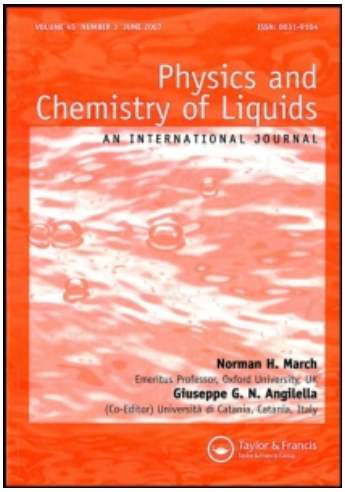

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Thermal Pressure Coefficients, of Liquid Polyvalent Metals Based on One-Component Plasma Model

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Thermal Pressure Coefficients of Liquid Polyvalent Metals Based on One-Component Plasma Model

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One-component plasma model is applied for predicting thermal pressure coefficients $\sqrt{_v}$ of liquid polyvalent metals at their melting points. The results are compatible with those obtained by other methods or experiments.

In recent years the one-component plasma (OCP) reference system has been widely used to understand the thermodynamic properties of liquid metals.[1-8] Ono and Yokoyama[4] and Montella *et al.*[6] have calculated thermal pressure coefficients $\sqrt{_v}$ using OCP reference system in the Gibbs-Bogoliubov (GB) formalism while Ono *et al.*[9] have made an attempt to estimate $\sqrt{_v}$ using OCP reference system in the Percus-Yervick (PY) phonon description, but their approaches are limited to liquid alkali metals. Yokoyama *et al.*[10] computed $\sqrt{_v}$ for simple liquid metals based on PY phonon description. However, results show a discrepancy between theoretical and experimental values except for In, Ga and Zn. Hasegawa and Watabe[11] have also calculated $\sqrt{_v}$ for simple liquid metals through the modified form of pressure equation appropriate to liquid metals using pseudopotential formalism for electron ion interaction.

In this communication we present a simple method based on one-component plasma reference system to calculate thermal pressure coefficients of liquid metals. The variation of $\sqrt{_v}$ with temperature (T) for different metals are studied over a wide range of temperature (up to

the boiling point). The aim of the present paper is to test the applicability of this procedure for liquid polyvalent metals having complicated liquid structure. The electronic contribution to entropy being appreciable in liquid polyvalent metals, seems to play an important role in the quantitative description of $\sqrt{}_v$. The results based on OCP reference system are compared with experimental as well as other theoretical estimates.

The thermal pressure coefficient defined through $\sqrt{}_v \equiv (\partial P/\partial T)_\Omega$, can be alternatively and equivalently given by

$$\sqrt{}_v \equiv \left(\frac{\partial S}{\partial \Omega}\right)_T \tag{1}$$

Here S denotes the entropy and Ω the atomic volume. The bulk entropy of the liquid metals in OCP reference system has already been discussed by Khanna and Shanker.[7] Therefore it is straight forwardly written as

$$S = S_{\text{gas}} + \Delta S_{\text{OCP}} + S_{\text{el}} \tag{2}$$

where, S_{gas} is the ideal gas entropy

$$\frac{S_{\text{gas}}}{NK_B} = \frac{5}{2} + \ln\left[\Omega\left(\frac{MK_BT}{2\pi\hbar^2}\right)^{3/2}\right] \tag{3}$$

ΔS_{OCP} is the excess entropy depends upon the plasma parameter Γ

$$\frac{\Delta S_{\text{OCP}}}{NK_B} = -2.83632\Gamma^{1/4} + 0.89770\Gamma^{-1/4} + 0.80049 \ln \Gamma + 1.78559 \tag{4}$$

here

$$\Gamma = \left[\frac{(Ze)^2}{K_BT}\right]\frac{1}{a} \tag{5}$$

with

$$\text{Winger-Seitz radius } a = \left(\frac{3\Omega}{4\pi}\right)^{1/3}$$

and S_{el} represents the electronic contribution to entropy

$$\frac{S_{\text{el}}}{NK_B} = \tfrac{1}{3}\pi^2 K_B T N(E_F) \tag{6}$$

Here $N(E_F)$ being the density of states (two per space orbital) at the Fermi level.

To evaluate thermal pressure coefficient $\sqrt{_v}$, the differentiation of Eq. (2) with respect to Ω at constant temperature leads to the formula

$$\sqrt{_v} = \frac{1}{\Omega}[1.0 + 0.23636\Gamma^{1/4} + 0.074808\Gamma^{-1/4} - 0.26683 + \tfrac{2}{9}\pi^2 K_B T N(E_F)] \quad (7)$$

To predict $\sqrt{_v}$, we need the plasma parameter Γ which is obtained by the procedure described in Khanna and Shanker.[8] The results are depicted in Table 1. A comparison between calculated and experimental values of $\sqrt{_v}$ reveals that discrepancies are typically of the order of 11% with fluctuations above and below the observed one. The results are in general better than recent theoretical results of Yokoyama *et al.*[10] (PY phonon description) and Hasegawa and Watabe[11] (HS model). Equation (7) clearly indicates that the plasma parameter Γ contributes and atomic volume Ω affects $\sqrt{_v}$. For the calculations of $\sqrt{_v}$ at different temperatures above melting, we have described the variation of Γ with the thermodynamic state by the simple expression

$$\Gamma = \Gamma_f \frac{T_f}{T}\left(\frac{n}{n_f}\right)^{1/3} \quad (8)$$

where, n is the number density of ions and subscript f refers to freezing.

