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The interpretation of hypersonic and ultrasonic 'velocities' in fluids

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Abstract. It is suggested that the conventional view of Brillouin light scattering and ultrasonic excitation in fluids in terms of phonon phase velocity and attenuation can be misleading and leads to spurious anomalies. A simple comparison is made of the two types of experiments from a fundamental point of view. The analysis of an ultrasonic experiment from first principles is given and is illustrated by an explicit example, the classical hydrodynamic fluid. It is pointed out that an important parameter is usually overlooked in the conventional ultrasonic experiment.

1. Introduction

Comparatively recent developments in light scattering techniques have led to a detailed study of the Brillouin lines in the spectrum of the light scattered from a fluid. It is usual and convenient to express such results in terms of a 'hypersonic' velocity and attenuation and to compare them with the velocity and attenuation of sound waves induced in the fluid in a 'supersonic' experiment (eg Fabelinskii 1968). This procedure has given rise to some apparent anomalies which, in our opinion, are quite spurious. Although, on the whole, the anomalies are now understood, there still seems to us to be room for a comparatively elementary discussion of this matter, which brings out the physical principles from the rather involved mathematical analyses available in the literature. It is felt that such a treatment may be helpful in promoting an appreciation of the difference between the two experiments which will lead to a proper understanding of these methods of studying the properties of a fluid.

In our analysis we shall include, in particular, a discussion of the supposed difference in the dispersion behaviour of the velocity of 'thermal' phonons and 'ultrasonic' phonons. This was exposed recently by Mountain (1966a) although, as he points out, the 'problem' was recognized considerably earlier (Markham *et al* 1951). Although this, in our opinion, is a non-problem, it excited considerable interest and controversy at the time (eg Selwyn and Oppenheim 1971), and indeed still does (numerous private communications). It is an interesting illustration of the great care and subtlety required in the comparison of experimental results in two different fields. Brillouin scattering is not ultrasonics at hypersonic frequencies and vice versa.

We shall also give a fundamental analysis of the ultrasonic experiment in rather simple terms which we hope may lead to an improved understanding and appreciation of the power and the limitations of this technique.

We now give a simple example of the dependence of a quantity on the way it is measured. If we have an isotropic continuous medium with a damping proportional to

velocity, we have the equation of motion for the elastic displacement, ξ (in one dimension), as follows,

$$\frac{\partial^2\xi}{\partial t^2}+\delta\frac{\partial\xi}{\partial t}-v^2\frac{\partial^2\xi}{\partial x^2}=0, \tag{1.1}$$

where v = (a modulus/a density)$^{1/2}$ and δ is a damping constant.

We obtain a dispersion relation by requiring that $\xi \propto \exp \mathrm{i}(\omega t+kx)$ so that

$$\omega^2-\mathrm{i}\delta\omega-v^2k^2=0. \tag{1.2}$$

For a steady wave in space we make k real so that ω must be complex and the wave decays in time, ie

$$\xi \propto \exp(-\tfrac{1}{2}\delta t)\cos k[x+v(1-\delta^2/4v^2k^2)^{1/2}t]. \tag{1.3}$$

For a steady wave in time we make ω real so that k must be complex and the wave decays in space and we get the quite different expression,

$$\xi \propto \exp\left(-\frac{x\omega}{v}(1+\delta^2/\omega^2)^{1/4}\sin(\tfrac{1}{2}\tan^{-1}\delta/\omega)\right)$$

$$\times\cos\omega\left(t+\frac{x}{v}(1+\delta^2/\omega^2)^{1/4}\cos(\tfrac{1}{2}\tan^{-1}\delta/\omega)\right). \tag{1.4}$$

Although a phase velocity cannot be directly measured it is convenient to define one. In the first case it seems natural to say,

$${}_tv_\mathrm{p}\equiv(\mathrm{Re}\,\omega)/k=v(1-\delta^2/4v^2k^2)^{1/2}, \tag{1.5}$$

which is directly obtained from (1.2).

In the second case one can also define a phase velocity,

$${}_xv_\mathrm{p}\equiv\omega/(\mathrm{Re}\,k)=v(1+\delta^2/\omega^2)^{-1/4}\sec(\tfrac{1}{2}\tan^{-1}\delta/\omega), \tag{1.6}$$

which is also obtained from (1.2). The two phase velocities are different because they are defined differently and no velocity is actually measured anyway. Indeed, we are in a grave difficulty in comparing the two velocities at all! If we are to compare the two expressions, what are we to use for k in the right-hand side of (1.5) and *at the same time* for ω in the right-hand side of (1.6)? The difficulty may perhaps be illustrated by considering the expansions of (1.5) and (1.6) for δ small which are,

$$\frac{{}_tv_\mathrm{p}}{v}=1-\frac{\delta^2}{8v^2k^2}-\frac{1}{2}\left(\frac{\delta^2}{8v^2k^2}\right)^2+\ldots \tag{1.5'}$$

and

$$\frac{{}_xv_\mathrm{p}}{v}=1-\frac{\delta^2}{8\omega^2}+\frac{7}{2}\left(\frac{\delta^2}{8\omega^2}\right)^2+\ldots. \tag{1.6'}$$

This is an interesting (and rather unusual) example in which there is a strong temptation to compare ${}_tv_\mathrm{p}$ and ${}_xv_\mathrm{p}$ by putting $vk=\omega$ in (1.5'), or $\omega=vk$ in (1.6') and assert that,

to order δ^2, ${}_tv_p$ and ${}_xv_p$ are the same. We consider this to be quite unjustified since we only have $\omega = kv$, from equation (1.2) when $\delta = 0$. If $\delta \neq 0$ the relation between ω and k is complex and a comparison of (1.5) and (1.6) becomes meaningless. The answer to this problem is that, in either case, the velocity and decay factor of the appropriate wave must be used to determine the properties of the material. In this particular case v and δ are the said properties of the material. Then no problem arises.

In some cases the difference between the two velocities can be very substantial (Mountain and Litovitz 1967, Gewurtz *et al* 1971). Then a comparison of the two methods can be very helpful in elucidating the properties of the material and/or determining whether the behaviour has been properly described, eg by an equation such as (1.1).

