

# SOME PROPERTIES OF COMPRESSIONAL WAVES IN LENNARD-JONES AND DEVONSHIRE LIQUIDS

## I. WEAK SOUND WAVES

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### Summary

The present paper describes some calculations of the speed of sound  $u$  in a theoretical Lennard-Jones and Devonshire liquid. It is found that  $u$  decreases as the temperature is raised, but increases if the liquid is compressed. When quantum effects are considered it is found that  $u$  decreases as the value of de Boer's quantal parameter  $\Lambda^*$  is increased. All these effects have been observed in experiments on real liquids.

### I. INTRODUCTION

The properties of compressional waves in a liquid are closely related to the forces acting between its molecules, and any theoretical treatment of such waves must start with a model for liquids which takes account of these forces. Kincaid and Eyring (1938) presented a treatment of this kind in which they assumed that the molecules are hard attracting spheres moving in a uniform potential field. The "smoothed" attractive forces between the molecules are represented by the uniform potential, and the repulsive forces are assumed to be zero except at the collision of molecules where they become infinite.

This is a crude model, but it was improved by Lennard-Jones and Devonshire (1937) who retained the simplification of spherical molecular symmetry but assumed that the molecules interact in pairs according to the more realistic function

$$\varepsilon = \varepsilon_0 [r_0/r]^{12} - 2(r_0/r)^6, \quad (1)$$

where  $\varepsilon$  is the interaction energy (relative to an energy zero at infinite separation) of two molecules whose centres are a distance  $r$  apart, and  $-\varepsilon_0$  is the minimum value of  $\varepsilon$  which occurs at the separation  $r=r_0$ . The first term in this potential represents a repulsive force which predominates at small separations and the second represents an attraction which outweighs the repulsion at larger separations. Lennard-Jones and Devonshire further postulated that the molecules in a liquid spend most of their time near the sites of a close-packed cubic lattice. Each molecule is imprisoned in a cell bounded by its nearest neighbours but it can move classically within the cell subject to the forces between it and its neighbours. To simplify the mathematics, Lennard-Jones and Devonshire assumed that the potential energy of a molecule at a distance  $a$  from the centre of the cell can be taken as its average potential over the surface of the sphere of radius  $a$ , calculated on the supposition that the neighbouring molecules are

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fixed at their lattice sites. From these assumptions they derived a general equation of state (designated here, the "LJD" equation) which can be written in the reduced form

$$P^* = f(V^*, T^*), \quad (2)$$

where  $f$  is a complicated function and  $P^*$ ,  $V^*$ , and  $T^*$  are dimensionless variables proportional to the pressure  $P$ , molar volume  $V$ , and temperature  $T$ , respectively. They are defined by

$$P^* = P / (2^{\frac{1}{2}} \epsilon_0 / r_0^3) = P / P_0, \quad (3)$$

$$V^* = V / (N r_0^3 / 2^{\frac{1}{2}}) = V / V_0, \quad (4)$$

$$T^* = T / (\epsilon_0 / k) = T / T_0, \quad (5)$$

where  $N$  is Avogadro's number and  $k$  is Boltzmann's constant (de Boer 1948). The molecular units  $P_0$ ,  $V_0$ ,  $T_0$  have been listed for several liquids in an earlier paper (Hamann 1960).

It has been found that the LJD theory gives a fair qualitative description of the thermodynamics of simple fluids (see, for instance, de Boer and Lunbeck 1948; Wentorf *et al.* 1950; Rowlinson 1959) and we have considered it worthwhile to use it as a basis of some calculations of the behaviour of compressional waves in liquids.

The present paper will be concerned with the speed of weak (sound) waves and Part II of this series will consider the properties of strong (shock) waves.

