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Abstract. Elastomers and gels are characterised by a large ratio of the bulk to the shear modulus, and are consequently capable of propagating shear waves of very low velocity. We have elsewhere examined the normal modes excited in gels contained in rectangular cells of infinite length with rigid boundary conditions, and have shown that the fundamental mode consists of a roller structure which is periodic along the long axis of the cell. Here we extend the variational analysis to include gels of semi-infinite length and of square cross-section with one end free; it is found that the fundamental is a localised mode, in which the motion of the gel is confined to the vicinity of the free surface. Gels of finite length with a free end are also investigated. Experimental observations are made both of quasi-longitudinal and of quasi-transverse modes in polyacrylamide gels; good agreement is found between the measured frequencies of the first few modes and the calculated eigenfrequencies for this system.

1. Introduction

In a recent article we described an investigation of the fundamental shear modes that can be excited in an incompressible elastic medium rigidly held inside an infinitely long prism of square cross-section (Ayant *et al* 1982—reference A). Experimental observations of similar modes have been reported (Brenner *et al* 1978, Nossal and Brenner 1978, Gelman and Nossal 1979, Nossal and Jolly 1982, Geissler and Hecht 1980), although limited to finite systems; these observations have furthermore generally been confined to gels with one free surface, a condition which could profoundly modify the eigenmodes. Until now, the normal modes for such systems with rigid boundaries have not been analysed.

An application of such investigations is to be found in the study of rubbers and elastomers, where a knowledge of the shear modulus G is of paramount importance. G, which depends on the microscopic configuration of the constituent polymer chains (Treloar 1975), defines the suitability of these materials in a wide range of industrial and other applications. It is frequently useful to know the shear modulus of an elastomeric polymer solution or gel at the same time as its optical properties. Since the latter are often most conveniently observed with cells of square cross-section, an *in situ* investigation of the shear modulus requires a knowledge of the allowed modes in this geometry. The determination of the shear modulus by the normal mode technique possesses certain well known advantages over other methods: the small amplitude of the motions necessary to obtain a measurable response, the precision of the frequency measurements, and the well defined boundary conditions (this last consideration is particularly important in the case of soft gels). It therefore seems appropriate to extend our previous investigation to include finite systems with a free end surface, and to compare the results with the observed resonances in the gel.

In the present article the variational techniques of reference A are extended to calculate not only the fundamental frequency, but also the next higher modes. In the previous cases, as also in the case of finite three-dimensional systems where all the boundaries are rigid, the task of obtaining an accurate numerical solution was straightforward, although tedious, using the Rayleigh variational theorem and a Fourier expansion for the trial functions. In the case of interest here, however, that of a prism with one end free, the truncated Fourier series method becomes intractable, because the displacement vector can no longer be expressed in terms of simple orthogonal basis functions in the form of products of sines and cosines. For this reason, we are forced to use an approximate variational treatment, using trial functions of the appropriate symmetry and chosen to satisfy the boundary conditions, while containing a single adjustable parameter. This procedure has been known since its inception to give very good approximations to the exact result (Rayleigh 1945). Tests between the approximate trial function method and the truncated Fourier series method, in the case of a finite three-dimensional gel with no free surfaces, gave a maximum difference of 0.7% in the estimation of the first six eigenfrequencies. Because of this accuracy, some confidence can be placed in the use of the single trial function method in the present case where a free surface exists.

The first part of the article, after a brief description of the variational method used, is devoted to solving the motion of the incompressible gel inside an infinitely long prism of square cross-section with one end surface free; the case of the gel of finite length is then investigated. The second part of the article concerns the experimental observations and their confrontation with the calculations.

2. Variational analysis of small oscillations in an incompressible medium

Our object is to determine the normal modes and eigenfrequencies of a gel which adheres, without slipping, to the walls of the containing cell. We shall, for the moment, neglect frictional effects; this omission is easily rectified, however, by the inclusion of a simple dissipation process.

In the problem investigated, we consider a vector $\boldsymbol{u}(\boldsymbol{x}, t)$ which describes the displacement of a point in the gel. We examine the case of a sample of volume ν of an isotropic body, with bulk compressional modulus K and shear modulus G. The potential energy of the sample may be expressed by means of the strain tensor

$$\tau_{ij} = \tfrac{1}{2}(\partial u_i/\partial x_j + \partial u_j/\partial x_i), \tag{1}$$

and of the stress tensor, which in this case is given by

$$T_{ij} = (K - \tfrac{2}{3}G)\sum_k \tau_{kk}\delta_{ij} + 2G\tau_{ij}. \tag{2}$$

As we are concerned with the limiting case where K tends to infinity, it is necessary that

$$\nabla \cdot \boldsymbol{u} = 0. \tag{3}$$

Hence we obtain directly the following expression for the potential energy V,

$$V = G \sum_{ij} \int \mathrm{d}^3x\, \tau_{ij}^2, \tag{4}$$

which, on account of equations (1) and (3) reduces to

$$V = \frac{G}{2} \sum_{ij} \int \mathrm{d}^3x \left(\frac{\partial u_i}{\partial x_j}\right)^2 + \frac{G}{2} \int_S \mathrm{d}S\, \boldsymbol{n} \cdot (\boldsymbol{u} \cdot \boldsymbol{\nabla})\boldsymbol{u}, \tag{5}$$

where S is the boundary surface of the sample and $\boldsymbol{n}$ is the outwards directed normal to the surface.

