omega) = \frac{1}{2} \frac{k(\rho_T - \rho_f)^2}{\eta V_0 \rho_T} \omega^2 = \frac{1}{2} \frac{k(1-\phi)^2 (\rho_f - \rho_s)^2}{\eta V_0 \rho_T} \omega^2. \quad (2.13g)$$

These expressions for the longitudinal acoustic mode are to be compared with similar expressions derived by Bacri and Rajaonarison<sup>15</sup> (BR) from a one-dimensional model of the gel acoustics. Equation (2) of Ref. 15 may be rewritten in the present notation as

$$V(\text{fast}) = V' [1 + (K_b + \frac{1}{3}N)/(2K_t)], \quad (2.14a)$$

where  $V'$ , the speed in the "sol" phase is simply

$$V' = \left[ \frac{K_t}{\rho_f + (1-\phi)\rho_s} \right]^{1/2}. \quad (2.14b)$$

Equation (2.14b) may be considered equivalent to Eq. (2.13b) simply by considering "the fluid" of Eq. (2.14b) to be "the suspension" of Eq. (2.13b). Thus,  $K_t$  in Eq. (2.14b) is actually  $K^*$  of (2.13b). Similarly, the total densities appearing in the denominator of Eqs. (2.13b) and (2.14b) may be considered to be the same depending on the definition of  $\rho_f$ . [cf. the discussion following Eq. (2.3b) above] I do, however, dispute the expression, Eq. (2.14a), for the change in velocity due to gelation. Presumably the compressibility of individual strands of the polymer network is comparable to that of the fluid; if they are exactly equal ( $K_s = K_t$ ) then one has, from Eqs. (2.13e) and (2.13f):

$$\xi_1(K_s = K_t) = 0,$$

$$\xi_2(K_s = K_t) = \frac{4}{3},$$

as opposed to  $\xi_1 = 1$ ,  $\xi_2 = \frac{4}{3}$  as implied by Eq. (2.14a). If, on the other hand, the individual polymer strands are completely incompressible, one has

$$\xi_1(K_s \gg K_t) = \phi,$$

$$\xi_2(K_s \gg K_t) = \frac{4}{3} \phi,$$

which is in essential agreement with BR in the dilute limit ( $\phi \approx 1$ ). Finally, if the polymer is very compressible  $K_s \ll K_t$  then one may have  $\xi_1 \gg 1$  and a small increase in  $K_b$ ,  $N$  can lead to a large change in  $V$ . It may prove quite difficult to measure  $K_s$  independently. Indeed, at this point one may well speculate on the validity of treating the gel as two interpenetrating elastic media which are describable by bulk moduli  $K_s$  and  $K_t$ . However, all previous treatments have implicitly assumed that the polymer molecules are incompressible ( $K_s \rightarrow \infty$ ) which is not true either.

Bacri and Rajaonarison<sup>15</sup> also derived an expression [their Eq. (3)] for that part of the attenuation due to the relative motion of fluid and solid components. In the current notation, this expression is

$$\gamma = \frac{1}{2} \frac{k(1-\phi)^2 \rho_f^2}{\eta V_0 \rho_T \phi^2} \omega^2. \quad (2.14c)$$

Again, if one can assume  $\rho_T = \rho_f + (1-\phi)\rho_s$  and  $\phi \approx 1$ , this expression agrees with Eq. (2.13g) derived herein.

As mentioned earlier, there is only one nontrivial shear mode whose phase velocity Eq. (2.5) is real in both the high and low frequency limits, according to the theory presented so far. In particular, in the low frequency limit the velocity and attenuation of the shear mode is

$$V(\text{shear}) = \left[ \frac{N}{(1-\phi)\rho_s + \phi\rho_f} \right]^{1/2}, \quad (2.15a)$$

$$\gamma(\text{shear}) = \frac{1}{2} \frac{k\rho_f^2}{\eta V(\text{shear})\rho_T} \omega^2. \quad (2.15b)$$

This is in radical disagreement with the derivation of THB, which was based on the assumption that the fluid remains stationary for the relevant gel network motion. They claim that this shear mode is much like the slow compressional mode considered here: diffusive at low frequencies but propagatory at high. They also claim an additional mode ("Type IV," a fluid based mode) which is propagatory at all frequencies. In order to comment on their result it is necessary to enlarge the scope of the basic theory, which is done in the next section.