The first case, (1.3), corresponds to a light scattering experiment because this is a diffraction process for which a real spacial wave must exist to give finite scattering intensity, ie k, or the scattering vector $\boldsymbol{Q}$ (see § 2), must be real. The amplitude of this wave varies with time because it is a component of a thermal fluctuation. This of course gives rise to the term thermal phonon. Since the wave has a limited lifetime its frequency is ill defined (the bandwidth theorem) which in the treatment above corresponds to a complex value for ω.

The second case, (1.4), corresponds to the usual ultrasonic experiment in which a transducer is continuously excited at a fixed frequency so that ω is real and precisely defined. However, owing to the decay processes, the wave is limited in space so that k is ill defined (the spacial analogue of the bandwidth theorem) and in the above treatment k is complex.

There is no reason in general why a standing wave of fixed k should not contain many frequencies and these are not necessarily distinct oscillations. In that case the definition of a phase velocity as in (1.5) fails, and the artificiality of the concept of a thermal phonon becomes apparent. One cannot then speak of a velocity and it has, wisely in our opinion, become usual in the light scattering experiment to consider the spectrum itself as being the experimental result from which the parameters of the scatterer are to be derived.

The same problem has not arisen in quite the same way in the ultrasonic experiment because the experiment tends not to be done if a reasonably well defined wave is not produced. One says that the system cannot sustain a propagating wave and one is no longer concerned with ultrasonics. We know that very interesting results in the light scattering experiment are still obtained even when the corresponding thermal phonons are ill defined. This suggests that ultrasonic type experiments should still be pursued and should give useful results even when a clearly propagated wave is not present.

In some ultrasonic experiments a pulsed disturbance is used and the velocity and attenuation of the propagated pulse is measured. This at least gives an actual measured velocity. But if it is to be compared with other 'velocities' then an extremely careful analysis is required and any detailed comparison will immediately reveal the well known inadequacy (eg Brillouin 1960) of the usual definition, of the group velocity, $v_g \equiv d\omega/dk$, when a dispersion relation such as (1.2) is involved.

The scattering experiment can be expressed in terms of a fundamental description of the properties of the fluid. The ultrasonic experiment ought also to be described in as similar and as fundamental a way as possible. This has been done implicitly for instance by Griffin (1968), but the essential similarity seems to us to have been obscured by mathematical complexity and, to our knowledge, no actual experimental arrangement in ultrasonics has been analysed by this method. In the next section we show how simple this connection is and illustrate it by means of an example in § 3.

2. Theoretical analysis

2.1. Introduction

The theoretical analysis of the light scattering experiment is very complex in the general case (Fabelinskii 1968, Selwyn and Oppenheim 1971, Griffin 1968). We shall consider the special case where the electric dipole induced by the field of the incident light is simply proportional to the local fluctuation in density of the scattering medium. This restricts us to the consideration of fully polarized scattered light. The fluctuations in (number) density are described by the density–density correlation function of Van Hove (1954):

$$G(\boldsymbol{r}, \tau) = \langle \rho \rangle^{-1} \langle \rho(\boldsymbol{r}+\boldsymbol{r}', t+\tau)\rho(\boldsymbol{r}', t) \rangle. \tag{2.1}$$

In order for light to be scattered with change of momentum $\hbar\boldsymbol{Q}$ and change in energy $\hbar\omega$ we have to select the appropriate Fourier component of $G(\boldsymbol{r}, \tau)$ which we write as

$$S(Q, \omega) = \frac{1}{2\pi} \int G(\boldsymbol{r}, \tau) \exp \mathrm{i}(\boldsymbol{Q} \cdot \boldsymbol{r} + \omega\tau)\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\tau. \tag{2.2}$$

$S(Q, \omega)$, in this case, describes the light scattering experiment, or for that matter a neutron scattering experiment. In the light scattering experiment Q is small ($\sim 2 \times 10^{-3}$ Å^{-1}) and then $S(Q, \omega)$ usually consists, for given Q, predominantly of two almost symmetrically placed Brillouin (1922) lines and a central Rayleigh line (Landau and Placzek 1934) as for instance in equation (3.12) below. The Brillouin lines are associated with propagated density fluctuations and the frequency at the peak, $\pm\omega_B$, is often taken to be Qv_B where v_B is called the velocity of hypersonic (since $\omega_B/2\pi \sim 10$ GHz) thermal phonons. This matter enjoys an extensive literature, and so will not be discussed further.

If one forces an oscillatory density variation one might expect that if a particular 'wave' is already strongly (or weakly) present in the spontaneous thermal fluctuations, ie in $S(Q, \omega)$, it will be correspondingly easy (or difficult) to excite that wave. Indeed this idea is the physical basis of the fluctuation–dissipation theorem (Callen and Welton 1951). We may expect therefore that there is a characteristic function for the ultrasonic experiment which is simply related to $S(Q, \omega)$. That function is the function $D(Q, \omega)$ defined in equation (2.15). The actual response function is given in (2.20). The response itself, here called $\delta\rho_\omega(\boldsymbol{r}, t)$, is given in (2.19); its form depends of course on how the sample is excited. In this sense the ultrasonic experiment is seen to be more complex than the scattering experiment. Indeed, it must always be more complex because the disturbance to the sample is always finite whereas one usually assumes 'linear response' as we do below (equation (2.9)). On the other hand, in the scattering experiment one must also bear in mind that the description of the scattering by the Van Hove function, $S(Q, \omega)$ and its generalizations, is only correct in so far as single scattering occurs. This requirement is comparatively easy to satisfy to a very good approximation in the light scattering experiment, except near a critical point.