Evidently with increasing temperature, the atomic volume (Ω) of the liquid will increase and can be obtained through the empirical relation

$$\Omega_T = \Omega(1 + \alpha\Delta T) \quad (9)$$

here α is the coefficient of thermal expansion. The variation of thermal pressure coefficient with temperature for different metals are displayed in Figure 1 using Eqs. (7), (8) and (9). The noticeable feature is that $\sqrt{_v}$ decreases with increasing temperature. A perusal of Figure 1 also shows that for liquid metals Zn, Cd and Mg the variation of $\sqrt{_v}$ with temperature is more linear than for Tl, Pb and Bi, but in the case of Al, Ga, In and Sn the decrease in $\sqrt{_v}$ with increasing temperature up to about 700 K beyond melting point is larger than for higher temperatures.

In summary, we can now say that one-component plasma (OCP) reference system accounts very well for the thermal pressure coefficients of liquid polyvalent metals at their melting points.

Table 1 Thermal pressure coefficients $\sqrt{\gamma_v}$ (in units of bar K^{-1}) for liquid polyvalent metals at their melting points

Metal	T (K)	Γ	S_{el} (NK_B)	$\sqrt{\gamma_v}$ (Calc)	$\sqrt{\gamma_v}$ Ref. (10)	$\sqrt{\gamma_v}$ Ref. (11)	$\sqrt{\gamma_v}$ (expt)	$\sqrt{\gamma_v}$(Calc)/$\sqrt{\gamma_v}$(expt)
Mg	923	107	0.12	37.8	30.2	—	33.9	1.11
Al	933	125	0.11	51.4	43.6	49.4	47.7	1.08
Zn	700	162	0.10	60.5	55.2	84.1	56.0	1.08
Cd	600	146	0.10	42.5	41.7	—	44.8	0.95
In	429	200	0.08	37.7	39.6	—	39.2	0.96
Sn	505	172	0.09	35.6	35.9	—	40.2	0.89
Pb	600	155	0.11	31.0	29.6	13.0	33.5	0.93
Ga	303	209	0.04	53.3	59.0	—	57.5	0.93
Tl	577	162	0.11	34.6	31.4	—	33.9	1.02
Bi	544	142	0.10	28.5	25.4	—	29.2	0.98

Experimental data are from Shimoji[12] and for liquid polyvalent metals S_{el} is evaluated in the Sommerfeld approximation.

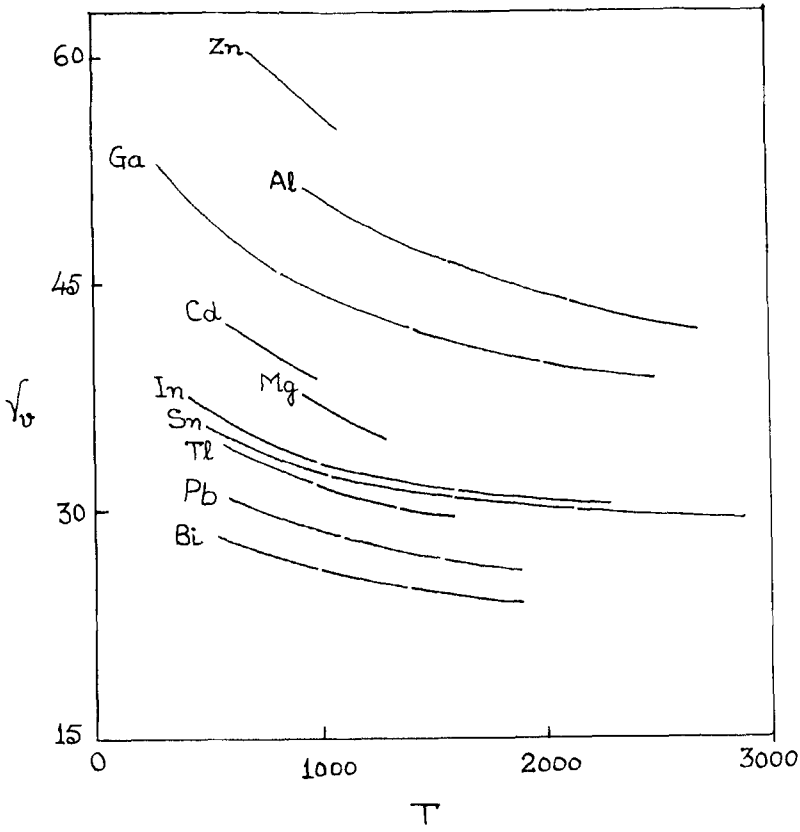

Figure 1 Variation of thermal pressure coefficient $\sqrt{\gamma_v}$ (in units of bar K^{-1}) with temperature $T(K)$.

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