### III. EFFECTS OF MACROSCOPIC VISCOSITY

In the basic model presented so far in Sec. II, attenuation is ascribed solely to the relative motion of fluid against solid and is ultimately due to the viscosity of the fluid acting on the scale of the pore size, a microscopic effect. It has been assumed explicitly that the fluid, the solid, and the skeletal frame are themselves nonattenuative ( $K_t$ ,  $K_s$ ,  $K_b$ , and  $N$  are all real valued). This approximation is obviously not strictly true. It can in principle be amended<sup>6,7</sup> though in practice there are in general no known gedanken experiments to relate the additional parameters to independent measurements; it is not valid simply to use the measured complex values of  $K_t$ ,  $K_s$ ,  $K_b$  and  $N$  in Eqs. (2.2) because those relations are derived from gedanken experiments in which the sample is statically stressed in a known manner and then allowed to equilibrate. In this section, I will explore the consequences of a particular additional model absorption mechanism on the normal modes predicted by the theory.

In many cases of interest the attenuation is indeed dominated by the relative fluid-solid motion essentially because of the smallness of the pores. Since a gel consists almost entirely of fluid, however, it is conceivable that the intrinsic attenuation in the fluid is comparable to that induced by the relative fluid-solid motion. By analogy with the case of a normal viscous fluid, one perhaps might also expect an additional fluid based shear mode,<sup>24</sup>  $q = \sqrt{i\omega\rho/\eta}$  ( $\eta$  is an effective fluid viscosity) to replace the trivial zero frequency mode predicted in the last section.

In order to systematically investigate these kinds of effects, it is informative to postulate, by analogy with normal fluids, a transverse attenuation mechanism

$-\eta' \nabla \times \nabla \times (\partial \mathbf{U} / \partial t)$  and a longitudinal attenuation mechanism  $(\zeta' + (4/3)\eta') \nabla [\nabla \cdot (\partial \mathbf{U} / \partial t)]$  which act on the fluid part only, in addition to the attenuation mechanism considered previously. The parameters  $\eta'$  and  $\zeta'$  are, then, effective shear and compressional fluid viscosities which are presumably (for the case of dilute gels) approximately equal to the viscosities of the pore fluid ( $\sim 0.01$  gm/(cm s) for water). [See Landau and Lifshitz,<sup>21</sup> Eq. (15.6) for a discussion of the two viscosities.] This, then, is a kind of macroscopic viscosity effect in which the attenuation is due to distortions that occur on the size scale of the wavelength, rather than that of the pores. This amended model continues to neglect any attenuation within the frame itself. The equations of motion, are, therefore:

$$\rho_{11} \frac{\partial^2 \mathbf{u}}{\partial t^2} + \rho_{12} \frac{\partial^2 \mathbf{U}}{\partial t^2} = P \nabla (\nabla \cdot \mathbf{u}) + Q \nabla (\nabla \cdot \mathbf{U}) - N \nabla \times \nabla \times \mathbf{u} + bF(\omega) \left( \frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right), \quad (3.1a)$$

$$\rho_{22} \frac{\partial^2 \mathbf{U}}{\partial t^2} + \rho_{12} \frac{\partial^2 \mathbf{u}}{\partial t^2} = R \nabla (\nabla \cdot \mathbf{U}) + Q \nabla (\nabla \cdot \mathbf{u}) + (\zeta' + \frac{4}{3}\eta') \nabla (\nabla \cdot \frac{\partial \mathbf{U}}{\partial t}) - \eta' \nabla \times \nabla \times \frac{\partial \mathbf{U}}{\partial t} - bF(\omega) \left( \frac{\partial \mathbf{U}}{\partial t} - \frac{\partial \mathbf{u}}{\partial t} \right). \quad (3.1b)$$

The quantities  $P$ ,  $Q$ , and  $R$  are still given by Eqs. (2.2) because the static gedanken experiments are unaffected by this additional mechanism.

