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ULTRASONIC PROPAGATION IN LIQUIDS

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TECHNICAL REPORT NO. 5

JUNE 10, 1946

NDRC DIVISION 14

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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ULTRASONIC PROPAGATION IN LIQUIDS

II. THEORETICAL STUDY OF THE
FREE VOLUME MODEL OF THE
LIQUID STATE

by

C. Kittel

Abstract

The free volume theory of liquids is applied to problems con-
nected with sound propagation. The equation of state derived by Tonks
for assemblies of hard elastic spheres may be written $pV_a \cong 3NkT$, where
the available volume V_a is the difference between the actual volume and
the volume corresponding to the closest possible packing. It is shown
that the molar available volume is approximately given by the increase
in molar volume of a substance on heating from $0°K$ to the temperature
considered, so that the pictorial concept of the available volume has a
real physical basis. Using the Tonks equation expressions are derived
for the sound velocity and the temperature and pressure coefficients of
sound velocity. These expressions are compared with experimental results.
Expressions are also given for the cubic expansion coefficient and the
difference of the specific heats on the free volume model. The Herzfeld-
Rice derivation of the sound absorption caused by phase shifts in the
vibrational specific heat is carried through for the Tonks equation of
state. The temperature and pressure coefficients of sound absorption are
discussed. Remarks are made on the relation of molecular structure to sound
absorption.

Title page
17 numbered pages

ULTRASONIC PROPAGATION IN LIQUIDS: II. THEORETICAL STUDY OF THE FREE VOLUME MODEL OF THE LIQUID STATE

I. Introduction

The purpose of this paper is to describe the velocity and absorption of ultrasonic waves in liquids in terms of the free volume theory of liquids and the relaxation theory of absorption processes. It is emphasized at the beginning that simple models of liquids may not be expected to give close numerical agreement with observation. We should, however, require that the model give the correct order of magnitude of physical quantities and their variations. This test we propose to apply to the free volume theory of liquids. The implications of the theory with respect to the mechanical properties of liquids have not previously been considered, to the author's knowledge.

The important experimental facts regarding ultrasonic propagation in liquids are summarized below:

(a) The velocity of sound in a liquid is commonly of the order of five to ten times the velocity in the vapor at the same temperature. For example, the velocity of sound in liquid oxygen[1] at 90°K is 910 m/sec, while the velocity in oxygen vapor[2] at the same temperature is 180 m/sec.

(b) The temperature coefficient of sound velocity $c^{-1}(\partial c/\partial T)_p$ is of the order of -3×10^{-3} °C^{-1}; in gases the temperature coefficient is of the same order but is positive.

(c) The pressure coefficient of sound velocity $c^{-1}(\partial c/\partial p)_T$ is of the order of $+5 \times 10^{-10}$ cm^2/dyne.

(d) The absorption of sound waves in liquids usually exceeds the classical value calculated on the basis of ordinary viscosity losses; in the case of CS_2, the observed value is several thousand times greater than the classical value.

(e) The temperature coefficient of sound absorption $\alpha^{-1}(\partial \alpha/\partial T)_p$ is of the order of ± 0.01 °C^{-1}. Both positive and negative signs occur, whereas on classical theory the sign is always negative, as the viscosity has a negative temperature coefficient.

(f) The pressure coefficient of sound absorption $\alpha^{-1}(\partial \alpha/\partial p)_T$ is -6×10^{-10} cm^2/dyne for toluene, the only liquid for which a determination has been reported.

The two traditional concepts of the liquid state regard a liquid as either a very dense gas or else as a solid in which the long range order between the molecules has broken down. Both of these concepts account qualitatively for the two distinguishing properties of liquids; namely, that a liquid combines the small shear modulus characteristic of gases with the small compressibility

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1. Liepmann, H. W., Helv. Phys. Acta 9, 507 (1936).
2. van Itterbeek, A., and Mariëns, P., Physica 4, 207 (1937).

characteristic of solids. To explain in a convenient and natural manner the origin of other physical properties of liquids, such as fusion, viscosity, dielectric constant, density and solution effects, sometimes the gas and sometimes the solid point of view is used.

In understanding the propagation of sound in liquids the gas model is particularly suitable. It turns out that sound velocities can be predicted qualitatively from this model; and further, the absorption of sound in liquids can be related to the absorption processes in gases, which are fairly well understood. On the other hand, the absorption processes in solids are poorly explained at the present time.

II. Sound Velocity

The relationship between the velocity of sound in the liquid and gaseous states has been made plausible by the work of Eyring and his collaborators[3], who have given a simple and useful explanation of the relation in terms of the gas model. The relation is derived by Eyring in a qualitative way and is not quite correct; later on we shall consider a rigorous equation of state for this model from which the sound velocity can be calculated unambiguously.

Eyring pictures the sound wave as traveling with infinite velocity within a molecule and with gas kinetic velocities through the space between the molecules of the liquid (Fig. 1). This space is termed the "available volume."
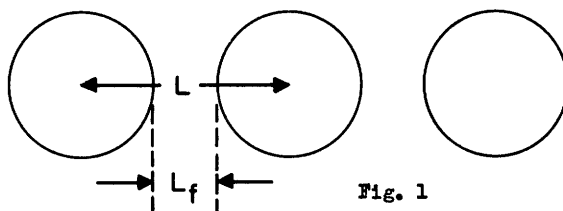

Fig. 1

The molecules effectively short-circuit a part of the path of the sound wave. If the intermolecular separation is L and the "free length" L_f, the molecules short-circuit all but the fraction L_f/L of the path. The sound velocity in the liquid is then given by

$$c_{liq} = (L/L_f) \, c_{gas} \tag{1}$$

where kinetic theory gives

$$c_{gas}^2 = \gamma_{gas}(RT/M) \tag{2}$$

with $\gamma_{gas} = C_p/C_v$, the ratio of specific heats in the gas.

