

JOURNAL OF  
THE  
INDIAN INSTITUTE OF SCIENCE  
SECTION A

---

VOLUME 37

OCTOBER 1955

NUMBER 4

---

SOUND VELOCITY IN A LENNARD JONES  
LIQUID MODEL

BY V. S. VENKATASUBRAMANIAN

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

Received July 25, 1955

ABSTRACT

Making use of the partition function derived by Lennard Jones for a plausible model of a liquid an expression for sound velocity is derived. This is applied to discuss some features regarding the dependence of velocity on chemical constitution and to calculate the ultrasonic velocities in liquid gases for which the requisite data are available. There is fair agreement with experimental values.

INTRODUCTION

With the availability of precise data regarding ultrasonic velocities in liquids, considerable attention has been devoted to the correlation between sound velocity and chemical constitution and molecular properties of the liquid. Thus the relationship between sound velocities in the liquid and gaseous states of the same substance has been examined by Eyring *et al.* (1937), (1938). Adopting an equation of state derived by Tonks (1936) on considerations of the statistical mechanics of an assembly of hard elastic spheres, Kittel (1946) has considered sound propagation in a "free volume" model of a liquid. Kittel finds fair agreement between estimates of the "available volume" from thermal expansion and sound velocity data. Another important work is that of Schaffs (1939) who has adopted the Van Der Waals equation of state, taking into account the variation of the constants with density. A satisfactory explanation has been given of the observations (1938) concerning the relation between sound velocity and chemical

constitution. In later papers, Schaffs derives an expression for sound velocity for members of homologous series of organic liquids in terms of a constant (denoted as the velocity for closest packing) and two other factors denoted by the "packing" factor, and the "distortion factor" which are characteristic of the series.

## 2. PARTITION FUNCTION AND DERIVATION OF SOUND VELOCITY

In the present paper, we consider the application of a more refined model for a liquid introduced by Lennard-Jones and Devonshire (1937). In this model, the molecule is regarded as being enclosed in a cell with a smoothed-out potential energy  $\chi(v)$ , this being naturally a function of the cell radius, and hence of the average volume per molecule =  $v$ . Denoting the molecular diameter by  $D$ , and considering the molecules to be situated on the surface of the cell, the partition function for each molecule

$$f = \frac{1}{h^3} \int \int \int e^{-p^2/2mkT} dp \int_0^{R-D} 4\pi r^2 \cdot e^{-\alpha(v)/kT} dr$$

$$= \frac{[2\pi mkT]^{3/2}}{h^3} \cdot e^{-\alpha(v)/kT} \cdot a.v. \left[ 1 - \left( \frac{D}{R} \right) \right]^3$$

where  $a.v. = 4\pi R^3/3$ ; and  $\alpha$  is a constant determined by the geometry of the packing. (Thus for a face centred cubic type  $\alpha = \frac{4\pi}{3} \sqrt{2}$ ).

Equating the partition function of the assembly of  $N$  molecules to  $f^N$  and calculating the pressure

$$p = kT \cdot \frac{\partial}{\partial v} \log f$$

$$= \frac{kT}{v \left[ 1 - \left( \frac{v_0}{v} \right)^{1/3} \right]} - \frac{\partial \chi}{\partial v}$$

where

$$\frac{v_0}{v} = \frac{D^3}{R^3} = \frac{D^3}{\sqrt{2} \cdot v}$$

Regarding the smoothed out potential energy, Lennard-Jones and Devonshire have dealt with the problem of a particle moving symmetrically in the field of a number of particles symmetrically arranged on the surface of a sphere, assuming a potential energy of the form

$$\phi(r) = -\frac{B}{r^6} - \frac{A}{r^{12}}$$

here the first term represents the effect of dispersion forces and the second the overlap forces.

The average potential corresponding to the equal probability of all the positions of the atoms on the surface of a sphere is,

$$\psi(0) = -\Lambda \left[ 1.2 \left( \frac{v'}{v} \right)^2 - \frac{1}{2} \left( \frac{v'}{v} \right)^4 \right]$$

where  $v' = \frac{r'^3}{\sqrt{2}}$  and  $\Lambda = z\epsilon'$

$r'$  and  $\epsilon'$  being the values of the molecular radius and potential energy corresponding to the potential energy minimum, and  $z$ , the co-ordination number.

Using this value of  $\psi$  and introducing the molar volume  $V = Nv$ ,

$$p = \frac{RT}{V} \cdot \frac{1}{1 - \left[ \frac{v_0}{v} \right]^{1/3}} - \frac{N\Lambda}{V} \cdot \left[ 2.4 \left( \frac{v'}{v} \right)^2 - 2 \left( \frac{v'}{v} \right)^4 \right].$$

The expression for sound velocity  $C$  is now given by

$$C^2 = \left( \frac{\partial p}{\partial \rho} \right)_s = - \frac{\gamma M}{\rho^2} \cdot \left( \frac{\partial p}{\partial V} \right)$$

where  $\gamma = C_p/C_v$ ,  $M = \text{Mol. wt.}$  and  $\rho = \text{density}$ , and becomes

$$C^2 = \gamma \frac{RT}{M} \cdot \left[ \frac{1}{1 - \left( \frac{v_0}{v} \right)^{1/3}} \cdot \left[ 1 + \frac{1}{3} \frac{\left( \frac{v_0}{v} \right)^{1/3}}{1 - \left( \frac{v_0}{v} \right)^{1/3}} \right] - \frac{N \cdot \Lambda}{RT} \left[ 7.2 \left( \frac{v'}{v} \right)^2 - 10 \left( \frac{v'}{v} \right)^4 \right] \right].$$

