

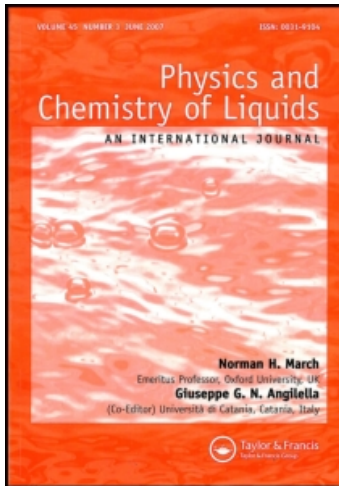
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I. Yokoyama<sup>a</sup>; I. Ohkoshi<sup>a</sup>; T. Satoh<sup>a</sup>

<sup>a</sup> Department of Mathematics and Physics, National Defense Academy, Yokosuka, Japan

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# Thermal Pressure Coefficients of Simple Liquid Metals Based on the Percus-Yevick Phonon Description

I. YOKOYAMA, I. OHKOSHI and T. SATOH

*Department of Mathematics and Physics,  
National Defense Academy, Yokosuka 239, Japan.*

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The Percus-Yevick phonon method appears to be applicable for predicting thermal pressure coefficients of simple liquid metals at the melting points. An accurate density-derivative of structure factor in the range  $(k_D, k_0)$  is important for a quantitative exploration of the present approach.

## 1 INTRODUCTION

The Percus-Yevick (PY) phonon theory of liquids has proven to be a useful approach for predicting certain thermodynamic properties of liquid metals.<sup>1-5</sup> To a good first approximation a liquid metal can be imagined to have  $3N$  normal modes of density fluctuation form. Thus, the zeroth order picture is of longitudinal phonons with  $\mathbf{k}$ -vectors occupying an enlarged Debye sphere of radius  $k_0 = 3^{1/3}k_D$  where  $k_D = (6\pi^2n)^{1/3}$ ,  $n$  the number density of ions. When phonon-phonon interactions are introduced, a leading order correction is obtained. So far we have reported a series of calculations of entropies,<sup>1,2</sup> specific heats,<sup>3</sup> phonon dispersion curves<sup>4</sup> and sound velocities<sup>5</sup> of liquid metals.

The purpose of the present paper is to calculate thermal pressure coefficients  $\gamma_V$  for a variety of simple liquid metals and to comment on the density-derivatives of structure factors. This seems to be a stringent test of the PY phonon approach because as Hasegawa and Watabe<sup>6</sup> pointed out previously  $\gamma_V$  is very sensitive to approximations on the temperature dependence of the structure factor. To our best knowledge Hasegawa and Watabe were the first

to work out  $\gamma_V$  of simple liquid metals from the fundamental point of view of the electron theory of metals. Using the pseudopotential formalism for the electron-ion interaction they calculated  $\gamma_V$  through the modified form of the pressure equation appropriate to liquid metals. The temperature derivative of the structure factor was evaluated by using the method of Andersen *et al.*<sup>7</sup> (hereafter referred to as the WCA method). Agreement between their results and experiments is found satisfactory for simpler metals though effective packing fractions  $\eta$  are not always reasonable.

In this paper we use, without recourse to the pressure equation, the PY phonon method which can account very well for the entropies of liquid metals. In the next section we derive an expression for  $\gamma_V$  and present a method to be employed. In §3, the results of numerical calculations are compared with experiments. Some conclusions are given in the last section.

## 2 FORMALISM

The total entropy from the PY phonon theory<sup>3</sup> reads

$$S = S_0 + S'_1 + S''_1 + S_{\text{elec}}, \quad (1)$$

where, with  $x \equiv \hbar\omega(k)/k_B T$ ,

$$S_0 = k_B \sum_{\mathbf{k}} \left\{ \frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right\} \quad (2)$$

$$S'_1 = \frac{k_B}{4N} \sum'_{\mathbf{k}, \mathbf{k}'} \left( \frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 a(\mathbf{k} - \mathbf{k}'), \quad (3)$$

$$S''_1 = \frac{k_B}{4N} \sum'_{\mathbf{k}, \mathbf{k}'} \left( \frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 \left\{ \frac{\partial \ln a(\mathbf{k} - \mathbf{k}')}{\partial \ln T} \right\}_V a(\mathbf{k} - \mathbf{k}'), \quad (4)$$

and, with  $N(E_F)$  being the density of states (two per space orbital) at the Fermi level,

$$S_{\text{elec}} = \frac{1}{3} \pi^2 N(E_F) N k_B^2 T. \quad (5)$$

The dashes on the summations indicate that all terms  $\mathbf{k} = \mathbf{k}'$  are omitted.  $S_0$  describes the independent phonon result and  $S'_1$  and  $S''_1$ , which include the structure factor  $a(\mathbf{k} - \mathbf{k}')$ , are due to the phonon-phonon interaction.  $S_{\text{elec}}$  arises from thermal excitation of the conduction electrons; it is small for simple metals and is adequately approximated by its Sommerfeld form.