2.2. Analysis of an ultrasonic experiment

To describe an ultrasonic experiment we consider the effect of the transducer as equivalent to some oscillating local 'field', $\boldsymbol{F}(\boldsymbol{r}, t)$ that couples to the number density of our

system (in an analogous sense to which electric field couples to charge density), namely,

$$\boldsymbol{F}(\boldsymbol{r}, t) = -\nabla\phi(\boldsymbol{r})\cos(\omega t) \tag{2.3}$$

so that $\phi(\boldsymbol{r})\cos(\omega t)$ is the 'potential' that gives this field. The effect of this external perturbation on the system may be represented by an additional term in the Hamiltonian of the form

$$K(t) = \cos(\omega t)\int \mathrm{d}\boldsymbol{r}\,\phi(\boldsymbol{r})\rho(\boldsymbol{r}). \tag{2.4}$$

If we imagine this perturbation to be switched on at time $t = 0$, when the system is in thermal equilibrium, then at a subsequent time, t, the expectation value of any operator, O, representing an observable†, may be written as

$$\langle O\rangle_t = \sum_m \frac{\mathrm{e}^{-\beta E_m}}{Z}\langle m|U^+(t)OU(t)|m\rangle \tag{2.5}$$

where $Z \equiv \Sigma_m \exp(-\beta E_m)$ and $\beta = 1/k_B T$ and we describe the equilibrium state at $t < 0$ by the canonical (or grand canonical) ensemble with energy eigenstates $|m\rangle$. $U(t)$ is the development operator that obeys the Schrödinger equation (with $\hbar = 1$):

$$\mathrm{i}\frac{\partial}{\partial t}U(t) = (H + K(t))U(t) \tag{2.6}$$

whose solution can easily be verified by differentiation to be

$$U(t) = T\exp\left(-\mathrm{i}\int_0^t [H + K(t_1)]\,\mathrm{d}t_1\right) = \mathrm{e}^{-\mathrm{i}Ht}T\exp\left(-\mathrm{i}\int_0^t \mathrm{d}t_1\,\hat{K}(t_1, t_1)\right) \tag{2.7}$$

where

$$\hat{K}(t_1, t_1) \equiv \mathrm{e}^{\mathrm{i}Ht_1}K(t_1)\,\mathrm{e}^{-\mathrm{i}Ht_1}, \tag{2.8}$$

and T is a time-ordering operator that orders operators of greater time arguments (in the expanded exponential form) to the left. Retaining terms up to linear order in $K(t)$ we find

$$U^+(t)OU(t) = \left(1 + \mathrm{i}\int_0^t \mathrm{d}t_1\,\hat{K}(t_1, t_1)\right)\mathrm{e}^{\mathrm{i}Ht}O\,\mathrm{e}^{-\mathrm{i}Ht}\left(1 - \mathrm{i}\int_0^t \mathrm{d}t_1\,\hat{K}(t_1, t_1)\right)$$

ie to linear order we obtain

$$U^+(t)OU(t) = \hat{O}(t) + \mathrm{i}\int_0^t \mathrm{d}t_1[\hat{K}(t_1, t_1), \hat{O}(t)] \tag{2.9}$$

where,

$$\hat{O}(t) = \mathrm{e}^{\mathrm{i}Ht}O\,\mathrm{e}^{-\mathrm{i}Ht}. \tag{2.10}$$

Inserting (2.9) in (2.5) we obtain the linear response expression originally due to Kubo (1957), namely

$$\langle O\rangle_t = \langle O\rangle + \mathrm{i}\hbar^{-1}\int_0^t \mathrm{d}t_1\,\langle[\hat{K}(t_1, t_1), \hat{O}(t)]\rangle. \tag{2.11}$$

As in (2.1) the angular brackets denote thermal equilibrium averages in the absence of the external perturbation.

† Those not interested in linear response theory may prefer to accept the result given in equation (2.11).

In an ultrasonic experiment one measures the density change due to the transducer† which is much larger than the spontaneous fluctuations (which are 'noise' in this experiment) but small enough for the response to be linear. We have then, $\delta\rho(r, t) = \langle\rho(r)\rangle_t - \langle\rho\rangle$ where $\langle\rho\rangle$ is the mean number density in the absence of the perturbation and $\langle\rho(r)\rangle_t$ is given by the appropriate form of (2.11).

Putting $O \equiv \rho(r)$ in (2.11) with $K(t)$ given by (2.4) we find

$$\delta\rho_\omega(r, t) = i\hbar^{-1} \int_0^t dt_1 \int dr' \cos(\omega t_1)\phi(r')\langle[\rho(r', t_1), \rho(r, t)]\rangle \tag{2.12}$$

$$= \mathrm{Re}\, i\hbar^{-1} \int_0^t dt_1\, e^{i\omega t_1} \int dr'\, \phi(r')\langle[\rho(r', t_1), \rho(r, t)]\rangle. \tag{2.13}$$

(2.13) follows from (2.12) since the expectation value of the commutator of two Hermitian operators is purely imaginary (Landau and Lifshitz 1965).

From space and time translational invariance in the fluid we have that

$$\langle[\rho(r', t_1), \rho(r, t)]\rangle$$

can depend only on $(r-r')$ and $(t-t_1)$ so that we may write it as follows:

$$\langle[\rho(r', t_1), \rho(r, t)]\rangle = \langle\rho\rangle(2\pi)^{-3} \int dQ \int d\omega'\, D(Q, \omega') \exp[-i\omega'(t_1 - t) + iQ \cdot (r' - r)]. \tag{2.14}$$

From isotropicity of the fluid, the function $D(Q, \omega)$ can depend only on $Q(=|Q|)$ and moreover is *odd* in its frequency argument as it is the transform of an imaginary function. As anticipated in § 2.1, the function $D(Q, \omega)$ arising in the ultrasonic experiment can be related very simply to $S(Q, \omega)$. $S(Q, \omega)$ and $D(Q, \omega)$ are the space–time Fourier transforms of $\langle\rho(r, \tau)\rho(0, 0)\rangle$ and $\langle[\rho(r, \tau), \rho(0, 0)]\rangle$ respectively. But

$$\langle[\rho(r, \tau), \rho(0, 0)]\rangle = \langle\rho(r, \tau)\rho(0, 0)\rangle - \langle\rho(0, 0)\rho(r, \tau)\rangle = \langle\rho(r, \tau)\rho(0, 0)\rangle - \langle\rho(-r, -\tau)\rho(0, 0)\rangle.$$

Hence

$$D(Q, \omega) = S(Q, \omega) - S(-Q, -\omega).$$

But $S(-Q, -\omega) = S(Q, \omega) \exp -(\hbar\omega/k_B T)$ so that,

$$D(Q, \omega) = S(Q, \omega)[1 - \exp(-\beta'\omega)] \tag{2.15}$$

where $\beta' = \hbar/k_B T$.