The reasoning leading to Eq. (1) from the specified properties of the model is not rigorous. It is possible to derive a rigorous equation of state

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3. Eyring, H. and Hirschfelder, J. O., J. Phys. Chem. **41**, 249 (1937); Kincaid, J. F., and Eyring, H., J. Chem. Phys. **5**, 587 (1937), **6**, 620 (1938); Hirschfelder, J. O., Stevenson, D. P. and Eyring, H., J. Chem. Phys. **5**, 896 (1937).

- 2 -

for the free volume model, and this has been done by Tonks[4] in a paper on the statistical mechanics of assemblies of hard elastic spheres. Recently, Rice[5] and Frank[6] have drawn attention to the importance of Tonks' work in relation to theories of the liquid state and have considered some of the thermodynamic consequences of the model.

The Tonks Equation of State

The Tonks equation of state for a classical three-dimensional gas of hard elastic spheres in the limit of close packing is

$$pV(1 - \Theta^{1/3}) = NkT \tag{3}$$

where Θ is the packing fraction with respect to the closest possible packing. We have $\Theta = V_0/V = 1 - (V_a/V)$, where V_0 is the minimum possible volume and V_a the available volume, is defined as $V - V_0$. For close packing as in a liquid

$$1 - \Theta^{1/3} = V_a/3V \quad . \tag{4}$$

In this approximation the equation of state becomes

$$pV_a = 3NkT \quad . \tag{5}$$

The form

$$p = (3RT/M)\rho_1 \quad . \tag{6}$$

where

$$\frac{1}{\rho_1} = \frac{1}{\rho} - \frac{1}{\rho_0} \tag{7}$$

is also useful. Here ρ_0 is the density corresponding to the closest possible packing.

The remarkable and simple form Eq. (5) which the equation of state assumes makes it easy to deduce various properties of the model. This form does not appear to have been stated explicitly before.

Before using Eq. (5) we shall consider its physical significance as applied to actual liquids. The pressure p is understood to be made up of two terms, one representing the effect of the attractive intermolecular forces and the other representing the external applied pressure. Let us imagine the intermolecular potential energy to be altered by removing the attractive part of the potential while leaving the repulsive part; the "internal pressure" may then be regarded as the pressure which would compress the system to the volume actually occupied. The implied relationship between internal pressure and temperature is plausible on the free volume model, since the internal pressure does balance the kinetic pressure of the molecules regarded as moving freely within the volume. It is not obvious, however, that the thermal expansion at constant external pressure should be given correctly by the Tonks equation. This amounts to the assumption that the balancing pressure due to potential energy is independent of the volume. The experimental checks of Eqs. (10) and (15) below may be taken as

4. Tonks, L., Phys. Rev. 50, 955 (1936).
5. Rice, O. K., J. Chem. Phys. 10, 653 (1942); 12, 1 (1944); 14, 335 (1946).
6. Frank, H. S., J. Chem. Phys. 13, 478 (1945).

justification of this assumption within the generous limits of error of this paper.

It is important to note that what is called the _available volume_ V_a in this paper is not identical with the _free volume_ V_f as customarily defined, although the same model is used. The available volume is the difference between the actual volume and the minimum possible volume and is given by $V(1 - 0)$; the free volume is defined[3,4,5] as the volume of possible motion of the center of a single molecule, and is given, per mole, by $V(1 - 0^{1/3})^3$. For close packing $V_f = V_a(V_a^2/27V^2)$. The available volume is a natural quantity to use in the equation of state; the free volume is a natural quantity to use in the partition function. The numerical values of the free volume given by Kincaid and Eyring are defined in terms of an approximate equation for sound velocity in liquids; the use of the more exact equation below will necessitate small changes in the numerical values.

The velocity of sound is given in the usual way by

$$c^2 = (\partial p/\partial \rho)_s = (\rho_1/\rho)^2(\partial p/\partial \rho_1)_s .$$

so that

$$c_{liq} = \left(\frac{V}{V_a}\right)\left(\frac{C_V + 3R}{C_V}\right)^{\frac{1}{2}}\left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{V}{V_a}\right)\left(\frac{3\gamma_{liq}}{\gamma_{gas}}\right)^{\frac{1}{2}} c_{gas} , \qquad (8)$$

where γ_{liq} has been set equal to $(C_V + 3R)/C_V$, in accordance with Eq. (16). It may be noted that C_{liq} and C_{gas} are to be taken at the same temperature.

Calculation of Sound Velocity

It is not practical to give a direct comparison of Eq. (8) with measurements of sound velocity in liquids since there is no really accurate independent method for determining the available or the free volume (see, however, Kincaid and Eyring[3]). We may, however, make an estimate of the available volume by considering the increase in volume between absolute zero and the temperature concerned.

If we are to take the free volume picture seriously there should exist some correlation between the _molar available volume_ as calculated using Eq. (8) from sound velocity measurements at room temperature and the actual _increase in molar volume_ of the material between 0 °K and room temperature. Such a relationship does in fact exist.

