ARCHIVES OF ACOUSTICS
3, 1, 49-56 (1978)

INVESTIGATION OF THE RELATION BETWEEN THE SOUND VELOCITY IN LIQUIDS AND THE MEAN VELOCITY OF THE THERMAL MOTION OF THEIR MOLECULES

FRANCISZEK KUCZERA

Institute of Physics, Silesian Technical Universty (44-100 Gliwice, ul. B. Krzywoustego 2)

It is shown in this paper that in assuming a rectangular potential well we also assume that the intermolecular compressibility of a liquid consists of a kinetic and a potential part. It was accepted that the kinetic part — as for a perfect gas — is independent of temperature at constant pressure. Hence, it can be concluded that the temperature coefficients of both the compressibility and the sound velocity depend almost exclusively on the space filling.

In considering the propagation of acoustic waves in gases attention has long been drawn to the close similarity of the expressions for the acoustic velocity and the mean velocity of the thermal translatory motion of the molecules

$$w = \sqrt{\gamma \frac{RT}{M}} \tag{1}$$

and

$$c = r\sqrt{\frac{RT}{M}}, \tag{1a}$$

where w denotes the propagation velocity of acoustic waves in a gas, c is the mean velocity of thermal motions, and r is a constant coefficient whose value depends on the method of averaging used. Thus there is a close relationship between the propagation velocity of the acoustic waves and the velocity of the thermal motion although the relationship between r and γ in formulae (1) and (1a) has not yet been reported. (The solution to this problem will be presented in section 1). In this situation there arises an obvious an interesting question as to whether and in what manner the velocities of the thermal motion of molecules in liquids are related to the velocity of propagation of acoustic waves in liquids (¹). This paper contains remarks and observations concerning this problem. In the first place attention will be drawn to the relation between the propagation velocity of acoustic waves in perfect gases and the thermal velocity (s. 1). Then after a brief recapitulation of some essential problems concerning the propagation of acoustic waves in solids (s. 2) attention is turned to the propagation of acoustic waves in liquids (s. 3).

1. In first considering the propagation of an acoustic wave in a perfect gas from a microscopic point of view it can be seen that within a system of hard, non-interacting molecules a continuous wave cannot propagate. An acoustic wave propagates in gas as a result of the volume elasticity which in this case is of a purely kinetic and static nature.

Consideration must thus be given to the volumes of such size that statistical quantities become meaningful. (This is in contrast to the analogous problem in solids where it is possible to start with a model confined to one molecule and its nearest environment). We thus have

$$w^2 = \left(\frac{\partial p}{\partial \varrho}\right)_s = \gamma \left(\frac{\partial p}{\partial \varrho}\right)_T, \tag{2}$$

where $\gamma = c_p/c_v$, and w is the velocity of acoustic waves in the gas. The other letters have their commonly accepted meanings. The gas pressure p can be expressed by the formula

$$p = \frac{1}{3} n\, m\overline{c^2} = \frac{1}{3} \varrho \overline{c^2}, \tag{3}$$

where n denotes the number of molecules per cubic centimetre, m is the mass of one molecule, and $\overline{c^2}$ is the mean square velocity of the thermal motion of the molecules. From (2) and (3) it can be seen that

$$w^2 = \gamma \frac{1}{3} \overline{c^2} = \frac{1}{3} [\overline{c^2} + (\gamma - 1)\overline{c^2}]. \tag{4}$$

If the acoustic disturbance is an isothermal process then the velocity of propagation w_T of such a disturbance will be given by

$$w_T^2 = \frac{1}{3} \overline{c^2} = \frac{1}{3} (\overline{c_x^2} + \overline{c_y^2} + \overline{c_z^2}) = \overline{c_x^2} \pm \overline{c_y^2} \pm \overline{c_z^2}. \tag{5}$$

(¹) In using the term "liquid" we shall always mean simple liquids as we hold that the properties essential for the liquid state occur in a simple liquid in an undisturbed form. By taking into consideration various side-effects such as association, solvation, hydrogen binding etc., we unnecessarily complicate the problem if we are only interested in the essence of the liquid state.

