Indian Journal of Pure & Applied Physics Vol. 51, July 2013, pp. 494-498

# Anharmonicity in thermal pressure for aluminium

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Received 12 December 2012; revised 4 April 2013; accepted 16 May 2013

An expression for the volume dependence of thermal pressure is formulated using basic thermodynamic identities. It is applied to aluminium metal for which sufficiently reliable data are available for comparison. The calculations are performed using the two models viz. the Thomas-Fermi model and the Stacey-Davis model. It is found that the values of thermal pressure for m=6 in both models are almost the same. Thermal pressure increases with the increase in pressure. The anhormonic effects are found to be dominant below about (P=60 GPa). While above this, harmonic effects become dominant. The anharmonic effects are very important at low pressures and become less significant as the pressure is increased. Values of thermal pressure have been calculated by taking into account the effect of the change in volume on melting. The results obtained for aluminium indicate that the present model is capable of predicting the volume dependence of thermal pressure, which is found to be in good agreement with the available data for a wide range of pressures and temperatures

Keywords: Metal, Thermodynamic properties, Anharmonicity

# **1** Introduction

The anharmonic behaviour can be studied by determining the volume dependence of thermal pressure which is responsible for the volume thermal expansion of a solid. The anharmonic term including in the Helmholtz free energy (F) affects all thermodynamic and thermoelastic properties of materials which are determined by the derivatives of F. The potential energy curve of the interatomic interactions in a solid departs from harmonic behaviour in the high temperature region approaching the melting temperature<sup>1</sup>. It is always interesting to know the sources and measure for anharmonicity, particularly, in metals; however, inclusion of true anharmonicity like vacancy formation, phononphonon interaction, etc in the equation of state through Grüneisen parameter ( $\gamma$ ). The anharmonic effect is related to the deviations from the linearity of the thermal pressure versus temperature plot. Deviation from the linearity of the thermal pressure in very high temperature region is accepted by various researchers<sup>2-6</sup>. Thermal pressure is defined as<sup>7</sup>:

$$P_{th} = -\left(\frac{\partial F}{\partial T}\right)_V \qquad \dots (1)$$

$$P_{th} = \frac{\gamma}{V} E_{th} \qquad \dots (2)$$

where  $\gamma$  is the Grüneisen parameter  $(=-\partial \ln \omega_i / \partial \ln V)_T$  which shows the measurement of anharmonicity due to lattice vibrations and  $E_{th}$  is thermal energy which includes the anharmonic effects due to thermal vibrations of atoms.

A widely used method of incorporating the temperature contribution to the equation of state is to add at each temperature the thermal pressure  $P_{th}$ , a term that accounts for the isochoric temperature effect on pressure<sup>8-10</sup>. The general expression for an equation of state<sup>7</sup> is:

$$P(V,T) = P_0(V) + P_{th}(V,T)$$
... (3)

 $P_{th}(V,T)$  may be calculated by the following equation:

$$\left(\frac{\partial P_{th}}{\partial T}\right) = \alpha K_T \qquad \dots (4)$$

 $\alpha$  is volume thermal expansivity

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P} \qquad \dots (5)$$

and

 $K_T$  is isothermal bulk modulus

$$K_T = -V \left(\frac{\partial P}{\partial V}\right)_T \qquad \dots (6)$$

Anderson<sup>7</sup> integrated Eq.(4) to evaluate

$$\Delta P_{th} = P_{th}(T,V) - P_{th}(Tr,V) = \alpha K_T (T - T_r) \qquad \dots (7)$$

where  $T_r$  is the reference temperature equivalent to 300K.

