CHAPTER 17

ACOUSTICS AND THE LIQUID STATE

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I. Introduction

It is well known that the structure of the liquid state has been more difficult to understand and predict theoretically than that of either solids or gases. Classical statistical mechanics and the kinetic theory have in the main proved adequate to handle gases, accounting successfully for equilibrium properties like the equation of state and specific heats, as well as nonequilibrium behavior like transport phenomena involving viscosity, thermal conductivity and diffusion. On the other hand quantum statistics gives a good account of the details of the solid state, particularly in its crystalline form. From their observed properties liquids appear to lie somewhere between the other two states. For a long time the theoretical study of liquids was approached from the standpoint of their alleged similarity to gases, since both have the ability to flow and possess no apparent shear elasticity. The van der Waals principle of continuity of state tends to favor this general viewpoint. On the other hand, the fact that liquids and gases obey different viscosity laws as far as temperature is concerned cannot be overlooked. More recently there has developed a tendency to attack the problem of the liquid state from the standpoint of the similarity between liquids and solids, particularly in the temperature range near the melting point.[1] The analogy between the viscous flow of liquids and the plastic flow of solids comes to mind at once. Moreover X-ray diffraction studies (like those of G. W. Stewart[2] and others) have indicated that though liquids have lost the high degree of distant-order characteristic of crystalline

[1] J. Frenkel, "Kinetic Theory of Liquids." Oxford Univ. Press, New York, 1946.
[2] G. W. Stewart, *Phys. Rev.* **37**, 9 (1931).

solids, they do possess a considerable degree of local or short-range order. The so-called liquid crystals are of particular interest in this connection since with increasing temperature these substances (e.g., *p-p'* azoxyanisole) pass from the crystalline solid form to a liquid state characterized by loss of long-range regular order but retaining long-range orientation order, which accounts for the optical anisotropy. Further increase in temperature destroys the orientation order and the liquid becomes optically isotropic with the retention of only local order.[3]

The attempt to extend the statistical mechanics of gases to liquids has not met with success as far as actual calculations are concerned, though the theory can be carried through formally. On the other hand the solid or crystal-like approach has been successful in leading to numerical results both for equilibrium and transport problems, though special and somewhat arbitrary assumptions are necessary. Thus, in the so-called cell-type theory[4] the liquid is viewed as a distorted crystal with a molecule located at or near each lattice point, with the recognition, however, that in a liquid some lattice sites may be vacant (hole theory). The relation between acoustical and other properties of the liquid state seems to be more understandable in terms of this sort of viewpoint.

II. General Survey of Acoustical Properties of Liquids

We begin with a brief survey of the acoustical properties of liquids of importance in connection with other physical characteristics of the liquid state. In so far as they behave like ideal fluids, liquids transmit compressional waves with velocity equal to the square root of the ratio of the adiabatic bulk modulus to the density. However, certain viscous liquids also propagate shear waves as well and therefore manifest shear elasticity. Hence the measurement of sound velocity can provide estimates of the elastic moduli of liquids together with their variation with temperature and pressure.

For all pure liquids save water the velocity of compressional waves decreases with temperature.[5] The same must therefore be true of the adiabatic bulk modulus. For water and salt solutions the velocity increases with temperature up to a certain characteristic temperature (74° C. for pure water) and thereafter decreases. The generally anomalous character of water with respect to its physical properties is well known. As might be expected, increase in pressure raises the compressional wave velocity in pure liquids, the effect in benzene, for example, corresponding to an in-

[3] M. G. Friedel, *Ann. phys.* **17**, 273 (1922); W. H. Bragg, *Nature* **133**, 445 (1934).

[4] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," p. 271 *ff*. Wiley, New York, 1954.

[5] L. Bergmann, "Der Ultraschall," 6th ed., Chapter 4. S. Hirzel, Stuttgart, 1954.

crease of about 17% for the pressure change from 1 to 500 atm. This is associated with the expected increase of the elastic modulus with pressure. Since it is the adiabatic bulk modulus which is given by sound-velocity measurements, independent static measurement of the isothermal bulk modulus provides a useful method of determining the ratio of the specific heats for a liquid. ($\gamma = K_{\text{ad.}}/K_{\text{iso.}}$, where K denotes the modulus). If $K_{\text{iso.}}$ is not known, knowledge of the thermal coefficient of expansion together with $K_{\text{ad.}}$ suffices, with the use of the well-known thermodynamic formula

$$\gamma = 1 + \frac{T\alpha^2 K_{\text{ad.}}}{\rho C_p} \tag{1}$$

where T = absolute temperature,
α = coefficient of expansion,
ρ = density, and
C_p = specific heat at constant pressure (expressed in energy units).