The isothermal disturbance thus propagates at a speed whose square is equal to the mean square of the component of the velocity of the thermal motion in the direction of propagation of the acoustic waves.

In the case of an adiabatic disturbance the mean square velocity increases. We then have

$$w^2 = \left(\frac{\partial p}{\partial \varrho}\right)_s = \frac{\partial}{\partial \varrho}\left(\frac{1}{3}\,\varrho\overline{c^2}\right)_s = \frac{1}{3}\left[\varrho\left(\frac{\partial \overline{c^2}}{\partial \varrho}\right)_s + \overline{c^2}\right] = \frac{1}{3}\left[\varrho\left(\frac{\partial \overline{c^2}}{\partial v}\right)_s \frac{\partial v}{\partial \varrho} + \overline{c^2}\right]. \tag{6}$$

In this expression we do not know the change in the mean square of the velocity during the adiabatic deformations $(\partial c^2/\partial v)_s$. It can however be determined by the following considerations.

It is known that the internal energy of one mole of a perfect gas is given by the expression

$$U = Nf\frac{1}{2}kT = Nf\frac{m\overline{c^2}}{6}, \tag{7}$$

where f denotes the number of degrees of freedom. We thus have

$$\left(\frac{\partial U}{\partial V}\right)_s = -p. \tag{8}$$

From (7) and (8) we obtain

$$Nf\frac{m}{6}\frac{\partial}{\partial V}(\overline{c^2})_s = \frac{1}{3}\,n\,m\overline{c^2},$$

and thus

$$\frac{\partial}{\partial V}(\overline{c^2})_s = \frac{2\overline{c^2}}{fV}. \tag{9}$$

Substituting (9) into (6) we obtain

$$w^2 = \frac{1}{3}\left[\frac{2}{f}\overline{c^2} + \overline{c^2}\right] = \frac{1}{3}\overline{c^2}\left[\frac{2}{f} + 1\right] = \ldots = \frac{1}{3}\overline{c^2}\gamma. \tag{10}$$

2. There is a widely held view that the liquid state is more similar to the solid state than to the gaseous state. At the same time it is stressed that liquids and solids have very similar densities. Furthermore, it is considered that:

(a) the short-range order in liquids is a remnant of the long-range order in crystals,

(b) the thermal motion of the molecules in liquids is similar to the thermal motion of the molecules in solids.

As we shall subsequently discuss these assumptions, and particularly their acoustic aspects, in section 3, some short remarks on the problem of the thermal motion of molecules (a one element solid) and the propagation of acoustic waves are needed.

It is generally considered that this problem is covered by the theory of the specific heats of a one element solid. It is assumed in this theory that a model of a lattice of coupled harmonic oscillators (one per atom) correctly describes the thermal motion. The internal energy is obtained accordingly by summing the quantized energies at all frequencies. An actual solution of the problem is obtained by the use of either Debye's method or the Bern-Kármán method.

Having reviewed briefly these well-known facts it should be stressed that — independent of the fundamental importance of both the acoustic theories of the specific heat — their significance for the problem of the velocity of acoustic waves and thermal motion should not be overestimated. The limitation arise for, among others, the following reasons:

(a) Using Debye's method we proceed from the assumption of an elastic continuum. In such a manner we thus immediately preclude the possibility of considering the elementary (molecular) mechanism of the transmission of an acoustic pulse.

(b) Using the Born-Kármán method we neglect the finite volume of the atoms. This leads consistently to an erroneous representation of the intermolecular forces, as may be seen from the following argument.