The relation is even simpler in the 'classical approximation', $\beta'\omega \ll 1$, since then,

$$D^{cl}(Q, \omega) = \beta'\omega S^{cl}(Q, \omega). \tag{2.15'}$$

Since $S^{cl}(Q, \omega)$ is even in ω, $D^{cl}(Q, \omega)$ is still odd in ω as required. We note then that the wealth of information in the literature about $S(Q, \omega)$ or $S^{cl}(Q, \omega)$ can be carried over directly to $D(Q, \omega)$ or $D^{cl}(Q, \omega)$. The relation between a light scattering experiment and an ultrasonic experiment is succinctly described by equation (2.15).

† The density change, $\delta\rho_\omega(r, t)$, is measured indirectly by observing a response proportional to it, such as the output of a detecting transducer in the liquid or via a change in the refractive index, as in the Debye–Sears method (1932).

However, the description of an *actual* ultrasonic experiment is somewhat more complex. Inserting (2.14) in (2.13) we have,

$$\delta\rho_\omega(\boldsymbol{r},t) = \mathrm{Re}\, i\hbar^{-1}\langle\rho\rangle(2\pi)^{-3}\int_0^t dt_1 \exp(i\omega t_1)\int d\boldsymbol{r}'\,\phi(\boldsymbol{r}')\int d\boldsymbol{Q} \times \int d\omega'\, D(Q,\omega')\exp i[-\omega'(t_1-t)+\boldsymbol{Q}\cdot(\boldsymbol{r}'-\boldsymbol{r})]. \tag{2.16}$$

In the usual ultrasonic experiment one waits for transients to die away. This means we require (2.16) for t sufficiently large. The relevant part of (2.16) is then

$$\lim_{t\,\mathrm{large}}\int_0^t dt_1 \exp(i\omega t_1)\exp -i\omega'(t_1-t)$$

$$= \exp(i\omega t)\lim\int_{-t}^{0} d(t_1-t)\exp[i(\omega-\omega')(t_1-t)]$$

$$= \exp(i\omega t)[i/(\omega'-\omega+i0^+)]. \tag{2.17}$$

Using (2.17) in (2.16) and writing,

$$\phi(\boldsymbol{r}') = (2\pi)^{-3}\int d\boldsymbol{Q}'\,\tilde{\phi}(\boldsymbol{Q}')\exp(i\boldsymbol{Q}'\cdot\boldsymbol{r}'), \tag{2.18}$$

we find

$$\delta\rho_\omega(\boldsymbol{r},t) = -\mathrm{Re}\exp(i\omega t)\hbar^{-1}\langle\rho\rangle(2\pi)^{-3}\int d\boldsymbol{Q}\,\tilde{\phi}(-\boldsymbol{Q})\exp(-i\boldsymbol{Q}\cdot\boldsymbol{r}) \times \int d\omega'\, D(Q,\omega')/(\omega'-\omega+i0^+). \tag{2.19}$$

Hence the ultrasonic experiment is described by the causal response kernel,

$$L(Q,\omega) = -i\pi D(Q,\omega)+\mathrm{Pr}\int d\omega'\, D(Q,\omega')/(\omega'-\omega), \tag{2.20}$$

where Pr means the principal value. It should be noted that, because of (2.19), $\delta\rho_\omega(\boldsymbol{r},t)$ involves a knowledge of $S(Q,\omega)$ for *all* Q and ω.

2.3. The analysis of a particular ultrasonic experiment

We now consider an explicit, although slightly idealized, ultrasonic experiment. We calculate the response of the fluid to excitation by a thin planar transducer. For the transducer face in the y–z plane the driving 'field', equation (2.3) takes the form

$$\boldsymbol{F}(\boldsymbol{r},t) = E\cos(\omega t)\delta(x)\boldsymbol{i}, \qquad \text{ie} \qquad \phi(\boldsymbol{r}) = -E\theta(x) \tag{2.21}$$

where $\theta(x)$ is the unit step function and E is a constant with dimensions of energy.

Hence

$$\tilde{\phi}(-\boldsymbol{Q})/E = \int d\boldsymbol{r}\,\theta(x)\exp(i\boldsymbol{Q}\cdot\boldsymbol{r}) = -i(2\pi)^2 Q_x^{-1}\delta(Q_y)\delta(Q_z). \tag{2.22}$$

(2.22) in (2.19) gives

$$\delta\rho_\omega(x,t) = \mathrm{Re}\, i\exp(i\omega t)E\hbar^{-1}\langle\rho\rangle(2\pi)^{-1}\int_{-\infty}^{\infty}\frac{dQ_x}{Q_x}\int_{-\infty}^{\infty}\frac{d\omega'\, D(Q_x,\omega')}{(\omega'-\omega+i0^+)}\exp(-iQ_x x). \tag{2.23}$$

We note that $\delta\rho_\omega(x, t)$ and $D(Q, \omega)$ do not form a Fourier pair as do $G(\boldsymbol{r}, \tau)$ and $S(Q, \omega)$. $\delta\rho_\omega(x, t)$ contains sufficient information to determine $D(Q, \omega)$ by inversion of (2.23) in principle although this would be difficult in practice. In this sense the ultrasonic experiment is at a disadvantage *vis-à-vis* the scattering experiment. On the other hand, in practice one can never actually get $G(\boldsymbol{r}, \tau)$ by measurement of $S(Q, \omega)$ because $S(Q, \omega)$ cannot be determined over a sufficient range of Q and ω. In both cases one has to revert to models and/or approximations to get $G(\boldsymbol{r}, \tau)$ or $S(Q, \omega)$. The ultrasonic experiment is then seen to involve an additional step, ie from $S(Q, \omega)$ or $D(Q, \omega)$ to $\delta\rho_\omega(\boldsymbol{r}, t)$. It is this additional step which makes the ultrasonic experiment more difficult to interpret in fundamental terms than the scattering experiment.