## II. METHOD OF CALCULATION

### (a) General

At low frequencies and low amplitudes the speed of sound  $u$  in a pure liquid is related to the thermodynamic properties of the substance by

$$u = V \left[ \frac{T}{M C_V} \left( \frac{\partial P}{\partial T} \right)_V^2 - \frac{1}{M} \left( \frac{\partial P}{\partial V} \right)_T \right]^{\frac{1}{2}}, \quad (6)$$

where  $M$  denotes the molar weight of the liquid and  $C_V$  is its molar heat capacity at constant volume. If the molecules interact according to the potential function (1), this relation can be written in the reduced form

$$u^* = V^* \left[ \frac{T^*}{C_V^*} \left( \frac{\partial P^*}{\partial T^*} \right)_V^2 - \left( \frac{\partial P^*}{\partial V^*} \right)_T \right]^{\frac{1}{2}}, \quad (7)$$

where  $P^*$ ,  $V^*$ , and  $T^*$  are defined by (3), (4), and (5), and

$$C_V^* = C_V / Nk, \quad (8)$$

$$u^* = u / (N \epsilon_0 / M)^{\frac{1}{2}} = u / (\epsilon_0 / m)^{\frac{1}{2}} = u / u_0, \quad (9)$$

$m$  being the molecular mass. Some values of  $u_0$  for several liquids have been listed previously (Hamann 1960).

For monatomic liquids or for simple diatomic liquids in which the molecular rotation is restricted,  $C_V^*$  can be calculated from the equation of state. It follows that  $u^*$  can also be derived from this equation.

*(b) Classical LJD Liquids*

In its original form the LJD theory assumed that the motion of each molecule within its cell obeys the laws of classical mechanics. This assumption is justifiable if the molecules are heavy (e.g. A, Kr, Xe, N<sub>2</sub>) but it is invalid for light molecules (e.g. H<sub>2</sub>, D<sub>2</sub>, He<sup>3</sup>, He<sup>4</sup>, Ne). Here we shall consider the classical model first and then treat the quantal generalization as a correction to the classical theory.

Wentorf *et al.* (1950) have published extensive tables of the thermodynamic properties of classical LJD fluids. Amongst the properties they listed were the compressibility factor  $P^*V^*/T^*$  ( $=PV/NkT$ ) and the heat capacity  $C_V^*$ , both as functions of  $V^*$  and  $T^*$ . Their data allow us to estimate the derivatives  $(\partial P^*/\partial T^*)_V$  and  $(\partial P^*/\partial V^*)_T$ , and hence to derive  $u^*$  for a wide range of pressures, volumes, and temperatures.

In the liquid region of the LJD theory  $P^*$  changes quite slowly with  $T^*$  at constant volume, and  $(\partial P^*/\partial T^*)_V$  can be found accurately by the method of differences. But at constant temperature  $P^*$  is a rapidly changing function of  $V^*$  and it is necessary to fit the tabulated values to an analytic expression in order to arrive at reliable values for  $(\partial P^*/\partial V^*)_T$ . By trial we have found that the polynomial

$$P^* = a + b/V^* + c/V^{*2} + d/V^{*3} \quad (10)$$

(at constant  $T^*$ ) gives a good description of the  $P^* - V^*$  relation over the range of volumes  $V^*$  between 0.9899 and 1.5556, and at temperatures  $T^*$  between 0.7 and 1.0. We therefore fitted the data to this formula by least squares, using a standard programme for the SILLIAC computer, and then derived  $(\partial P^*/\partial V^*)_T$  by straightforward differentiation.

*(c) Quantal LJD Liquids*

In liquids composed of light molecules it is not justifiable to assume that the molecules move classically within their cells: it is necessary to allow for the finite spacing of the energy levels. de Boer (1948) has shown in a general way that this correction makes the thermodynamic functions dependent on a quantal parameter  $\Lambda^*$  as well as on  $V^*$  and  $T^*$  (or  $P^*$  and  $T^*$ ). The quantity  $\Lambda^*$  is defined by

$$\Lambda^* = 2^{1/2} h / r_0 (m \epsilon_0)^{1/2}, \quad (11)$$

where  $h$  is Planck's constant. It is the reduced de Broglie wavelength of relative motion of two molecules of mass  $m$  and relative kinetic energy  $\epsilon_0$ , and it is a characteristic property of the molecules. The greater its value the more will the liquid deviate from classical behaviour. Values of  $\Lambda^*$  for some simple liquids have been listed in an earlier paper (Hamann 1960).