One can use the following thermodynamic identity<sup>7</sup> to compute the values of volume dependence of thermal pressure.

$$\left(\frac{d\ln\alpha K_T}{d\ln V}\right)_T = \delta_T - K_T$$
 ...(8)

On integration of Eq.(8) and using Eq.(7), we get:

$$\Delta P_{th} = (T - T_r) \alpha_0 K_0 \exp \int \left( \delta_T - K_T \right) \frac{\partial V}{V} \qquad \dots (9)$$

where  $\alpha_0$  and  $K_0$  are the values of volume thermal expansivity ( $\alpha$ ) and isothermal bulk modulus ( $K_T$ ) at atmospheric pressure, respectively and at a reference temperature.  $\delta_T$  is isothermal bulk modulus:

$$\delta_T = -\frac{1}{\alpha K_T} \left( \frac{\partial K_T}{\partial T} \right)_P \qquad \dots (10)$$

and  $K'_T$  is the first order pressure derivative of isothermal bulk modulus:

$$K'_{T} = \left(\frac{\partial K_{T}}{\partial P}\right)_{T} \qquad \dots (11)$$

In the present paper, we formulate an expression to evaluate values of volume dependence of thermal pressure for aluminium. Aluminium (Al) is an important metal due to its simple s-p nearly-free electronic structure calculations. and has been the subject of numerous experimental and theoretical investigation. Aluminium does not have any d or f electrons which will contribute to the thermodynamic properties either magnetically or electronically, so it is a good choice to establish criteria based only on vibrational contributions. It is found that the values of thermal pressure are very close to those values reported in the literature<sup>11,12</sup>.

#### **2** Theoretical Model

Sharma and Sharma<sup>13</sup> used the following expression for the volume dependence of  $\delta_T$ .

$$\delta_T = \delta_T^{\infty} + \left(\delta_T^0 - \delta_T^{\infty}\right) \left(\frac{V}{V_0}\right)^m \qquad \dots (12)$$

where  $\delta_T^0$  and  $\delta_T^\infty$  are the values of  $\delta_T$  at P = 0 and at  $P \to \infty$  or  $V \to 0$ , respectively and the exponent *m* is an adjustable parameter.

Srivastava and Sinha<sup>14</sup> considered the following expression for first pressure derivative of isothermal bulk modulus.

$$K'_{T} = K'_{\infty} + \left(K'_{0} - K'_{\infty}\right) \left(\frac{V}{V_{0}}\right)^{K'_{0}} \qquad \dots (13)$$

where  $K_0$  and  $K_{\infty}$  are the values of  $K_T$ , respectively at P = 0 and at  $P \to \infty$  or  $V \to 0$ .

Equation (9) at  $T = T_m$ , the melting temperatures becomes;

$$\Delta P_{th} = \alpha_0 K_0 \left( \exp \int \left( \delta_T - K_T \right) \frac{\partial V}{V} \right) (T_m - T_r) \qquad \dots (14)$$

Using Eqs (9,12-14), we get the following relationship:

$$\Delta P_{th} = \alpha_0 K_0 \left[ \exp\left\{A \ln \frac{V(T_m, P)}{V(T_r, 0)} + \left\{B\left(\frac{V(T_m, P)}{V(T_r, 0)}\right)^m - 1\right\} - C\left\{\left(\frac{V(T_m, P)}{V(T_r, 0)}\right)^{K_0'} - 1\right\}\right\} \right] (T_m - T_r) \qquad \dots (15)$$

where *A*, *B* and *C* are constants for given material. We have

$$A = \left(\delta_T^{\infty} - K_{\infty}^{'}\right) \qquad \dots (16)$$

$$B = \left(\frac{\delta_T^0 - \delta_T^\infty}{m}\right) \qquad \dots (17)$$

$$C = \left(\frac{K_{0}^{'} - K_{\infty}^{'}}{K_{0}^{'}}\right) \qquad \dots (18)$$

One can find the values of  $V(T_m, P)/V(T_r, 0)$  in Eq. (15) from the following expression:

$$\frac{V(T_m, P)}{V(T_r, 0)} = \frac{V(T_m, P)}{V(T_r, P)} \times \frac{V(T_r, P)}{V(T_r, 0)} \qquad \dots (19)$$