We write

$$V = V_0 + V_a , \qquad (9)$$

where V_0 is the molar volume corresponding to the closest possible packing in a geometrical sense, and V_a is the molar available volume. Let

$$V_a = V_1 + V_2 + V_3 , \qquad (10)$$

where:

-4-

V_1 = molar volume change on heating solid from 0 °K to the melting point;

V_2 = molar volume change on fusion;

V_3 = molar volume change on heating liquid from melting point to the temperature concerned.

Unfortunately, the expansion data from which the V's can be calculated are inadequate, and a certain amount of guesswork enters into any estimate of the available volume based on the thermal expansion data. A comparison of available volumes as calculated from sound velocity and thermal expansion data is given in Table 1. The agreement is as good as can be expected.

This evidence shows that the pictorial concept of the available volume has a real physical basis. It is in principle possible to give an approximate calculation of sound velocities from thermal expansion data alone.

Table 1

Comparison of Available Volume as Calculated from Thermal Expansion and Sound Velocity Data for 300 °K

| | Available Volume Increments cc/mole | | | Calculated Available Volume in cc/mole derived from: | |
| | V_1 0°K to Melting Point | V_2 Fusion Volume Change | V_3 Melting Point to 300 °K | Thermal Expansion [Eq.(10)] | Sound Velocity [Eq.(8)] |
Substance					
$CHBr_3$	8	10	(2)	20	19
CCl_4	11	4	5	20	28
Benzene	10	10.3	2.5	23	25

Notes: Thermal expansion and fusion volume change data are from the Landolt-Bornstein tables. V_1 is based on a linear extrapolation of measured values obtaining between 80 °K and 200 °K; this overestimates the change at low temperatures (since by the Nernst theorem the expansion coefficient must vanish at 0 °K) and underestimates the change at high temperatures. No allowance has been made for any effective "zero-point" available volume.

Temperature Coefficient of Sound Velocity

We may determine the available volume from the sound velocity at one temperature and using this value compare the calculated with the experimental value of the temperature coefficient of sound velocity $c^{-1}(\partial c/\partial T)_p$. The velocity of sound in liquids has usually a _negative_ temperature coefficient; that is, the velocity decreases with increasing temperature. This is contrary to the position with gases, which show a positive temperature coefficient. In terms of the free volume picture of a liquid the effect of the increased distance the molecules have to travel, owing to thermal expansion, dominates the increase in molecular velocity.

We may derive an expression for the temperature coefficient of sound velocity on the free volume model. From Eqs. (2) and (8),

$$c^{-1}(\partial c/\partial T)_p = r^{-1}(\partial r/\partial T)_p - r_a^{-1}(\partial r_a/\partial T)_p + (1/2T) + (1/2 \gamma_{liq})(\partial \gamma_{liq}/\partial T)_p. \quad (11)$$

where the change in $\mathcal{T}_{gas}$ is neglected. Now ΔV is essentially equal to ΔV_a, since the expansion of the molecules themselves may be neglected in comparison with the expansion of the available volume. Writing A for the temperature coefficient of cubic expansion[7], we have

$$c^{-1}(\partial c/\partial T)_p = (1/2T) - A[(V/V_a) - 1] + (2\mathcal{T}_{liq})^{-1}(\partial \mathcal{T}_{liq}/\partial T)_p \; ; \quad (12)$$

this equation may be written in terms of observables by using Eq. (8):

$$c^{-1}(\partial c/\partial T)_p = (1/2T) - A\left\{\left(\frac{\mathcal{T}_{gas}}{3\mathcal{T}_{liq}}\right)^{1/2}\left(\frac{c_{liq}}{c_{gas}}\right) - 1\right\} + (2\mathcal{T}_{liq})^{-1}(\partial \mathcal{T}_{liq}/\partial T)_p. \quad (13)$$

A detailed comparison of experimental values of the temperature coefficient with calculated values from Eq. (13) is given in Table 2. The purpose in giving this and other tables is not in order to emphasize specific cases of agreement or disagreement, but rather to exhibit the consequences of the free volume equation of state. It seems likely that Eq. (5) will find wide use in problems of the liquid state, so that it is well to understand some of the limitations and capabilities of the equation.

It is seen that the calculated values are in order of magnitude agreement with the measurements, but that the calculated values underestimate the value somewhat. It is significant that the order of magnitude of the results derived from the simple model of hard elastic spheres is correct, and that the existence of an "anomalous" positive temperature coefficient for water is correctly indicated by the theory.

Pressure Coefficient of Sound Velocity

It is of interest to consider the pressure coefficient of sound velocity $c^{-1}(\partial c/\partial p)_T$. Using the Tonks equation we find

$$c^{-1}(\partial c/\partial p)_T = \beta_T[(V/V_a) - 1] = \beta_T\left\{\left(\frac{\mathcal{T}_{gas}}{3\mathcal{T}_{liq}}\right)^{1/2}\left(\frac{c_{liq}}{c_{gas}}\right) - 1\right\} , \quad (14)$$

where β_T is the isothermal compressibility and is equal to $\mathcal{T}_{liq}$ times the adiabatic compressibility. The variation of $\mathcal{T}_{liq}$ with pressure should probably be considered, but relevant data could not be found. A comparison of experimental with theoretical values is given in Table 3, from which it appears that the predictions of the theory are slightly low. The positive sign of the pressure coefficient arises because the sound path through the available volume is shortened by compressing the volume. The fact that both the temperature and pressure coefficients of velocity as calculated are somewhat low suggest that the available volume is overestimated by the sound velocity equation.

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7. The conventional symbol for both the cubic expansion coefficient and the pressure attenuation coefficient is α; in this paper A is used for the cubic expansion coefficient to avoid confusion.

