Ultrasound attenuation in liquid mercury, zinc and gallium metals

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Ultrasonic attenuation in liquid mercury, zinc and gallium metals has been studied using the concept of a two-state thermodynamical model for the liquids near the melting points. Our theoretical results, so obtained, have been compared with the experimental values and necessary explanations have been offered for any deviations in the results.

Keywords: Liquid metals, Ultrasonic relaxation, Transport properties, Ultrasonic attenuation

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1 Introduction

The study of attenuation of ultrasonic waves in the liquid metals gives us the information about their structure and other related parameters. Recent investigations of the structures of the liquid metals by X-ray, neutron diffraction techniques and computations of inter ionic potentials from radial distribution functions are providing a basis for interpretation of the bulk viscosities. This is determined from ultrasonic attenuation measurements.

The liquid metals are monoatomic in character and ultrasonic attenuation measurements have shown that vibrational or rotational isomeric relaxation does not occur but a structural relaxation similar to that in monometallic liquid does. Almost, all the liquid metals show the existence of the excess ultrasonic attenuation over the classical value. We are using the thermodynamical theory of relaxation processes incorporating the concept of a two-state model for the liquid near the melting point.

The classical attenuation (\(\alpha_{cl}\)) coefficient is given by the addition of the viscous (\(\alpha_S\)) and the thermal (\(\alpha_T\)) attenuation coefficients, such that

\[
\alpha_{cl} = \alpha_S + \alpha_T
\]

Here, the value of \(\alpha_{cl}\) is written as:

\[
\alpha_{cl} = \frac{2\pi^2}{\rho c_i^3} \left( \frac{\eta_s k_T T}{c_p^3 f} \right) \frac{c_p^2 J}{c_p^2 J} \]

the values of \(\alpha_S\) and \(\alpha_T\) are obtained by the following relations:

\[
\alpha_S = \frac{3\pi^2}{3\rho c_i^3} h_i f^2,
\]

or we can write

\[
\alpha_S = \frac{3\pi^2}{3\rho c_i^3} h_i f^2,
\]

and

\[
\alpha_T = \frac{2\pi^2}{\rho c_i^3 k_T T} \frac{c_p^2 J}{c_p^2 J} \]

or this can be written as:

\[
\alpha_T = \frac{2\pi^2}{\rho c_i^3 k_T T} \frac{c_p^2 J}{c_p^2 J} \]

where, \(\rho\) is the density of the liquid metal, \(c_i\) the ultrasonic velocity of the longitudinal wave in [100] direction, \(\eta_s\) the shear viscosity, \(\alpha_p\) the expansion coefficient, \(k_T\) the thermal conductivity, \(c_p\) the specific heat at constant pressure, \(f\) the ultrasonic frequency and \(J\) is the joules constant.

The excess attenuation coefficient (\(\alpha_B\)) is usually attributed to a bulk viscosity \(\eta_B\) and defined by:

\[
\alpha_B = \alpha - \alpha_{cl} = \frac{3\pi^2}{3\rho c_i^3} h_i f^2,
\]

\[
\alpha_B = \alpha - \alpha_{cl} = \frac{3\pi^2}{3\rho c_i^3} h_i f^2,
\]

where \(\alpha\) is the experimental value of the ultrasonic attenuation coefficient.

2 Two-state Model and Structural Relaxation Theory

To describe the structural relaxation processes in monoatomic fluids, a simplest two-state model is assumed. According to this model, two structures are present near the melting point having different coordination numbers, corresponding, respectively, to
the order of packing in the solid state and to a hard sphere like packing in the liquid state.

State I is the one having lower free energy and higher packing fraction and corresponds to the solid phase on freezing. State II has higher free energy and lower packing fraction and corresponds to the liquid phase above the melting point.

At a particular temperature and pressure, a certain fraction of the number of atoms would be in state I, and the remaining fraction would be in another state. When sound wave passes through the medium, the equilibrium distribution of the number of atoms in the two states is perturbed.

