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# The pressure and temperature dependence of the velocity of sound in liquid metals

Ravinder Kumar, Piyush Kuchhal and Narsingh Dass

Physics Department, University of Roorkee, Roorkee 247667, India

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**Abstract.** In the present paper, a relation is developed to study the velocity of sound in liquid metals as a function of pressure at different temperatures. The relation obtained is applied in the cases of liquid Na, K, Rb, Cs and Hg. The calculated and experimental results in each liquid are found to be in very good agreement throughout range of pressure and temperature studied. Furthermore, several thermodynamic parameters are also calculated.

## 1. Introduction

Shaw and Caldwell [1] recently reported sound velocity measurements in liquid Na, K, Rb and Cs as a function of pressure at different temperatures. Earlier, Davis and Gordon [2] reported the sound velocity data in the case of liquid Hg. One way of analysing the sound velocity data in liquid metals is to develop a polynomial in pressure and that is exactly what those authors did. In this method, the parameters involved may be quite large.

The other approach is to develop an analytical relation on some physical basis so that the sound velocity measurements can be represented as a function of pressure at different temperatures. Such a relation may be useful in obtaining the volume compression data of the liquid metals.

From the above-mentioned sound velocity measurements, we find that the velocity of sound in a liquid metal increases with increasing pressure and decreases with rising temperature. Moreover, the first pressure derivative of the velocity of sound is always positive and the second derivative is always negative. All these facts have to be combined together to obtain the desired relation which is capable of representing the pressure-dependence of the velocity of sound at different temperatures. This is exactly the aim of the present paper.

## 2. Theory

To study the pressure dependence of the velocity of sound, $V_s(P, T_R)$, at an ambient temperature, $T_R$, in the liquid metals, we propose that the ratio of second to first pressure derivatives of the velocity of sound is a pressure-independent parameter, namely

$$\left(\frac{\partial^2 V_s(P,T_R)}{\partial P^2}\right)_{T_R} \Bigg/ \left(\frac{\partial V_s(P,T_R)}{\partial P}\right)_{T_R} = -Z. \tag{1}$$

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Successive integration of equation (1) within the limit from $P = P$ to $P = 0$ gives

$$V_s'(P, T_R) = \left(\frac{\partial V_s(P, T_R)}{\partial P}\right)_{T_R} = V_s'(0, T_R)\exp(-ZP) \tag{2}$$

$$V_s(P, T_R) = V_s(0, T_R) + \frac{V_s'(0, T_R)}{Z}[1 - \exp(-ZP)] \tag{3}$$

where $V_s'(0, T_R)$ is the first pressure derivative of $V_s(P, T_R)$ at $P = 0$.

It is evident from equation (3) that $V_s(P, T_R)$ increases with increasing pressure. Moreover, the value of the velocity of sound corresponding to $P \to \infty$ is given by

$$V_s(\infty, T_R) = V_s(0, T_R) + \frac{V_s'(0, T_R)}{Z}. \tag{4}$$

In the present problem the thermal effect is considered in the same way as it is considered in the volume compression study [3, 4] of solids and liquids, namely

$$P(T) = P(T_R) + P_{th} \tag{5}$$

where $P_{th}$ is the thermal pressure and the simplest form of it is taken as

$$\begin{aligned} P_{th} &= \alpha(0, T_R)B_T(0, T_R)(T - T_R) \\ &= \xi(T - T_R) \end{aligned} \tag{6}$$

where $\alpha(0, T_R)$ and $B_T(0, T_R)$ are the volume expansion coefficient and the isothermal bulk modulus, respectively, at $P = 0$ and $T = T_R$.

To take into account the thermal effect, equations (2) and (3) can be written as

$$V_s'(P, T) = V_s'(0, T_R)\exp\{-Z[P - \xi(T - T_R)]\} \tag{7}$$

$$V_s(P, T) = V_s(0, T_R) + \frac{V_s'(0, T_R)}{Z}\{1 - \exp\{-Z[P - \xi(T - T_R)]\}\}. \tag{8}$$

However, $Z$ is also taken as a temperature-independent parameter in writing equations (7) and (8).