First, let us note that to high accuracy, the summand of Eq. (2) can be expanded for small  $x$  to give  $1 - \ln x$ , and we obtain

$$S_0 = k_B \sum_{\mathbf{k}} (1 - \ln x). \tag{2}$$

We are concerned with the thermal pressure coefficient  $\gamma_V \equiv (\partial P / \partial T)_V$ , which can be alternatively and equivalently defined by

$$\gamma_V \equiv \left( \frac{\partial S}{\partial V} \right)_T = -n^2 k_B \left\{ \frac{\partial(S/Nk_B)}{\partial n} \right\}_T. \tag{6}$$

In the computationally convenient form (6),  $\gamma_V$  is very evidently a property of the interatomic forces and independent of the so-called volume term (in the pseudopotential formalism) which is inadequately known to us at the present time. Using the scaled variable  $k/k_0$ , differentiation of Eq. (1) with respect to  $n$  at constant temperature leads to the formula

$$\gamma_V = \gamma_V^0 + \gamma_V^{1'} + \gamma_V^{1''} + \gamma_V^{\text{elec}}, \tag{7}$$

where

$$\gamma_V^0 = nk_B - \frac{9}{2} nk_B \int_0^1 d \left( \frac{k}{k_0} \right) \frac{(k/k_0)^2}{a(k/k_0)} n \left\{ \frac{\partial a(k/k_0)}{\partial n} \right\}_T, \tag{8}$$

$$\gamma_V^{1'} = -\frac{81}{32} nk_B \int_0^1 \frac{d(k/k_0)}{(k/k_0)} \int_0^1 \frac{d(k'/k_0)}{(k'/k_0)} \left[ \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\}^2 \Phi_1 - 2 \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\} \Phi_3 + \Phi_5 \right], \tag{9}$$

$$\Phi_\alpha = \int_{|k-k'|/k_0}^{k+k'/k_0} d \left( \frac{q}{k_0} \right) \left( \frac{q}{k_0} \right)^\alpha n \left\{ \frac{\partial a(q/k_0)}{\partial n} \right\}_T, \alpha = 1, 3, 5.$$

$$\gamma_V^{1''} = -\frac{81}{32} nk_B \int_0^1 \frac{d(k/k_0)}{(k/k_0)} \int_0^1 \frac{d(k'/k_0)}{(k'/k_0)} \left[ \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\}^2 \Psi_1 - 2 \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\} \Psi_3 + \Psi_5 \right], \tag{10}$$

$$\Psi_\alpha = \int_{|k-k'|/k_0}^{k+k'/k_0} d \left( \frac{q}{k_0} \right) \left( \frac{q}{k_0} \right)^\alpha n \left\{ \frac{\partial}{\partial n} \left[ a \left( \frac{q}{k_0} \right) \left( \frac{\partial \ln a(q/k_0)}{\partial \ln T} \right)_V \right] \right\}_T,$$

$$\alpha = 1, 3, 5.$$

and

$$\gamma_V^{\text{elec}} = \frac{2}{3} nk_B \left( \frac{S_{\text{elec}}}{Nk_B} \right). \tag{11}$$

Here we used the Egelstaff<sup>8,9</sup> independent-phonon formula

$$\omega(k) = k \left[ \frac{k_B T}{ma(k)} \right]^{1/2} \quad (12)$$

in the derivation of Eq. (8),  $m$  as the mass of an ion and the Sommerfeld free-electron form in Eq. (11). In order to apply Eqs. (8)–(10) to the actual metals some approximations are necessary on the density-derivative of  $a(k/k_0)$  since little is known to us about it.† Hasegawa and Watabe used the WCA method for this purpose (the isochoric temperature-derivatives of structure factors in their cases). The WCA structure factor, however, has a spurious bump<sup>6,13</sup> around the phonon region. This is a vital defect in view of the present approach because harmonic effects are dominant in the description of the entropy, the most important region of  $k$ -space being  $k_D < k < k_0 \equiv 3^{1/3}k_D$  which is peculiar to liquids. Furthermore they frequently obtained unreasonable values of packing fractions  $\eta$  in the WCA calculations.‡

In the present work we evaluate  $\{\partial a(k/k_0)/\partial n\}_T$  using a hard-sphere structure factor  $a_{HS}(k/k_0)$  (the only established route known to us at the present time) and test the ability of the PY method to predict  $\gamma_V$ . In this approximation we obtain

$$\gamma_V^0 = nk_B - \frac{9}{2}nk_B \int_0^1 d \left( \frac{k}{k_0} \right) \left( \frac{k}{k_0} \right)^2 \left\{ \frac{\partial \ln a_{HS}(k/k_0)}{\partial \ln \eta} \right\}, \quad (13)$$

$$\begin{aligned} \gamma_V^1 = & -\frac{81}{32}nk_B \int_0^1 \frac{d(k/k_0)}{(k/k_0)} \int_0^1 \frac{d(k'/k_0)}{(k'/k_0)} \left[ \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\}^2 \xi_1 \right. \\ & \left. - 2 \left\{ \left( \frac{k}{k_0} \right)^2 + \left( \frac{k'}{k_0} \right)^2 \right\} \xi_3 + \xi_5 \right], \quad (14) \end{aligned}$$

$$\xi_\alpha = \int_{|k-k'|/k_0}^{k+k'/k_0} d \left( \frac{q}{k_0} \right) \left( \frac{q}{k_0} \right)^\alpha a_{HS} \left( \frac{q}{k_0} \right) \left\{ \frac{\partial \ln a_{HS}(q/k_0)}{\partial \ln \eta} \right\}, \quad \alpha = 1, 3, 5$$