Kushwah *et al*<sup>15</sup>. obtained the following isobaric equation of state:

$$\frac{V(T_m, P)}{V(T_r, P)} = 1 - \frac{1}{\delta(T_r, 0) + 1} \times \ln \left[ 1 - \alpha(T_r, P) \left( \delta(T_r, 0) + 1 \right) (T_m - T_r) \right] \dots (20)$$

We can predict the values of  $\alpha(T_r, P)$  through the following relationship<sup>13</sup>:

$$\alpha(T_r, P) = \alpha(T_r, 0) \left( \frac{V(T_r, P)}{V(T_r, 0)} \right)^{\delta_{T_{\infty}}} \\ \times \exp\left[ \left( \frac{\delta_{T_0} - \delta_{T_{\infty}}}{m} \right) \left\{ \left( \frac{V(T_r, P)}{V(T_r, 0)} \right)^m - 1 \right\} \right] ...(21)$$

where  $\alpha(T_r, 0)$  is the volume thermal expansivity at the reference temperature  $T_r$  and at zero pressure. We can easily compute the values of  $V(T_m, P)/V(T_r, 0)$ through Eq. (19-21). The values of volume dependence of thermal pressure are calculated through Eq. (15).

## **3** Results and Discussion

**3.1** Values of  $\delta_{T_{\infty}}$  and  $K_{\infty}$ 

A well known thermodynamic identity <sup>16</sup> is given by:

$$\delta_T = K_T + q - 1 + C_T$$
 ...(22)

where  $K_T$  is first order pressure derivative of isothermal bulk modulus  $K_T$ .

$$K_{T}^{'} = \left(\frac{\partial K_{T}}{\partial P}\right)_{T} \qquad \dots (23)$$

and q is second Grüneisen parameter.

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T \tag{24}$$

and  $C_T$  is the volume derivative of heat capacity at constant volume along isotherm.

$$C_{T}' = \left(\frac{\partial \ln C_{V}}{\partial \ln V}\right)_{T} \qquad \dots (25)$$

At infinite pressure i.e.,  $P \rightarrow \infty$  or  $V \rightarrow 0$ , Eq. (22) takes the form:

$$\delta_{T_{\infty}} = K_{\infty}' + q_{\infty} - 1 + C_{T_{\infty}}' \qquad \dots (26)$$

 $q_{\infty}$  tends to zero<sup>16</sup> and  $C_{T_{\infty}}$  tends to zero<sup>17</sup> at  $P \to \infty$  or  $V \to 0$ , now Eq. (26) becomes:

$$\delta_{T_{n}} = K_{\infty} - 1$$
 ...(27)

If we Follow the Thomas-Fermi model<sup>18-21</sup>, i.e.,  $K_{\infty}^{'} = 5/3$  then Eq. (27) results into  $\delta_{T_{\infty}} = 2/3$ . While for the Stacey-Davis model<sup>22</sup> i.e.,  $K_{\infty} = 2.652$  which is calculated<sup>22</sup> through  $K_{\infty} = 0.6K_0$  where  $K_0$  is the first order pressure derivative of isothermal bulk modulus at  $T_r$  and zero pressure, now Eq. (27) gives  $\delta_{T_{\infty}} = 1.652$ . The values of  $\delta_{T_{\infty}}$  for both models<sup>18-22</sup> the constraint<sup>23</sup>  $0 < \delta_T < K_{\infty}$ . Input satisfy parameters used in calculations are presented in Table 1. The predicted thermal pressure of aluminium through Eq. (15) for both models i.e.,  $K_{\infty} = 5/3$  or  $\delta_{T_{\infty}} = 2/3$  and  $K_{\infty} = 2.652$  or  $\delta_{T_{\infty}} = 1.652$  for the different values of m such as 1, 3, 6, 8, 10 and 12. According to the Thomas-Fermi model  $\delta_T^{\infty}$  and  $K_{\infty}$ are the same for all the materials, while according to the Stacey-Davis model  $\delta_T^{\infty}$  and  $K_{\infty}$  depend on the

Table 1 — Input parameters <sup>11,31-33</sup> used in calculations	
Parameter	Values
$\delta_{T_0}$	4.8 δ
K <sub>0</sub> IGPa)	77.2
$\alpha_0 (10^{-1} \mathrm{K}^{-1})$	6.9
<i>K</i> ′ <sub>0</sub>	4.42

material. This behaviour is similar to that found for the Grüneisen parameters  $\gamma_{\infty}$  and  $\lambda_{\infty}$  (Ref. 24).