2.4. The determination of $S(Q, \omega)$ from an ultrasonic experiment

It is of interest to show explicitly how one can obtain $D(Q, \omega)$, or $S(Q, \omega)$, from the measured values of $\delta\rho_\omega(x, t)$. We write $L(Q, \omega)$ of equation (2.20) in the form,

$$L(Q, \omega) = \int_{-\infty}^{\infty} \frac{d\omega' D(Q, \omega')}{(\omega' - \omega + i0^+)} \equiv -iA(Q, \omega) \exp(i\Phi(Q, \omega)). \tag{2.24}$$

where $A(Q, \omega)$ and $\Phi(Q, \omega)$ are real and even in Q. Inserting (2.24) in (2.23) we find

$$\delta\rho_\omega(x, t) = E\hbar^{-1}\langle\rho\rangle(2\pi)^{-1} \int_{-\infty}^{\infty} \frac{dQ_x}{Q_x} A(Q_x, \omega) \cos(\omega t - Q_x x + \Phi(Q_x, \omega)). \tag{2.25}$$

From the experimental result, $\delta\rho_\omega^{exp}(x, t)$, we can evaluate the function

$$\delta\rho_\omega^{exp}(Q_x, t) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} dx\, \delta\rho_\omega^{exp}(x, t) \exp(i Q_x x). \tag{2.26}$$

By comparing the inverse of (2.26) with (2.25) we find,

$$\delta\rho_\omega^{exp}(Q_x, t) = E\hbar^{-1}\langle\rho\rangle(2\pi)^{-1} \frac{i}{Q_x} A(Q_x, \omega) \sin(\omega t + \Phi(Q_x, \omega)). \tag{2.27}$$

Hence $A(Q_x, \omega)$ and $\Phi(Q_x, \omega)$ can be determined from experiment. Then using (2.20) and (2.24) and the fact that $D(Q, \omega)$ is real we have,

$$D(Q, \omega) = \pi^{-1} A(Q, \omega) \cos(\Phi(Q, \omega)). \tag{2.28}$$

This analysis is carried out for a particular case in § 3.2.3.

We can see from (2.19) that in view of the Fourier integral over Q the behaviour of $\delta\rho_\omega(x, t)$ is determined by the complex poles of Q of $D(Q, \omega)$ which are the same as those of $S(Q, \omega)$. This explicitly justifies the use of dispersion relations such as (3.7), with ω real, for predicting the general form of the ultrasonic response.

3. Illustrative examples

3.1. The ideal fluid

We first consider the case where we have a classical hydrodynamic fluid whose viscosities (η_s and η_v) and thermal conductivity (λ) are vanishingly small (equation (3.12) for a and

$b \to 0$) when $S(Q, \omega)$ may be written as

$$S(Q, \omega) = R\delta(\omega) + B(\delta(\omega - C_0 Q) + \delta(\omega + C_0 Q)), \tag{3.1}$$

ie the two Brillouin lines and the Rayleigh line are all delta functions. Since this is a classical result we use (2.15′) to obtain $D^{c1}(Q, \omega)$ and insert it in (2.23) with the result,

$$\delta\rho_\omega(x, t) \propto \cos[\omega(t - x/C_0)]. \tag{3.2}$$

This represents one unattenuated travelling wave with phase velocity C_0 which is the same as the phase velocity derived from the peak of the Brillouin line, ie $v_B = \omega/Q = C_0$. The two experiments give the same result except that the sharp Rayleigh line has no observable effect in the ultrasonic experiment.

3.2. The classical hydrodynamic fluid

3.2.1. The velocity dispersion relations. For a classical fluid the linearized hydrodynamic equations for the fluid velocity, $\boldsymbol{v}$, the deviation ρ_1 from the mean mass density $\rho_0 (= m\langle\rho\rangle)$ and the deviation T_1 from the mean temperature T_0 are as follows (consistent with the special case of § 2 we have put curl $\boldsymbol{v} = 0$) (Mountain 1966a, b):

$$\frac{\partial \rho_1}{\partial t} + \rho_0 \operatorname{div} \boldsymbol{v} = 0 \tag{3.3}$$

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\frac{C_0^2}{\gamma} \operatorname{grad} \rho_1 - \frac{C_0^2 \alpha \rho_0}{\gamma} \operatorname{grad} T_1 + (\tfrac{4}{3}\eta_s + \eta_v) \operatorname{grad} \operatorname{div} \boldsymbol{v} \tag{3.4}$$

$$\rho_0 c_v \frac{\partial T_1}{\partial t} - [c_v(\gamma - 1)/\alpha] \frac{\partial \rho_1}{\partial t} - \lambda \operatorname{div} \operatorname{grad} T_1 = 0 \tag{3.5}$$

where $\gamma = c_p/c_v$, λ is the thermal conductivity, α is the coefficient of volume thermal expansion, $C_0 = (\gamma/\rho_0 \chi_T)^{1/2}$, is a velocity to be identified below and χ_T is the isothermal compressibility of the fluid.