Let the volume of a solid be V, of this V_M accounts for the proper volume of the molecules themselves. Let us call $V_s = V - V_M$, the free volume. We then have

$$\frac{\partial V}{\partial p} = \frac{\partial V_s}{\partial p} + \frac{\partial V_M}{\partial p}, \quad \frac{1}{V}\frac{\partial V}{\partial p} = \frac{V_s}{V}\frac{1}{V_s}\frac{\partial V_s}{\partial p} + \frac{V_M}{V}\frac{1}{V_M}\frac{\partial V_M}{\partial p},$$

that is

$$\beta = \frac{V_s}{V}\beta_s + \frac{V_M}{V}\beta_M. \tag{11}$$

From formula (11) it is evident that the measured (effective) compressibility β_M differs considerably from the "real" intermolecular compressibility β_s. The second term on the right-hand side of the equation can usually be neglected.

3. A relation between the velocity of propagation of acoustic waves in liquids and the thermal motion of the molecules should be based on the information already available on the thermal motion of molecules in liquids. Unfortunately, such information is very scarce and thus no theory of the specific heat of a one element liquid has so far been elaborated.

Following FRENKEL [3] it has been suggested that the similar values of the specific heat c_v, of liquids and relevant solids in the neighbourhood of the solidification temperature, give evidence for the similarity of the thermal motion in both states. This information is too general for the present purpose since it conveys no clear idea as to whether the molecules are moving at a uniform speed while reflected from the walls of the cells formed by the closest molecules, or are vibrating sensu stricto, and are thus under the action of, for example harmonic, forces. However, the molecular mechanism of the propagation of acoustic waves in liquids depends on the nature of these motions. In the former case the propagation of an acoustic wave can to some extent be explained by reference to the "gas model", i.e. to the state presented in section 1. However, in the latter case use shoulds be made of the quasi-crystalline model.

Thus it can be clearly seen that even qualitative considerations concerning the elementary mechanism of the propagation of acoustic waves in liquids must be based on reliable information on the nature of the thermal motion of the molecules. It has been suggested that the existence of short range order in liquids points explicitly to the fact that an explanation of the manner in which acoustic waves propagate in liquids should be based on the quasi-crystalline model, the short range order being interpreted as an expression of the tendency of the intermolecular forces to develop crystalline structures. However, as long ago as 1922 **Gans** [4] showed that in systems of non-interacting rigid balls there is a distinct probability of finding the molecules at a definite distance from each other. This probability depends on amongst other factors the ratio V_s/V. From expression (11) it can be seen that the intermolecular "real" compressibility is considerably higher than the effective (measured) compressibility, than the assumption of a flat bottomed potential for the interacting forces of the molecules cannot be regarded as a course approximation. In assuming a flat potential bottom, i.e. assuming that the liquid molecules are moving freely from collision to collision, it can be supposed that the relationship between the wave propagation velocity and the mean velocity of thermal motion, substantiated in section 1, can also be used for a liquid [5].

However, this description is not satisfactory. If the liquid compressibility is considered to be exclusively of a kinetic nature, derived from the energy in a manner similar to that of the gas molecules, then by considerations of space filling, the relation

$$\beta = \frac{V_s}{V} \beta_s$$

should be satisfied, as can be seen from formula (11). Now the ratio V_s/V varies from approximately 1/5 to 1/10, and the liquid compressibility should thus be from 1/5 to 1/10 that of the gas compressibility. This obviously does not occur and it is therefore evident that even under the assumption of a flat potential well, the relationships derived in section 1 cannot be used for liquids. The main reason for this can be seen in the fact that the flat potential bottom lies below the axis of the abcissae, while the depth of the well depends also (under the condition of constant pressure that we are considering), on the temperature.

