

*(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.