If we demand solutions of the form,

$$\boldsymbol{v} = \boldsymbol{v}_0 \exp[\mathrm{i}(\omega t + \boldsymbol{Q}.\boldsymbol{r})] \tag{3.6}$$

and similarly for ρ_1 and T_1 we obtain the dispersion equation,

$$-\mathrm{i}\omega^3 - \omega^2(a + b)Q^2 + \mathrm{i}\omega(C_0^2 + abQ^2)Q^2 + \frac{C_0^2}{\gamma} aQ^4 = 0 \tag{3.7}$$

where $a \equiv \lambda/\rho_0 c_v$ and $b \equiv (\tfrac{4}{3}\eta_s + \eta_v)/\rho_0$. For the light scattering case, as explained in § 1, we require the solution of (3.7) for Q real. This is extremely complex in general (Mountain 1966b) but if, with Mountain (1966a), we take $a = 0$ (for most fluids $a \ll b$) we find his result,

$$\omega = C_0 Q(1 - b^2 Q^2/4C_0^2)^{1/2} + \tfrac{1}{2}\mathrm{i}bQ^2 \tag{3.8}$$

ie according to the definition (1.5)

$$_t v_p = C_0(1 - b^2 Q^2/4C_0^2)^{1/2} \tag{3.9}$$

$$= C_0(1 - b^2 Q^2/8C_0^2 + \mathrm{O}(Q^4)). \tag{3.9′}$$

(3.9) and (3.9′) are the analogues of (1.5) and (1.5′). Again we find for a 'driven' oscillation (ω real) using (3.7) and $a = 0$ that,

$$Q^2 = \omega^2(C_0^2 - ib\omega)/(C_0^4 + b^2\omega^2) \tag{3.10}$$

and according to the definition (1.6)

$$_xv_p = \frac{\sqrt{2}C_0(1 + b^2\omega^2/C_0^4)^{1/2}}{[1 + (1 + b^2\omega^2/C_0^4)^{1/2}]^{1/2}} \tag{3.11}$$

$$= C_0(1 + \tfrac{3}{8}b^2\omega^2/C_0^4 - \dots). \tag{3.11′}$$

(3.11) and (3.11′) are the analogues of (1.6) and (1.6′). This identifies C_0 as the phase velocity for vanishing Q or ω, as the case may be. We emphasize again that no comparison can be made, strictly speaking, between (3.9) and (3.11) because one is a function of the independent variable Q and the other of the independent variable ω. The comparison is indeed often made however, since when the second term in (3.9′) is small, one is tempted to substitute $Q = \omega/C_0$ and then apparently

$$_tv_p = C_0(1 - \tfrac{1}{8}b^2\omega^2/C_0^4 + \dots). \tag{3.9″}$$

It is then asserted (Mountain 1966a) that $_tv_p$ shows negative dispersion and $_xv_p$ positive dispersion. Those who feel our objection to such comparisons of $_tv_p$ and $_xv_p$ is pedantic should investigate what to do when b is not small, eg for viscous liquids, and even more when a is not small.

3.2.2. The light scattering spectrum and the ultrasonic response. The light scattering spectrum corresponding to equations (3.3) to (3.5) and the equivalent of the dispersion relation (3.7) has been investigated in great detail. We quote here an approximate result, and refer the reader elsewhere for the general case (Mountain 1970). One finds†, for Q small,

$$S^{c1}(Q, \omega)\left(\frac{2\pi m\beta\gamma}{\rho_0\chi_T}\right)$$

$$= (\gamma - 1)2\Gamma_R Q^2/[(\Gamma_R Q^2)^2 + \omega^2] + \Gamma Q^2/[(\Gamma Q^2)^2 + (\omega \pm C_0 Q)^2]$$

$$+ dQ(C_0 Q \pm \omega)/[(\Gamma Q^2)^2 + (\omega \pm C_0 Q)^2], \tag{3.12}$$

where $\pm$ indicates two terms one with each sign. The first term is the Rayleigh line with,

$$\Gamma_R = a/\gamma. \tag{3.13}$$

The next two terms are the Brillouin lines with

$$\Gamma = \frac{1}{2}\left(b + \frac{\gamma - 1}{\gamma}a\right). \tag{3.14}$$

The last two terms are the 'skew' lines with

$$d = \frac{1}{2}\left(b + 3\frac{\gamma - 1}{\gamma}a\right)C_0^{-1}. \tag{3.14′}$$

If we use the peaks of the Brillouin lines to define the hypersonic phase velocity we get $_tv_p = C_0$, ie no dispersion. But we know that there is dispersion, eg as in equation (3.9), which is the exact result for $a = 0$.

† $S(Q, \omega)$ is normalized so that $\int_{-\infty}^{\infty} S(Q, \omega)\,d\omega \to \rho_0\chi_T/m\beta$ as $Q \to 0$.

However, this recipe is artificial since it is only algebra to separate what we have called, for convenience, the Brillouin and skew lines in (3.12). A more realistic procedure is to find ω for the maximum of the non-central lines (the effect of the Rayleigh line may be ignored because usually $\Gamma_R \ll \Gamma$). The peaks are at $\pm\omega_p$ where,

$$ {}_{l}v_p \simeq \frac{\omega_p}{Q} = C_0\left(1-\frac{\Gamma}{dC_0}\{[1+(Qd)^2]^{1/2}-1\}\right) \tag{3.15} $$

$$ = C_0[1-\tfrac{1}{2}\Gamma dQ^2/C_0+O(Q^2)]. \tag{3.15'} $$

If $a = 0$, ie thermal conductivity effects are neglected, then (3.15') gives for ${}_{l}v_p$ the result (3.9'). Hence (3.12) is indeed an approximation for small Q.

We now predict the result of the idealized ultrasonic experiment *for this approximation* by inserting (3.12) for $S(Q, \omega)$ in (2.15') and the result in (2.23). The result is the following, for $x > 0$:

$$ \begin{aligned} \delta\rho_\omega(x,t)[2\gamma/(E\langle\rho\rangle^2\chi_T)] &= (\gamma-1)\exp[-(\omega/2\Gamma_R)^{1/2}x]\cos[\omega t-(\omega/2\Gamma_R)^{1/2}x] \\ &+\tfrac{1}{2}\mathrm{Re}\,\mathrm{i}\exp[\mathrm{i}(\omega t-fgx)]\exp(-fhx)[1-\mathrm{i}fd(g-\mathrm{i}h)][g-(2+h)\mathrm{i}](1+h+\mathrm{i}g)^{-1} \\ &+\tfrac{1}{2}\mathrm{Re}\,\mathrm{i}\exp[\mathrm{i}(\omega t-fgx)]\exp[-f(2+h)x]\{1+\mathrm{i}fd[g-(2+h)\mathrm{i}]\}(g-\mathrm{i}h) \\ &\times(1+h+\mathrm{i}g)^{-1} \end{aligned} \tag{3.16} $$