Equation (5) is applicable to the case of a gel with a free surface. When all the surfaces are held rigid, the second term in (5) vanishes and the potential energy reduces to

$$V = \frac{G}{2} \sum_{ij} \int \left(\frac{\partial u_i}{\partial x_j}\right)^2 \mathrm{d}^3x. \tag{6}$$

In order to determine the normal modes of the system, we use a variational technique due to Rayleigh (1945), which is applicable to all problems of small movements, and which relies on the stationary properties of the eigenfrequencies. The principle of the technique is outlined as follows.

The potential energy of the system, defined according to (5) or (6) may be re-expressed in the form

$$V = \tfrac{1}{2} GI. \tag{7}$$

The kinetic energy T is given in the present case by

$$T = \frac{\rho}{2} \int \dot{\boldsymbol{u}}^2\, \mathrm{d}^3x, \tag{8}$$

where ρ is the density of the medium and $\dot{\boldsymbol{u}}$ represents the time derivative of $\boldsymbol{u}(\boldsymbol{x}, t) = \boldsymbol{u}(\boldsymbol{x}) \sin(\omega t)$. The requirement that the total energy $T + V$ be time independent is ensured by equalising the coefficients of $\sin^2(\omega t)$ and $\cos^2(\omega t)$ in $T + V$: this can be done be defining a function S, associated to T, such that

$$\begin{aligned} S &= \frac{\rho}{2} \int \boldsymbol{u}(x)^2\, \mathrm{d}^3x \\ &= \tfrac{1}{2}\rho J. \end{aligned} \tag{9}$$

The required time independence of $T + V$ is then obtained when

$$\omega^2 = V/S, \tag{10}$$

and the condition that $\boldsymbol{u}$ be a normal mode is that V/S be stationary, i.e.

$$\omega^2 = (V/S)_{\text{extremum}}. \tag{11}$$

It should be emphasised that, although Rayleigh does not formally define the associated function S as in (9), this method is entirely equivalent; the presentation chosen here is simply for the purpose of convenience.

The variational approximation introduced by Rayleigh then consists of substituting for $\boldsymbol{u}(\boldsymbol{x})$ in relation (11) a suitable trial function containing one or more adjustable parameters; the approximate stationary values of V/S are found on varying these parameters.

The task is thus reduced to looking for a vector field $\boldsymbol{u}(\boldsymbol{x})$ which obeys the incompressibility condition (3) and the boundary condition $\boldsymbol{u}(\boldsymbol{x})=0$ at the cell walls. Hence the frequencies ω of the corresponding approximate normal modes are given by the Rayleigh condition (11).

For convenience, we use the integrals I and J as defined by relations (7) and (9). Designating by E the stationary value of I/J, we obtain from (11)

$$E=(I/J)_{\text{extremum}}, \tag{12}$$

where $E=\omega^2\rho/G$ has the dimensions of the square of a wave vector.

In reference A (Ayant *et al* 1982), it was shown that the formulation of (12) is equivalent to the standard equation of motion for an incompressible medium, namely

$$\boldsymbol{\nabla}\wedge(\boldsymbol{\nabla}^2+E)\boldsymbol{u}=0. \tag{13}$$

3. Three-dimensional cell with free surface

3.1. General considerations

Here we examine the case of an incompressible gel contained in a cell of square cross-section, with one end free. The effects of surface tension are neglected (see § 6). Two situations are investigated, a gel of semi-infinite length in the $+z$ direction, and a gel of finite length b in the $+z$ direction. The limits of the gel in the x and y directions are taken to be at ± 1, and the free surface is placed at $z=0$.

It is worthwhile remarking that the symmetry of such samples with a free surface is C_V^4; thus, according to group theory, the normal modes should fall into five distinct symmetry types: A_1, A_2, B_1, B_2 and E. Of these the first, A_1, will be excluded from consideration since it is totally symmetric, and involves a volume change in the sample which is supposed to be incompressible. The second, which corresponds to a rotation about the C_4 or z axis, defines modes which we shall call quasi-transverse (QT). The second type of mode investigated in this paper involves movement along the z axis and belongs to the representation E; these are designated quasi-longitudinal (QL). B_1 and B_2 are similar to the QL modes, but are described by wave numbers much larger than those considered here, and consequently lie beyond the region of interest close to the fundamental frequency. Since the QT modes involve movements approximately parallel to the x–y plane, the trial functions proposed will have zero z component: the surface integral in (5) thus vanishes, and the problem simplifies considerably. This case will be treated after the discussion of the QL modes.

We emphasise the fact that the distinction between QL and QT modes is linked to the concept of a continuous variation between the present case and that of the infinitely long prism: either mode can be written in the form $u_j(x,y,z)=u_j(x,y)\exp(\mathrm{i}k_z z)$, where $j=x,y,z$. One examines what happens when k_z tends to zero. Reference A shows that either the components u_x and u_y tend to zero (QL), or the component u_z tends to zero (QT).

3.2. Quasi-longitudinal modes

In this case the displacement of the gel perpendicular to the free surface is non zero, and the surface contribution to the potential energy in (5) must be taken into account. Using (7), we rewrite (5) as

$$\begin{aligned} I &= \int \sum_{ij} \left(\frac{\partial u_i}{\partial x_j}\right)^2 \mathrm{d}^3x + \int_S \boldsymbol{n} \cdot [(\boldsymbol{u} \cdot \boldsymbol{\nabla})\boldsymbol{u}]\,\mathrm{d}S \\ &= I_V + I_S. \end{aligned} \tag{14}$$

In the case of the QL modes, the displacement $\boldsymbol{u}$ is approximately confined to a plane parallel to one of the sides of the prism. Because of the square cross-section, we may choose the y-axis to lie perpendicular to this side, and then $u_y \simeq 0$. The components of the trial function obeying the boundary conditions may be chosen as

$$\begin{aligned} u_x &= u_x(x, z)\cos(\pi y/2) \\ u_y &= 0 \\ u_z &= u_z(x, z)\cos(\pi y/2). \end{aligned} \tag{15}$$