Differentiation of equation (8) with respect to temperature gives

$$\left(\frac{\partial V_s(P, T)}{\partial T}\right)_P = -V_s'(0, T_R)\exp\{-Z[P - \xi(T - T_R)]\}. \tag{9}$$

Thus, it is evident from equation (9) that, at a given pressure, $V_s(P, T)$ decreases with rising temperature.

Hence, it is clear that the velocity of sound in a liquid metal can be easily computed as a function of pressure at different temperatures with the help of equation (8), provided that the values of $V_s(0, T_R)$, $V_s'(0, T_R)$, $Z$, $\alpha(0, T_R)$ and $B_T(0, T_R)$ are known.

Insofar as the values of $\alpha(0, T_R)$ and $B_T(0, T_R)$ are concerned, these may be easily available in the literature. Sometimes, there may be a difficulty in finding the value of $B_T(0, T_R)$, in which case, $B_T(0, T_R)$ can be evaluated from the thermodynamic relation

$$\frac{1}{B_T(0, T_R)} = \frac{1}{B_s(0, T_R)} + \frac{[\alpha(0, T_R)]^2 T_R}{\rho(0, T_R)C_P(0, T_R)} \tag{10}$$

where the adiabatic bulk modulus, $B_s(0, T_R)$, can be computed from

$$B_s(0, T_R) = [V_s(0, T_R)]^2 \rho(0, T_R). \tag{11}$$

Thus, knowing the value of the density, $\rho(0, T_R)$, and the heat capacity at constant pressure $C_P(0, T_R)$, the value of $B_T(0, T_R)$ can be easily calculated.

Before making use of equation (8), it will be worthwhile to justify the assumption given in equation (1). In this connection, the following points are to be noted.

(i) The calculations for the velocity of sound up to 0.7 GPa in the case of liquid alkali metals and up to 1.3 GPa in the case of mercury agree well with the experimental data (see table 1). Furthermore, the various thermodynamic parameters computed are also in very good agreement with the results of other workers (see table 2). Hence, the calculations of the present paper definitely give confidence in the correctness of the assumption.

**Table 1.** Input data.

| Liquid | $T_R$ (°C) | $V_s(0, T_R)$ (km s$^{-1}$) | $V_s'(0, T_R)$ (km s$^{-1}$ GPa$^{-1}$) | $Z$ (GPa$^{-1}$) | $\alpha(0, T_R)$ ($10^{-4}$ K$^{-1}$) | $B_T(0, T_R)$ (GPa) | RMSD in $V_s$ (m s$^{-1}$) | Reference for $\alpha$ and $B_T$ |
|---|---|---|---|---|---|---|---|---|
| Na | 148.9 | 2.500 | 1.068 | 0.4389 | 2.43 | 5.14 | 1.8 | [1] |
| K | 114.2 | 1.848 | 1.671 | 0.8847 | 2.73 | 2.49 | 1.4 | [1] |
| Rb | 130.9 | 1.220 | 1.373 | 0.8518 | 2.85 | 1.90 | 1.4 | [1] |
| Cs | 108.3 | 0.952 | 1.387 | 1.2917 | 2.91 | 1.47 | 1.0 | [1] |
| Hg | 40.5 | 1.4415 | 0.2185 | 0.3234 | 1.80825 | 24.31 | 0.82 | [2] |

(ii) We developed recently an equation of state based on the assumption that the ratio of second to first pressure derivatives of the isothermal bulk modulus is a pressure-independent parameter. The equation of state (EOS) so developed has been applied successfully for various types of materials [5–7]. Therefore, it is natural for us to see that the ratio of second to first pressure derivatives of the velocity of sound is also a pressure-independent parameter. The present computations favour this assumption.

(iii) Under the condition that $Z$ is quite small, equation (3) becomes

$$V_s(P, T_R) = V_s(0, T_R) + V_s'(0, T_R)P.$$

Thus, the variation of the velocity of sound with pressure becomes linear and indicates a special case of equation (3)

Taking all these points into consideration, we feel that the present assumption represents a good working assumption.