where

$$ f = C_0/2\Gamma \tag{3.17} $$

$$ g = [(1+16\omega^2\Gamma^2/C_0^4)^{1/2}-1]^{1/2}\,\mathrm{sgn}(\omega)/\sqrt{2} \tag{3.18} $$

$$ = 2\omega\Gamma/C_0^2+\ldots \tag{3.18'} $$

$$ h = [(1+16\omega^2\Gamma^2/C_0^4)^{1/2}+1]^{1/2}/\sqrt{2}-1 \tag{3.19} $$

$$ = 2\omega^2\Gamma^2/C_0^4+\ldots. \tag{3.19'} $$

The first term in (3.16) comes from the Rayleigh term in (3.12) which is physically mainly fluctuation in temperature. If the wavelength of this component of $\delta\rho$ is λ_R its attenuation factor may be written $\exp(-2\pi x/\lambda_R)$. This wave is therefore attenuated severely within a wavelength and is evanescent. It is reminiscent of the electromagnetic wave in a conductor or a cut-off waveguide. Moreover, λ_R is small since usually Γ_R is small and so the wave is unlikely to be observed in most fluids. This is the thermal wave referred to by Landau and Lifshitz (1959) and investigated many years ago by Hertzfeld (1938) and Hertzfeld and Litovitz (1959). It is possible that this 'wave' could be important at low frequencies and in materials with high thermal conductivity.

The last two terms in (3.16) correspond to harmonic waves with the same phase velocity but, in general, very different attenuation factors and amplitudes. The wavelength λ_B of these waves is given by,

$$ \begin{aligned} \lambda_B = 2\pi/fg &= 4\pi\sqrt{2}(\Gamma/C_0)[(1+16\omega^2\Gamma^2/C_0^4)^{1/2}-1]^{-1/2} \\ &= 2\pi C_0/\omega+4\pi\omega\Gamma^2/C_0^3+\ldots \end{aligned} \tag{3.20} $$

ie the ultrasonic phase velocity is

$$ {}_{x}v_p = C_0(1+2\omega^2\Gamma^2/C_0^4+\ldots). \tag{3.21} $$

As expected, this ultrasonic phase velocity shows what some would describe as positive dispersion relative to the hypersonic phase velocity, given in (3.15′):

$$_{x}v_{p} = C_0[1+\tfrac{1}{2}b^2\omega^2/C_0^4+O(\omega^4)], \tag{3.21′}$$

which is almost the same as (3.11′). The difference arises because we have used an approximate $S(Q, \omega)$.

The usual situation is that $h \ll 1$ and so of the last two waves in (3.16), arising from 'Brillouin' and 'skew' lines in $S(Q, \omega)$, the second is more severely attenuated than the first. The first wave (second term in (3.16)) is of the form

$$\exp(-x/l)\cos(\omega t - 2\pi x/\lambda_B) \tag{3.22}$$

where $l/\lambda_B = (2\pi)^{-1}(g/h)$. (3.22) is the analogue of (1.4) for $\delta/\omega \ll 1$. To first order in η and λ we find that,

$$\alpha \equiv \frac{1}{l} = \frac{\omega^2}{\rho_0 C_0^3}[\tfrac{2}{3}\eta+\tfrac{1}{2}(\gamma-1)\lambda/\rho_0 C_p], \tag{3.23}$$

which is the classic expression for ultrasonic attenuation in a classical hydrodynamic fluid (eg Hertzfeld and Litovitz 1959, equation (7-17)).

If we consider a light scattering experiment with Q adjusted to give a Brillouin shift roughly corresponding to the ultrasonic frequency ω then from (3.12) we have $\Delta\omega \simeq \Gamma Q^2$ where $\Delta\omega$ is the width of the Brillouin line. Hence using (3.18′) for g, and (3.19′) for h, we find,

$$l/\lambda_B \simeq (2\pi)^{-1}(\omega/\Delta\omega)+ \ldots . \tag{3.24}$$

Thus, if the light scattering experiment reveals a sharp Brillouin line, the *corresponding* ultrasonic experiment reveals a weakly attenuated wave. For the second wave, the third term in (3.16), we find in the same approximation,

$$l/\lambda_B \simeq (2\pi)^{-1}(\Delta\omega/\omega)+ \ldots \tag{3.24′}$$

which corresponds to severe attenuation when the Brillouin line is narrow. Moreover, the amplitude of the latter wave is smaller than that of the former in the ratio $2\Delta\omega/\omega$, in the same approximation.

However, our result, (3.21), for the ultrasonic phase velocity, does not reproduce the ultrasonic velocity dispersion predicted by Hertzfeld and Litovitz (1959) where, for small attenuation per wavelength it is found that when viscosity dominates ($a \to 0$) the dispersion is positive whereas if thermal conductivity dominates ($b \to 0$), the dispersion is negative†. We attribute this to the fact that we have used the approximate expression, (3.12), for $S(Q, \omega)$. The phase velocity to be expected in an ultrasonic experiment is therefore sensitive to the form of $S(Q, \omega)$ and vice versa.

We see that, as one would expect on general grounds, the broader the Brillouin line, the more dominant ultrasonic excitation is attenuated. It is not so obvious that *two* ultrasonic waves are to be expected. However, the two waves have the same phase velocity which is still well defined.

3.2.3. $S(Q, \omega)$ from an ultrasonic experiment. As noted above if the losses, ie Γ and Γ_R, are not large, then the second term in equation (3.16) dominates $\delta\rho_\omega(x, t)$ and it may be

† This statement is true but equation (7-18) of Hertzfeld and Litovitz (1959) is incorrect.

written in the form,

$$\delta\rho_\omega(x,t) \simeq B(\omega)\exp(-fhx)\cos(\omega t - fgx + \psi(\omega)) \tag{3.16'}$$

where $B(\omega)\exp(i\psi(\omega))$ can be expressed in terms of f, g, h, and d. In those circumstances this decaying wave is what will be measured in the ultrasonic experiment. We note that it is *essential to measure the phase shift*, $\psi(\omega)$, as well as the wavelength, $2\pi/fg$, and the decay length, $1/fh$. This is seldom done in ultrasonic experiments. It is usual to measure only the wavelength, $2\pi/fg$, and the attenuation coefficient, fh.