Measurement of the sound velocity in electrolytes leads to knowledge of the variation of bulk modulus with concentration; this is found to be complicated in form but constitutes an increase in every case.[5]

Much study has been directed toward the acoustic understanding of the elastic constants of organic liquids as a function of their chemical constitution.[5] Certain generalizations have been seen as plausible, for example: (1) aromatic compounds have in general higher bulk moduli than aliphatic compounds; (2) the bulk modulus appears to increase with the size of the molecule; (3) the bulk modulus appears to increase in general with the viscosity. There is some evidence that for a good many liquids the velocity of compressional waves is nearly proportional to the cube of the density. This would mean that the adiabatic compressibility is inversely proportional to the seventh power of the density. For several liquids (e.g., benzene, ether, carbon tetrachloride, heptane, toluene) the coefficient of proportionality is approximately independent of temperature for each liquid separately, though at the same temperature the coefficients vary considerably from liquid to liquid. There are indeed order-of-magnitude regularities. Thus, for the alcohols $C_nH_{2n+1}OH$ at 20°, all values of $\beta_{\text{ad.}}\rho^7$ lie between 19.57×10^{-12} c.g.s. (for CH_3OH) and 17.40×10^{-12} c.g.s. (for $C_{12}H_{25}OH$). (The compressibility is denoted by β.) On the other hand the corresponding value for heptane at 20° is 7.57×10^{-12} c.g.s. So one must beware of generalizing![5]

Since the velocity V of a compressional wave in a fluid is always given by

$$V^2 = \left(\frac{dp}{d\rho}\right)_{\text{ad.}} \tag{2}$$

knowledge of the equation of state should be sufficient to calculate V as a function of γ, the molecular weight, the density, and the volume of the molecule. Unfortunately, the equation of state of liquids is not well known in closed form. Actually, precise knowledge of the sound velocity could well be a help in the determination of the equation of state.

It has been hoped that light may be shed on the structure of liquids by the study of the sound velocity behavior in liquid mixtures. For it is very rare that the velocity varies linearly from that of the first component to that of the second as the concentration of the second varies from 0 to 100%. Usually the simpler linear variation is replaced by curves showing maxima or minima in the region in question. For example, as has been shown by R. Parshad,[5] in a mixture of ethyl alcohol and water (for which by themselves the compressional wave velocities at 20° C. are 1180 and 1485 m./sec. respectively) the velocity actually has a maximum value of 1600 m./sec. for a mixture containing approximately 25% alcohol by volume. For the same mixture the adiabatic compressibility has a minimum for the same relative concentration. The attempt has been made to connect such phenomena with the degree of association of the liquids concerned and its disturbance by the mixture, which should have an effect on the compressibility. Much theoretical work remains to be done, however.

Where reference is made to sound waves in liquids it is almost always with compressional waves in mind. However, as has been suggested earlier, transverse shear waves are possible and may ultimately have great significance in unraveling the structure of high polymers. A long time ago Stokes[6] called attention to the possibility of producing transverse waves in a viscous liquid by rotating a disk parallel to its own plane. It can readily be shown that if the liquid possesses viscosity but no shear elasticity, harmonic transverse waves of this type travel with a phase velocity $V = \sqrt{2\omega\nu}$, where ω is the angular frequency and ν is the kinematic viscosity (the shear viscosity divided by the density), and are damped with a spatial attenuation coefficient $\alpha = \sqrt{\omega/2\nu}$. The fluid displacement ξ in the direction perpendicular to that of propagation has the form

$$\xi = \xi_0 e^{-\alpha x} e^{i(\omega t - \omega x/V)}. \tag{3}$$

Unless the viscosity is very high or the frequency very low, these waves are too highly damped to be easily studied by propagation techniques, though they have been detected by W. P. Mason[7] and his collaborators through their loading influence on the crystal source. Indeed the viscosity of the liquid can be determined from the measured change in the resonant

[6] Lord Rayleigh, "Theory of Sound," Vol. 2, para. 347. Dover, New York, 1945.