Equations (3.1) are similar to those considered by Marqusee and Deutch<sup>32</sup> who specialized to the case where it is assumed that: (i)  $\rho_{12} = 0$  and (ii)  $P$ ,  $R$  are given by their values in the limit of a dilute concentration ( $\phi \approx 1$ ) of incompressible polymer strands ( $K_s \rightarrow \infty$ ), namely  $P = K_s + \frac{4}{3}N$ ,  $R = K_s$ . The parameter  $Q$  ( $\equiv \beta$  in their notation) is left as a free parameter although it is clear from Eq. (2.2b) that the appropriate value in this limit is  $Q = (1 - \phi)K_s$ .

It is straightforward to derive the dispersion relations from Eqs. (3.1) which I shall do for the limits appropriate to the gel problem, namely small frame moduli ( $K_s, N \ll K_f, K_a$ ) and low frequency ( $\omega \ll \omega_c$ ) so that the viscous skin depth is large compared to the pore sizes.

$$q^2 = \frac{\bar{\rho}_{22} N \omega^2 - i\eta' \bar{\rho}_{11} \omega^3 \pm [(\bar{\rho}_{22} N \omega^2 - i\eta' \bar{\rho}_{11} \omega^3)^2 + 4i\eta' \omega^5 N(\bar{\rho}_{11} \bar{\rho}_{22} - \bar{\rho}_{12}^2)]^{1/2}}{-2i\eta' \omega N} \quad (3.3)$$

As stated in the introduction to this section, it is assumed that the viscous skin depth is much larger than the pore size, i.e.,  $\omega \ll \omega_c$  and so  $F(\omega) = 1$ . There is, however, another crossover frequency in the problem which occurs when the macroscopic viscous skin depth  $\delta = \sqrt{2\eta' / \rho_T} \omega$  is comparable to the shear wavelength predicted by Eq. (2.15a),  $\lambda / 2\pi = (1/\omega)(N/\rho_T)^{1/2}$ . Ignor-

**A. Longitudinal modes**

The complex phase velocities are still given by Eqs. (2.4) except that the quantity  $R$  is replaced by  $\bar{R}(\omega)$ , where

$$\bar{R}(\omega) = R - i\omega(\zeta' + \frac{4}{3}\eta'),$$

as is obvious from Eq. (3.1b). It is implicitly assumed that  $R \gg \omega(\zeta' + \frac{4}{3}\eta')$  which is reasonable since  $R \approx K_f \sim 10^{10}$  dyn/cm<sup>2</sup> and  $(\zeta' + \frac{4}{3}\eta') \approx 10^{-2}$  poise, for water based dilute gels.

**1. Slow compressional wave**

To lowest order in frequency the slow wave is still diffusive with the same diffusivity as before, i.e., Eqs. (2.8a) and (2.8b) are unaffected. Therefore, the diffusivity in the weak frame limit applicable to the gel problem, Eq. (2.11), is unaffected.

**2. Fast compressional wave**

The wave vector of the fast compressional wave is still of the form  $q(\omega) = \omega/V + i\gamma(\omega)$  in the low frequency limit. The speed  $V$  of the fast wave in the low frequency, weak frame, limits, Eqs. (2.13a)-(2.13f), is unaffected by the additional attenuation mechanism. The attenuation, however, is modified from that given by Eq. (2.13g) by the inclusion of an additional term:

$$\gamma(\omega) = \frac{1}{2} \frac{\zeta' + \frac{4}{3}\eta'}{V_0^3 \rho_T} \omega^2 + \frac{1}{2} \frac{(\rho_T - \rho_f)^2 k}{V_0 \rho_T \eta} \omega^2. \quad (3.2)$$

This result, though formally similar to that derived by Bacri and Rajaonarison,<sup>15</sup> differs in the first term in that: (i) the speed  $V_0$  is the speed in the suspension and, (ii) the longitudinal viscosity  $\zeta' + \frac{4}{3}\eta'$  need not be the same as that of the solvent; the differences in the second term have already been discussed in connection with Eq. (2.13g).