Several attempts have been made to generalize the LJD theory to allow for the influence of  $\Lambda^*$ . de Boer and Lunbeck (1948) worked out the quantum correction to  $P^*$  in the form of an infinite power series in  $\Lambda^{*2}$ , but unfortunately the series often fails to converge. Hamann (1952) proposed an alternative treatment which involved some physical and mathematical simplifications but had the advantage of giving the quantum correction in a simple closed form.

Recently Levelt and Hurst (1960) have presented an exact calculation based on numerical computations of the energy eigen values for molecular motion in the complex LJD field. But it is doubtful whether the work involved in these computations is justified by the crude nature of the original LJD model, and we have preferred here to use the approximate, but convenient, algebraic correction (Hamann 1952). In the reduced units, the correction to the pressure is (David and Hamann 1953).

$$\frac{P^*}{(\text{quantal})} - \frac{P^*}{(\text{classical})} = T^* \left( 1 + \frac{3}{2} \frac{V^*}{y^*} \frac{dy^*}{dV^*} \right) / V^*(x^* - 1), \quad (12)$$

provided that  $x^* \geq 1.5$ , where

$$x^* = 9.071 y^{*3} T^{*3} V^{*3} \Lambda^{*-1}, \quad (13)$$

and  $y^*$  is related to  $V^*$  by

$$(1 + 12y^* + 25 \cdot 2y^{*2} + 12y^{*3} + y^{*4}) / (1 + y^*)(1 - y^*)^6 - 2V^{*2} = 0. \quad (14)$$

The corresponding correction to the heat capacity is

$$\frac{C_V^*}{(\text{quantal})} - \frac{C_V^*}{(\text{classical})} = 3(x^* - 2) / 4(x^* - 1)^2. \quad (15)$$

We have applied the correction (12) to the classical LJD pressures listed by Wentorf *et al.* (1950) and then calculated the derivatives  $(\partial P^* / \partial T^*)_V$  and  $(\partial P^* / \partial V^*)_T$  in the same way as before.

### III. RESULTS AND DISCUSSION

#### (a) Liquids at Low Pressures

If a liquid is at a temperature below its normal boiling point then its reduced vapour pressure  $P^*$  is very small and can be assumed to be zero. Under these conditions  $V^*$  and  $u^*$  depend only on  $T^*$  and  $\Lambda^*$  (Hamann 1960). We have used equation (10) to find the zero pressure values of  $V^*$  and applied equation (7) to calculate the corresponding values of the reduced speed of sound. The results are listed in Table 1.

It will be seen that  $u^*$  decreases with increasing temperature, in contrast to its behaviour in a perfect gas (Hamann 1960), and that at a particular temperature it decreases with an increase in the quantal parameter  $\Lambda^*$ . This last effect arises from the fact that the zero-point energy inflates the volume of the liquid and makes it much more compressible than a classical liquid.

The theoretical results are compared with experimental data in Figure 1. It is clear that the experiments show the predicted dependence of  $u^*$  upon  $T^*$  and  $\Lambda^*$  although the numerical agreement is not very good. The lack of agreement evidently arises from the faults of the "cell" model rather than from the mathematical approximations of the LJD theory. We find that Dahler and Hirschfelder's (1961) improved cell theory gives even worse agreement with experiment, the calculated values of  $u^*$  being about 20% higher than those for the LJD theory. Barker's (1961) new "tunnel" model gives good results for classical liquids but is not easily applied to quantal ones.

