An Investigation of the Viscosities of Various Groups of Liquid Metals

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The viscosities of four groups of liquid metals have been calculated at various temperatures using the Gas-like model of viscosity of liquid metals. The groups of liquid metals considered include alkali metals, transition metals, the main group metals and the lanthanides. The results obtained show that the model reproduces in general the temperature dependence of the viscosity of these groups of liquid metals. The trend of the viscosity in general follows an exponential decrease as temperature rises. There is generally both quantitative and qualitative agreement between the experimental and the calculated viscosities. However, there is a significant quantitative disparity between theory and experiment for liquid Li perhaps due to the anomalous behaviour of this metal.

1. Introduction

The study of the properties of various groups of liquid metals has been of interest to researchers over the years [1-7]. This no doubt stems from the importance of these metals in science and technology even in modern times. For example, these metals are employed in nuclear energetics, emission electronics, new power-intensive chemical current sources, medicine, electricity, semiconductors, jewellery, electromagnetism, petroleum and plastic production, optics, and other fields [8-12].

The viscosity of liquid metals is an important physical property that influences the activities of refining, casting and solidification as well as the general behaviour of liquids [13]. Viscosity is one of the atomic transport properties which plays an important role in fluid flow and reaction mechanism in metallurgy. It is essential not only from the practical viewpoint, but also from the theoretical viewpoint as a property which reflects the structure of the liquid state.

The viscosity of liquid metals belonging to different groups of the periodic table and their alloys have been determined by different researchers using a number of models. For example, Chiong [14], Hsu and Eyring [15], and Tosi [16] have determined the viscosities of the liquid alkali metals, while Anusionwu [17] has calculated the viscosity of liquid alkali metal alloys. Morioka et al. [18] and Morioka [19, 20] have determined the viscosities of some liquid transition metals and liquid main group metals. Kondrat’ev et al. [6] have also determined the viscosities of some liquid lanthanide metals. These researchers have employed different models in their work. However, there has not been any conclusive model for the determination of the viscosity of liquid metals and alloys in general. In this paper, we attempt to calculate the viscosities of the aforementioned groups of liquid metals at different temperatures by means of a particular model, the Gas-like model, proposed recently by Morioka et al. [18]. Recently, we calculated the viscosities of a number of liquid metals and alloys using this model [21].

2. Theoretical Background

The Gas-like model has been described in detail by Morioka et al. [18]. The model employs both kinetic and rate theories to describe the viscosity of liquid metals with known physical properties and involves two adjustable parameters. The adjustable parameters $k$ and $z$, according to Morioka, respectively relate to the effective atomic diameter and the coordination number of nearest neighbour atoms in the liquid metals.

Morioka assumes that the collision cross-section $\sigma$, of the atoms is defined by

$$\sigma = \pi kd^2$$

(1)

where $d$ is the diameter of the atom in Å, $k$ is an adjustable parameter as defined above and is considered a correction factor due to deviation from a hard-sphere picture of the atom. The hard-sphere model of atoms applies correctly to describe the viscosity of the ideal gas. Thus the viscosity of the
gas phase in the gas-like model is written as

$$\eta_g = \frac{2}{3N_A\sigma} \sqrt{\frac{MRT}{\pi}}$$  \hspace{1cm} (2)

The difference between the viscosity of a gas and a liquid is that the viscosity of the liquid is associated with the exponential term of the activation energy which is the height of a potential energy barrier for the movement of the atom presented by nearest neighbour atoms in the liquid. As a result, the activation energy for the atom to surmount this potential can be related to the cohesive energy of atoms in the liquid. Morioka therefore assumes that this cohesive energy is constant in temperature and thus is related to the latent heat of evaporation. Thus we can write

$$E_{vis} = \frac{H_{evap}}{z}$$  \hspace{1cm} (3)

Consequently, the model assumes that $\eta_g$ is not constant as is the case in the Arrhenius type viscosity, but has the same temperature dependence of the viscosity of a gas. Hence the gas-like model of viscosity for a liquid metal is given by

$$\eta = \frac{2}{3N_A\pi(kd)^2} \sqrt{\frac{MRT}{\pi}} \exp\left(\frac{H_{evap}}{zRT}\right)$$  \hspace{1cm} (4)

where $\eta$ is the viscosity, $N_A$ is the Avogadro number, $M$ is the atomic mass of the atom, $d$ is the atomic diameter, $R$ is the Universal gas constant, $T$ is the absolute temperature and $H_{evap}$ is the enthalpy of evaporation of each liquid metal. According to Morioka et al, $k$ and $z$ are adjustable parameters obtained by fitting the experimental viscosity data. The model is based on the viscous activation energy $E_{vis}$ which is given by

$$E_{vis} = \frac{H_{evap}}{z}$$  \hspace{1cm} (5)