Table 2

Temperature Coefficient of Sound Velocity $c^{-1}(\partial c/\partial T)_p$

Comparison of Eq.(13) Deduced from the Tonks Equation with Experimental Values

(Data for T = 300 °K)

Substance	C_p/C_v gas	C_p/C_v liq.	Cubic Exp. Coef. °C^{-1}	$\dfrac{c_{liq}}{c_{gas}}$	V/V_g	$\gamma_{liq}^{-1}(\partial\gamma_{liq}/\partial T)_p$	Temp. Coef. of Sound Velocity °C^{-1} Exper.	Temp. Coef. of Sound Velocity °C^{-1} Calc.
Amyl Acetate	(1.2)	1.33	1.16 × 10^{-3}	7.47	4.1	?	-4.8 × 10^{-3}	-1.9 × 10^{-3}
Benzene	1.08	1.44	1.24	7.00	3.5	-0.6 × 10^{-3}	-3.6	-1.7
Carbon Disulfide	1.24	1.56	1.20	5.54	2.8	+1.2	-2.8	-0.0
Carbon Tetrachloride	1.08	1.46	1.23	6.93	3.4	-0.5	-3.4	-1.6
Chlorobenzene	(1.2)	1.35	0.98	7.42	4.0	-0.3	-2.9	-1.7
Ethyl Alcohol	1.11	1.18	1.10	6.12	3.4	-0.2	-3.0	-1.1
Heptane	(1.2)	1.19	1.24	6.35	3.6	?	-3.7	-1.6
Methyl Iodide	(1.2)	(1.3)	1.24	5.40	3.1	?	-3.1	-0.9
Nitrobenzene	(1.2)	(1.3)	0.83	8.96	5.0	?	-2.3	-1.6
Toluene	(1.2)	1.34	1.1	6.92	3.8	-1.5	-3.3	-2.1
Water	1.32	1.00	0.117	3.50	2.3	?	+1.7	+1.5

Notes: Values of C_p/C_v in parentheses are assigned arbitrarily; other values from E. Hiedemann, Ultraschallforschung (Walter de Gruyter and Co., Berlin, 1939). Cubic expansion coefficients are from the Landolt-Bornstein tables. Temperature variation of γ_{liq} from E. B. Freyer, J. C. Hubbard and D. H. Andrews, J. Am. Chem. Soc. 51, 759 (1929). Experimental values of the temperature coefficient of sound velocity are taken from Hiedemann's book and from the preceding paper by J. R. Pellam and J. K. Galt. The values used for c_{gas} are calculated from Eq. (2).

Table 3

Pressure Coefficient of Sound Velocity $c^{-1}(\partial c/\partial p)_T$

Comparison of Calculated Values from Eq.(14) with Experimental Values

Substance	Adiabatic Compressibility $cm^2/dyne$	Pressure Coefficient of Sound Velocity $cm^2/dyne$	
		Experimental	Calculated
Carbon Disulfide	59.0×10^{-12}	3.7×10^{-10}	1.7×10^{-10}
Carbon Tetrachloride	74.5	4.7	2.7
Ether	138.7	7.7	3.1
Ethyl Bromide	88.1	5.7	2.1
Methyl Acetate	80.9	2.7	2.0
Benzene	64.9	3.1	2.3
Toluene	68.3	3.2	2.7

Notes: Values of the adiabatic compressibility are from Hiedemann's book. Experimental values of the pressure coefficient of sound velocity are from J. C. Swanson, J. Chem. Phys. **2**, 689 (1934), except for the value for methyl acetate, which is from P. Biquard, Comptes rendus (Paris) **206**, 897 (1938).

III. Discussion of Free Volume Theory

It is appropriate at this point to discuss the basis for the application of the Tonks equation of state to actual liquids. Four main assumptions underlie this application:

(a) It is assumed that the internal structure of a molecule is "hard" – that is, the internal compressibility of a molecule is neglected in comparison with the compressibility of the system as a whole. This assumption is justifiable.[*]

(b) It is assumed that the molecules are spherical. It should be possible to generalize the derivation of the equation of state to describe other shapes.

(c) It is assumed that the compressibility of the molecules with respect to each other – that is, the intermolecular compressibility – is purely kinetic in origin. The repulsive forces are imagined to rise sharply at the

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[*] The internal compressibility of a molecule β_{mol} is of the order of L/k, where L is the length of the molecule and k is the force constant. The force constant is given by $k = (2\pi f)^2 m$, where the frequency f is a fundamental vibration frequency of the molecule and is of the order of 1000 cm^{-1} or 3×10^{13} cps; m is the reduced mass of the molecule and is of the order of 3×10^{-23} gm for a light molecule. With these values $k \sim 10^6$ dynes/cm, so that $\beta_{mol} \sim 10^{-14} cm^2/dyne$, which is to be compared with $\beta_{gas} \sim 10^{-10} cm^2/dyne$ under the equivalent pressures obtaining in a liquid.

boundary of the hard sphere. This is quite a drastic assumption.

(d) It is assumed that the internal pressure arising from the attractive intermolecular forces is approximately independent of volume. This is also a drastic assumption.

(e) The Tonks derivation is based on classical mechanics, and no account is given of quantum effects. It is almost certain that quantum effects are of considerable importance in liquids, since the spacing between the energy levels of a molecule confined within its own free volume is of the order of kT for room temperature.[8]

In the light of the assumptions which have been made, it is of interest to consider further consequences of the Tonks equation. We have already seen that the equation leads to values of the temperature and pressure coefficients of sound velocity which are correct to within an order of magnitude at least.