[7] W. P. Mason, "Piezoelectric Crystals and their Application to Ultrasonics," p. 339 *ff*. Van Nostrand, New York, 1950.

resistance of the crystal with precision equal to that of standard viscosimeter methods.

For very viscous liquids like some of the high polymers, Mason has shown that $\alpha \neq \omega/V$ as in the simple theory of Stokes, and that this can be most readily explained by the assumption that the liquid exhibits shear elasticity as well as viscosity. By interpreting the propagation properties of the liquid by means of an equivalent electric transmission line he has been able to measure the equivalent shear elasticity. Thus, for polymerized castor oil the shear elasticity for frequencies in the neighborhood of 30 kc. turns out to be approximately 10^7 dynes/cm.^{2} This type of elasticity has been termed *configurational* and is attributed to the tendency of the long-chain molecules composing the polymer to return to their most probable configuration after having been distorted by the action of the radiation. If the liquid behaved like a crystalline substance we should expect its shear modulus to be much higher (recall that most solids have moduli in the neighborhood of 10^{11} dynes/cm.^{2}. Actually some liquids like arochlor (pentachlordiphenyl) do have shear moduli as high as 10^9 dynes/cm.^{2} Of course it should be emphasized that these values are functions of the frequency. Thus the shear elasticity of polyisobutylene at room temperature is 3×10^9 dynes/cm.^{2} at 10 megacycles and 5.5×10^9 dynes/cm.^{2} at 60 mc. In general shear elasticities of polymers increase as the temperature decreases.

In solutions of high polymers the shear modulus for given frequency and temperature is a function of concentration. Thus when polyisobutylene is dissolved in cyclohexane, Mason has shown that the shear elasticity can be expressed as the sum of a term varying linearly with the concentration and a term varying as the cube of the concentration. From a theoretical point of view the linear dependence seems attributable to the shear stiffness of single-chain molecules, whereas the cube term may be said to correspond to the entanglement of the chains. This concentration dependence thus provides a way of separating out the effects of single-chain action and interchain reactions, respectively, as functions of temperature, frequency, etc. It should prove a valuable tool in the more precise physical characterization of polymers.

Mason comments that very high shears of liquids can be obtained by employing large shear displacements of the oscillating crystal at high frequency. It should indeed prove theoretically possible to produce maximum shearing strains in the liquid in the vicinity of the crystal of as much as ½. It would seem that this might permit the estimation of shear strengths of polymers, though there are mathematical difficulties in the way of precise evaluation.

Mention of the attenuation of shear waves suggests reverting to the problem of the damping (as distinct from scattering) of compressional

waves in liquids. The classical theory attributes this primarily to viscosity, heat conduction, and radiation. However, it is readily shown that the effects of heat conduction and radiation are negligible compared with the effects of viscosity. Increased accuracy in the measurement of sound attenuation since 1940 has decisively shown that shear viscosity is not a sufficient explanation. It is true that over wide frequency ranges the compressional wave absorption coefficient for liquids varies directly as the square of the frequency, just as the classical theory predicts, but the actual magnitude for practically all liquids is much smaller than that observed.[8] For associated liquids like water and the alcohols the observed absorption is of the order of two or three times the viscous absorption; whereas for nonassociated liquids, e.g., the organic compounds like benzene, the observed absorption may be several hundred times the classical value. Indeed it is only for monatomic liquids like mercury and the liquefied rare gases on the one hand and very viscous liquids like glycerine on the other that the classical value is actually observed. It therefore seems clear that the absorption of sound in liquids is not a simple transport phenomenon. The somewhat similar behavior of gases has been explained in terms of the transfer of some of the increased kinetic energy of translational motion of the molecules, brought about by the sound radiation, into internal rotational and vibrational states of the molecules. There is a lag in the attainment of equilibrium in this process, in other words, a finite time of relaxation, which makes itself evident in attenuation of the average flow of energy in the sound. The success of this relaxation point of view for gases has led to its application to liquids as well. Various forms of relaxation processes are possible. The one just mentioned is usually termed *thermal*, since the results can be expressed in terms of an internal specific heat associated with the internal energy states of the molecule along with the usual external specific heat connected with molecular translation. This type cannot of course apply to monatomic liquids like mercury. Moreover, it does not work for water, which, as in so many of its properties, is also anomalous with respect to sound absorption. Hall[9] has explained absorption in water by a kind of structural relaxation in which local molecular rearrangement is brought about by the sound radiation with a relaxation time of the order of 10^{-12} sec. This theory involves two interesting consequences for the structure of water: (1) the existence of a structural or dynamic compressibility, which shows relaxation, in addition to the instantaneous static compressibility of ordinary measurement, and (2) the existence of a bulk or volume viscosity in addition to the usual shear viscosity. The latter is the ratio of excess

[8] J. J. Markham, R. T. Beyer, and R. B. Lindsay, *Revs. Modern Phys.* **23**, 353 (1951).