† Egelstaff *et al.*<sup>10</sup> have reported the isothermal density-derivatives of structure factors for liquid Rb which are the only available data at the present time. Quite recently Cummings and Egelstaff<sup>11</sup> have confirmed the uniform fluid model (proposed by Egelstaff *et al.*<sup>12</sup> and used in their analysis<sup>10</sup>) to be well supported by more sophisticated models for liquid Rb. However, the uniform fluid model can not give a correct description of  $\gamma_V$ . For further details in this respect see Hasegawa and Watabe<sup>9</sup> and the footnote on p.170.

‡ McLaughlin and Young,<sup>14,15</sup> quite recently, have reported in their low-angle structure factor calculations that the modified WCA formalism of Jacobs and Andersen<sup>16</sup> can remove the spurious bump at low  $k$ . Therefore the situation mentioned here might change for the better.

and

$$\begin{aligned} \gamma_V^{1''} = & -\frac{81}{32}nk_B\frac{T}{\eta}\left(\frac{\partial\eta}{\partial T}\right)_V\int_0^1\frac{d(k/k_0)}{(k/k_0)}\int_0^1\frac{d(k'/k_0)}{(k'/k_0)}\left[\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}^2\zeta_1\right. \\ & \left.-2\left\{\left(\frac{k}{k_0}\right)^2+\left(\frac{k'}{k_0}\right)^2\right\}\zeta_3+\zeta_5\right], \quad (15) \\ \zeta_\alpha = & \int_{|k-k'|/k_0}^{k+k'/k_0}d\left(\frac{q}{k_0}\right)\left(\frac{q}{k_0}\right)^\alpha a_{HS}\left(\frac{q}{k_0}\right)\left\{-\frac{\partial\ln a_{HS}(q/k_0)}{\partial\ln\eta}\right. \\ & \left.+\left[\frac{\partial\ln a_{HS}(q/k_0)}{\partial\ln\eta}\right]^2+\frac{\partial^2\ln a_{HS}(q/k_0)}{\partial\ln\eta^2}\right\}, \alpha=1,3,5. \end{aligned}$$

where we assumed that the density-derivative of hard-sphere diameter  $(\partial\sigma/\partial n)_T=0$ , and that the temperature-derivative of packing fraction  $(\partial\eta/\partial T)_V$  is independent of  $\eta$ . We return again to the former assumption when considering its possible effect on  $\gamma_V$  in conjunction with ab initio calculations based on the Gibbs-Bogoliubov variational method.<sup>17</sup> As for the latter assumption it is well supported in view of the smallness of the term  $\gamma_V^{1''}$  (see Table II).

### 3 RESULTS AND DISCUSSIONS

The total thermal pressure coefficient given in Eq. (7) as well as the total entropy given in Eq. (1) have been calculated using the hard-sphere structure factor  $a_{HS}(k/k_0)$  for various packing fractions which encompass a large majority of conceivable applications. The results are shown in Figures 1-6 where the left-side scale is for the entropy and the right-side scale is for the thermal pressure coefficient. As is seen from the figures the calculated entropies between  $\eta=0.38$  and  $\eta=0.50$  are within 10% of the observed ones for all cases except for Ga, In and Sn. This means that the entropies of simple liquid metals are moderately well described by  $a_{HS}(k/k_0)$  for any given  $\eta$  in the range (0.38, 0.50).<sup>18</sup> For Ga, the calculated entropies are larger than the experiment by 23% with  $\eta=0.38$ , and by 5% with  $\eta=0.5$ .

On the other hand the calculated pressure coefficients vary sensitively with  $\eta$  over quite a wide range. A clear trend is that the entropy decreases with increasing  $\eta$ , while the thermal pressure coefficient increases with increasing  $\eta$ . Here we are interested in a correlation between the two. By fitting the calculated entropy to the observed one, a packing fraction  $\eta_{ph}$  can be obtained and this is used to find the corresponding calculated thermal pressure coefficient through the diagrams 1-6. The results of such an exercise for seventeen metals at the melting points are summarized in Table I. On