**B. Shear modes**

The nature of the shear modes is radically changed from that discussed in the previous section; there are two nontrivial modes where there had only been one and their dispersion relations are given by

ing factors of order unity, this crossover occurs at a frequency  $\omega_x = N/\eta' (\ll \omega_c)$ . I should point out that the added attenuation terms basically represent a Taylor's series expansion in frequency; for frequencies comparable to  $\omega_x$ , it is really not valid to neglect terms with higher order time derivations, (e.g.,  $\nabla(\nabla \cdot \partial^3 \mathbf{u} / \partial t^3)$  etc.) as has been done here.

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TABLE I. Shear modes of a porous medium in the low and in the high frequency limit as derived from Eq. (3.3). In all cases it is assumed that the viscous skin depth is much larger than a typical pore size. The displacement of the fluid component is  $U(\mathbf{r}, t)$  whereas that of the solid is  $u(\mathbf{r}, t)$ . The complex wave-vector is  $q(\omega)$ .

	$\omega \ll N/\eta'$ ( $\delta \ll \lambda/2\pi$ )	$\omega \ll N/\eta'$ ( $\delta \gg \lambda/2\pi$ )
A mode	$q^2 = \frac{\rho_T}{N} \omega^2$ $u = U$	$q^2 = i \frac{\rho_T \omega}{\eta'}$ $u = U$
B mode	$q^2 = \frac{-\eta \phi^2}{\eta' k} + i \left( \frac{\eta \phi^2}{kN} + \frac{\alpha \phi \rho_f}{\eta'} \right) \omega$ $u = i \frac{\eta' \omega}{N} U$ $ u  \ll  U $	$q^2 = i \frac{\eta \phi^2}{kN} \omega$ $u = i \frac{\eta' \omega}{N} U$ $ u  \gg  U $

In Table I, I have presented the low frequency and high frequency limits (relative to  $\omega_c$ ) of the shear modes, which are derivable in a straightforward, if tedious, manner from Eq. (3.3). These results are in disagreement with those of THB who assumed that, for the relevant motion of the solid matrix, the fluid can be assumed stationary; their dispersion relation [Eq. (12) of Ref. 2 but in the present notation] is

$$\omega^2 - i \left[ \frac{\eta \phi^2}{k(1-\phi)\rho_s} \right] \omega - \frac{N}{(1-\phi)\rho_s} q^2 = 0. \quad (3.4)$$

THB predict that the shear mode is diffusive at low frequencies ( $q^2 = -i\omega C$ ) and propagatory at high ( $q^2 = \omega^2/V^2$ ). According to Table I, the "A" branch has exactly the reverse behavior. At low frequencies, the two components are locked together by the viscosity of the fluid and so the mode is propagatory, identical in all respects with the shear mode derived in the previous section, Eq. (2.15a). On the other hand, this branch is in fact *diffusive* at high frequencies, with a diffusivity  $\eta'/\rho_T$ , characteristic of the usual diffusive shear mode present in any viscous fluid, at high frequencies. (See Landau and Lifshitz<sup>21</sup> Sec. 24.) The other, B branch, has a diffusivity  $kN/\eta\phi^2$  identical to that of THB ( $=\rho c^2/f$  in their notation) at high frequencies (relative to  $\omega_c$ ); in this case the fluid part is essentially immobile by virtue of its inertia. This same branch has the unusual characteristic that it tends to a static, permanent distortion at low frequencies. This distortion, however, applies essentially to the fluid component only and occurs on a distance scale ( $k^{1/2}$ ) which is comparable to the pore size and so the continuum treatment of the dynamics breaks down. In fact, in the high frequency limit this branch has much the same problem because if  $\omega \gg \omega_c$  then

$$|q^2| \gg \frac{\eta}{\eta'} \frac{\phi^2}{k}$$

and the distance scale on which this model varies is also of the order of a pore size. Thus, only the A branch appears to have physical significance. Whether the other branch has physical significance or is simply

an artifact of the approximations that went into Eq. (3.1) is unclear at present; it is clear that it violates the long wavelength assumption upon which Eqs. (3.1) are based. Because the wavelength of this branch is small on the scale of the pore size, the microscopic flow pattern of the fluid around the polymer strands is clearly altered<sup>22</sup> [ $F(\omega)$  is not constant]. At the very least, other terms that are second order derivatives in position and first order in time  $\{\nabla \times \nabla \times (\partial u / \partial t)$  and  $\nabla[\nabla \cdot (\partial u / \partial t)]\}$  should also be included in Eqs. (3.1).