TABLE I  
 SOME REDUCED PROPERTIES OF CLASSICAL AND "QUANTIZED" LJD LIQUIDS AT ZERO PRESSURE

LJD Liquids	Temperature $T^*$	Volume $V^*$	Coefficient of Thermal Expansion $\frac{1}{V^*} \left( \frac{\partial V^*}{\partial T^*} \right)_P$	Isothermal Compressibility $-\frac{1}{V^*} \left( \frac{\partial V^*}{\partial P^*} \right)_T$	Heat Capacity $C_V^*$	Speed of Sound $u^*$
(a) Classical: $\Lambda^*=0$	0	0.916	0	0.0133	0	8.30†
	0.70	1.037	0.244	0.0348	2.61	6.63
	0.75	1.050	0.261	0.0386	2.58	6.47
	0.80	1.065	0.287	0.0433	2.55	6.34
	0.85	1.081	0.316	0.0493	2.53	6.17
	0.90	1.099	0.352	0.0571	2.50	5.98
	0.95	1.120	0.405	0.0683	2.47	5.78
	1.00	1.145	0.491	0.0851	2.43	5.60
(b) Quantal: $\Lambda^*=0.5$	0.70	1.090	0.319	0.0454	2.71	6.00
	0.75	1.109	0.358	0.0527	2.68	5.77
	0.80	1.130	0.408	0.0626	2.64	5.52
	0.85	1.155	0.477	0.0771	2.59	5.24
	0.90	1.186	0.584	0.1004	2.54	4.92
	0.95	1.226	0.784	0.1458	2.47	4.53
	1.00	1.290	1.366	0.286	2.38	3.99
(c) Quantal: $\Lambda^*=1.0$	0.70	1.213	0.474	0.0819	2.46	4.87
	0.75	1.245	0.586	0.1061	2.47	4.58
	0.80	1.288	0.780	0.1516	2.45	4.22
	0.85	1.353	1.287	0.280	2.38	3.71

† This value was derived previously (Hamann 1960).

Our calculations on quantal liquids were limited to values of  $\Lambda^*$  less than 1.5 for two reasons:

(i) If  $\Lambda^*$  is much greater than one, the stable range of the liquid state is shifted to lower reduced temperatures than are covered by the tables of Wentorf *et al.* (1950).

(ii) Equations (12) and (15) were based on an Euler-Maclaurin expansion of the partition function (Hamann 1952) which is only valid when  $x^*$  is greater than 1.5. If  $\Lambda^*$  is large,  $x^*$  becomes less than this value. We have therefore not been able to apply the theory directly to  $H_2$  and the helium isotopes, but the trend of the curves to  $\Lambda^*=1$  is certainly sufficient to explain the behaviour of the lighter liquids.

#### (b) Liquids at High Pressures

The computation of  $u^*$  is easily extended to compressed liquids. Using the polynomial form (10) of the  $P^*-V^*$  relation, we can derive values of the derivative  $(\partial P^*/\partial V^*)_T$  over a wide range of temperatures and densities. As before, the derivative  $(\partial P^*/\partial T^*)_P$  and the corresponding values of  $P^*$  and  $C_V^*$  can be taken directly from the tables of Wentorf *et al.* (1950). The results are