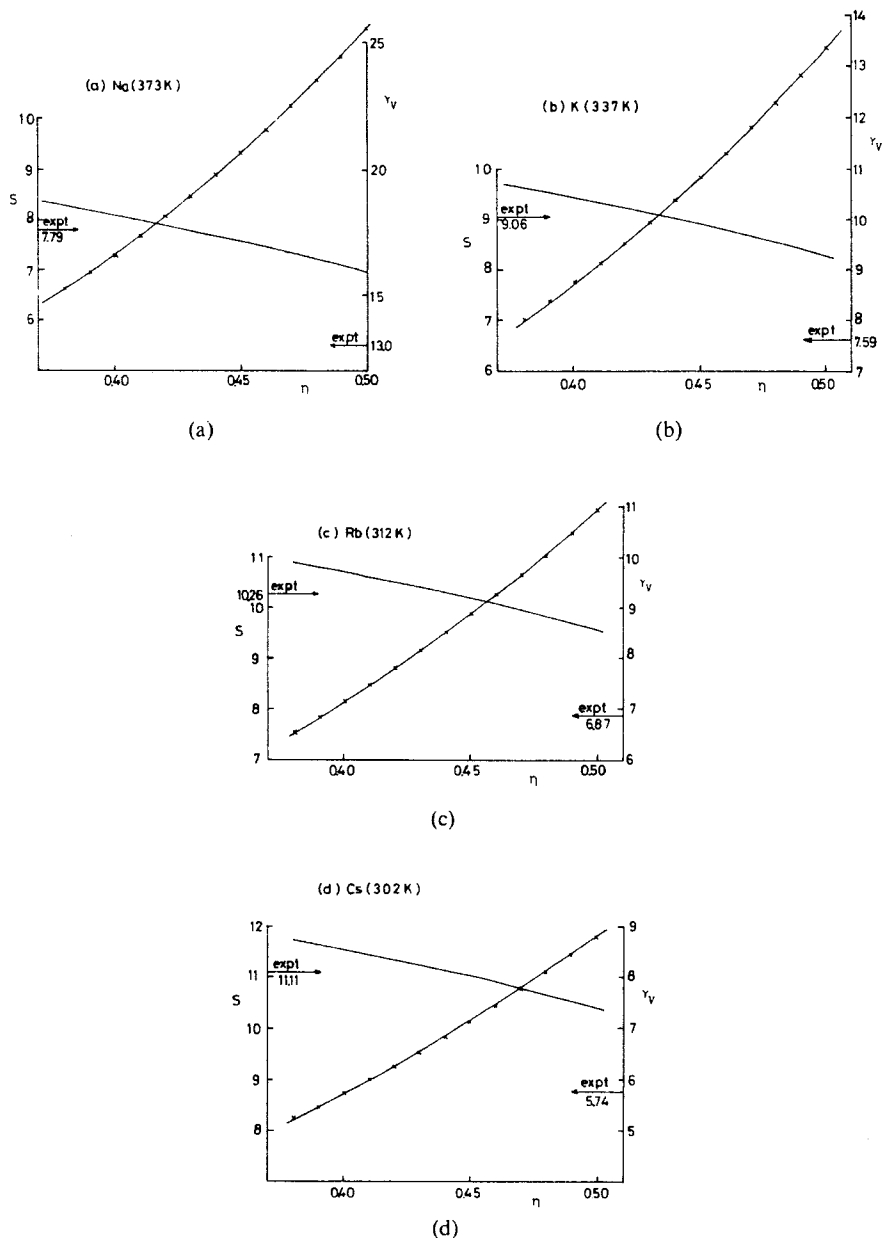


FIGURE 1 Entropies  $S$  (in units of  $Nk_B$ ) and thermal pressure coefficients  $\gamma_v$  (in units of  $\text{bar} \cdot \text{K}^{-1}$ ) versus packing fractions  $\eta$  for the alkali metals: the left-side scale is for  $S$ , (—) and the right-side scale is for  $\gamma_v$ , (x—x—x). Experimental data are taken from Hultgren *et al.*<sup>19</sup> for  $S$  and from Webber and Stephens<sup>20</sup> for  $\gamma_v$  (see also Table I).