Thermal Expansion Coefficient

The measure of agreement with experiment attained by the calculated values of the temperature coefficient of velocity may be attributed in part to the use of experimental values of the cubical expansion coefficient when substituting in Eq. (13) to obtain the results displayed in Table 2; this is particularly true with respect to water. We may, however, calculate the cubical expansion coefficient from the Tonks equation of state, obtaining

$$A = V^{-1}(\partial V/\partial T)_p = (V_a/V)(1/T) \tag{15}$$

A comparison of experimental with theoretical values is given in Table 4. The agreement is excellent for the organic liquids, but is poor for water and mecury,

Table 4

Cubical Expansion Coefficient

Comparison of Calculated Values from Eq. (13) with Experimental Values

$$V^{-1}(\partial V/\partial T)_p \text{ in } °C^{-1}$$

Substance	V/V_a	Cubical Expansion Coefficient Experimental	Calculated
Benzene	3.5	1.24×10^{-3}	0.95×10^{-3}
Carbon Disulfide	2.8	1.20	1.19
Carbon Tetrachloride	3.4	1.23	0.98
Chlorobenzene	4.0	0.98	0.84
Ethyl Alcohol	3.4	1.10	0.98
Mercury	6.4	0.18	0.52
Methyl Iodide	3.1	1.24	1.07
Water	2.3	0.12	1.45
Water (400 °K)	(2.3)	0.97	(1.1)

Notes: The data are for $T = 300$ °K. The values of the ratio of the volume to the free volume (V/V_a) are from Table 2.

as might be expected. We have neglected entirely the role of the metallic electrons, so that the present discussion is often inapplicable to liquid metals. Water is

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8. Bartholomé E., and Eucken, A., Trans. Far. Soc. 33, 45 (1937).

anomalous in general behavior at room temperature and below, but near the boiling point the calculated value of the cubic expansion coefficient is in good agreement with experiment.

Difference of Specific Heats $(C_p - C_v)$

Using Eq. (5) we may compute the difference $(C_p - C_v)$ for the Tonks equation, finding

$$C_p - C_v = p(\partial V_a/\partial T)_p = 3R \tag{16}$$

instead of simply R which obtains for an ideal gas. A comparison is given in Table 5 of experimental with theoretical values of the difference $(C_p - C_v)$.

Table 5

Comparison of Experimental Values of $(C_p - C_v)$ with Calculated Values from Eq.(16)

Substance	C_p Expt.	C_p/C_v Expt.	$(C_p - C_v)$ cal/mole/°C	
			Expt.	Calc.
Argon (87°K)	10.0	2.2	5.5	6
Oxygen (90°K)	13.0	1.7	5.3	6
Nitrogen (76°K)	13.6	2.0	6.6	6
Hydrogen (20°K)	6.9	1.5	2.5	6
Benzene	31.6	1.44	9.7	6
Carbon Tetrachloride	30.7	1.46	9.7	6
Ether	40.6	1.33	10.0	6
Ethyl Alcohol	27.	1.18	4.2	6
n-Heptane	49.	1.19	7.8	6
n-Propyl Alc.	35.6	1.16	5.0	6
Toluene	37.8	1.34	10.0	6

Notes: The data are for 300°K unless otherwise specified. Experimental values of C_p/C_v are from L. Bergmann, Der Ultraschall (Edwards Bros. reprint, Ann Arbor, 1944)
The agreement in the case of the liquefied gases is good except for the case of hydrogen, where quantum effects are of importance. For the organic liquids the calculated $(C_p - C_v)$ of 6 cal/mole/°C is generally low. With regard to C_v, one might expect on the basis of the free volume model that C_v would be equal in the liquid and gaseous states at the same temperature. It is well known[8] that C_v is greater in the liquid state, however.

IV. Sound Absorption

The two principal mechanisms responsible for the absorption of sound in liquids are the ordinary shearing viscosity and the energy loss associated with incomplete excitation of vibrational energy states of the molecules. In many liquids the latter mechanism is the dominant cause of attenuation. A detailed bibliography of the literature concerned with incomplete vibrational excitation in gases has been given by Richards.[9] The theory developed for gases was first

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9. Richards, W. T., Rev. Mod. Phys. 11, 36 (1939).

applied to liquids by Mandelstam and Leontovic[10], and later extended by Kneser[11].
Herzfeld[12] has given an interesting discussion of absorption in liquids, while
Tisza[13] has considered the important implications of the subject with respect to
the hydrodynamical equations.

The program of this section is to give a physical order-of-magnitude
estimate of the maximum absorption expected from relaxation processes; to go through
a detailed calculation of the absorption for the Tonks equation of state; to con-
sider the temperature and pressure coefficients of absorption; and, finally, to
discuss the relation between sound absorption and molecular structure.

It is possible to make a simple estimate of the maximum absorption
caused by relaxation of a vibrational mode. The work done by the compressional
cycle of a sound wave is of the order of $\Delta p \Delta V$. Now $\Delta p/p = -\Delta V/V + \Delta T/T$, for an
ideal gas where the first term on the right represents "mechanical" effects and
the second term "thermal" effects of the pressure. For an adiabatic process the
ratio of the thermal term to the mechanical term is $(\gamma - 1)$, where γ is the ratio
of the specific heats. Let C_i be the specific heat associated with the relaxing
degree of freedom; then C_i/C_v represents the fraction of thermal energy in the
mode concerned, and $(C_i/C_v)(\gamma - 1)/\gamma$ is an approximate upper limit to the
fraction of the total energy of the sound wave dissipated in one cycle. We should,
of course, find absorptions of this order of magnitude only in the neighborhood of
the relaxation frequency characterizing the exchange of energy between translational
and vibrational degrees of freedom.