I should like to point out that, regardless of the actual mechanisms that are operative, any additional shear branch (such as the "B-mode" of Table I) must have the property that the wave vector  $q$  tends to a finite limit as  $\omega$  tends to zero. Otherwise the number of hydrodynamic modes would exceed the number of hydrodynamic variables.<sup>34</sup> Following Ref. 34, there is a total of nine hydrodynamic variables: density, gel concentration, total momentum (3), displacement of the gel network from equilibrium (3), and energy density. Hydrodynamic modes are those for which the characteristic frequency tends to zero in the limit of long wavelengths i. e.,  $\lim_{q \rightarrow 0} \omega(q) = cq^n$  for some  $n \geq 1$ . The hydrodynamic modes for the gel are: thermal diffusion (not explicitly considered in this article); two longitudinal fast waves  $\omega = \pm V(\text{fast})q$ ; one longitudinal slow wave  $\omega = iC_D q^2$ ; and four shear waves  $\omega = \pm (N/\rho_T)^{1/2}$  (two different polarizations). In addition, the model presented in this article predicts another hydrodynamic mode<sup>13</sup>  $\omega(q) \equiv 0$  corresponding to a static deformation in gel density; were a realistic model for vacancy diffusion in the gel network included in our analysis, this mode would acquire a nonzero diffusivity. In all, then, there are nine hydrodynamic modes, as expected. If the B branch (or any other) had the property  $\lim_{\omega \rightarrow 0} q(\omega) = K\omega^m$  for some nonzero  $m$ , this would be an additional hydrodynamic mode (both  $\omega$  and  $q$  tending to zero together) which is not allowed.

It should be emphasized that the propagatory shear mode with speed  $\sqrt{N/(1-\phi)\rho_s}$  claimed by THB [high frequency limit of Eq. (3.4)] is not physically realizable. This limit occurs mathematically when the frequency is so high that the viscous skin depth is small compared to a pore size  $\omega \gg \omega_c$  and  $\lim_{\omega \rightarrow \omega_c} \bar{\alpha}(\omega) = \alpha$  [cf. Eq. (2.3c')]. For a dilute concentration of scatterers (polymer strands) the real parameter  $\alpha$  is nearly unity<sup>28</sup> i. e.,  $\lim_{\phi \rightarrow 1} \lim_{\omega \rightarrow \omega_c} \bar{\alpha}(\omega) = 1$ . Thus, in this double limit the speed of the shear mode is, indeed,  $\sqrt{N/(1-\phi)\rho_s}$  as can be seen from Eq. (2.5). This result also follows from the B branch of Eq. (3.3) in the limit  $\omega \gg \omega_c$  ( $\gg \omega_c$ ) as can be checked. It has already been pointed out, however, that this limit is unphysical in that the wavelength of the mode is small compared to the average pore size.

#### IV. COMPARISON WITH EXPERIMENTAL DATA

##### A. Slow compressional wave

Using static techniques, Tanaka and co-workers (THB) have independently measured the two parameters  $b$  and  $K_b + \frac{4}{3}N$  needed for a description of the diffusive slow

wave in the low frequency, weak frame limit. Their results for two polyacrylamid gels of volume concentration  $1 - \phi = 0.025$  and  $0.05$  are listed in Table II, as are the diffusivities calculated from Eq. (2.11). This expression is clearly appropriate because  $K_T = 2.2 \times 10^{10}$  dyn cm<sup>-2</sup> is indeed much larger than  $K_b$ ,  $N$ . By light scattering techniques THB observed a mode which was clearly diffusive in nature and whose diffusivity is also included in Table II. That the two diffusivities agree to within experimental uncertainties is gratifying confirmation of the theory. [THB noted that their result, Eq. (2.12), is also in essential agreement.]