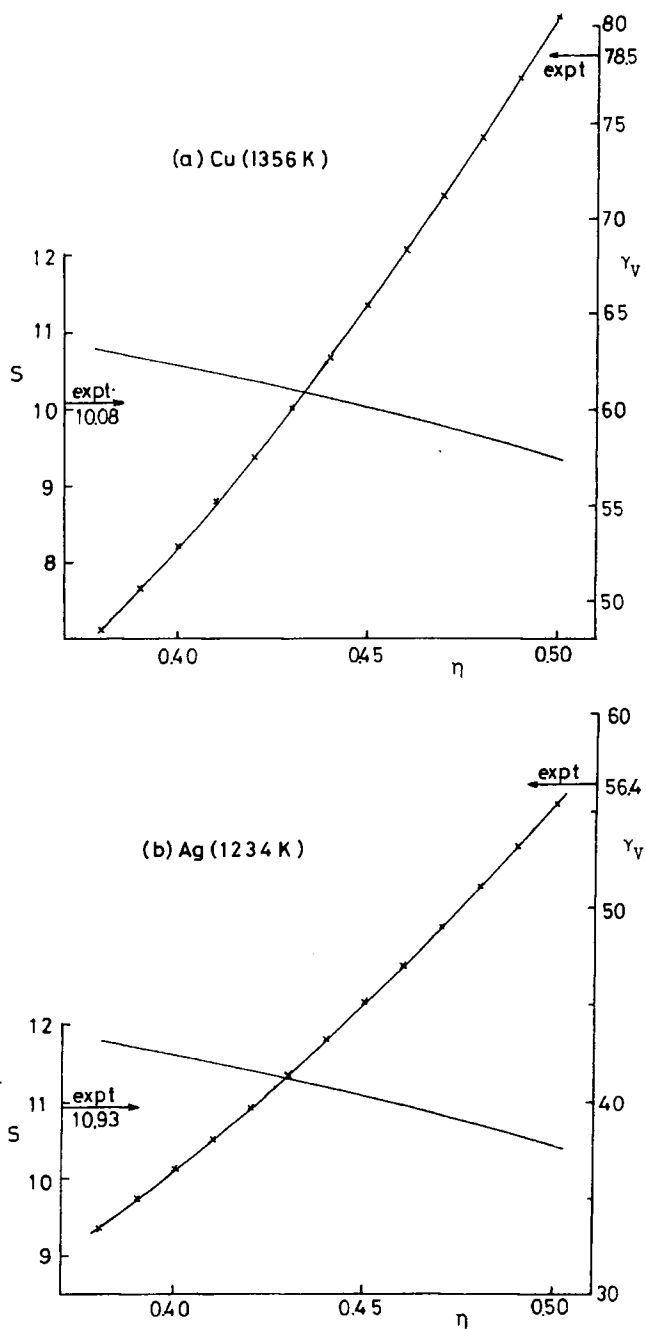


FIGURE 2 As Figure 1, for the noble metals.



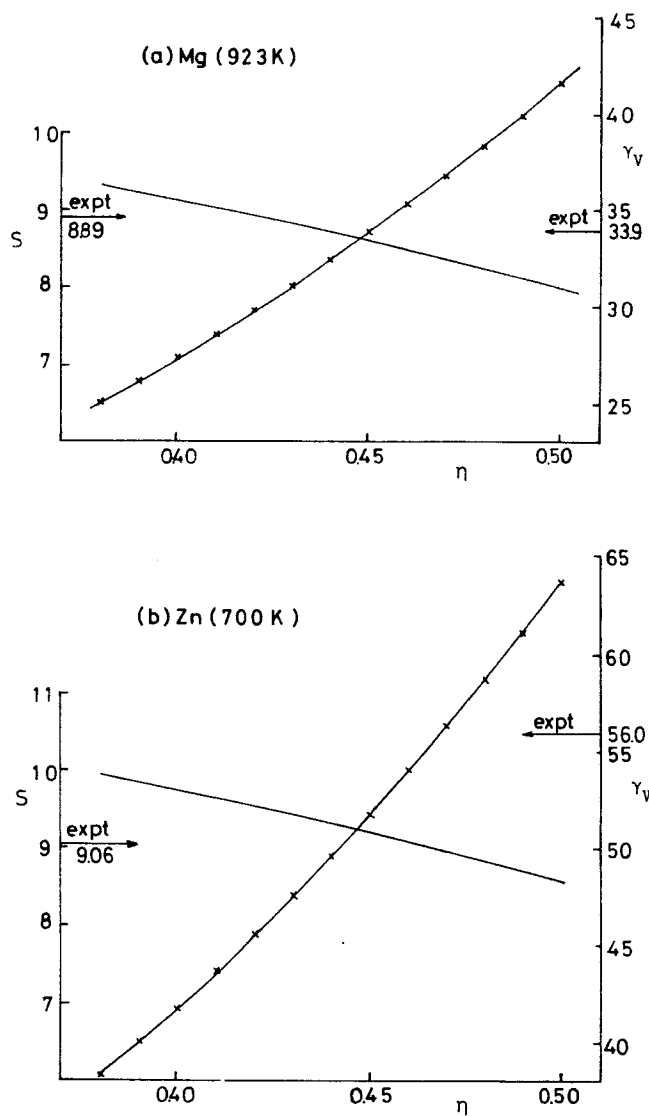


FIGURE 3 As Figure 1, for the divalent metals.

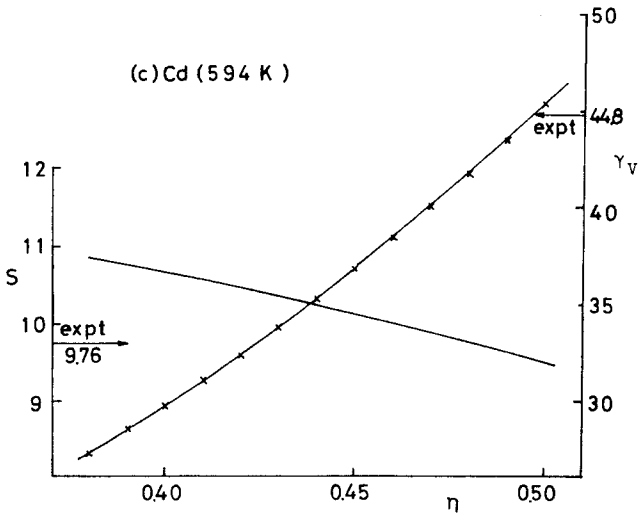


FIGURE 3(c)