Let us compare this estimate of the peak absorption with some ex-
perimental values. For CO_2 gas we have $(\gamma - 1)/\gamma \sim 0.23$, and $C_i/C_v \sim 0.3$, so
that about 0.07 of the energy is dissipated per cycle. This means that the in-
tensity is down $1/e$ in about 14 wave lengths; using data for high frequencies we
should estimate 8 wave lengths. Measurements by Fricke[14] show that at the re-
laxation frequency of 20 kc/sec the intensity is down by $1/e$ in about 4 wave
lengths, indicating that our order of magnitude estimate is generally correct. The
famous example of a highly absorbing low viscosity liquid is CS_2, for which the
measured absorption[15] at 1 mc/sec is about 2000 times the classical value as cal-
culated from viscosity and heat conduction losses alone; yet at this frequency the
intensity is only down by $1/e$ in 50 wave lengths. At 7 mc/sec the intensity[16] is
down by $1/e$ in about 12 wave lengths; this value appears quite reasonable in the
light of the above estimates.

Absorption in Liquids on Free Volume Model

It is instructive to calculate the absorption in detail for the
free volume model of the liquid state, applying the method of Herzfeld and Rice[17]

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to the Tonks equation of state, Eq. (5). In a sense the calculation is but a formal extension of the treatment of absorption in gasses developed by Herzfeld and Rice, and others. Let C_1 be the specific heat of the relaxing mode of vibration, and C_e the specific heat of all the other degrees of freedom of the molecule. Let T' denote the effective temperature of the energy associated with C_1, and T the temperature associated with C_e. Losses owing to ordinary viscosity and heat conduction are not considered; it can be shown that these are additive to the first approximation.

From the Tonks equation of state,

$$p = 3RT\rho_1/M \quad ; \quad (1/\rho_1) = (1/\rho) - (1/\rho_0) . \tag{17}$$

The force equation gives

$$\partial u/\partial t = - (1/\rho)(\partial p/\partial x) = - (3RT/M)(\rho_1/\rho)[(\partial \ln T/\partial x) + (\partial \ln \rho_1/\partial x)] , \tag{18}$$

while the conservation equation is

$$\partial \ln \rho/\partial t = - \partial u/\partial x = (\rho/\rho_1)(\partial \ln \rho_1/\partial t). \tag{19}$$

From the first law of thermodynamics

$$C_e(\partial T/\partial t) + C_1(\partial T'/\partial t) = (pM/\rho_1^2)(\partial \rho_1/\partial t). \tag{20}$$

The relaxation time constant τ' is introduced* through the equation

$$C_1(\partial T'/\partial t) = C_1(T - T')/\tau' . \tag{21}$$

We consider small changes in ρ_1, T and T', and suppose that the small changes are of the form $\exp[j(\omega t - kx)]$, where $k = k_1 - jk_2$. On substituting in Eqs. (17) through (21) we find an expression for k^2. For the technique of the calculation Herzfeld and Rice may be consulted. The imaginary part of k^2 is $-2k_1 k_2$, where

$$2k_1 k_2 = \omega^2(M/3RT)(\rho/\rho_1)^2 \left\{ \frac{\omega \tau}{1 + (\omega \tau)^2} \cdot \frac{\gamma^\infty - \gamma^0}{\gamma^0 \gamma^\infty} \right\} . \tag{22}$$

Here $\tau = \tau'(C_1/C_v^0)(\gamma^\infty/\gamma^0)$; $\gamma^0 = C_p^0/C_v^0$; $\gamma^\infty = C_p^\infty/C_v^\infty$. The low frequency specific heat C_v^0 is given by $C_1 + C_e$, while the high frequency specific heat C_v^∞ is simply C_e.

Now $k_1 \cong \omega/c_{liq}$, where the sound velocity c_{liq} is given by Eq. (8). Also, $k_2 = \alpha$, where α is the ordinary pressure attenuation coefficient in the expression $p = p_0 \exp[-\alpha x]$ for the damping of a plane wave. We have finally

$$\alpha = (\pi f^2/c_{liq}) \left\{ \frac{3R}{C_p^\infty} \frac{C_1}{C_v^0} \frac{f_0}{f^2 + f_0^2} \right\} \tag{23}$$

where $f = \omega/2\pi$ and $f_0 = 1/2\pi\tau$; here $C_p - C_v = 3R$ from Eq. (16).

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* For simplicity all of the modes of internal motion are supposed to relax at the same frequency, in which case C_1 includes the whole of the vibrational specific heat.

The maximum absorption per wave length occurs when $f = f_0$ and is given by

$$(c_{liq}/f)\alpha_{max} = \frac{\pi}{2} \frac{C_p - C_v}{C_p^{\infty}} \frac{C_1}{C_v^0} , \qquad (24)$$

which is of the same form as the previous estimate reached by a qualitative argument.

At low frequencies $(f \ll f_0)$ we have

$$\alpha = f^2(\pi/f_0 c_{liq}) \frac{C_p - C_v}{C_p^{\infty}} \frac{C_1}{C_v^0} , \qquad (25)$$

so that at low frequencies α/f^2 is constant for the attenuation caused by the relaxation mechanism, just as for viscosity and heat conduction. These results are in agreement with those of Kneser and Herzfeld, when slight differences in definitions are taken into account.