The physical conditions, represented by means of a geometrically simple potential are very complicated. It must be taken into consideration that it is not possible, in this case, to use the equipartition principle. The application of this principle requires that the energy of a molecule should be a linear homogeneous function of the squares of the position coordinates and of the momenta. It can be seen from the model that the liquid compressibility is both kinetic and potential. However, we do not know the way in which these two components combine to form the resultant compressibility. We can only make an estimate for subsequent use. We are of the opinion that the kinetic component of the intermolecular compressibility is considerably higher than the potential component, although the temperature dependence of the intermolecular compressibility is defined by the temperature dependence of the potential component. We thus can write

$$K_s = K_{sk} + K_{sp}, \tag{12}$$

where K_{sk} and K_{sp} denote the moduli of the kinetic and potential intermolecular compressibility, respectively.

Neglecting the compressibility of the molecules themselves, the measured compressibility β can, using formula (11), take the form

$$\beta = \frac{V_s \beta_s}{V}. \tag{13}$$

The question arises as to the relation of the change of the ratio V_s/V to the change in the compressibility β, and the dependence of this effect on temperature at constant pressure. It can be seen that

$$\frac{1}{\beta}\frac{\partial\beta}{\partial T} = \frac{1}{V_s}\frac{\partial V}{\partial T} - \frac{1}{V}\frac{\partial V}{\partial T} + \frac{1}{\beta_s}\frac{\partial\beta_s}{\partial T}$$

or, by neglecting the third term on the right-hand side of the above equation,

$$\frac{1}{\beta}\frac{\partial\beta}{\partial T} = \left(\frac{V}{V_s} - 1\right)\alpha, \tag{14}$$

where α denotes the volume expansion coefficient.

From formula (14) it is evident that the temperature dependence of the change in the measured compressibility β is defined almost exclusively by a change in the space filling. Table 1 contains numerical data of the relevant coefficients. From the table it can be seen, that for benzene, for example, $\beta^{-1}(\partial\beta/\partial T_p \times \alpha^{-1} \simeq 6$, in agreement with the values obtained by other methods (2).

---

(2) The values of the volumes of the actual molecules determined by various methods differ slightly from one to another because it is evident that the quantity to be measured is defined by the method of measurement. In this interpretation we consider that, for example, two values of the ratio V_s/V equal to 1/6 and 1/7, respectively, are in agreement.

Table 1. Thermal coefficients of some normal liquids

Name of liquid	$\frac{1}{\beta}\left(\frac{\partial\beta_T}{\partial T}\right)_p\times 10^4$ [deg^{-1}]	$\frac{1}{w}\left(\frac{\partial W}{\partial T}\right)_p\times 10^4$ [deg^{-1}]	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\times 10^4$ [deg^{-1}]	$\frac{1}{\gamma}\left(\frac{\partial\gamma}{\partial T}\right)_p\times 10^4$ [deg^{-1}]
Benzene	+74.6 [6]	−35.5 [7]	12.2 [8,9]	−7.4 [10] −6.6*
Carbon tetrachloride	+73.0 [6]	−33.7 [7]	12.2 [8,9]	−6.1 [10]
Ethyl ether	+99.2 [6]	−46.3 [7]	16.4 [8,9]	+2.5* −0.5 [10]
Carbon disulphide	+77.4 [6]	−27.9 [7]	12.0 [8,9]	+10.8 [10] +9.2*
Ethylo-benzene	+57.8 [11]	−28.4 [7]	10.1 [8,9]	−3.3*
Chloro-benzene	+57.3 [6]	−28.8 [7]	9.8 [8,9]	−8.6 [10] −3.8*
Cyclohexane	+78.1 [9]	−36.0 [7]	12.0 [8,9]	−9.8 [12]
Aminobenzene	+50.0 [6]	−24.4 [7]	8.5 [8,9]	−2.3 [8,9] −1.5*
Ethyl acetate	+88.5 [9]	−38.3 [7]	13.6 [8,9]	−2.4 [8,9]
n-pentane	+99.2 [9], [13]	−44.5 [7]	16.2 [13]	−5.4*
Nitrobenzene	+56.2 [11]	−22.4 [7]	8.3 [8]	+1.2 [11]
m-xylene	+67.3 [11]	−30.6 [7]	10.1 [8]	−1.8 [11]