The component

$$\eta_g = \frac{2}{3N_A\pi(kd)^2} \sqrt{\frac{MRT}{\pi}}$$  \hspace{1cm} (6)

is the viscosity of the gas phase in line with the simple model of viscosity of liquids according to Kittel [22] given by

$$\eta = \eta_g \exp\left(E_{vis}/RT\right)$$  \hspace{1cm} (7)

3. Results and Discussion

The model was applied to liquid alkali metals, liquid transition metals, liquid main group metals, and liquid lanthanide metals to calculate the viscosities at different temperatures. We discuss the results obtained as follows:

**Liquid Alkali Metals**

The viscosities of the liquid alkali metals Li, Na, K, Rb, and Cs were calculated at various temperatures using Eqn.(3). Table 1 shows the heat of evaporation, atomic mass and atomic diameter of the individual liquid metals obtained from Iida and Guthrie [23] and [29]. The experimental viscosity data were obtained from Waseda [24], Iida and Guthrie [23] and Grosse [26] for Li; Iida and Guthrie [23] and Waseda [24] for Na; Iida and Guthrie [23], Waseda [24] and Wonsoo and Tong-Seek [25] for K, Rb and Cs.

Our result shows that the viscosity of liquid alkali metals decreases exponentially with the increase of temperature as shown in Fig. 1. The figure shows that the model reproduces closely and to a good extent the experimental viscosity values for the liquid alkali metals. However, Li shows a significant quantitative disparity between measured and calculated values especially above 500K.
Table 1: The physical parameters used in the calculations and the adjustable parameters obtained.

<table>
<thead>
<tr>
<th>Metal</th>
<th>At.Dia (Å)</th>
<th>$H_{\text{evap}}$ (KJmol$^{-1}$)</th>
<th>At.Mass (g)</th>
<th>$k$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.95</td>
<td>148.00</td>
<td>6.94</td>
<td>0.448</td>
<td>16.920</td>
</tr>
<tr>
<td>Na</td>
<td>3.62</td>
<td>99.20</td>
<td>22.99</td>
<td>0.460</td>
<td>13.190</td>
</tr>
<tr>
<td>K</td>
<td>4.48</td>
<td>79.10</td>
<td>39.10</td>
<td>0.460</td>
<td>11.850</td>
</tr>
<tr>
<td>Rb</td>
<td>4.79</td>
<td>75.70</td>
<td>85.47</td>
<td>0.480</td>
<td>11.720</td>
</tr>
<tr>
<td>Cs</td>
<td>5.17</td>
<td>66.50</td>
<td>132.91</td>
<td>0.490</td>
<td>10.700</td>
</tr>
<tr>
<td>Fe</td>
<td>2.48</td>
<td>340.00</td>
<td>55.84</td>
<td>0.600</td>
<td>6.900</td>
</tr>
<tr>
<td>Cu</td>
<td>2.56</td>
<td>307.00</td>
<td>63.54</td>
<td>0.665</td>
<td>8.860</td>
</tr>
<tr>
<td>Ag</td>
<td>2.90</td>
<td>258.00</td>
<td>107.80</td>
<td>0.488</td>
<td>10.200</td>
</tr>
<tr>
<td>Hg</td>
<td>3.03</td>
<td>59.10</td>
<td>200.50</td>
<td>0.409</td>
<td>14.609</td>
</tr>
<tr>
<td>Al</td>
<td>2.78</td>
<td>291.00</td>
<td>26.98</td>
<td>0.600</td>
<td>11.040</td>
</tr>
<tr>
<td>In</td>
<td>3.32</td>
<td>231.80</td>
<td>114.82</td>
<td>0.456</td>
<td>27.000</td>
</tr>
<tr>
<td>Sn</td>
<td>3.10</td>
<td>296.00</td>
<td>118.60</td>
<td>0.400</td>
<td>38.400</td>
</tr>
<tr>
<td>Pb</td>
<td>3.33</td>
<td>178.00</td>
<td>207.20</td>
<td>0.500</td>
<td>14.680</td>
</tr>
<tr>
<td>Sb</td>
<td>3.18</td>
<td>193.43</td>
<td>121.76</td>
<td>0.600</td>
<td>11.900</td>
</tr>
<tr>
<td>Bi</td>
<td>3.40</td>
<td>179.00</td>
<td>208.98</td>
<td>0.460</td>
<td>21.300</td>
</tr>
<tr>
<td>La</td>
<td>3.29</td>
<td>406.00</td>
<td>138.91</td>
<td>0.600</td>
<td>15.600</td>
</tr>
<tr>
<td>Ce</td>
<td>3.17</td>
<td>350.00*</td>
<td>140.12</td>
<td>0.450</td>
<td>17.550</td>
</tr>
</tbody>
</table>

Values were obtained from Iida and Guthrie [23] while *value was obtained from the Internet [29].