Temperature Coefficient of Sound Attenuation

Experimental determinations of the temperature coefficient of attenuation in different liquids show both positive and negative values. Where relaxation is a minor factor, a negative coefficient is found owing to the decrease in viscosity with increasing temperature. Where relaxation is the predominant factor a positive coefficient is expected when the frequency is above the relaxation frequency, and a negative coefficient when the frequency is below the relaxation frequency. This is because a rise in temperature increases the probability of energy transfer and thus increases the relaxation frequency. If $f > f_0$, an increase in f_0 brings the region of maximum absorption nearer to the measurement frequency; the opposite holds if $f < f_0$. The actual situation, however, may be more complicated.

Considering only relaxation losses we find from Eq. (23):

$$\alpha^{-1}(\partial\alpha/\partial T)_p \cong \pm f_0^{-1}(\partial f_0/\partial T)_p + C_1^{-1}(\partial C_1/\partial T)_p - 2C_v^{-1}(\partial C_v/\partial T)_p - c_{liq}^{-1}(\partial c_{liq}/\partial T)_p, \quad (26)$$

where the plus sign before the term $f_0^{-1}(\partial f_0/\partial T)_p$ applies to the case $f \gg f_0$, and the minus sign applies when $f \ll f_0$. The intermediate case is more complicated. Consider now the magnitude of the term in $f_0^{-1}(\partial f_0/\partial T)_p$: Landau and Teller[18] shown that under certain assumptions

$$f_0 \propto \exp[-3(\pi a \nu)^{2/3}(M/2kT)^{1/3}] , \qquad (27)$$

where a is the atomic radius, M the mass of the molecule, and ν the frequency of the vibrational mode. The exponential factor gives essentially the probability of exchange of vibrational and translational energy in a collision, and comes out to be of the order of 10^{-4} to 10^{-6}, in agreement with the experimental results for gases, where a collision frequency of the order of 10^{10} collisions per second is associated with relaxation frequencies of the order of 10^5 cycles per second. From Eq. (27) we have

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18. Landau, L. and Teller, E., Phys. Zeit. d. Sow. <u>10</u>, 34 (1936); cf. Zener, C., Phys. Rev. <u>38</u>, 277 (1931).

$$f_0^{-1}(\partial f_0/\partial T)_p = q/3T \ , \tag{28}$$

where q is the argument of the exponential factor in the above equation. Since q is of the order of 10, we have $f_0^{-1}(\partial f_0/\partial T)_p \sim 10^{-2}$.

Let us consider the order of magnitude of the other terms in Eq. (26). The term arising from c_{11q} is of the order of 3×10^{-3} and may usually be neglected. The two terms in the specific heat may be combined in one, since $\Delta C_v = \Delta C_1$, giving $(\partial C_1/\partial T)_p (C_1^{-1} - 2C_v^{-1})$. Since the specific heat C_1 usually corresponds to a vibration, it is given by an Einstein function. The relative slope of an Einstein function varies from very steep at low temperatures to flat at high temperatures. For molecules containing at least two non-hydrogen atoms, we are up near the flat part of the curve at room temperature and the contribution of the change in specific heat to $\alpha^{-1}(\partial \alpha/\partial T)_p$ will be of the order of 5×10^{-3} or less. It therefore appears that the term arising from f_0 often may be the most important single contribution; in some cases, however, the term in the specific heat may be significant.

In liquids for which the viscosity is a major factor contributing to the attenuation, a term arising from η of the order of 10^{-2} must be considered. Including viscosity, the attenuation α as given by Eq. (23) is increased by the additive Stokes term $8\pi^2 f^2 \eta /3c^3 \rho$.

Measurements of the temperature coefficient of absorption have been reported by Pellam and Galt[19], Bazulin[20], Sorenson[21], Baumgardt[22] and Hunter[23]. An interpretation of the results of Pellam and Galt is given in Table 6.

Study of the table suggests that the temperature coefficient of sound absorption is a useful quantity in the study of molecular relaxation times. The indications are not always unambiguous, but in the absence of more complete experimental knowledge of the acoustic absorption spectrum of liquids the temperature coefficient provides pertinent information.

Pressure Coefficient of Sound Attenuation

The pressure coefficient of sound attenuation in toluene has been determined by Biquard[24] who measured the absorption at 7 mc/sec between pressures of 1 to 500 atm, giving $\alpha^{-1}(\partial \alpha/\partial p)_T = 6 \times 10^{-10}$ cm^2/dyne. At one atmosphere $\alpha/f^2 = 80 \times 10^{-17}$ sec^{2}cm^{-1}, as compared with the classical value 8×10^{-17}, suggesting that the principal part of the absorption may be ascribed to relaxation processes. On the assumption that $f \ll f_0$ and that changes in specific heat may be neglected, we have from Eq. (25)

$$\alpha^{-1}(\partial \alpha/\partial p)_T = - f_0^{-1}(\partial f_0/\partial p)_T - c^{-1}(\partial c/\partial p)_T \tag{29}$$

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19. Pellam, J. R. and Galt, J. K., "Ultrasonic Propagation In Liquids, Part I. Application of Pulse Technique to Velocity and Absorption Measurements at 15 mg," R. L. E. Technical Report 4.
20. Bazulin, P., C. R. (Doklady) Acad. Sci. URSS 14, 273 (1937).
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22. Baumgardt, E., Comptes Rendus (Paris) 202, 203 (1936).
23. Hunter, J. L., J. Acous. Soc. Am. 13, 36 (1941).
24. Biquard, P., Rev. d'Acoustique 8, 130 (1939).