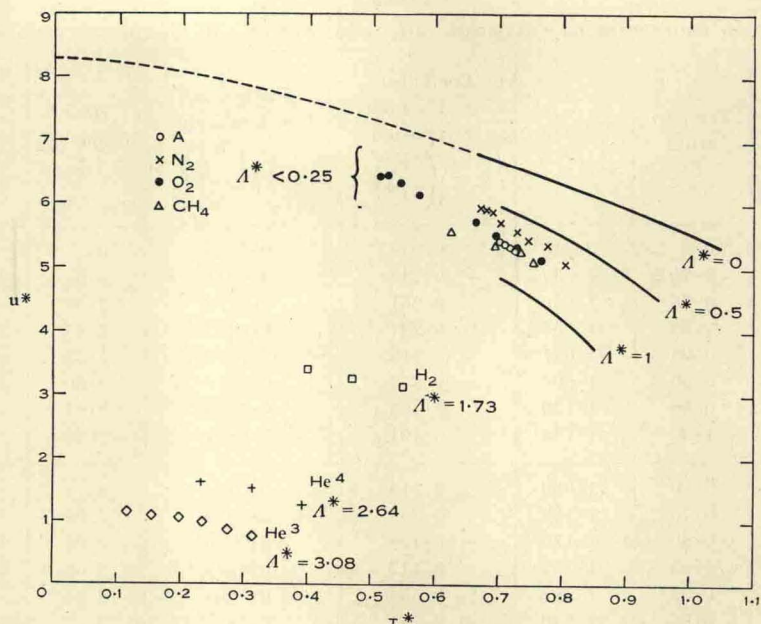


Fig. 1.—A comparison of the calculated and experimental speeds of sound in simple liquids. The sources of the experimental data for A, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and He<sup>4</sup> have been given in an earlier paper (Hamann 1960). The data for He<sup>3</sup> have been taken from a paper by Atkins and Flicker (1959).

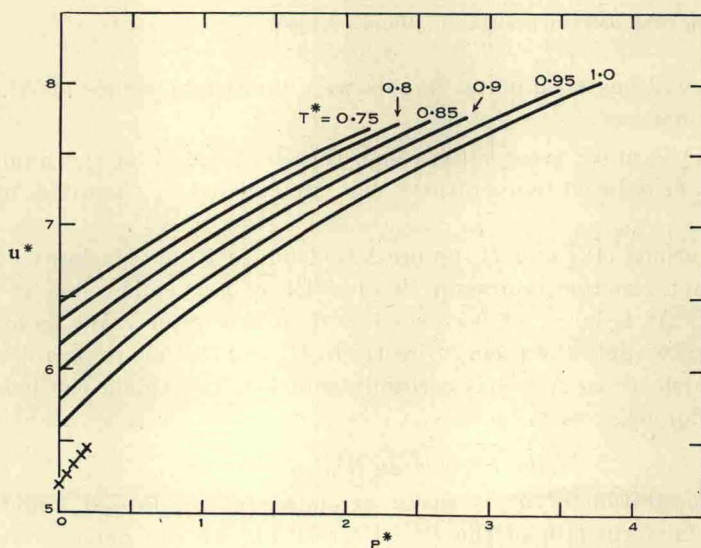


Fig. 2.—The effect of pressure on the speed of sound. The curves represent the theoretical Leonard-Jones-Devonshire relations and the crosses denote the experimental data for argon at  $T^*=0.75$ .

plotted in Figure 2, which also shows some experimental data for liquid argon, obtained by van Itterbeek, van Dael, and Grevendonk (1959) in the pressure range 1 to 72 atm. Again the theory predicts the right kind of trend in  $u^*$  with increasing pressure. The agreement between theory and experiment would probably be better at higher pressures ( $P^* > 2$ ; that is,  $P > 1000$  atmospheres for argon), where the cell model becomes a more realistic one. There is a clear need for some experiments in this pressure range.

(c) Rao's (1940) Relation

Rao (1940) found empirically that the thermal coefficient of the speed of sound in many liquids is close to three times the thermal coefficient of the density. Expressed in a reduced form this relation becomes

$$\frac{1}{u^*} \left( \frac{\partial u^*}{\partial T^*} \right)_P = -A \frac{1}{V^*} \left( \frac{\partial V^*}{\partial T^*} \right)_P, \quad (16)$$

where  $A \approx 3$ . Later Carnevale and Litovitz (1955) observed that a parallel relation applies if the density is changed, not by temperature, but by pressure: that is

$$\frac{1}{u^*} \left( \frac{\partial u^*}{\partial P^*} \right)_T = -A' \frac{1}{V^*} \left( \frac{\partial V^*}{\partial P^*} \right)_T, \quad (17)$$

where again  $A' \approx 3$ . These relations are very simple and we considered it worthwhile to see whether they have any basis in the LJD theory.

We find that for classical LJD liquids in the temperature range  $T^* = 0.7$  to 1.0, the relation (16) fails rather badly. The factor  $A$  is only about 1.7 and it decreases with increasing temperature. On the other hand, the relation (17) is obeyed quite accurately.  $A'$  has the value  $2.7 \pm 0.1$  and is independent of both the temperature and the pressure, to at least  $P^* = 2.5$  (equivalent to an absolute pressure of 1000 atm in liquid argon).

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