## 3. Calculations

The calculations were performed for the cases of liquid Na, K, Rb, Cs and Hg. Equation (8) was first applied at the ambient temperature, $T_R$, to obtain the best-fitted values of $V_s(0, T_R)$, $V_s'(0, T_R)$ and $Z$. The values of these parameters obtained in each liquid are reported in table 1 together with the values of $\alpha(0, T_R)$ and $B_T(0, T_R)$. Equation (8) can now be applied to compute the velocity of sound as a function of pressure at different temperatures.

However, it may be mentioned here that the maximum discrepancies between the calculated and the experimental measurements of sound velocity throughout the range of pressure and temperature studied for each liquid metal were ±1.2% for Na, ±1.8% for K, ±2.5% for Rb, ±2.5% for Cs and ±0.6% for Hg. The discrepancy in each liquid appears to

**Table 2.** Some thermodynamic properties of liquid metals.

| | | $V_s(0,T)$ (km s$^{-1}$) | | $V_s'(0,T)$ (km s$^{-1}$ GPa$^{-1}$) | | $B_s(0,T)$ (GPa) | | $B_s'(0,T)$ | | $B_T(0,T)$ (GPa) | | $B_T'(0,T)$ | | $\gamma(0,T)$ | $\delta_T(0,T)$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Liquid | $T$ (°C) | Present | Theory | Present | Theory | Present | Theory | Present | Theory | Present | Theory | Present | Theory | Present | Present | Theory |
| Na | 148.9 | 2.500 | 2.503 | 1.067 | 1.01 | 5.724 | 5.74 | 6.004 | 3.7 | 5.135 | 5.14 | 6.265 | 3.8 | 1.119 | 6.771 | 3.87 |
| | 129.7 | 2.526 | 2.508 | 1.057 | 1.06 | 5.868 | 5.79 | 6.019 | 3.8 | 5.291 | 5.22 | 6.226 | 3.9 | 1.125 | 6.572 | 3.85 |
| | 109.4 | 2.552 | 2.519 | 1.045 | 1.05 | 6.022 | 5.87 | 6.033 | 3.6 | 5.462 | 5.33 | 6.102 | 3.7 | 1.126 | 6.366 | 3.81 |
| K | 150.2 | 1.807 | 1.832 | 1.708 | 1.68 | 2.639 | 2.71 | 6.122 | 3.8 | 2.328 | 2.38 | 6.412 | 4.8 | 1.136 | 6.850 | 4.27 |
| | 114.2 | 1.848 | 1.852 | 1.671 | 1.62 | 2.789 | 2.80 | 6.165 | 3.8 | 2.486 | 2.49 | 6.354 | 4.0 | 1.154 | 6.534 | 4.16 |
| | 100.0 | 1.865 | 1.854 | 1.657 | 1.64 | 2.849 | 2.82 | 6.180 | 3.9 | 2.549 | 2.52 | 6.337 | 4.0 | 1.160 | 6.427 | 4.14 |
| | 84.8 | 1.881 | 1.863 | 1.642 | 1.65 | 2.913 | 2.86 | 6.196 | 3.9 | 2.618 | 2.57 | 6.314 | 4.1 | 1.169 | 6.295 | 4.09 |
| Rb | 150.11 | 1.206 | 1.215 | 1.386 | 1.44 | 2.083 | 2.11 | 5.920 | 3.9 | 1.837 | 1.86 | 6.232 | 4.1 | 1.099 | 6.739 | 4.22 |
| | 130.9 | 1.220 | 1.218 | 1.373 | 1.43 | 2.144 | 2.14 | 5.954 | 3.9 | 1.902 | 1.90 | 6.207 | 4.1 | 1.105 | 6.575 | 4.18 |
| | 108.3 | 1.237 | 1.225 | 1.379 | 1.42 | 2.217 | 2.18 | 5.993 | 3.9 | 1.981 | 1.95 | 6.188 | 4.1 | 1.112 | 6.382 | 4.12 |
| | 78.8 | 1.258 | 1.235 | 1.341 | 1.36 | 2.314 | 2.23 | 6.040 | 3.8 | 2.088 | 2.20 | 6.162 | 4.0 | 1.113 | 6.163 | 4.04 |
| | 60.1 | 1.272 | 1.241 | 1.329 | 1.33 | 2.377 | 2.26 | 6.069 | 3.8 | 2.157 | 2.06 | 6.154 | 3.9 | 1.114 | 6.029 | 3.99 |
| Cs | 108.3 | 0.952 | 0.954 | 1.387 | 1.38 | 1.670 | 1.64 | 5.862 | 3.6 | 1.464 | 1.47 | 6.084 | 3.9 | 1.023 | 6.448 | 4.36 |
| | 89.4 | 0.963 | 0.959 | 1.373 | 1.34 | 1.678 | 1.66 | 5.888 | 3.5 | 1.515 | 1.50 | 6.061 | 3.8 | 1.028 | 6.276 | 4.29 |
| | 71.8 | 0.974 | 0.964 | 1.359 | 1.34 | 1.723 | 1.67 | 5.912 | 3.6 | 1.563 | 1.53 | 6.045 | 3.8 | 1.0347 | 6.126 | 4.23 |
| | 49.7 | 0.986 | 0.969 | 1.343 | 1.33 | 1.779 | 1.72 | 5.939 | 3.6 | 1.625 | 1.57 | 6.028 | 3.8 | 1.0352 | 5.953 | 4.17 |
| Hg | 50.9 | 1.4294 | 1.4358 | 0.2224 | 0.2275 | 27.513 | 27.759 | 9.578 | — | 27.081 | 23.96 | 9.648 | 9.17 | 2.689 | 9.303 | — |
| | 40.5 | 1.4415 | 1.4415 | 0.2185 | 0.2242 | 28.043 | 28.043 | 9.517 | — | 27.614 | 24.31 | 9.552 | 9.14 | 2.727 | 9.130 | — |
| | 21.9 | 1.4592 | 1.4501 | 0.2128 | 0.2208 | 28.834 | 28.474 | 9.413 | — | 28.410 | 24.84 | 9.404 | 9.10 | 2.782 | 8.882 | — |