Table 6

Temperature Coefficient of Sound Absorption

Interpretation of Results in Terms of Eq.(26) - Frequency 15 mc/sec.

Substance	Temp. Coef. $\alpha^{-1}(\partial\alpha/\partial T)_p$ °C^{-1}	$\frac{\alpha_{exper}}{\alpha_{classical}}$	Tentative Interpretation
Ethyl Bromide	+ 0.010	7	Dominant factor is change in f_o, the relaxation frequency. $f_o < 15$ mc/sec.
Methyl Iodide	+ 0.0087	30	Fundamental vibrational frequency of CH_3I molecule is fairly low (534 cm^{-1}), so that specific heat change is not important; f_o is dominant factor. $f_o < 15$ mc/sec.
Methyl Alcohol	– 0.011	3	Change in viscosity contributes only –0.004; velocity contributes +0.003; specific heat term is positive, so that at least –0.010 must be accounted for by f_o change. $f_o \gg 15$ mc/sec, in agreement with Herzfeld[12], who concludes on other grounds that $f_o \sim 3 \times 10^4$ mc/sec.
n–Propyl Alcohol	– 0.0086	2	As for methyl alcohol, $f_o \gg 15$ mc/sec.
n–Amyl Alcohol	– 0.014	1.5	Changes in both viscosity and f_o are probably effective here. The absorption is nearly classical. $f_o \gg 15$ mc/sec.
Benzene	+ 0.011	90.	The evidence of the temperature coefficient of absorption is that $f_o < 15$ mc/sec, yet Herzfeld indicates that $f_o \sim 2000$ mc/sec. It is possible that these figures represent two different relaxation modes, the mode with a weak absorption peak near 10 mc/sec having a predominant effect on the temperature coefficient. Such a peak is suggested by a plot of α vs f based on collected results. Kneser[11] gives $f_o > 55$ mc/sec.

Now f_o at constant temperature is proportional to the collision frequency, so that

$$f_o^{-1}(\partial f_o/\partial p)_T = L_f^{-1}(\partial L_f/\partial p)_T = - (V/3V_a)\beta_T , \qquad (30)$$

where L_f is the free length as in Fig. 1. The magnitude of the term in f_o is 1×10^{-10}, while the term in the sound velocity c is 3×10^{-10}. The calculated value of $\alpha^{-1}(\partial\alpha/\partial p)_T$ comes out to be 4×10^{-10} cm^2/dyne, in fair agreement with the experimental value 6×10^{-10} cm^2/dyne.

The physical interpretation of the result is that the molecules are brought closer together by the application of pressure, thus increasing the collision

and relaxation frequencies. If $f < f_0$ an increase in f_0 moves the region of maximum absorption away from the working frequency. Also, the wave length is increased by pressure, so that the absorption per unit length will decrease even if the absorption per wave length is constant.

Sound Absorption and Molecular Structure

According to present ideas the magnitude of the non-classical part of the attenuation is determined by the position and magnitude of the relaxation frequencies of the molecule. It is difficult to calculate these frequencies since they are dependent upon the detailed coupling between different modes of motion. In gases it is well-confirmed experimentally that the relaxation mechanism accounts for most of the non-classical absorption. Relaxation frequencies in pure gases are of the order of $10^3 - 10^5$ cps; since "collisions" in liquids are at least 10^3 more frequent than in gases we would expect relaxation frequencies in liquids to be of the order of 10^7 cps. The indication of the present evidence is that the actual frequencies are of this order or higher. The existence of well-defined vibrational states in liquid molecules is known from infra-red and Raman spectra evidence.

A review of the absorption of sound in various liquids at 15 mc/sec shows several regularities with regard to molecular structure: a) The three most absorbing liquids of low viscosity are non-polar: CS_2, CCl_4, Benzene.

Substance	$\alpha_{exper}/\alpha_{classical}$
CS_2 (7 mc/sec)	600
CCl_4	25
Benzene	90

Other non-polar liquids are highly absorbing — heptane, hexane, toluene. This tendency suggests that the coupling of translational and vibrational motion is small in molecules with small electrostatic interactions, giving a long lifetime to the vibrational state and a low relaxation frequency. b) Highly associated liquids tend to show low, near-classical absorption at 15 mc/sec. The alcohols and water are good examples of associated liquids, and they show the following values:

Substance	$\alpha_{exper}/\alpha_{classical}$
Methyl Alcohol	3
Ethyl "	1
Propyl "	2
Butyl "	1
Amyl "	1.5
Water "	3

This tendency suggests that the formation of molecular groups is conducive to the transfer of vibrational energy and therefore leads to high relaxation frequencies. This is expected. In the limiting case of a solid there is little distinction between translational energy of molecules with respect to one another and vibrational energy internal to a molecule. In solids we have relaxation times of the order of 10^{-12} sec, as estimated from heat conductivity data.

CONCLUSIONS

It is found that the Tonks equation of state as applied to liquids is a suitable framework for making close order-of-magnitude estimates concerning quantities involved in sound propagation. The detailed numerical agreement is usually unsatisfactory, thus indicating the limitations of the model. In particular the temperature and pressure dependence of the compressibility is given only roughly by this model. On the other hand, the thermal expansion coefficient is given quite accurately; also, it is possible to attach physical significance to the concept of the available volume.

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