I should mention that Patterson and co-workers<sup>17,18</sup> have also reported diffusivities in the range  $10^{-7}$ – $10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> on polymer gels and on (noncrosslinked) polymer solutions of the same concentrations as the gels. They have not reported independent measurements of  $K_b + \frac{4}{3}N$  and  $k/\eta$ , however. Because their values for diffusivities are independent of whether the polymer is cross linked into a gel or remains as a solution, they have concluded that: (i) Since the value of  $N$  is obviously very different in a gel as compared to a solution (for which  $N = 0$ ), it is apparent that  $K_b$  is much larger than  $N$  and (ii) the value of  $K_b$  does not depend on whether the polymer chains are cross linked or not. Thus, Tanaka's argument<sup>2</sup> that  $K_b$  and  $N$  are comparable to each other (Poisson's ratio for the gel network is zero) may not be borne out by Patterson's gels. In particular, the static measurement of the Young's modulus of the gel ( $E \approx 3N$ ) is not enough information to deduce  $K_b$ , in such systems.

In Table III, I have summarized those porous systems in which the slow wave has been observed in one form or another. Because the mode has been observed in such disparate systems as 4th sound and gels, it is clear that the mode is a fairly common one. According to the theory, the additional compressional mode, whether propagatory or diffusive, exists in any permeable, fluid saturated system, except for special values of the parameters, an example of which occurs when  $K_b \equiv N = 0$ . It remains to be explained why this mode is not always observed in every porous fluid saturated solid.

## B. Shear mode

Measurements of the shear moduli have been reported on a variety of gels. Probably the most extensive measurements are those of Ferry and Fitzgerald<sup>35</sup> on gels consisting of polyvinyl chloride (the solid) in dimethyl-

TABLE II. Experimental data on the diffusive mode in polyacrylamid/water gels as determined by steady state macroscopic methods and by dynamic light scattering. From Ref. 2.

$1 - \phi$	0.05	0.025
$b = \eta \phi^2 / k$ (dyn s cm <sup>-4</sup> )	$2.2 \pm 0.3 \times 10^{11}$	$3.5 \pm 0.1 \times 10^9$
$K_b + \frac{4}{3}N$ (dyn cm <sup>-2</sup> )	$5.2 \pm 0.3 \times 10^4$	$4.4 \pm 0.9 \times 10^2$
$C_D$ (cal) = $(K_b + \frac{4}{3}N)k/\eta$ (cm <sup>2</sup> s <sup>-1</sup> )	$2.1 \pm 0.3 \times 10^{-7}$	$1.2 \pm 0.2 \times 10^{-7}$
$C_D$ (exptl) (cm <sup>2</sup> s <sup>-1</sup> )	$2.4 \pm 0.1 \times 10^{-7}$	$1.6 \pm 0.1 \times 10^{-7}$

TABLE III. Systems in which the slow wave has been observed.

	Weak frame	Stiff frame
Low freq. (diffusive) (dominance of $\eta_T$ )	Polymer gels <sup>a</sup>	Rocks <sup>b</sup> Fused glass beads <sup>b</sup>
High freq. (propagatory) (dominance of $\rho_T$ )		4th sound in He II <sup>c</sup> Fused glass beads <sup>d</sup> Other artificial media <sup>d</sup>

<sup>a</sup>Present article and Ref. 2.

<sup>b</sup>References 29 and 30.

<sup>c</sup>References 12 and 27.

<sup>d</sup>Reference 10.

thianthrene (the fluid) at concentrations of  $1 - \phi = 0.10$  and  $0.40$  (the latter is considered a "plastic" rather than a "gel"). They measured the complex shear modulus  $\tilde{N}(\omega)$  as a function of frequency (30 Hz–5 kHz) and temperature ( $-23$  °C to  $+25$  °C).

Their analysis of the data indicates that the room temperature shear modulus is highly frequency dependent and could vary from  $10^5$  (dyn cm<sup>-2</sup>) at 30 Hz to  $10^{10}$  (dyn cm<sup>-2</sup>) at  $10^8$  Hz, if their scaling hypothesis proves correct by extending the measurements to higher frequency. The imaginary part of  $\tilde{N}$  can also be quite large. These effects do not appear to be describable by Eq. (3.3) and, indeed, seem to lie outside the realm of this article because it has been explicitly assumed here that the shear modulus is frequency independent. It would appear that there is direct evidence that the modulus in a gel can be highly frequency dependent.