# **3.2** Effect of m parameter on thermal pressure

*P-V* relationship for Al at 300K based on experimental data is shown in Fig. 1. Values of thermal pressure obtained through Eq. (15) along with those values obtained by Hanstrom and Lazor<sup>11</sup> and Boehler and Ross<sup>12</sup> for the sake of comparison, is

shown in Fig. 2. It is apparent from Fig. 1 that thermal pressure increases with the increase in m. It also reflects that thermal pressure increases with increase in pressure. As the value of m increases, the values of thermal pressure increases throughout the wide range of pressure. It explores that both models give almost the same results for m=6 at every pressure and near to those values of thermal pressure obtained by Hanstrom and Lazor<sup>11</sup> and Boehler and Ross<sup>12</sup>. Values



Fig. 1 — Pressure versus volume for aluminium at reference temperature based on experimental data<sup>11,12</sup>



Fig. 2 — Pressure dependence of thermal pressure at different values of m for two models (the Thomas-Fermi model and the Stacey-Davis model) at reference temperature  $T_r$  for aluminium

of thermal pressure for m>6 deviate more than m>6from data<sup>11,12</sup> at higher pressures. It is also observed from Fig. 2 that the values of thermal pressure for above m>6 come closer to each other throughout the pressure range. At constant temperature, thermal pressure increases with the increase in pressure by virtue of the reduction in amplitude of atomic vibrations..

### **3.3** Anharmonic effects in thermal pressure

Figure 2 shows the non-linearity at low pressures. It could be seen below about (P=60 GPa) for the metal under consideration, however, for (P>60 GPa) inearity takes place. It is clear from Eq. (2) that there must be anharmonicity in thermal pressure. Thermal pressure in Eq. (2) is the function of Grüneisen parameter  $\gamma (=-\partial \ln \omega / \partial \ln V)_T \gamma$  a and thermal energy  $E_{\rm th}$ . Out of which Grüneisen parameter is the crucial measurement of anharmonicity. This anharmonicity is arised from strong asymmetry of atomic vibrations. At low pressures, anharmonic effects are higher and decrease with increase in pressure. The values obtained through Eq. (15) are consistent with those explanations given by many researchers<sup>25-29</sup>. Isaak et al.<sup>29</sup> and Karki et al.<sup>30</sup> also explained that these effects are limited to low pressure. This is proved by Hardy theory<sup>25</sup>, which shows that the application of pressure extends the boundary between the anharmonic and the classical regime to higher temperatures. Thus, anharmonic effects disappear with increasing *P*.

## **4** Conclusions

We have thus formulated an Expression (Eq. 15) using basic thermodynamic identities for estimating the values of volume dependence of thermal pressure. The present model has been applied to aluminium. The results have been obtained for different values of parameter m viz. 1, 3, 6, 8, 10, 12 and reasonably good agreement with the available data<sup>11,12</sup> has been obtained for m>6. This is true for the Thomas –Fermi model as well as for the Stacey-Davis model. For m>6, both the models yield almost identical results. For m>6, the results obtained from the two models are also quite close to each other. It should be mentioned that values of m>6, the results based on the two models deviate significantly with each other, and also deviate from the data. It is also revealed that the anharmonic effects are more significant below 60 GPa and the anharmonicity is suppressed at higher pressures.

#### Acknowledgement

The authors are also grateful to Prof J Shanker, IBS, Khandari, Agra, Uttar Pradesh, India, for his valuable discussion and suggestions. Dr S K Sharma is thankful to Shivalik Institute of Engineering and Technology, Ambala (H.R.) for providing the facility to this research.

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