[9] L. H. Hall, *Phys. Rev.* **73**, 775 (1948).

pressure to the fractional time rate of change of density. It was set equal to zero in Stokes' original treatment of viscous damping. Actually, in Hall's theory, its value for water is several times that of the shear viscosity.

A somewhat similar type of relaxation theory is that employed by J. Lamb[10] and his co-workers to explain absorption in certain organic liquids, like cyclohexane derivatives, which form rotational isomers. The sound wave perturbs the equilibrium between such isomers, with effective flow of energy in the process. Relaxation times of the order of 10^{-5} sec. have been detected for these substances, corresponding to frequencies of the order of 100 kc., readily observable by acoustic means.

Still another possible form of relaxation mechanism is the chemical reaction (e.g., dissociation) proposed by Liebermann[11] for electrolytes like magnesium sulfate solutions. This is still in the testing stage.

All relaxation mechanisms lead to velocity dispersion as well as absorption. As in the case of shear viscosity the dispersion turns out to be a second-order effect compared with absorption. Actually, there is no clear-cut experimental evidence for the existence of genuine dispersion in liquids.

III. Some Other Properties of Liquids Subject to Acoustic Influence and Study

1. Cavitation[12]

Many phenomena associated with the effect of acoustic radiation in liquids, especially at high intensity, can be attributed to the occurrence of cavitation, that is to say, the appearance in a liquid subject to high stresses of cavities or bubbles. Cavitation produced by ultrasound is of two kinds: (1) When the liquid through which the radiation passes contains dissolved air or other gases the changes in pressure produced by the sound cause the dissolved gas to come out of solution. This is called pseudo cavitation or sometimes gassy cavitation. (2) If the liquid is thoroughly degassed, cavities can still be formed if the change in pressure is sufficient to overcome the tensile strength of the liquid: it ranges from about 1.5 atm. for liquids of very low viscosity like carbon tetrachloride to about 4 atm. for castor oil. This is termed the cavitation threshold. Why it is in general so much lower than the tensile strength of a liquid as associated with its compressibility would indicate, remains a puzzle. It has been suggested that even a so-called gasfree liquid possesses nuclei in the form of very small bubbles containing gas under extremely high pressure, and that cavitation starts on such nuclei. Possibly the hole theory of liquids may provide another explanation (cf. Section IV). There has also been much experimental and theoretical

[10] J. Karpovich, *J. Acoust. Soc. Amer.* **26**, 818, 951 (1954); cf. also *J. Chem. Phys.* **22**, 1767 (1954).

[11] L. Liebermann, *Phys. Rev.* **76**, 1520 (1949).

[12] L. Bergmann, "Der Ultraschall," 6th ed., p. 837*ff*. S. Hirzel, Stuttgart, 1954.

work on the threshold of pseudo cavitation. E. Meyer[13] of Göttingen believes that it is caused by the adhesion of the air or other dissolved gases to fine solid particles. On the other hand, Fox and Herzfeld[14] have developed the notion that the cavitation nuclei are genuine air or gas bubbles whose persistence in the liquid in equilibrium despite surface tension is to be attributed to the protection of a monomolecular layer or skin; the cavitation threshold is the sound intensity just sufficient to break the skin so that gas can diffuse into the bubble and cause it to grow. This theory still awaits experimental confirmation.

The effects of ultrasonically induced cavitation are often spectacular: at high intensity it can bring about the complete mixing of otherwise immiscible liquids, such as water and mercury, into a rather stable emulsion. The precise mechanism is not yet well understood. In addition to the large forces released in the collapse of the bubbles, the vigorous hydrodynamic streaming produced by the sound radiation in the neighborhood of cavitation bubbles probably plays an important role (cf. Section III-2).