We recall that Li has some anomalous behaviour. Among the alkali metals the pseudopotential of Li has rather large non-local component because p states are missing in the core [4]. Again, while the other alkali metals are characterized by weak electron-ion interaction, the absence of p electrons in Li core is responsible for strong scattering of itinerant electrons in the sp conduction band [27]. This may also be responsible for the high melting point of Li (452.15K) among the other alkali metals [12]. It can be seen that for any given temperature within the liquid range, Li has the highest viscosity as can be seen in Fig. 1. Table 1 shows that Li has the smallest atomic diameter, smallest atomic mass and highest heat of evaporation. Thus the relatively high viscosity value at any given temperature is evident in Eqn.1, where we see that the viscosity should increase with a decrease in the atomic diameter $d$ and an increase in $H_{\text{evap}}$ for any given temperature. A small atomic diameter suggests high packing density for a given volume and should give rise to high inter-molecular (cohesive) force and therefore high viscosity at any given temperature. This also results in high heat of evaporation and associated high melting point as is evident in Li. These peculiar properties of Li may account for the disparity in the calculated and experimental viscosity. It should be recalled that the experimental viscosity data of Li used in this work were obtained from different sources as with the other metal as stated above. The values of the adjustable parameters $k$ and $z$ are in Table 1.

Liquid Transition Metals
For the transition metals, we considered liquid Fe, Cu, Ag, and Hg. We obtained the heat of evaporation, atomic mass and atomic diameter of the individual liquid metals from Iida and Guthrie [23] for Fe and Hg and Morioka [19, 20] for Cu and Ag. Morioka et al. [18] and Morioka [19, 20] had earlier determined the viscosities of liquid Cu and Ag but we repeated the calculation. The experimental viscosities of the liquid transition metals were obtained from [20] for Cu and Ag; [23] for Fe, and [23, 24] for Hg.

In Fig. 2, the temperature dependence of the viscosity of this group of liquid metals decreased
exponentially. However, we observed that Hg has the lowest viscosities within its liquid range, while Fe on the other hand, has the highest viscosities within the liquid range. It is also observed from Table 1 that Fe with very high viscosities near the melting point, has the highest heat of evaporation and the smallest atomic diameter and atomic mass, while Hg with the lowest viscosities near the melting point, has the lowest heat of evaporation and the largest atomic diameter and atomic mass among the transition metals under consideration. Generally however, there are both qualitative and quantitative agreement between the calculated and experimental values of viscosities for this group of metals. The values of the adjustable parameters $k$ and $z$ obtained are shown in Table 1.

Liquid Main Group Metals

For this group of liquid metals, we considered Al, Pb, Sb, Sn, Bi, and In. Table 1 shows the physical parameters used. Experimental viscosity values were obtained from [19] for Sb, Sn, Bi, and In; and from [23, 24] for Al and Pb. Fig. 3 shows that the calculated and experimental viscosity values for these liquid metals have both good qualitative and quantitative agreement.

Al is seen to have the highest viscosity value near the melting point. In this group, a critical observation shows that liquid Bi which has the largest atomic diameter and atomic mass, and the smallest heat of evaporation, should have the lowest viscosity near the melting point. But, Sb rather has this property even though Sb has smaller atomic diameter and atomic mass as well as larger heat of evaporation than Bi. We may attribute this to the anomalous behaviour of Bi which expands when solidifying [12]. The values of $k$ and $z$ obtained are shown in Table 1.

Liquid Lanthanides

Due to the difficulty associated with the availability of experimental viscosity data, we only considered liquid Lanthanum and Cerium in the lanthanide group. Our results, however, show that the agreement between experimental viscosity and calculated viscosity values is better in liquid Ce than in La as is evident from Fig. 4.

There is a slight shift in the calculated viscosity from the experimental values beyond the temperature of $1300 K$ for La. This divergence gradually increases as the temperature increases. Experimental viscosity data for La and Ce were obtained from Wittenberg and De Witt [28] as employed in [6], while physical parameters employed are shown in Table 1.
Viscosity (mPa s) vs. Temperature (K)

FIG. 4: Viscosity of liquid Lanthanide metals at different temperatures. Squares represent experimental values while lines represent calculated values. Experimental values were obtained from [6] and [28].

4. Conclusion

Our studies show that the viscosities of the mono-component liquid metals belonging to the alkali, transition, main group, and lanthanide groups can be predicted to a reasonable extent by the gas-like model. However, the limitations of the model are observed when applied to mono-component liquid metals, which manifest some form of anomalous properties such as that of Li. However, the peculiar properties of Li may account for the disparity in the calculated and experimental viscosity. We also observed that generally viscosities of various groups of liquid metals increase with an increase in the atomic diameter and heat of evaporation, and a decrease in atomic mass.

References