By means of this separation of the variable y, it is shown in the appendix how the three-dimensional expression for I in (14) can be reduced to a two-dimensional one by the use of a two-variable potential $\phi(x, z)$ defined by

$$u_x(x, z) = \partial\phi/\partial z, \qquad u_z(x, z) = -\partial\phi/\partial x. \tag{16}$$

The three-dimensional eigenfrequencies are related to the two-dimensional ones by

$$E(\mathrm{3D}) = E(\mathrm{2D}) + \tfrac{1}{4}\pi^2. \tag{17}$$

We may then try

$$\phi(x, z) = (1 + \cos \pi x)g(z), \tag{18}$$

which satisfies the boundary conditions. The stationary condition now concerns only the variable function $g(z)$.

The integrals of the variational procedure can now be written

$$J = \int (\pi^2 g^2 + 3g'^2)\,\mathrm{d}z \tag{19}$$

and

$$I_V = \pi^2 J + I_V^* \tag{20}$$

with

$$I_V^* = \int (3g''^2 - \pi^2 g'^2)\,\mathrm{d}z, \tag{21}$$

$$I_S = -2\pi^2 g(0)g'(0), \tag{22}$$

where g' and g'' represent respectively the first and second derivatives of g, and the free surface is located at the end $z = 0$; the rigid end is located at $z = b$. The rigid boundary constraint at $z = b$ requires that

$$g(b) = g'(b) = 0. \tag{23}$$

It is of interest to note that the variational treatment used here does not impose any explicit boundary conditions at the free surface; nevertheless, a treatment based on the standard propagation equation (13), together with the incompressibility condition (3), should make use of well known boundary conditions that cancel certain components of the stress tensor at the free surface. We have verified that these cancellations are inherent in the variational treatment.

We now apply the variational procedure. Introducing a small variation δg in g, with attendant variations δI and δJ in I and J respectively, and integrating by parts, one gets from (19) and (21)

$$\tfrac{1}{2}\delta J=\int_0^b(\pi^2 g-3g'')\delta g\,\mathrm{d}z-3g'(0)\delta g(0) \tag{24}$$

and

$$\tfrac{1}{2}\delta I_V^*=\int_0^b(3g''''+\pi^2 g'')\delta g\,\mathrm{d}z-3g''(0)\delta g'(0)+(3g'''(0)+\pi^2 g'(0))\delta g(0). \tag{25}$$

From (22) we likewise obtain

$$\tfrac{1}{2}\delta I_S=-\pi^2(\delta g(0)g'(0)+g(0)\delta g'(0)). \tag{26}$$

This allows us to set the stationary condition as

$$\delta I^*=E^*\delta J, \tag{27}$$

where

$$E^*=E-\pi^2, \qquad \text{and } \delta I^*=\delta I_V^*+\delta I_S. \tag{28}$$

Combining equations (23)–(26), we find that $g(z)$ satisfies the fourth-order equation

$$3g''''+(\pi^2+3E^*)g''+\pi^2E^*g=0, \tag{29}$$

together with the following boundary conditions at $z=0$

$$3g''(0)+\pi^2 g(0)=0 \tag{30}$$

$$g'''(0)+E^*g'(0)=0. \tag{31}$$

We are now in a position to consider the two cases, that of the semi-infinite cell, and secondly the cell of finite length.

3.2.1. Semi-infinite cell. When b is allowed to go to infinity, (29) allows solutions of the form $\exp(\mathrm{i}kz)$, with k given by

$$k_\pm^2=\pi^2[\tfrac{1}{2}t-\tfrac{1}{3}\pm(\tfrac{1}{4}t^2-\tfrac{2}{9})^{1/2}], \tag{32}$$

where

$$t=E/\pi^2.$$

When $t^2<8/9$, complex values of k occur; this implies a localised mode. We shall set $\lambda=\mathrm{i}k$, where it is understood that $R\lambda<0$. Thus

$$g(z)=A\exp(\lambda z)+\bar{A}\exp(\bar{\lambda}z), \tag{33}$$

where the bar denotes the complex conjugate.

To ensure the boundary conditions (30) and (31), we must have the determinant

$$\begin{vmatrix}3\lambda^2+\pi^2 & 3\bar{\lambda}^2+\pi^2\\ \lambda^3+E^*\lambda & \bar{\lambda}^3+E^*\bar{\lambda}\end{vmatrix}=0. \tag{34}$$

This gives, on simplifying

$$3|\lambda|^4 - \tfrac{1}{3}\pi^4 - (\pi^4/3|\lambda|^2) - 3E^*|\lambda|^2 = 0 \tag{35}$$

with

$$|\lambda|^4 = \pi^4(1-t)/3. \tag{36}$$

By setting $t = 1 - u^2/3$ in (35) and (36), we get

$$1 - u - u^2 - u^3 = 0, \tag{37}$$

which contains only one real root, namely

$$u = 0.5437,$$

that is,

$$E = 8.897. \tag{38}$$

This value for E falls significantly below the lowest value obtained in the case of an infinitely long gel in two dimensions with no free surfaces (reference A), namely 9.27, and this is related to the fact that the mode is localised. Figure 1 shows a sketch of the gel displacement incurred in this mode. It is worth remarking that at the stationary condition the value of the wave vector corresponding to the imaginary part of λ is 1.214, only slightly shifted from the value of $k = 1.200$ for the repetitive roller structure found in the infinite case with no free surfaces.

