

VELOCITY OF SOUND IN LIQUID HYDROGEN AT LOW PRESSURES*

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Hamann¹ has shown that for simple liquids the velocity of sound conforms to the principle of corresponding states. David and Hamann² have applied this treatment to the classical cell theory of Lennard-Jones and Devonshire. In addition, they have used the cell model to calculate approximately the velocity of sound in quantum liquids. However, they have made no calculations for liquid hydrogen because the quantum parameter, Λ^* , was too large for liquid hydrogen to be reasonably treated by their approximate method.

Recently, Henderson and Reed³ have formulated a reliable and computationally convenient method whereby the influence of quantum effects in the Lennard-Jones and Devonshire theory may be taken into account. In their procedure the energy levels of the molecule in its cell were numerically obtained by the WKB method and the resulting thermodynamic properties evaluated for temperatures and volumes characteristic of liquid hydrogen.⁴ In this communication we have applied these data to obtain the velocity of sound in liquid hydrogen at low pressures.

The reduced speed of sound for small amplitudes and frequencies in a pure liquid can be written²

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

where the reduced quantities u^* , V^* , P^* , T^* , and C_V^* have been defined by David and Hamann.² Since the cell potential is complicated, it is not possible to obtain explicit expressions for the energy levels. As a result the pressure has been obtained by fitting a polynomial in V^* by the least squares method to the Helmholtz free energy (at constant T) and then differentiating in a straightforward manner. The quantity $(\partial P^*/\partial T^*)_{T^*}$ may then be obtained by differentiating once more. The quantity $(\partial P^*/\partial T^*)_{V^*}$ was most conveniently calculated from one of Maxwell's relations

$$\left(\frac{\partial P^*}{\partial T^*} \right)_{V^*} = \left(\frac{\partial S^*}{\partial V^*} \right)_{T^*} \quad (2)$$

where $(\partial S^*/\partial V^*)_{T^*}$ was obtained by fitting a polynomial in V^* to S^* by the least squares method and then differentiating. We calculated the thermodynamic proper-

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¹ Hamann, S. D., *Aust. J. Chem.*, 1960, **13**, 325.

² David, H. G., and Hamann, S. D., *Aust. J. Chem.*, 1961, **14**, 1.

³ Henderson, D., and Reed, R. D., *J. Chem. Phys.*, 1964, **40**, 975.

⁴ Reed, R. D., Ph.D. Thesis, 1964, Arizona State University.

ties in intervals of 0.01 in the range $1.35 \leq V^* \leq 1.50$ and used polynomials of degree five, six, and seven for the least squares fit. The calculations were performed on a GE225 digital computer. The resulting polynomials gave good descriptions of the free energy and entropy. We have made an estimate of the accuracy of our differentiation by calculating the velocity of sound for each of these polynomials and believe that our values are accurate to about 2%.

The results of these calculations for the velocity of sound in liquid hydrogen ($\Lambda^* = 1.729$) at zero pressure are shown in Figure 1. The corresponding results for

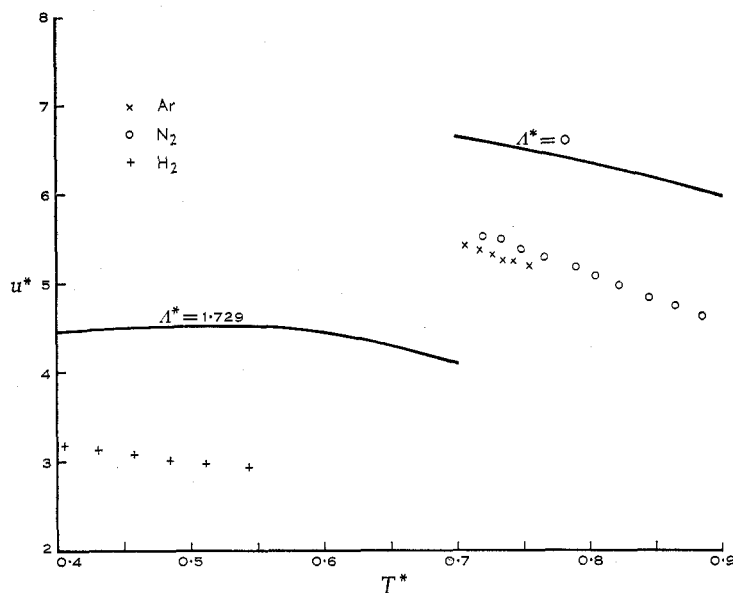


Fig. 1.—Calculated and experimental values of the velocity of sound for liquid hydrogen ($\Lambda^* = 1.729$) and for classical liquids ($\Lambda^* = 0$) at low pressures. The experimental values for Ar, N₂, and H₂ were taken from refs.^{5,6,7} respectively.

the classical cell theory² ($\Lambda^* = 0$) are also shown for comparison. It can be seen that the quantum corrections are given quite well. The difference between the theoretical curve and the experimental values for hydrogen is about the same as for classical liquids and presumably results from the limitations of the cell model itself.

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⁵ Van Itterbeek, A., Grevendonk, W., Van Dael, W., and Forrez, G., *Physica, 's Grav.*, 1959, **25**, 1255.

⁶ Van Itterbeek, A., and Van Dael, W., *Physica, 's Grav.*, 1962, **28**, 861.

⁷ Van Itterbeek, A., Van Dael, W., and Cops, A., *Physica, 's Grav.*, 1961, **27**, 111.