If necessary,  $\Lambda$  can be eliminated by making use of the expression for  $p$  and equating it to zero, since at ordinary pressures  $p \ll V \partial p / \partial V$ , then

$$C^2 = \gamma \cdot \frac{RT}{M} \cdot \frac{1}{1 - \left( \frac{v_0}{v} \right)^{1/3}} \left[ 1 + \frac{\left( \frac{v_0}{v} \right)^{1/3}}{1 - \left( \frac{v_0}{v} \right)^{1/3}} - \frac{7.2 \left( \frac{v'}{v} \right)^2 - 10 \left( \frac{v'}{v} \right)^4}{2.4 \left( \frac{v'}{v} \right)^2 - 2 \left( \frac{v'}{v} \right)^4} \right].$$

Further, making use of the above equation of state,  $\gamma$  can be expressed in terms of  $C_p$  (or  $C_v$ )

$$(C_p - C_v) = T \cdot \left( \frac{\partial v}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial T} \right)_v - T \cdot \frac{(\partial p / \partial T)_{p,v}^2}{(\partial p / \partial v)_T}$$

Neglecting the variation of  $\Lambda$  and  $v'$  with  $T$ , this yields

$$C_p - C_v = \frac{R}{\left[1 - \left(\frac{v_0}{v}\right)^{1/3}\right] \left[1 + \frac{1}{3} \frac{(v_0/v)^{1/3}}{1 - (v_0/v)^{1/3}} - \frac{7.2 \left(\frac{v'}{v}\right)^2 - 10 \left(\frac{v'}{v}\right)^4}{2.4 \left(\frac{v'}{v}\right)^2 - 2 \left(\frac{v'}{v}\right)^4}\right]}$$

$$= \beta R$$

$$\therefore \gamma = C_p/[C_p - \beta R].$$

#### DISCUSSION

Formula (5) can be used to explain in a qualitative way the results on the relation of sound velocity to the chemical constitution of a liquid. Thus, the observed increase in velocity with increasing chain length in a homologous series is to be attributed to the corresponding increase in  $(v_0/v) = (D/R)^3$ , this effect predominating over that due to increase in molecular weight. Similarly, the increase in velocity in Nitrobenzene (1,477 met./sec.) and Aniline (1,659 met./sec.) over that in benzene (1,333 met./sec.) is due to the increase in molecular volume. As pointed out by Schaffs, a striking example is provided by the pair  $C_2H_5 OH$  (1,173 met./sec.) and  $NO_2 CH_2 OH$  (1,578 met./sec.) where the replacement of the H atom by the  $NO_2$  group increases the velocity by 35%.

For comparison of the formula with experimental results, we shall first consider the case of liquefied gases Argon (in particular) and  $N_2$  in which the assumptions of the Lennard Jones formula are most nearly fulfilled, and further the values of  $D$ ,  $v'$  and  $\Lambda$  have been given by Lennard Jones and Devonshire, on the basis of data obtained from isotherms for the gases. These values can be compared with the experimental results of Liepmann (1939) and Galt (1948) who have also given values of  $C_p$  and  $\gamma$  calculated from the ultrasonic velocities.

TABLE

Liquefied gas	D	$\gamma$ (Calc.)	C (Calc.)	$\gamma$ (Obs.)	C (Obs.)
Argon .. ..	3.41 A	2.0	830	2.2	837
Nitrogen .. ..	3.72 A	2.0	910	1.96	929

It is seen that the agreement between calculated and observed values is satisfactory.

Comparison with other liquids is vitiated by absence of knowledge of  $\Lambda$  and  $v'$ . When this term is neglected, the equation of state essentially goes over to that of Tonks, which has been found to give results of the right order of magnitude.

ACKNOWLEDGMENTS

I thank Professor R. S. Krishnan for guidance and useful suggestions.

REFERENCES

1. Eyring and Hirschfelder .. *J. Phys. Chem.*, 1937, **41**, 250.
2. Kincaid and Eyring .. *J. Chem. Phys.*, 1938, **6**, 620.
3. Tonks .. *Phys. Rev.*, 1936, **50**, 955.
4. Kittel, C. .. *Rep. Prog. Phys.*, 1946, **11**, 205.
5. ————— .. *J. Chem. Phys.*, 1946, **14**, 614.
6. Schaffs, Ch. .. *Ann. d. Physik*, 1941, **40**, 393.  
Summary, *Bergmann Ultraschall*, 1954, 384, et  
seq. (Hirzel Verlag).
7. Parthasarathy .. *Curr. Sci.*, **6**, 322.
8. Lennard Jones and  
Devonshire  
Fowler and Guggenheim .. *Statistical Thermodynamics*, p. 336 (Cambridge  
University Press).
9. Liepmann .. *Helv. Phys. Acta*, 1939, **12**, 421.
10. Galt .. *J. Chem. Phys.*, 1948, **16**, 505.