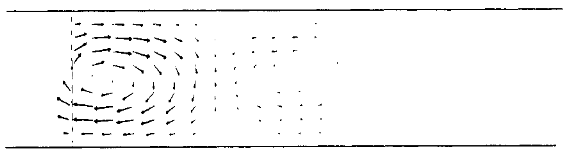

Figure 1. Displacement vectors of the localised mode in a semi-infinite two-dimensional gel. The free surface is represented by a discontinuous straight line, to the right of which extends the gel. On the scale used in the figure, the length of the displacement vectors becomes vanishingly small at depths greater than about twice the width of the cell.

3.2.2. Finite cell. The fundamental mode in a cell of finite length can be seen by continuity from the semi-infinite case. It is convenient to reverse the previous arrangement, and to locate the *fixed* surface at $z = 0$, and the *free* surface at $z = b$. Then the solution $g(z)$ of (29) is a linear combination of four functions

$$u(z) = \exp(\gamma z)\cos(qz) \qquad v(z) = \exp(\gamma z)\sin(qz)$$

$$w(z) = \exp(-\gamma z)\cos(qz) \qquad r(z) = \exp(-\gamma z)\sin(qz)$$

(here the $u(z)$ should not be confused with the displacement vector), where $k = q + \mathrm{i}\gamma$, and

$$k^2 = \pi^2\{\tfrac{1}{2}t - \tfrac{1}{3} + \mathrm{i}[(\tfrac{2}{9} - \tfrac{1}{4}t^2)]^{1/2}\}. \tag{39}$$

Writing, for brevity, $u(b) = u_l$, etc., the boundary conditions give

$$\Delta = \begin{vmatrix} 1 & 0 & 1 & 0 \\ \gamma & q & -\gamma & q \\ u_l'' + \frac{1}{3}\pi^2 u_l & v_l'' + \frac{1}{3}\pi^2 v_l & w_l'' + \frac{1}{3}\pi^2 w_l & r_l'' + \frac{1}{3}\pi^2 r_l \\ u_l''' + E^* u_l' & v_l''' + E^* v_l' & w_l''' + E^* w_l' & r_l''' + E^* r_l' \end{vmatrix} = 0 \tag{40}$$

where Δ is a function of E for a given b, since γ, q, u_l, u_l' etc., can be expressed as a function of E. Thus the required eigenvalues of E are obtained from the zero values of the determinant Δ. In order for k in (39) to be complex, t^2 must be smaller than 8/9, i.e. E must lie below the baseline value of the infinite cell with no free surfaces, E_{lim}. It can be shown that this condition holds for $b > 1.86$. Table 1 shows the value of E of the fundamental mode for various values of b. Modes lying higher than E_{lim} can be handled be defining a single new function $u(z)$

$$u(z) = (1/k_+) \sin k_+ z - (1/k_-) \sin k_- z \tag{41}$$

and

$$g(z) = u(z) + \alpha u'(z). \tag{42}$$

Table 1. Calculated values of the minimum energy parameter $E(2\text{D})$ of the fundamental quasi-longitudinal mode for a gel contained in a rigid cell of dimensions $2 \times 2 \times b$ units with fixed boundary conditions, and a free surface at b. To obtain the three-dimensional values $E(3\text{D})$ corresponding to these results, the required operation is $E(3\text{D}) = E(2\text{D}) + \pi^2/4$.

b	E
1.9	9.248
2.0	9.160
2.5	8.972
3.0	8.950
4.0	8.927
6.0	8.900
10.0	8.8971
∞	8.8970

Condition (42) automatically takes account of the rigid boundary conditions at $z = 0$. The free surface conditions (30) and (31) lead to the relation

$$AD - BC = 0 \tag{43}$$

where

$$A = u_l'' + \tfrac{1}{3}\pi^2 u_l, \qquad B = u_l''' + \tfrac{1}{3}\pi^2 u_l',$$
$$C = u_l''' + E^* u_l', \qquad D = u_l'''' + E^* u_l''. \tag{44}$$

If $E > \pi^2$, one of the values of k becomes purely imaginary, and in order to keep all the quantities real, we set

$$k_-^2/\pi^2 = (\tfrac{1}{4}t^2 - \tfrac{2}{9})^{1/2} - (\tfrac{1}{2}t - \tfrac{1}{3}),$$

while

$$k_+^2/\pi^2 = (\tfrac{1}{4}t^2 - \tfrac{2}{9})^{1/2} + (\tfrac{1}{2}t - \tfrac{1}{3}).$$

Thus (41) becomes

$$u(z)=(1/k_+)\sin(k_+z)-(1/k_-)\sinh(k_-z). \tag{45}$$

In figure 2 are shown the displacement vectors characteristic of the first seven quasi-longitudinal modes for the specific case $b=6$ (i.e. the ratio length/width of the cell equal to 3). Clearly for the fundamental mode (QL 0), most of the displacement is confined near the surface; this contrasts with the next two excited modes QL 1 and QL 2, in which the displacement at the surface is small. To obtain the values of E corresponding to the three-dimensional rectangular cell, as indicated in (17) the constant $\pi^2/4$ must be added to the values of E(2D) quoted in the figure.