The energy required by an atom to jump from one state to another is known as the activation energy and is equal to the difference in the free energy \( \Delta F \) of the two states. The equilibrium would be established again after a lapse of a finite time. This finite time is known as the relaxation time of the process and can be represented by \( \tau \).

Under the structural relaxation process, the liquid possesses a compressibility \( \beta_o \) which is constituted by the two components as follows:

\[
\beta_o = \beta_r + \beta_s \quad \ldots (5)
\]

\( \beta_o \) is the total compressibility, \( \beta_r \) the relaxation compressibility, \( \beta_s \) is the instantaneous compressibility.

Ultrasonic energy is attenuated in the liquid metals and the ultrasonic attenuation coefficient \( \alpha_B \) (for \( \omega \tau << 1 \)) due to structural relaxation, can be written as:

\[
\alpha_B = \frac{C\omega^2}{c_1} \frac{\rho \tau}{\beta_o} \frac{g^2}{\xi^2} \]

or

\[
\alpha_B / f^2 = \frac{C\omega^2}{c_1} \frac{\rho \tau}{\beta_o} \frac{g^2}{\xi^2} \quad \ldots (6)
\]

In order to obtain the expression for \( \beta_r \) and \( \tau \), we use a relaxation treatment for the configurational component of the compression. The simple assumption of a relaxation process with the two energy states is necessary in this case.

Using a relaxational treatment discussed\(^{12,13} \), we obtain the following expression for \( \beta_r \):

\[
\beta_r = \frac{V}{2RT} \left[ 1 + \cosh \left( \frac{\Delta F}{RT} \right) \right] \quad \ldots (7)
\]

where \( V \) is the molar volume of the liquid metal and \( \Delta V/V \) is the relative change in the volume, under structural relaxation for the liquid metal concerned. \( \Delta V/V \) essentially represents the difference in the packing fractions of state I (solid phase) and state II (liquid phase) above the melting point. The value of \( \Delta V/V \) for the Hg, Zn and Ga are estimated on the basis of the structure of these metals. Hg is rhombic structure, hence, for Hg, \( \Delta V/V = 0.29 \), Zn has a \( hcp \) structure, hence for Zn, \( \Delta V/V = 0.30 \) and Ga has a orthorhombic (complex) structure, so we estimate \( \Delta V/V = 0.29 \) as for other metals in the literature\(^{10,11} \).

The relaxation time \( \tau \) can be obtained using Erying’s theory of relaxation rates\(^{12,13} \) giving the following expression for \( \tau \):

\[
\tau = \frac{V}{\eta_s} \frac{1}{RT} \left[ 1 + \exp \left( \frac{\Delta F}{RT} \right) \right] \quad \ldots (8)
\]

In order to obtain the values of \( \alpha_B \), the attenuation coefficient due to structural relaxation using Eq. (6), we need the values of \( \beta_o \) and \( \beta_r \) and \( \tau \), which can be obtained independently.

\( \beta_o \) can be obtained using the following relation:

\[
\beta_o = 1 / (c_1^2 \rho_s) \quad \ldots (9)
\]

where, \( \rho_s \) is the density of the liquid metal and \( c_1 \) is the velocity of the ultrasonic wave in the concerned liquid metal.

Similarly, \( \beta_s \) can be calculated from the following relation:

\[
\beta_s = 1 / (c_s^2 \rho_s) \quad \ldots (10)
\]

where \( c_s \) is the longitudinal ultrasonic velocity in the solid phase of the liquid metal concerned and \( \rho_s \) is the density of the solid metal.

The values of \( \rho_s \), \( c_s \) and \( \rho_l \), \( c_l \) are taken from the literature\(^{14-20} \) for Hg, Zn and Ga. We have calculated the values of \( \beta_0 \) and \( \beta_s \) by Eqs (9) and (10), respectively and then calculated \( \beta_r \) by using Eq. (5).

The value of \( \Delta F \) is calculated by using Eq. (7) and \( \tau \) has been calculated by using Eq. (8).

The values of \( \eta_s \) is taken from literature\(^{15,16} \). We have calculated the value of classical attenuation coefficient \( \alpha_{cl} / f^2 \) by using Eq. (1).