Data for Na, K, Rb and Cs were taken from [1]; data for Hg were taken from [2].

be reasonable, taking into account the simplicity of the present theory on the one hand and the experimental error involved in the measurement on the other. In figure 1, the velocity of sound $V_s(P, T)$ is plotted against pressure at that temperature at which the root mean-square deviation is at its maximum in each liquid metal. Thus, it can be said that the agreement is very good between the calculated and the experimental values of the velocity of sound. Moreover, the discrepancy could be further reduced provided that more accurate values of $\alpha(0, T_R)$ and $B_T(0, T_R)$ become available, particularly of the former.

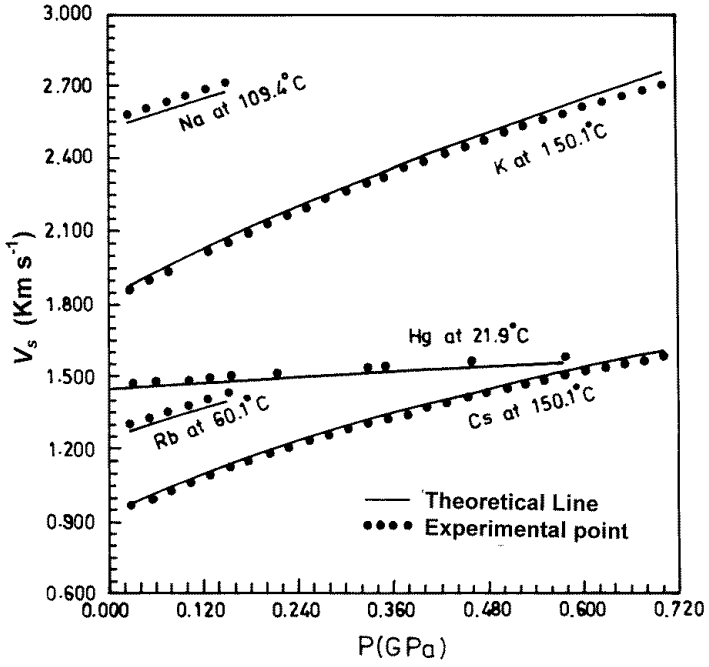


**Figure 1.** The velocity of sound versus pressure in liquid metals, having a maximum value of the root mean square deviation at the indicated temperature.