3.3. *Quasi-transverse modes*

For the quasi-transverse modes we select a trial function which approximates the motion to a movement parallel to the xy plane:

$$u_x=u_x(x,y)g(z), \qquad u_y=u_y(x,y)g(z), \qquad u_z=0. \tag{46}$$

We calculate the quantities J and I so as to take account of the free surface contribution at $z=b$. As in the last section, the fixed end is located at $z=0$. One gets

$$\begin{aligned} J&=J(\mathrm{2D})\int_0^b g(z)^2\,\mathrm{d}z \\ I&=I(\mathrm{2D})\int_0^b g(z)^2\,\mathrm{d}z+J(\mathrm{2D})\int_0^b g'(z)^2\,\mathrm{d}z. \end{aligned} \tag{47}$$

Now the solution to the two-dimensional problem of the square was obtained in reference A: the eigenvalue found for E in this case was $E_0=13.087$. Thus we may set

$$J(\mathrm{2D})=1$$

with

$$I(\mathrm{2D})=E_0\,(=13.087).$$

This gives from (47)

$$\delta J=2\int_0^b g\delta g\,\mathrm{d}z$$

and

$$\begin{aligned} \delta I&=E_0\delta J+2\int_0^b g'\delta g'\,\mathrm{d}z \\ &=E_0\delta J+2g'(b)\delta g(b)-2\int_0^b g''\delta g\,\mathrm{d}z. \end{aligned}$$

In order for I to be an extremum for any δg,

$$g'(b)=0, \tag{48}$$

and hence

$$g''+(E-E_0)g=0. \tag{49}$$

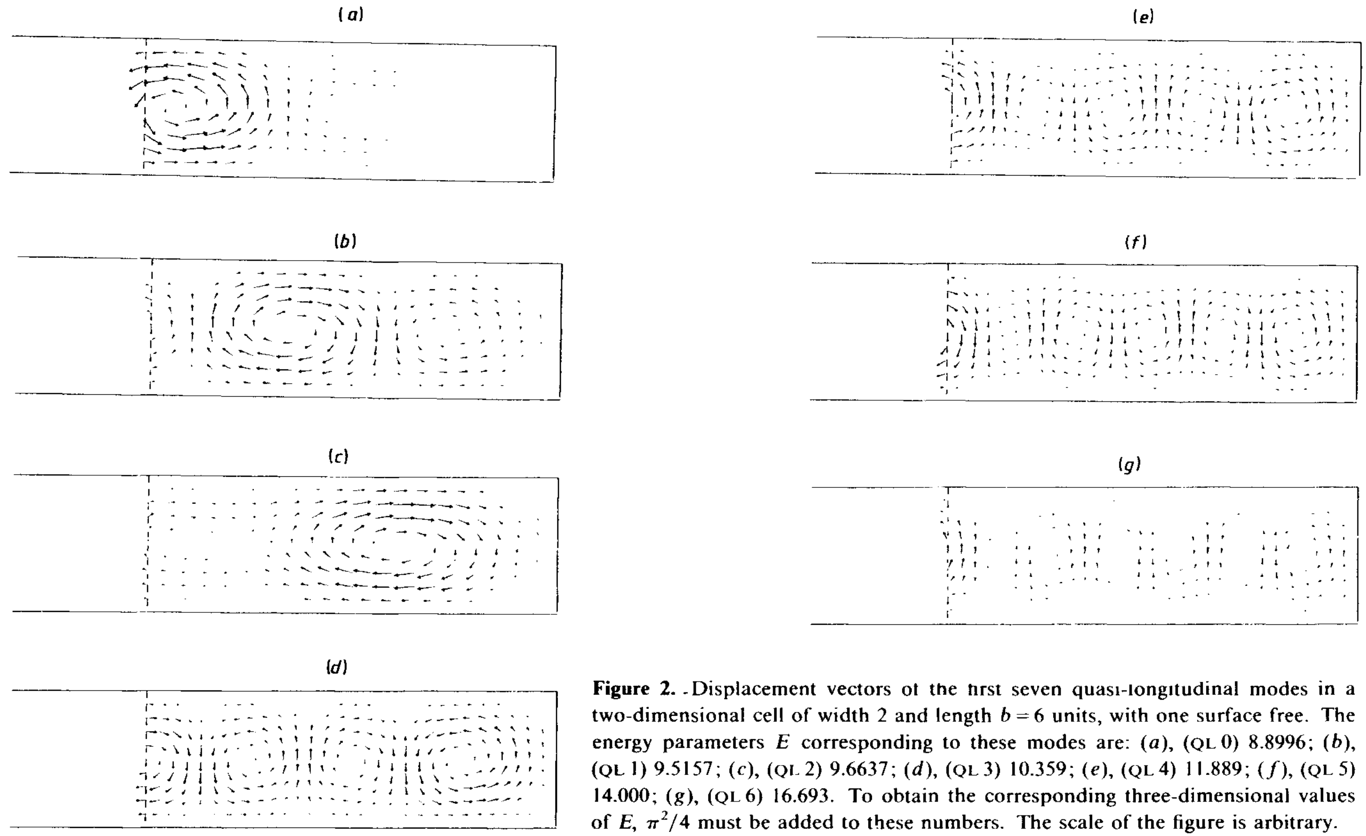

Figure 2. Displacement vectors of the first seven quasi-longitudinal modes in a two-dimensional cell of width 2 and length $b = 6$ units, with one surface free. The energy parameters E corresponding to these modes are: (*a*), (QL 0) 8.8996; (*b*), (QL 1) 9.5157; (*c*), (QL 2) 9.6637; (*d*), (QL 3) 10.359; (*e*), (QL 4) 11.889; (*f*), (QL 5) 14.000; (*g*), (QL 6) 16.693. To obtain the corresponding three-dimensional values of E, $\pi^2/4$ must be added to these numbers. The scale of the figure is arbitrary.

