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DEPENDENCE OF IONIC MOBILITIES IN LIQUID $^3$He ON TEMPERATURE AND DENSITY.

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DEPENDENCE OF IONIC MOBILITIES IN LIQUID $^3$He ON TEMPERATURE AND DENSITY

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We have measured the mobility of positive and negative ions in liquid $^3$He as a function of the temperature and the density of the liquid. Previous measurements had been performed by Meyer, Davis, Rice, and Donnelly\textsuperscript{1} and in this laboratory\textsuperscript{2,3} but they were not so extensive as those presented here.

We used two different techniques in performing the mobility measurements. The first technique—the same used to obtain the measurements reported by Modena\textsuperscript{2} and de Magistris\textsuperscript{3}—is based on the method devised by Cunsolo\textsuperscript{4} for $^4$He and consists of the measurement of the time-of-flight of ions between two electrodes, whose distance is known. Recently one of us (F.S.) developed a new method based on the measurements of the voltage-current characteristics of a diode under a condition of complete space charge limitation. This condition is defined by having zero electric field at the ion source electrode. The integration of the Poisson's equation gives the following simple relation:

$$i = \alpha \mu V^2$$

where $i$ is the measured current, $V$ the applied potential, $\mu$ the ionic mobility, and $\alpha$ a coefficient depending on the geometry of the cell. This method has been successfully used in the measurement of ionic mobilities in $^4$He.\textsuperscript{5} The latest measurements have been performed with this method, which is faster and simpler to use, and gives smaller errors. The time-of-flight method requires that the distance between two electrodes be known. The complete space charge method requires, besides this, the knowledge of the absolute values of the current and the voltage. We have preferred to calibrate the complete space charge cell with respect to one experimental point taken with the time-of-flight method; the agreement for the other data is satisfactory. The electric fields used with the complete space charge method are rather lower than those used for the other method; they were never above 30 V/cm.

The technique used to increase the pressure in the experimental cell has been described by de Magistris and Modena.\textsuperscript{3} Briefly, it consists of a stainless steel Toepler pump (a bellows filled with mercury), which enabled us to reach pressures up to 25 atm using not more than 2 liters NTP of $^3$He. Before entering the cell, the $^3$He was passed through a trap at liquid $^4$He temperature. A standard type of continuous $^4$He refrigerator enabled us to reach the temperature of 0.39°K.

In Figs. 1 and 2 the values of the mobility for positive and negative ions, respectively, are reported as a function of the density of the liquid, for different temperatures. For negative ions the vapor pressure values are indicated by a dotted line (Fig. 2). For positive ions this has not been made, as the vapor pressure mobilities had already been presented by de Magistris and Modena.\textsuperscript{3} Both the straight lines
Fig. 1. Positive ion mobility at different constant temperatures vs. the density of the liquid.

Fig. 2. Negative ion mobility at different constant temperatures vs. the density of the liquid.
in Fig. 1 and the curves in Fig. 2 must be considered as a rough attempt to find an empirical best fit to the data for a fixed temperature. The errors reported in both figures are not to be intended as statistical errors, but as a measure of the uncertainty with which the straight lines can be drawn through the experimental points. In both methods it is necessary to draw a straight line (see Cusolo and Scaramuzzi).

It is not possible at present to fit our experimental data to any satisfactory theory. We will limit ourselves to pointing out a few considerations about the limits within which a classical model can fit the data. The classical approach to this problem can be summarized in the two formulas describing the motion of an extraneous particle in a fluid, due to Einstein:

$$\mu = \frac{eD}{KT}$$

and to Stokes–Einstein:

$$D = \frac{KT}{6\pi\eta R}$$

Combining them, we get the well-known Walden’s rule

$$\eta\mu = \text{constant}$$

valid in the hypothesis that the radius of the particle is constant. Table I shows the values of $\eta\mu$ in arbitrary units calculated for positive and negative mobilities at vapor pressure as a function of temperature. From Table I it appears that equation (3) is satisfied only for positive ions for temperatures down to $\sim 1.4^\circ\text{K}$. The lack of data for $\eta$ values under pressure prevents us from extending this kind of computation to larger liquid densities.

Another quantity which can be calculated in the approximation of this model is the diffusion coefficient of the ion, $D_{i+}$, from equation (1). As already noted by de Magistris and Modena, $D_{i+}$ exhibits the same temperature dependence of the self-diffusion coefficient down to $\sim 1.4^\circ\text{K}$ (the ratio of the absolute values $D/D_{i+}$ is about 7), but the values at lower temperatures show a complete disagreement.

### Table I. The $\eta\mu$ Product in Arbitrary Units for Positive and Negative Ions Computed from Smoothed Values of $\mu$ at Vapor Pressure and from the Viscosity Measurements by Betts et al.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\eta\mu_+$</th>
<th>$\eta\mu_-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>17.7</td>
<td>6.3</td>
</tr>
<tr>
<td>2.5</td>
<td>18.5</td>
<td>7.0</td>
</tr>
<tr>
<td>2.0</td>
<td>18.5</td>
<td>7.5</td>
</tr>
<tr>
<td>1.5</td>
<td>18.6</td>
<td>7.9</td>
</tr>
<tr>
<td>1.3</td>
<td>19.9</td>
<td>8.5</td>
</tr>
<tr>
<td>1.0</td>
<td>22.2</td>
<td>9.4</td>
</tr>
<tr>
<td>0.8</td>
<td>23.9</td>
<td>10.0</td>
</tr>
<tr>
<td>0.5</td>
<td>30.0</td>
<td>12.2</td>
</tr>
</tbody>
</table>
between the two diffusion coefficients. In particular, in the $D_{1+}$ curve there is not any minimum corresponding to that in the $D$ curve.

Referring to the density dependence of the mobility, we want to point out that even the data for the self-diffusion coefficient under pressure, given by Garwin and Reich,\textsuperscript{7} show a behavior almost linear in the same range of densities as ours, like the mobility of positive ions (see Fig. 1).

A simple model for the positive ion was given by Atkins,\textsuperscript{8} who computed the effective mass of the ion due to polarization forces. Although the model is very rough, we may suppose the radius of the ion to be the distance at which the pressure equals the melting pressure. This implies the picture of the "snowball," or solid cluster ion. The values of $R$ thus calculated and those from the values of $\mu$ using the Stokes formula

$$R = \frac{e}{6\pi \eta \mu}$$

are reported in Table II. The two sets of values are in good agreement as far as the magnitude is concerned, but the dependence in temperature is opposite.

To conclude, we want to point out that, recently, theoretical work has appeared in which the motion of the ions is considered in systems made up of bosons\textsuperscript{9} or fermions,\textsuperscript{10} but it is impossible to test these theories making use of our data, because they are valid only at temperatures lower than those we had to deal with. Work is in progress to extend the temperature range of our measurements.

References