When cavitation is produced ultrasonically, luminescence is often observed. The explanation is still a matter of speculation: one point of view takes the stand that enough electric charge can be produced by friction between the cavities and the surrounding liquid to build up sufficient electrostatic potential for an electric discharge; another point of view developed by V. Griffing[15] insists that all cavitation luminescence is chemiluminescence.

This suggests a reference to the interesting influence of ultrasound on chemical reactions in liquids. Thus, in water containing dissolved oxygen, hydrogen peroxide is formed by ultrasonic radiation. Similarly water and carbon tetrachloride in the presence of dissolved gases like argon, oxygen, and nitrogen react under ultrasonic radiation to produce free chlorine. Here is a rapidly expanding field which has already led to numerous industrial applications. Many theories have been proposed, most of them invoking cavitation. The best substantiated theory so far appears to be that of V. Griffing[15] and co-workers, which assumes that ultrasonic chemical effects in liquids are gas-phase thermal reactions taking place in the cavitation bubbles. Although the actual temperature rise associated with sound intensity of 5 to 10 watts/cm.^{2} in a homogeneous medium is only a few degrees centigrade, the adiabatic compression of small bubbles by the sound can lead to temperature increases of several hundred degrees. For gas bub-

[13] R. Esche, *Akustische Beihefte* Heft 4, p. AB208 (1952); cf. also *J. Acoust. Soc. Amer.* **27**, 173 (1955).

[14] F. E. Fox and K. F. Herzfeld, *J. Acoust. Soc. Amer.* **26**, 984 (1954).

[15] V. Griffing, *J. Chem. Phys.* **20**, 939 (1952); cf. also *J. Acoust. Soc. Amer.* **27**, 173 (1955).

bles of higher specific-heat ratio, one would then expect greater chemical yields and this is found to be so.

2. Streaming[16]

It has been known for a long time that liquids (as well as gases, for that matter) when irradiated by high-frequency harmonic sound not only are sinusoidally disturbed but exhibit hydrodynamic flow in the form of circulating currents, which may either be on a scale comparable with the dimensions of the vessel containing the liquid or may be small-scale whirling motions taking place in the vicinity of cavitation bubbles and possibly affecting the darting motion of the bubbles themselves. Calculation indicates that the streaming velocity is directly proportional to the total attenuation coefficient. Hence, study of streaming provides an indirect method for the measurement of attenuation. Eckart[17] believes that the computation which makes the streaming velocity proportional to the *total* absorption (whether due to viscosity or thermal or structural relaxation, etc.) is only an approximation and that it will probably break down in the case of chemical reactions taking place near an obstacle in a liquid. The matter is still controversial. Eckart's original theory[18] made the streaming velocity proportional to the bulk viscosity only. Nyborg,[16] who has studied streaming extensively, has paid particular attention to streaming in the neighborhood of air bubbles in water at frequencies near bubble resonance. Here, because of the enormously increased attenuation coefficient, streaming velocities of very great magnitude (e.g., 50 m.p.s.) can be realized. It is believed that these may be one of the reasons for the strong biological influence of ultrasonic radiation.

3. High-Intensity Radiation

The complexity of the problem of the interaction of high-frequency sound radiation and the liquid medium through which it passes becomes even more evident when one considers the effect of high-intensity radiation. Of course, very intense radiation can lead to cavitation and the various concomitant phenomena already mentioned. But it is well known that the cavitation threshold goes up markedly with frequency:[19] whereas in water at 15 kc.p.s. it is only of the order of 2 watts/cm.^{2}, at 3 mc.p.s. it is already approaching 35 kw./cm.^{2}. A similar result holds for short, high-intensity pulses. At the same time it has been discovered that the effective attenuation coefficient increases with intensity even when cavitation has not been

[16] W. L. Nyborg, *J. Acoust. Soc. Amer.* **25**, 68 (1953).
[17] C. Eckart, *J. Acoust. Soc. Amer.* **27**, 173 (1955).
[18] C. Eckart, *Phys. Rev.* **73**, 68 (1948).
[19] L. Bergmann, "Der Ultraschall," 6th ed., p. 847. S. Hirzel, Stuttgart, 1954.