The boundary condition (48) ensures that the solutions correspond to even modes in an analogous cell of length $2b$ which is closed at both ends. (This is a result of the approximation adopted here that $u_z = 0$.) It follows from (48) and (49) that

$$g(z) = \cos[(n+\tfrac{1}{2})(\pi z/b)],$$

and hence

$$E = E_0 + (n+\tfrac{1}{2})^2(\pi^2/b^2). \tag{50}$$

4. Viscosity effects

The effects of viscosity in an oscillating gel have been considered by Nossal (1979), and it is not necessary to reproduce his results here. On the simplest assumption, that of a Newtonian polymer–polymer viscosity described by the single parameter η, the angular frequencies of the resonances ω can be shown to be shifted to lower values ω'

$$\omega' = c_{tr}E^{1/2}[1-(\eta^2/4G^2)c_{tr}^2E]^{1/2} \tag{51}$$

where c_{tr} is the transverse velocity of sound.

The characteristic width of these resonances is given by

$$\gamma = (\eta/2G)c_{tr}^2E. \tag{52}$$

The measurements reported in the following section of this paper show resonances with quite high quality factors ($Q \geqslant 20$), and therefore the frequency shifts are expected to be, at most, of the order of a few tenths of a percent.

5. Experimental observations

In reference A, experimental evidence was shown of the quasi-transverse mode in a gel contained in a transparent cell of square cross-section. No comparison was made, however, with the frequencies of other modes in the system. Nossal and Jolly (1982), on the other hand, were able to compare the frequency of the quasi-transverse mode in a rectangular cell with that of a simple torsional mode for a gel of similar composition in a cylindrical cell. For the cell geometry used by these authors, the observed ratio of these two frequencies was 1.21; the calculated ratio, using (51) above, is 1.226.

The present experimental investigation is intended to examine the relationship between the quasi-transverse and the quasi-longitudinal oscillations in a rectangular sample with an open end. The dimensions of the sample ($1 \times 1 \times 3$ cm^3) were such that, in the nomenclature of § 3.2.2 above, the effective half-length of the cell (6 units—recalling that the surface is free) was greater than 1.86 units, and therefore the fundamental quasi-longitudinal mode corresponds to a localised mode with a value of E lying below that of an infinitely long sample with both ends closed.

The experimental arrangement is shown in figure 3. The glass cell containing the gel is fixed either horizontally or vertically on a wheel the vertical axle of which is the rotor of a small (2 W) DC electric motor. The motor was powered by a programmable low-frequency signal generator (ENERTEC), and the frequency output of the generator monitored with a frequency counter. When the cell is in the horizontal position, a small (1 mm $\times$ 0.5 mm) mirror, consisting of a fragment of gold plated microscope cover

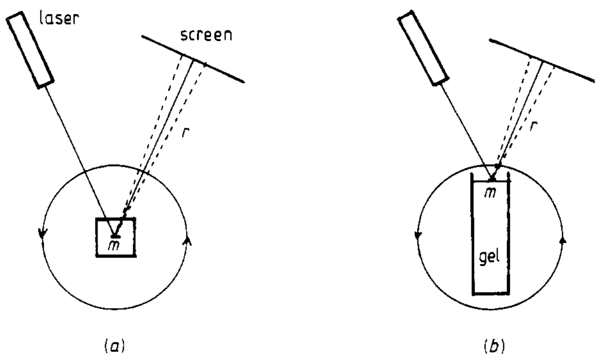

Figure 3. Experimental arrangement. The laser beam is reflected from a small mirror (m), placed on or in the surface of the gel, onto a screen at a distance r from the sample. The rectangular glass cell is mounted rigidly on a wheel either vertically (a) or horizontally (b), and the wheel is oscillated about its axis by the DC motor, thereby exciting quasi-transverse (a) or quasi-longitudinal (b) modes in the gel. The horizontal plane lies in the plane of the paper.

slide, was placed flat on the surface of the gel, oriented so that the long axis was vertical. Illumination of the mirror with a low-power helium–neon laser caused a bright spot to be reflected on a suitable screen. When the driving frequency supplied to the motor coincided with a resonance, the spot broadened out into a line whose length was measured with a tape rule.

For the quasi-transverse modes, the cell was fixed vertically with its z-axis coincident with the axle of the motor. The small mirror was inserted vertically into the material of the gel. This insertion cuts the surface of the gel, but the small size of the mirror reduces the extent of the damage. As the polyacrylamide gels used in these experiments have adhesive surfaces, not only do they stick to the glass cell, but also to the mirror, and also small cuts tend to heal; this further reduces the perturbation introduced by the mirror.

The gels used in this investigation were prepared using a ratio of acrylamide to bisacrylamide of 37.5 by weight, using a procedure which has been described previously (Hecht and Geissler 1978). Observation on gels with an acrylamide concentration of 3% gave spectra with poorly resolved resonances, presumably due to dissipative processes in the gel. To circumvent this difficulty, 5% gels were used. Even though the precursor fluid in the optical cells was capped with a thin (~3 mm) layer of water in order to limit contact with the air during gelation and to obtain a flat surface, perfectly flat upper surfaces were not obtained. It was also obvious to the naked eye from the refractive index gradient that polymerisation within the first millimetre below the top surface was inhomogeneous. Although in principle this inhomogeneous region could be sliced off, the consistency of the gels is such that the resulting surface deviates grossly from flatness, thus leading to spurious resonances at frequencies below the fundamental QL mode. It was found that such spurious resonances could be greatly reduced by carefully removing the gel from the cell using a hypodermic syringe, and then reinserting it upside down, so that the flat surface moulded by the cell bottom now becomes the free surface. After a few minutes the gel readheres to the glass surface, and resonances again become visible. In figure 4 it can be seen that the spurious resonances (below 160 Hz) have been reduced to an unresolved shoulder.