* Author's calculations

The temperature coefficient of the velocity of sound,

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p=\left(2-\frac{V}{T_s}\right)\alpha\,\frac{1}{2},$$

is, as can be seen, expressed exclusively by a change in the volume. This fact should be stressed since, from a formal computation of the value

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p=\left[\alpha-\frac{1}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_p\right]\frac{1}{2}$$

(see Table 1), some workers conclude that a change in the coefficient of compressibility primarily accounts for the temperature change of the sound velocity. If the intermolecular compressibility is to be considered as a real measure of the elastic properties, it can be easily seen that almost the only reason for a temperature dependent sound velocity at a constant pressure is the change in volume.

4. In conclusion it can be said that if we consider only the effect of the temperature dependent change in volume at constant pressure, then we obtain:

(a) good agreement, as regards the sign and the absolute value, of the "measured" temperature coefficient of the liquid compressibility (³),

---

(³) In view of the slight difference in the numerical values of the ratio V_s/V obtained by different various methods the estimates presented above do not at present permit the isothermal and adiabatic compressibilities (cf. Table 1) to be descerned.

(b) good agreement, as regards the sign and the absolute value, of the temperature coefficient of the sound velocity, and that

(c) it can be accepted to a good approximation over the whole range of the liquid state that the intermolecular compressibility changes only very slightly with temperature, at constant pressure. The change in the "measured" compressibility is simulated by a change of volume.

The conclusions (a), (b) and (c) result from the assumption that the intermolecular compressibility of a liquid consists of a kinetic compressibility, which is independent of temperature at constant pressure, and of a potential compressibility which is considerably lower than the kinetic compressibility.

The relation between the velocity of the thermal translational motion of the molecules in a liquid and the sound velocity is more complex than the similar relation for perfect gases. The considerations presented in this paper are thus the first approximation of the dependencies between these quantities which as yet are undetermined.

References

[1] B.B. Kudriawcew, *Primienienije ultrazwukow pri issliedowaniji gazoobraznych wieszczestw*, Primienienije ultraakustiki k issliedowaniji wieszczestwa, MOPI, Moskwa, 4, 25 (1957).

[2] W.W. Riewienko, *O wywodie skorosti zwuka na osnowie molekularno-kinieticzeskoj tieoriji*, Akusticzeskij Żurnał, 5, 153 (1959).

[3] J. Frenkel, *Kinieticzeskaja tieorija żidkostiej*, Nauka, Leningrad 1975, 112.

[4] R. Gans, *Über den Abstand der Molekulen*, Phys. Zeitschr., 23, 108 (1922).

[5] J.F. Kincaid, H. Eyring, *Free volumes and free angle ratios of molecules in liquids*, The Journal of Chemical Physics, 6, 620 (1938).

[6] D. Tyrer, *Einige Beziehungen zwischen Kompressibilität und anderen physikalischen Eigenschaften von Flüssigkeiten*, Z. Phys. Chem., 37, 182 (1914).

[7] Landolt-Bornstein, *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, II.5, Molekularakustik, Springer-Verlag, (1967).

[8] Landolt-Bornstein, *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, II.1, Mechanisch-thermische Zustandsgrössen, Springer-Verlag, (1971).

[9] J. Timmermans, *Physico-chemical constants of pure organic compounds*, New York 1950.

[10] E.B. Freyer, J.C. Hubbard, D.H. Andrews, *Sonic studies of the physical properties of liquids*, Jour. Am. Chem. Soc., **51**, 759 (1929).

[11] International Critical Tables of Numerical Data, New York-London 1933.

[12] I.B. Rabinowicz, *Wlianije izotopiji na fizyko-chemiczeskije swojstwa żidkostiej*, Nauka, Moskwa 1968.

[13] N.B. Wargaftik, *Sprawocznik po tieplofiziczeskim swojstwam gazow i żidkostiej*, Nauka, Moskwa 1972.

Received on April 8th, 1977