observed. In recent work by D. M. Towle[20] it has been found that the absorption coefficient for distilled water, for example, increases almost linearly with the sound excess pressure as the latter ranges from 2 to 7 atm., the slope of α/ν^2 versus pressure being approximately 20×10^{-17} cm.$^{-1}$-sec.^{2} per atmosphere and nearly independent of frequency over the range from 4 to 9 mc.p.s. It is interesting that no change in velocity with intensity was detected in these experiments. Similar results have been obtained by Fox and Wallace.[21] The theoretical explanation is still in an embryonic state. Fay's solution of the nonlinear wave equation for finite-amplitude waves predicts such an increase in absorption in a purely viscous medium, but it does not appear that the predicted order of magnitude agrees with Towle's experimental results. At the same time Fay's theory predicts a frequency dependence which is not experimentally observed. No one has worked out in detail the theory of the absorption of high-amplitude acoustic waves for a thermal or structural relaxation mechanism. The suggestion that in the high-intensity radiation very small cavitation bubbles are produced—too small to give rise to obvious cavitation phenomena but sufficient to absorb sound by scattering or by resonant action—probably is worth further study, though exploratory studies do not hold out too much hope of agreement with presently available experimental data unless some radically new mechanism is postulated. This provides a challenging domain for study.

IV. Theories of the Liquid State and Connection with Acoustics

As has been suggested in the foregoing, the type of theory which has been most successful in accounting for the observed acoustical behavior of liquids, particularly absorption, is that which assumes one or more relaxation mechanisms in addition to the presence of shear viscosity. Numerous reviews of these mechanisms are available.[8, 22] The simplest approach to an understanding of relaxation is the phenomenological one. For all relaxation mechanisms the equation of state of a liquid is not simply the static equilibrium relation connecting pressure, density, and temperature; rather it takes the form of a dynamical equation in which one side contains an expansion of the form $\rho_e + a_1\dot{\rho}_e + a_2\ddot{\rho}_e + \cdots$ and the other side an expansion of the form $b_0p_e + b_1\dot{p}_e + b_2\ddot{p}_e + \cdots$. Here p_e is the excess pressure and ρ_e the excess density. The static equation of state is obtained if $a_i = b_i = 0$ for all i save 0, and $b_0 = \rho_0\,\beta_0$, where ρ_0 is the mean density and β_0 the static compressibility. This yields no relaxation and no dispersion or absorption of sound. On the other hand, if all the a's and b's are zero save a_1, b_0, and b_1, we get the model of a simple relaxation mechanism. Thus,

[20] D. M. Towle and R. B. Lindsay, *J. Acoust. Soc. Amer.* **27,** 530 (1955).
[21] F. E. Fox and W. A. Wallace, *J. Acoust. Soc. Amer.* **26,** 994 (1954).
[22] H. O. Kneser, *Kolloid-Z.* **134,** 20 (1953).

to take a special case, if p_e = constant so that the state equation becomes

$$\rho_e + a_1 \dot{\rho}_e = b_0 p_e \tag{4}$$

the solution for ρ_e yields

$$\rho_e = b_0 p_e (1 - e^{-t/a_1}) \tag{5}$$

where a_1 now appears as the relaxation time τ in which ρ_e rises to within $1 - e^{-1}$ of its final equilibrium value $b_0 p_e$. The significance of the relaxation time in terms of the parameters a_1, b_0, b_1, etc., will of course depend on the process envisaged. In the application to sound transmission the dynamical equation of state is used in conjunction with the hydrodynamic equation of motion and equation of continuity. If it is assumed that p_e corresponds to a plane harmonic wave of the form $p_0 e^{i(\omega t - kx)}$, it then turns out that the wave parameter k is a complex quantity depending on the angular frequency ω. The excess pressure or density of the wave takes the form given in equation (3), where α is the absorption coefficient and V the phase velocity of the wave.

If, after adopting an appropriate definition of relaxation time τ, we plot α/ω as a function of $\omega\tau$, the result in any relaxation process is a rather broad maximum occurring for a value of $\omega\tau$ which depends on the type of mechanism, i.e., on the relative values of b_0, b_1, a_1 in the dynamical equation of state. It is only in the special case in which b_1 and b_0 are very close together that the maximum value of α/ω occurs for $\omega = 1/\tau$, or what may be called the angular relaxation frequency.

From a pictorial point of view the various relaxation mechanisms can be classified in roughly four categories: thermal, structural, chemical, and orientational. The first three have been mentioned in passing in Section II. The fourth refers to a mechanism in which the long-chain molecules in high polymers have their equilibrium orientation disturbed by the radiation. Thus, external tension may tend to stretch the chains out into parallel lines, where previously in equilibrium they had been more or less curled up. This is obviously not a simple relaxation mechanism and could hardly lead to a single relaxation time.