If we regard (3.16') as an experimental result for $\delta\rho_\omega(x,t)$, so that $B(\omega)$, $\psi(\omega)$, 'fh' and 'fg' are all now experimentally determined quantities, we can use the procedure described in § 2.4 to find the corresponding $D_{\exp}(Q,\omega)$. The result is

$$\begin{aligned} D_{\exp}(Q,\omega)(\pi\rho_0 E\hbar^{-1}/m) &= QB(\omega)\cos\psi(\omega)\left(\frac{fh}{(fh)^2+(Q-fg)^2}-\frac{fh}{(fh)^2+(Q+fg)^2}\right) \\ &\quad -QB(\omega)\sin\psi(\omega)\left(\frac{Q-fg}{(fh)^2+(Q-fg)^2}+\frac{Q+fg}{(fh)^2+(Q+fg)^2}\right). \end{aligned} \tag{3.25}$$

In the limit of small Γ it may be shown by the comparison of (3.16') and the second term in (3.16) that

$$B(\omega)\exp(i\psi(\omega)) \to \frac{E\langle\rho\rangle^2\chi_T}{2\gamma}\left(1-i\frac{\omega}{C_0}\left(dt\frac{\Gamma}{C_0}\right)\right). \tag{3.26}$$

Using (3.26), (3.17), (3.18') and (3.19') in (3.25) and the result in (2.15') we find an 'experimental' $S(Q,\omega)$ corresponding to the assumption of (3.16') that only the principal wave is observed when Γ is small. The result for $S(Q,\omega)$ is precisely the second (double) term of (3.12) corresponding to the Brillouin lines and a term of the same form as the third (double) term of (3.12) coming from the second term in large parentheses in (3.25) except that d is replaced by $(d+\Gamma/C_0)$. Of course, the Rayleigh term is missing. If, further, $a \ll b$, ie thermal conductivity effects are neglible as is often the case, then by (3.14) $d = \Gamma/C_0$ and so the small skew terms in $S(Q,\omega)$ deduced from (3.16') are too large by a factor of two.

It is significant that the approximation (3.16') which many would expect only to correspond to the Brillouin lines only in $S(Q,\omega)$ in fact also generates the skew terms. This emphasizes the essential unity and common physical basis of all these terms in the spectrum. In particular this further justifies the statement preceding (3.15).

If the losses are very large, the two 'Brillouin' ultrasonic waves become identical, but are then evanescent since $l/\lambda_B \to (2\pi)^{-1}$.

3.3. Concluding remarks

As we have already noted, equation (3.12) is an approximation for the correct result even in the rather simple case of a hydrodynamic fluid. In the next approximation Γ and C_0 in (3.12) are replaced by functions of Q and the evaluation of the integrals in (2.23) becomes complex. For the particular case of a simple classical hydrodynamic fluid it is probably easier to carry out the conventional ultrasonic analysis as given for instance in Hertzfeld and Litovitz (1959), although many approximations have to be made even there before a comprehensible answer can be obtained.

4. Conclusion

The method used here will be valuable when dealing with more fundamental models of fluids which lead naturally to $S(Q, \omega)$ and its generalizations. The result of an ultrasonic experiment can then be predicted with the help of equations (2.15) and (2.19). In this method one need not worry about such matters as whether the process is adiabatic, where the energy goes, etc, etc. All the assumptions are in $S(Q, \omega)$ and thereafter only mathematical approximations, if any, are made.

An important conclusion from our analysis is that the conventional ultrasonics experiment, in which only attenuation and wavelength are measured, ignores an important additional measurable parameter ($\psi(\omega)$ in equation (3.16′)). Moreover, it would appear that the actual ultrasonic signal is in general much more complex than is usually assumed to be the case (eg equation (3.16)).

We intend, in a subsequent publication, to apply this method to other types of fluid and in particular to one with a relaxing bulk modulus, which is of considerable interest in ultrasonic work.

References

Brillouin L 1922 *Ann. Phys., Lpz* **17** 88
——1960 *Wave Propagation and Group Velocity* (New York: Academic Press)
Callen H B and Welton T A 1951 *Phys. Rev.* **83** 34
Debye P and Sears F 1932 *Proc. Natl Acad. Sci. US* **18** 409
Fabelinskii I L 1968 *Molecular Scattering of Light* (New York: Plenum Press)
Gewurtz S, Gornall W S and Stoicheff B P 1971 *J. Acoust. Soc. Am.* **49** 994
Griffin A 1968 *Rev. Mod. Phys.* **40** 167
Hertzfeld K F 1938 *Phys. Rev.* **53** 899
Hertzfeld K F and Litovitz T A 1959 *Absorption and Dispersion of Ultrasonic Waves* (New York: Academic Press) p 44
Kubo R 1957 *J. Phys. Soc. Japan* **12** 570
Landau L D and Lifshitz E M 1959 *Fluid Mechanics* (London: Pergamon) p 304 and footnote on p 201
——1965 *Quantum Mechanics* (London: Pergamon) p 15
Landau L D and Placzek G 1934 *Phys. Z. Sov.* **5** 172
Markham J J, Bayer R T and Lindsay R B L 1951 *Rev. Mod. Phys.* **23** 353
Mountain R D 1966a *Rev. Mod. Phys.* **38** 205
—— 1966b *J. Res. Natl Bur. Stand.* A **70** 207
—— 1970 *Critical Reviews in Solid State Science* vol 1 (Cleveland, Ohio: Chemical Rubber Company) p 5
Mountain R D and Litovitz T A 1967 *J. Acoust. Soc. Am.* **42** 516
Selwyn Ph A and Oppenheim I 1971 *Physica* **54** 161
Van Hove I 1954 *Phys. Rev.* **95** 249