## C. Fast compressional wave

Bacri and co-workers<sup>15,36</sup> have measured the ultrasonic ( $\sim 10^8$  Hz) properties of gels similar to Tanaka's. The measured change in attenuation upon gelation agrees with Eq. (2.13g) [or (2.14c)] in the sense that the  $(1 - \phi)^2$  dependence was observed and the deduced values of the damping  $\eta/k$  were comparable to those measured by THB. Left unexplained is why  $\eta/k$  deduced ultrasonically from Eq. (2.14c) does not appear to depend on gel concentration, (i. e.,  $1 - \phi$ ) although this dependence was clearly seen by THB. Furthermore, Jarry and Patterson<sup>16</sup> reported essentially no change in attenuation (deduced from Brillouin scattering widths) on their gels and they attribute attenuation as due to the first term of Eq. (3.2), at least at hypersonic frequencies.

More puzzling is the change in velocity due to gelation which BR<sup>15</sup> observed to be a few percent. (This is too small to be seen by Brillouin scattering.) Eq. (2.13a) with  $\xi_i$  of order unity implies that  $K_b$ ,  $N$  are  $\sim 10^9$  dyn cm<sup>-2</sup> which is at least four orders of magnitude larger than  $K_b + \frac{4}{3}N$  measured by THB. BR offer the explanation that the difference could be due to a large dependence of  $K_b + \frac{4}{3}N$  on frequency similar to that which apparently occurs in the shear modulus of some gels (Sec. IV B above). Although this is possible, it should be verified experimentally. There are also two other possibilities: (i) If  $[(1 - \phi)/\phi] K_T \ll K_b \ll K_T$  (dilute gel of very compressible molecules) then  $\xi_1 \gg 1$  and a small  $K_b$  can have a large effect on  $V$ . This is not a large enough effect, however, to explain the data. (ii)

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Upon gelation the concentration of monomer in the fluid obviously decreases. It is known that a 1% change in the salt concentration of seawater can change the velocity by almost one percent, albeit in the wrong direction for our purposes.<sup>37</sup> Thus it is at least conceivable that the change in velocity upon gelation is due largely to a change in  $V_0$  and not  $K_b$  or  $N$ . It will be difficult to monitor the properties of the pore fluids because they are thought to consist of a fairly large concentration of free carriers, preferentially of one sign (+), which balances the bound changes (-) on the gel networks.<sup>1</sup> Thus it will be difficult to study a pore fluid separate from a polymer network.

## V. SUMMARY

The elastodynamic modes of a porous and permeable fluid saturated system have been analyzed in terms of models which treat the motions of the two components separately. The models were specialized to the cases of interest for most gels, namely small frame moduli of the solid skeleton, but with arbitrary polymer concentration and with arbitrary compressibility of the polymer strands. Difficulties encountered in these models are due to the apparently large frequency dependence of the frame moduli which, in turn, are presumably due to internal degrees of freedom in the polymer network not considered here.

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<sup>1</sup>T. Tanaka, *Sci. Am.* **244**, 124 (1981).

<sup>2</sup>T. Tanaka, L. O. Hocker, and G. B. Benedek, *J. Chem. Phys.* **59**, 5151 (1973).

<sup>3</sup>T. Tanaka, S. Ishiwata, and C. Ishimoto, *Phys. Rev. Lett.* **38**, 771 (1977).

<sup>4</sup>M. A. Biot, *J. Acoust. Soc. Am.* **28**, 168 (1956); **28**, 179 (1956).

<sup>5</sup>M. A. Biot and D. G. Willis, *J. Appl. Mech.* **24**, 594 (1957).

<sup>6</sup>M. A. Biot, *J. Appl. Phys.* **33**, 1482 (1962).

<sup>7</sup>M. A. Biot, *J. Acoust. Soc. Am.* **34**, 1254 (1962).