It may be of interest to note the values of the coefficients a_1, b_0, b_1 for thermal and structural relaxation. For thermal relaxation we have[8]

$$a_1 = \frac{1}{\omega_0} = \frac{\tau C_p^{\,e}}{C_p^{\,t}} \tag{6}$$

$$b_0 = \rho_0 \beta_s^{\,0}, \qquad b_1 = \frac{\rho_0 \beta_s^{\,\infty}}{\omega_0} \tag{7}$$

where ω_0 = the angular relaxation frequency,

τ = the relaxation time,
C_p^e = the external molar heat capacity at constant pressure,
C_p^t = the total molar heat capcity at constant pressure (including that due to intramolecular energy changes),
β_s^0 = the low-frequency adiabatic compressibility, and
β_s^∞ = the high-frequency adiabatic compressibility. The latter two quantities are further given by

$$\beta_s^0 = \frac{\beta}{1 + T^e b^2 V_m/\beta C_v^t} \tag{8}$$

$$\beta_s^\infty = \frac{\beta}{1 + T^e b^2 V_m/\beta C_v^e} \tag{9}$$

where β = the isothermal compressibility,
T^e = the temperature corresponding to intermolecular equilibrium,
b = the volume coefficient of thermal expansion,
V_m = the molecular volume,
C_v^t = the total molar heat capacity at constant volume for low frequencies, and
C_v^e = the external (intermolecular) molar heat capacity at low frequencies. In this case the expression for the absorption coefficient α becomes

$$\alpha = \frac{V\omega^2\omega_0}{2V_0^2(\omega^2 + \omega_0^2)}\left(1 - \frac{\beta_s^\infty}{\beta_s^0}\right) \tag{10}$$

where V_0 is the limiting phase velocity of the wave at very low frequencies (i.e., neglecting relaxation processes), whereas V is the frequency-dependent phase velocity given by

$$V^2 = \frac{\omega^2 + \omega_0^2}{\rho_0(\beta_s^\infty\omega^2 + \beta_s^0\omega_0^2)} \tag{11}$$

which reduces to V_0^2 for $\omega = 0$.

For structural relaxation $C_p^e = C_p^t$ since $C_p^i = 0$ and hence

$$a_1 = \frac{1}{\omega_0} = \tau \tag{12}$$

Further, in this case, the compressibilities are given by

$$\beta_s^0 = \frac{\beta^t C_v^t}{C_p^e} \tag{13}$$

$$\beta_s^\infty = \frac{\beta^e C_v^e}{C_p^e} \tag{14}$$

where β^t = total isothermal compressibility and β^e = isothermal compressi-

bility associated with intermolecular processes. With these changes in meaning the absorption and dispersion formulas for structural dispersion are of the same form as (10) and (11). It should of course be emphasized that α in equation (10) must be interpreted as supplying attenuation in *addition* to that caused by shear viscosity.

Hall's application of structural relaxation[9] to water implies that water is essentially a two-state liquid: one state is a broken-down ice structure in which the local order is that of a tetrahedral arrangement of nearest neighbors about each water molecule, the coordination being maintained by intermolecular hydrogen bonds; the other state corresponds roughly to cubic close packing, a state of higher relative energy and smaller molar volume. The compressional effect of the sound radiation is to increase the relative number of water molecules in the second or "excited" state; this is the structural relaxation process. Unfortunately, there is no decisive alternative evidence for the two-state theory; X-ray studies of water subject to ultrasonic radiation have been proposed but have, so far as the author is aware, not been carried out. It has been argued by Mavroides[23] that the influence of sinusoidal pressure changes on the dielectric constant of water favors the one-state rather than the two-state theory, but careful examination has served to cast considerable doubt on the cogency of the argument. The matter obviously needs further investigation. It must be admitted that structural relaxation of the Hall type has not been successful in accounting for absorption in other associated liquids like the alcohols[24] where it might conceivably be expected to show up. One reason is probably the very small change in volume associated with the pressure change. Structural relaxation of the orientational type has been successful in describing high polymer absorption.