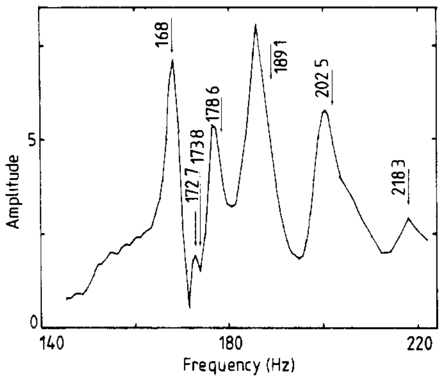

Figure 4. Spectrum of the quasi-longitudinal modes excited in a $1 \times 1 \times 3\ \mathrm{cm}^3$ gel having a free surface. The observed fundamental frequency occurs at 168.2 Hz (QL 0). The arrows indicate the expected frequencies of the modes QL 1 to QL 6, on the assumption that the gel is held rigidly at all the boundaries below the free surface.

Before discussing the results, two further points should be raised. Firstly, the presence of the mirror must obviously perturb the results. To calculate this effect approximately, we assume that a thin mirror of density $\sigma\ \mathrm{g\,cm^{-2}}$ and breadth a is embedded in an infinite medium of zero density and of shear modulus G. It is easy to show that the fundamental frequency of this oscillating system is roughly $(6\pi G/\sigma a)^{1/2}$. The ratio of this frequency to the characteristic fundamental frequency calculated above for the unperturbed system is therefore approximately $(3\pi\rho/2E\sigma a)^{1/2}$, where ρ is the density of the gel ($\sim 1\ \mathrm{g\,cm^{-3}}$), and σ is measured to be $0.036\ \mathrm{g\,cm^{-2}}$. For a mirror of width $a = 0.05$ cm, it can be seen that the perturbing frequency is some 14 times higher than the fundamental QT mode investigated in this paper, and therefore may be neglected. A similar argument shows that the depression in the fundamental frequency caused by the presence of the mirror is also extremely small.

A second point of interest concerns the excitation and detection system used here. Like the pioneering arrangement of Brenner *et al* (1978), the excitation system does not generate harmonics of the driving frequency, unless of course it is overdriven, which is not the case here. In contrast, however, Nossal's detection system analyses the characteristic frequencies of a diffraction fringe produced by a bright spot in the sample: if the maximum brightness of the fringe is located close to the detector, then a strong contribution from harmonics will be detected. The present arrangement, although somewhat tedious, is not susceptible to harmonics, since the whole of the trajectory of the bright fringe is followed. The absence of harmonics makes the interpretation of the spectra simpler. Another important advantage of the present system is that not only the magnitude but also the direction of the displacement vector is displayed on the screen; this provides a check on whether the displacement is parallel to the excitation.

6. Results and discussion

In figure 4 is shown the spectrum of the quasi-longitudinal mode in a 5% polyacrylamide gel with the fundamental mode QL 0 at 168 Hz. The programmable generator gives frequencies with a precision of 0.2 Hz up to 200 Hz, but the measurements shown are represented in steps of 0.8 Hz. Above 200 Hz, the minimum step length was 2 Hz.

The expected frequencies of QL 1–6 are shown with arrows, on the basis of the QL 0 assignment. The minimum occurring at 171.8 Hz does not in fact correspond to a linear motion of the reflection spot, but to a small ellipse, suggesting a combination of two weak close-lying resonances; two possible close-lying resonances are QL 1 and 2, whose spatial distribution (figure 2) would be favourable to such a combination. If this interpretation is correct, the poorly resolved weak resonance observed at 172.6 Hz can be identified with QL 2, and QL 1 would be hidden in the unresolved shoulder at about 171.5 Hz. The shift to lower frequencies may be explained by imperfect contact of the rougher gel surface at the lower end of the cell; the observed weakness of these two resonances is in qualitative agreement with the amplitude of the function $g(z)$ at the free surface (figure 2).

The remaining four resonances are relatively strong, and also show a small shortfall in comparison with the calculated frequencies (table 2).

Table 2. Quasi-longitudinal waves in a finite gel: comparison between theory and experiment.

Mode	Calculated (Hz)	Observed frequency (Hz)	
		Sample 1	Sample 2
QL 0	(basis for calculation)	168.2	168.2
QL 1	172.7	not resolved	—
QL 2	173.8	? 172.6	—
QL 3	178.6	176.6	—
QL 4	189.1	185.8	185
QL 5	202.5	200.0	198
QL 6	218.3	218 ± 1	—

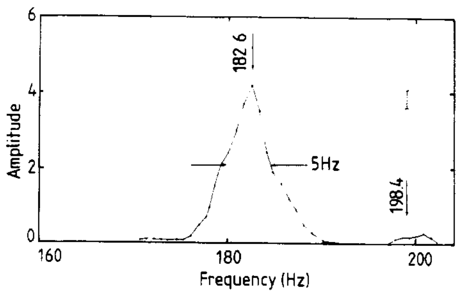

Figure 5. Spectrum (in arbitrary units) of the quasi-transverse modes excited in the same gel as in figure 4. The vertical arrows indicate the expected positions of the modes QT 0 and QT 1 on the basis of the identification of the resonance occurring at 168.2 Hz in figure 4 with the QL 0 mode. The experimental uncertainty in the amplitude measurement is estimated to be about one quarter of the width of the principal diffraction fringe generated by the mirror: the width of this fringe for this experiment is shown in the upper right part of the figure.

In figure 5 is shown the spectrum of the quasi-transverse modes, obtained with the cell fixed vertically on the mounting. No measurable response was observed anywhere below 170 Hz, and consequently only the corresponding part of the spectrum is shown here. The main resonance occurs at 182.5 Hz, with a quality factor of about 35, while a broad secondary resonance is just visible between 196 and 204 Hz. Using as basis frequency the QL mode at 168.2 Hz, the following correspondence can be calculated.