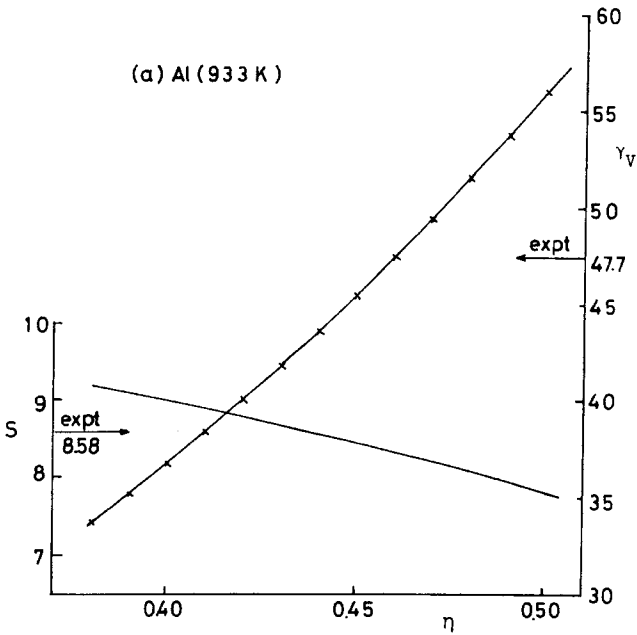
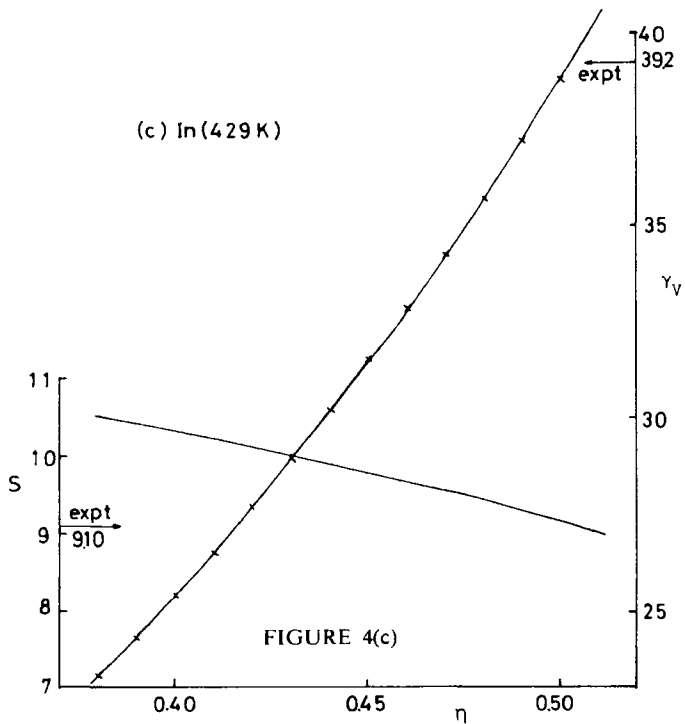
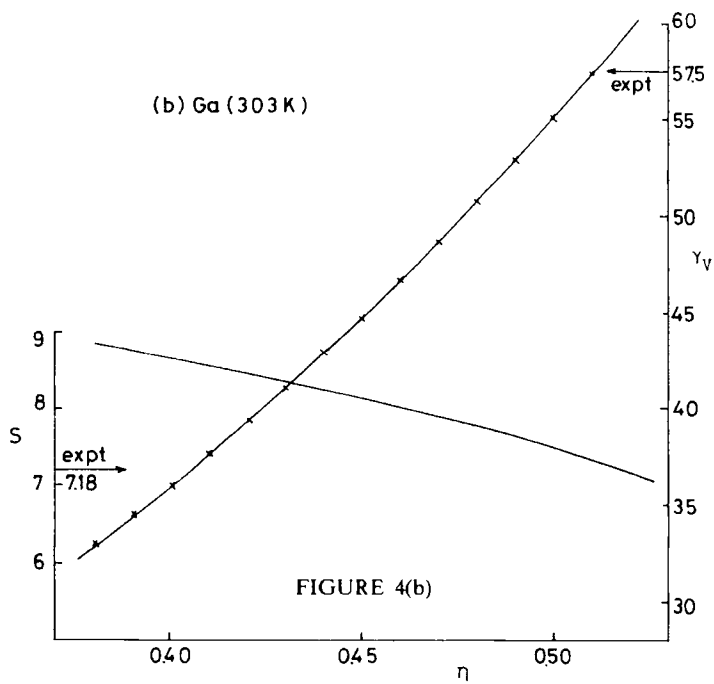


FIGURE 4 As Figure 1, for the trivalent metals.



