

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 Λ^* 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

$$\epsilon = \epsilon_0 [r_0/r]^{12} - 2(r_0/r)^6, \quad (1)$$

where ϵ is the interaction energy (relative to an energy zero at infinite separation) of two molecules whose centres are a distance r apart, and $-\epsilon_0$ is the minimum value of ϵ 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

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

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

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

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

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

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

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

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

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

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

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.