<sup>8</sup>M. R. J. Wyllie, G. H. F. Gardner, and A. R. Gregory, *Geophysics* **27**, 569 (1962).

<sup>9</sup>R. D. Stoll in *Physics of Sound in Marine Sediments*, edited by L. Hampton (Plenum, New York, 1974).

<sup>10</sup>T. J. Plona, *Appl. Phys. Lett.* **36**, 259 (1980); T. J. Plona and D. L. Johnson in 1980 *Ultrasonic Symposium Proceedings*, edited by J. deKlerk and B. R. McAvoy (IEEE, New York, 1980), p. 868.

<sup>11</sup>D. L. Johnson and T. J. Plona, *J. Acoust. Soc. Am.* (to be published).

<sup>12</sup>D. L. Johnson, *Appl. Phys. Lett.* **37**, 1065 (1980); *ibid.* **38**, 827 (1980) (E).

<sup>13</sup>J. M. Deutch and D. L. Johnson, *J. Chem. Phys.* (to be published).

<sup>14</sup>P. G. DeGennes, *Macromolecule* **9**, 587 (1976).

<sup>15</sup>J. -C. Bacri and R. Rajaonarison, *J. Physiq. Lett.* **40**, L-5 (1979).

<sup>16</sup>J. -P. Jarry and G. D. Patterson, *Macromolecules* **14**, 1281 (1981).

<sup>17</sup>G. D. Patterson, J. R. Stevens, J. -P. Jarry, and C. P. Lindsey, *Macromolecules* **14**, 86 (1981).

<sup>18</sup>G. D. Patterson, D. S. Pearson, J. -P. Jarry, *Macromolecules* (to be published).

<sup>19</sup>R. J. S. Brown and J. Korrington, *Geophysics* **40**, 608 (1975).

<sup>20</sup>J. Geertsma and D. C. Smit, *Geophysics* **26**, 169 (1961).

<sup>21</sup>L. D. Landau and M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959), p. 31 ff.

<sup>22</sup>J. G. Berryman, *Appl. Phys. Lett.* **37**, 382 (1980).

<sup>23</sup>Reference 21, Eq. (17.10) gives the flow resistance through a single tube from which  $k = \phi r^2/8$  follows.

<sup>24</sup>Reference 21, p. 88 ff.

<sup>25</sup>J. M. Hovem and G. D. Ingram, *J. Acoust. Soc. Am.* **66**, 1807 (1979).

<sup>26</sup>C. H. Yew and P. N. Jogi, *Exp. Mech.* **18**, 167 (1978).

<sup>27</sup>K. A. Shapiro and I. Rudnick, *Phys. Rev. A* **137**, 1383 (1965).

<sup>28</sup>D. L. Johnson and P. N. Sen, *Phys. Rev. B* **24**, 2486 (1981).

<sup>29</sup>R. N. Chandler and D. L. Johnson, *J. Appl. Phys.* **52**, 3391 (1981).

<sup>30</sup>R. N. Chandler, *J. Acoust. Soc. Am.* **70**, 116 (1981).

<sup>31</sup>A. W. Wood, *A Textbook of Sound* (MacMillan, New York, 1941).

<sup>32</sup>J. A. Marqusee and J. M. Deutch, *J. Chem. Phys.* **75**, 5239 (1981).

<sup>33</sup>I am grateful to M. H. Cohen for pointing this out to me.

<sup>34</sup>P. C. Martin, O. Parodi, and P. S. Pershan, *Phys. Rev. A* **6**, 2401 (1972). I am most grateful to B. I. Halperin for pointing out the relevance of this work to me.

<sup>35</sup>J. D. Ferry and E. R. Fitzgerald, *J. Colloid Sci.* **8**, 224 (1953).

<sup>36</sup>J. -C. Bacri, J.-M. Courdille, J. Dumas, and R. Rajaonarison, *J. Physiq. Lett.* **41**, L-369 (1980).

<sup>37</sup>H. Medwin, *J. Acoust. Soc. Am.* **58**, 1318 (1975); V. A. Del Grosso, *J. Acoust. Soc. Am.* **47**, 947 (1970).