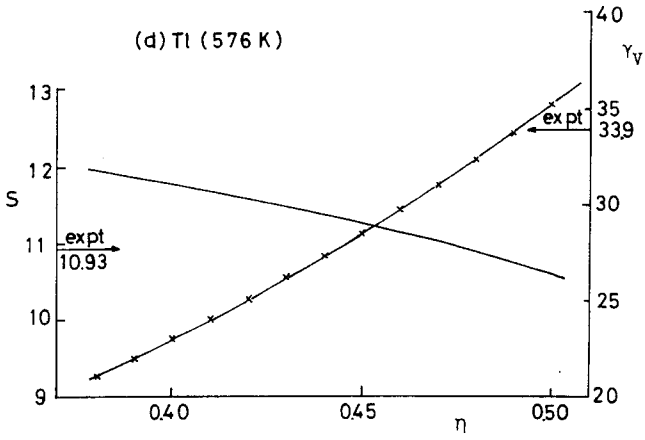


FIGURE 4(d)

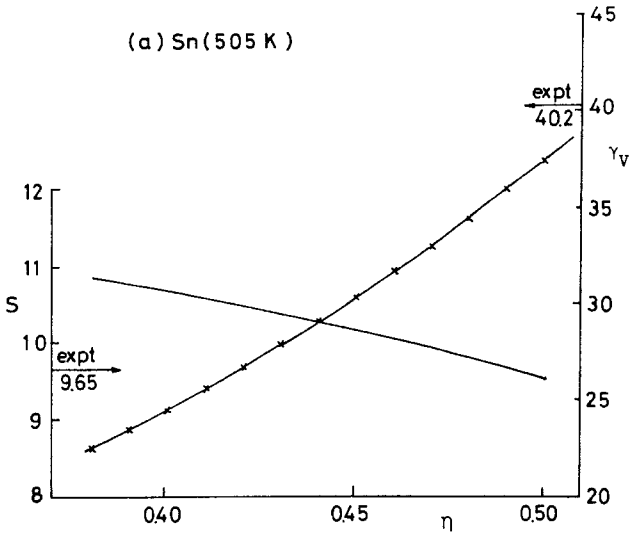


FIGURE 5 As Figure 1, for the tetravalent metals.

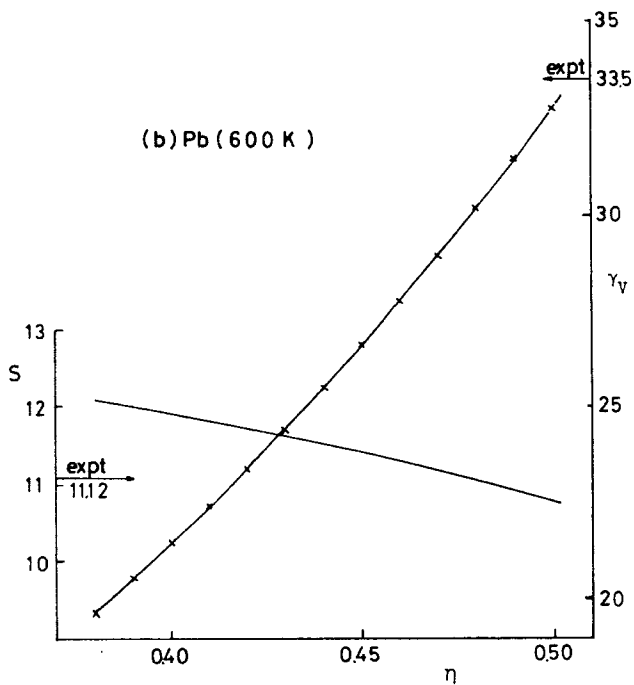


FIGURE 5(b)

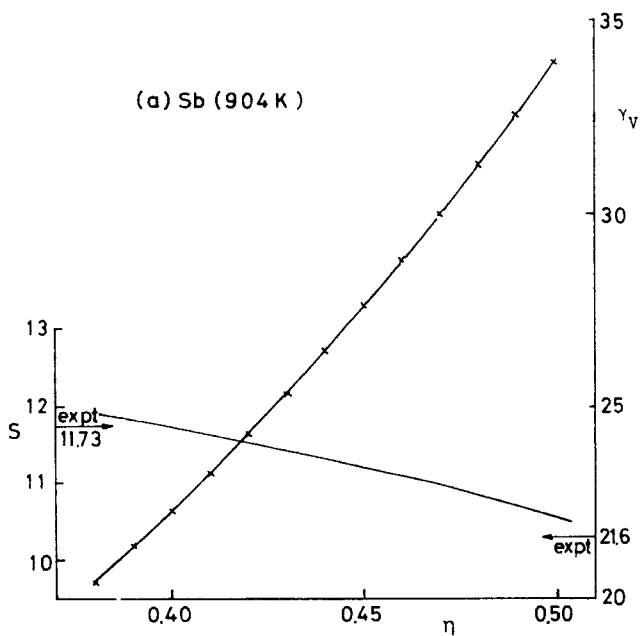


FIGURE 6 As Figure 1, for the pentavalent semimetals.