Mode	Theoretical value (eq. (50)), based on QL 0 = 168.2 Hz	Observed value (Hz)
QT 0	182.6	182.5
QT 1	198.4	197–202

The gels were finally extracted from the cell and their shear modulus measured directly as described by Geissler and Hecht (1980). This gave

	Sample 1	Sample 2
G (dyn cm^{-2})	$(2.68 \pm 0.3) \times 10^4$	$(2.90 \pm 0.4) \times 10^4$
Density (g cm^{-3})	1.019	
Estimated QT 0 from G and eq. (50) (Hz)	188 ± 10	196 ± 14
Observed QT 0 (Hz)	182.5	183.4

As these samples were prepared under identical conditions, the two results for G give a measure of the error involved in the direct method, which is clearly greater than the error in the frequency measurement.

A final remark concerns the theoretical analysis developed above, in which the effects of surface tension were explicitly excluded. This exclusion requires justification. It can be seen that for a localised mode of wave number k, the energy of the displacement associated with the surface tension is roughly A/k^2, where A is the coefficient of surface tension. The contribution to the energy coming from the shear elastic modulus G of the bulk medium is, in the same approximation, G/k^3. The ratio of these contributions Ak/G, is very small for the gels investigated here ($A \sim 80$ dyn cm^{-1}, $G \sim 2.5 \times 10^4$ dyn cm^{-2}, $k \sim 1$ cm^{-1}), and consequently the effects of surface tension may be neglected.

We conclude that the experimental results are in good agreement with the frequencies predicted by the variational analysis proposed here. The disparities between the calculated and the observed frequencies of the higher excited modes are very small, and can be explained either by slight departures from the fixed boundary conditions at the lower end of the gel, or by the inadequacy of the trial functions used in the calculation. The agreement between the theoretical ratio of the QT 0 to the QL 0 mode and the observed ratio is excellent. Finally, our measurements confirm the theoretical prediction of the novel localised mode described in this paper.

Appendix

This appendix sets forth the method whereby the three-dimensional quasi-longitudinal case may be reduced to a two-dimensional problem. We specify an approximate form for the displacement vector which is consistent both with the boundary conditions and with the observed nature of the vibrations. We are here interested in the movement generated by a rotational excitation about the y-axis (i.e. perpendicular to the $C_4(z)$ axis of the cell); this mode is called quasi-longitudinal, since it involves motion along the length of the cell. This approximation, which neglects the small component u_y in $\boldsymbol{u}$, must satisfy the rigid boundary condition at $y = \pm 1$, and is written in the form of the vector potential

$$A_x = 0, \qquad A_y = -\phi(x, z) \cos \tfrac{1}{2}\pi y, \qquad A_z = 0, \tag{A1}$$

which yields

$$u_x = u_x(x, z) \cos \tfrac{1}{2}\pi y, \qquad u_y = 0, \qquad u_z = u_z(x, z) \cos \tfrac{1}{2}\pi y. \tag{A2}$$

In (A2), $u_x(x, z)$ and $u_z(x, z)$ represent the solutions to the two-dimensional case. One thus obtains for the volume integral

$$\begin{aligned} J &= J(\text{2D}) \\ I_V &= I_V(\text{2D}) + \int\int \left[\left(\frac{\partial u_x}{\partial y}\right)^2 + \left(\frac{\partial u_z}{\partial y}\right)^2 \right] \mathrm{d}x\, \mathrm{d}y \\ &= I_V(\text{2D}) + \frac{\pi^2}{4} J(\text{2D}), \end{aligned} \tag{A3}$$

where

$$I_V(\text{2D}) = \int\int \sum (\partial u_i / \partial x_j)^2 \, \mathrm{d}z\, \mathrm{d}x, \qquad \text{with } i, j = x \text{ or } z.$$

To obtain I_S, we insert $n = (0, 0, -1)$ into (14), giving at $z = 0$

$$\begin{aligned} I_S &= -\int\int \mathrm{d}x\, \mathrm{d}y \left(u_x \frac{\partial u_z}{\partial x} + u_z \frac{\partial u_z}{\partial z} \right)_{3\text{D}} \\ &= -\int_{-1}^{+1} \mathrm{d}x \left(u_x \frac{\partial u_z}{\partial x} + u_z \frac{\partial u_z}{\partial z} \right)_{2\text{D}}. \end{aligned}$$

Integration by parts gives

$$\int_{-1}^{+1} u_x \frac{\partial u_z}{\partial x} \mathrm{d}x = -\int_{-1}^{+1} u_z \frac{\partial u_x}{\partial x} \mathrm{d}x,$$

and the incompressibility condition, together with relation (A2) gives

$$\partial u_z / \partial z = -\partial u_x / \partial x.$$

Hence,

$$\begin{aligned} I_S &= 2 \int_{-1}^{+1} u_z \frac{\partial u_x}{\partial x} \mathrm{d}x \\ &= I_S(\text{2D}). \end{aligned} \tag{A4}$$

Thus the problem reduces to the two-dimensional one of a rectangle with a free end at $z=0$, with the following definitions

$$J=\int\int \boldsymbol{u}^2\,\mathrm{d}x\,\mathrm{d}z$$
$$I=\int\int \sum_{ij}\left(\frac{\partial u_i}{\partial x_j}\right)^2 \mathrm{d}x\,\mathrm{d}z+2\int_{-1}^{+1} u_z\frac{\partial u_x}{\partial x}\,\mathrm{d}x \tag{A5}$$

calculated at $z=0$. It follows from (A3), (A4) and (A5) that

$$E(3\mathrm{D})=E(2\mathrm{D})+\tfrac{1}{4}\pi^2.$$

It should be recalled that the choice of the approximate function (A1) limits us to the quasi-longitudinal modes.

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