Another interesting proposal of a relaxation mechanism employs the hole theory of liquids,[25, 26] which assumes that any apparently continuous liquid medium is actually full of cavities, which may be treated effectively as vacant lattice sites. If spherical, the holes are of the order of magnitude of a few Ångstrom units in diameter and in number such that their total volume for a normal liquid is around 0.5% of the total volume of the liquid. Nolle[27] has recently developed a structural relaxation theory for the absorption of sound in water under large hydrostatic pressure (e.g., up to 1300 atm.) in which one state of the liquid is that containing holes while the other

[23] J. Mavroides, Ph.D. Thesis, Brown University, Providence, R. I. 1953.

[24] D. Sette, *Phys. Rev.* **78**, 476 (1950).

[25] J. Frenkel, "Kinetic Theory of Liquids," p. 74*ff*. Oxford Univ. Press, New York, 1946.

[26] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," p. 311*ff*. Wiley, New York, 1954.

[27] A. W. Nolle, *J. Acoust. Soc. Amer.* **27**, 173 (1955).

state corresponds to an irregular close packing of the molecules. Harmonic sound radiation disturbs the equilibrium between the two states. Nolle assumes that the negative energy of hole formation is analogous to the free-energy difference between the two states of water in Hall's theory. The variation of the absorption coefficient with applied hydrostatic pressure as calculated agrees in a general way with the experimental results. Further work along this line has recently been reported by T. A. Litovitz and E. H. Carnevale,[28] who have measured ultrasonic absorption in water up to pressures of 2000 atm., indicating that both shear and compressional attenuation increases with pressure. To account for these results theoretically it appears necessary to modify Hall's theory in the direction of associating the open or icelike packing with the higher free-energy state, which is the reverse of Hall's postulate. It is also necessary to assume that the free-energy difference between the two states is dependent on temperature. With these modifications excellent agreement is obtained between theory and experiment. All this, of course, casts further doubt on the details of Hall's theory and suggests further intensive research into structural relaxation.

The hole theory has also been invoked by Lukasik[29] to account for the temperature dependence of sound velocity in liquids. He is able to show that the hole-theory equation of state for orthocresol can lead to the observed temperature dependence for reasonable values of hole size (e.g., 57×10^{-24} cm.^{3}) and energy of hole formation (e.g., 1 kcal./mole). It appears that acoustics may ultimately provide a useful way of testing the validity of the hole theory.

Another valuable tool which may be used in conjunction with acoustics in the study of the liquid state is the influence of magnetic fields on sound absorption. As an illustration may be mentioned some exploratory work by D. R. Curran at Brown University on the liquid crystal *p-p'* azoxyanisole in which a sharp attenuation peak for 10-mc. radiation is observed in the neighborhood of the transition temperature from the anisotropic to the isotropic form. A magnetic field of only 800 oersteds is sufficient to shift the temperature at which the peak occurs by 0.5° C. or 1° C. depending on whether the field is directed parallel or perpendicular to the direction of sound propagation. Further study is demanded, but the preliminary results are not inconsistent with a two-state relaxation process.

[28] T. A. Litovitz and E. H. Carnevale, *J. Acoust. Soc. Amer.* **27**, 547 (1955).
[29] S. J. Lukasik, *J. Acoust. Soc. Amer.* **27**, 173 (1955).

Nomenclature

C_p Specific heat at constant pressure (expressed in energy units)
C_p^e External molar heat capacity at constant pressure
C_p^t Total molar heat capacity at constant pressure (including that due to intramolecular energy-changes)
C_v^t Total molar heat capacity at constant volume for low frequencies
C_v^e External (intramolecular) molar heat capacity at low frequencies
K Bulk modulus
T Absolute temperature
T^e Temperature corresponding to intermolecular equilibrium
V Velocity
V_0 Limiting phase velocity
V_m Molecular volume

a Relaxation constant
b_0 ρ_0 β_0 (rho, beta)
k Wave parameter
p_e Excess pressure

α Coefficient of thermal expansion, acoustic absorption coefficient
β Isothermal compressibility
β_0 Static compressibility
β_s^0 Low-frequency adiabatic compressibility
β_s^∞ High-frequency adiabatic compressibility
β^t Total isothermal compressibility
β^e Isothermal compressibility associated with intermolecular processes
ν Kinematic viscosity
ρ Density
ρ_e Excess density
ρ_0 Mean density
τ Relaxation time
ξ Fluid particle displacement
ω Angular frequency
ω_0 Angular relaxation frequency