### *3.1. Thermodynamic parameters*

A number of thermodynamic parameters can be easily evaluated. Equations (7) and (8) can be used to obtain the values of $V_s(0, T)$ and $V_s'(0, T)$, respectively, whereas equations (10) and (11) will give the values of $B_s(0, T)$ and $B_T(0, T)$, respectively, because all other parameters needed for calculation are available in the literature. To calculate $B_s'(0, T)$, we start with the relation

$$[V_s(P, T)]^2 = B_s(P, T)/\rho(P, T). \tag{12}$$

By differentiating equation (12) with respect to pressure and putting $P = 0$, we get

$$B_s'(0, T) = V_s(0, T)\rho(0, T)\left(2V_s'(0, T) + \frac{V_s(0, T)}{B_T(0, T)}\right). \tag{13}$$

Thus, all the data being known, $B_s'(0, T)$ can be computed from equation (13).

The Anderson–Grüneisen parameter

$$\delta_T(0,T) = -\frac{1}{\alpha(0,T)B_T(0,T)}\left(\frac{\partial B_T(0,T)}{\partial T}\right)_{P=0} \tag{14}$$

is calculated assuming a linear variation of $B_T(0,T)$ with temperature whereas the values of $B'_T(0,T)$ are computed with the help of Overton's [8] relation. The Grüneisen parameter given by

$$\gamma(0,T) = \frac{\alpha(0,T)B_s(0,T)}{\rho(0,T)C_P(0,T)} \tag{15}$$

is also calculated.

The values of all these parameters are reported in table 2 and compared with the results of other workers. It is evident from table 2 that the values of $\delta_T(0,T)$ and $B'_T(0,T)$ obtained by Shaw and Caldwell have some formulational error otherwise our results should not differ from theirs. The possible formulational error appears to be that they have taken a negative sign in the bracket of equation (13) instead of a positive one.

## 4. Discussion

The values of $V_s(0,T)$, $V'_s(0,T)$, $B_s(0,T)$ and $B_T(0,T)$ for liquid alkali metals are in very good agreement with the values reported by Shaw and Caldwell. However, the values of $B'_s(0,T)$, $B'_T(0,T)$ and $\delta_T(0,T)$ differ due to a possible error in the formulation as discussed above.

Furthermore, the values of $V_s(0,T)$, $B_s(0,T)$, $B'_s(0,T)$ (except in Hg), $B_T(0,T)$, $B'_T(0,T)$, $\gamma(0,T)$ and $\delta_T(0,T)$ decrease whereas those of $V'_s(0,T)$ and $B'_T(0,T)$ increase with rising temperature. The most compressible of liquid alkali metals is Cs and the least compressible is Na, The values of $B_s(0,T)$ and $B'_T(0,T)$ are greater than $B_T(0,T)$ and $B'_s(0,T)$, respectively. All the liquid metals are found to have $B'_T(0,T)$ greater than 4 which appears not to be an unusual result.

The decrease in the value of $B'_s(0,T)$ with rising temperature in liquid alkali metals can be explained on the basis of equation (13), in which the value of the $[V_s(0,T)\rho(0,T)]$ term is found to decrease faster than the value of $2V'_s(0,T) + V_s(0,T)/B_T(0,T)$ increases with rising temperature. The reverse is true in the case of Hg. The interesting result of the present study is that $B'_T(0,T) \approx \delta_T(0,T)$ which is in agreement with the idea of Dass and Kumari [9].

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