Tables 1-3 show our acoustical data for liquid Hg, Zn and Ga.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Liquid metal</th>
<th>( \beta_0 \times 10^{-12} )</th>
<th>( \beta_s \times 10^{-12} )</th>
<th>( \beta_r \times 10^{-12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hg</td>
<td>3.419</td>
<td>2.332</td>
<td>1.087</td>
</tr>
<tr>
<td>2</td>
<td>Zn</td>
<td>1.856</td>
<td>0.6613</td>
<td>1.245</td>
</tr>
<tr>
<td>3</td>
<td>Ga</td>
<td>1.992</td>
<td>2.254</td>
<td>-0.260</td>
</tr>
</tbody>
</table>
Table 2 — List of values of temperature, ultrasonic wave velocity, density, $\Delta V/V$, $\Delta F$, $\eta_s$ (shear viscosity) and $\tau$ (the relaxation time) for three liquid metals with their units

<table>
<thead>
<tr>
<th>Metal</th>
<th>$T$ (K)</th>
<th>$c_1$ ($10^3$ cm/s)</th>
<th>$\rho_0$ (g/cm$^3$)</th>
<th>$\Delta V/V$</th>
<th>$\Delta F$</th>
<th>$\eta_s$ (kcal mol$^{-1}$)</th>
<th>$\tau$ (10$^{-2}$ poise)</th>
<th>$\tau$ (10$^{12}$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>298</td>
<td>1.470</td>
<td>13.534</td>
<td>0.29</td>
<td>2.235</td>
<td>1.610</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>723</td>
<td>2.790</td>
<td>06.920</td>
<td>0.30</td>
<td>3.180</td>
<td>3.027</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>303</td>
<td>2.870</td>
<td>06.095</td>
<td>0.29</td>
<td>—</td>
<td>1.950</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 — Experimental and theoretical values (from the two-state model) of the ultrasonic attenuation ($a/f^2$) in three liquid metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>$T$ (K)</th>
<th>$a/f^2$ ($10^{-17}$ Neper cm$^{-1}$ s$^2$)</th>
<th>$a_{cl}/f^2$ classical value</th>
<th>$a_{cl}/f^2$ excess</th>
<th>$a_{th}/f^2$ present theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>298</td>
<td>5.71±0.1</td>
<td>5.27</td>
<td>0.44</td>
<td>0.90</td>
</tr>
<tr>
<td>Zn</td>
<td>723</td>
<td>3.7±0.6</td>
<td>4.00</td>
<td>0.30</td>
<td>2.19</td>
</tr>
<tr>
<td>Ga</td>
<td>303</td>
<td>1.58±0.03</td>
<td>1.40</td>
<td>0.18</td>
<td>—</td>
</tr>
</tbody>
</table>

3 Results and Discussion

The excess ultrasonic attenuation in Hg is around 8% of the classical value (Table 3). This suggests that the ultrasonic attenuation in Hg is caused mainly due to the classical processes, namely, due to viscosity and thermal conductivity of the liquid mercury. Our theoretical values of excess ultrasonic attenuation in Hg, however, are twice of the experimental values$^{21}$. The reason for this discrepancy lies mainly in the uncertainty involved with the thermodynamic parameters used for calculations of the ultrasonic attenuation due to classical processes.

Liquid zinc and gallium also possess very small amount of excess ultrasonic attenuation. It is, therefore, certain that in these two liquid metals also the ultrasonic attenuation is caused mainly due to classical processes.

Our estimate of excess ultrasonic attenuation in zinc using a two-state model gives a value, which is 7 times higher than that of the experimental estimate. In this case also, there is a great amount of uncertainty in the experimental values of various thermodynamic parameters used for the calculations of the classical attenuation in zinc. This makes the classical attenuation values in liquid zinc quite uncertain, hence this discrepancy. In Ga, we are unable to estimate the exact theoretical values for excess ultrasonic attenuation due to great uncertainties involved in the relevant data.

References