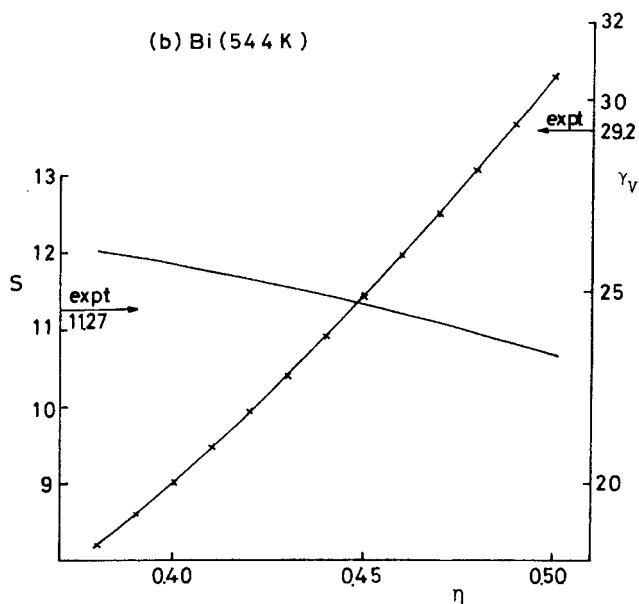


FIGURE 6(b)

comparing  $\gamma_V(\text{calc})$  with  $\gamma_V(\text{expt})$  in the table it is found such a correlation, to some extent, exists between the two. An interesting point is that there is a marked trend between alkalis and polyvalent metals. A glance at the final column shows that  $\gamma_V$  for polyvalent metals are fairly well described by  $a_{HS}(k/k_0)$ , while those for alkalis are poorly described by it though somewhat more favourable values are obtained for heavy alkalis. This may be interpreted as the pair potentials in alkali metals being much softer than those in polyvalent metals. Therefore the results here are in qualitative agreement with the previous publications.<sup>23,24</sup> The packing fractions  $\eta_{ph}$  thus obtained are compatible with those from the structural information<sup>25</sup> except for Ga, Sn and In† where the structure factor evidence points to significant departures from hard-sphere character.

Various contributions to the entropies and the thermal pressure coefficients are given in Table II. It is seen from the table that most of the former (up to 93%–95%) is harmonic,<sup>26</sup> and that the same is true for the latter (up to 96%–98%). To look at this in more detail let us go back to Eq. (8). The first term on the right-hand side in that equation describes the ideal gas result

† For In,  $a_{HS}(k/k_0)$  roughly approximates, on the whole, to the observed structure factor with  $\eta = 0.45$  but differs, to a great extent, from the latter in the important phonon region between  $k_D$  and  $k_0$ .

TABLE I

Thermal pressure coefficients  $\gamma_V$  at the melting points.

	$T$ (K)	$\eta_{ph}$	$\gamma_V(\text{calc})$ (bar · K <sup>-1</sup> )	$\gamma_V(\text{expt})$ (bar · K <sup>-1</sup> )	$\gamma_V(\text{calc})/\gamma_V(\text{expt})$
Na	373	0.430	19.0	13.0	1.46
K	337	0.437	10.2	7.59	1.34
Rb	312	0.444	8.62	6.87	1.25
Cs	302	0.443	6.92	5.74	1.21
Cu	1356	0.445	64.2	78.5	0.82
Ag	1234	0.463	47.6	56.4	0.84
Mg	923	0.423	30.2	33.9	0.89
Zn	700	0.465	55.2	56.0	0.99
Cd	594	0.480	41.7	44.8	0.93
Al	933	0.440	43.6	47.7	0.91
Ga	303	0.518	59.0	57.5	1.03
In	429	0.505	39.6	39.2	1.01
Tl	576	0.473	31.4	33.9	0.93
Sn	505	0.490	35.9	40.2	0.89
Pb	600	0.475	29.6	33.5	0.88
Sb	904	0.400	22.3	21.6	1.03
Bi	544	0.455	25.4	29.2	0.87

The packing fractions  $\eta_{ph}$  have been extracted by the fitting of calculated entropies to experimental ones. These give  $\gamma_V(\text{calc})$  in the fourth column. In order to obtain  $\gamma_V(\text{expt})$ , we have used, wherever possible, the Webber and Stephens values<sup>20</sup> of isothermal compressibilities  $\chi_T$  and thermal expansion coefficients  $\alpha_p$  for the sake of uniformity. In the case of Mg, however, for which these authors do not give sufficient information, we have taken  $\alpha_p$  from Allen<sup>21</sup> and  $\chi_T$  from McAlister *et al.*<sup>22</sup> (appropriate to the elevated temperature of 938 K) and calculated  $\gamma_V = \alpha_p/\chi_T$ .

which is too small (by a factor of about 4 for Na at the melting point) to explain the experimental values of liquid metals. The most important contribution stems from the second term. As stated in the previous section little is known about the density-derivative of structure factors, and we used the hard-sphere approximations in the present analysis. For illustrative purposes we first show, in Figure 7, the profiles of  $n\{\partial a_{HS}(k/k_0)/\partial n\}_T$  over the whole range  $(0, 2k_0)$  of interest for three packing fractions. They are slightly negative about up to  $k \approx k_0$ , rise sharply at  $k \approx 1.1k_0$  and reach maxima at  $k \approx 1.25k_0$ †. In view of the dominant harmonic term we are interested in their behaviours at low  $k$  rather than those beyond  $k = k_0$ , and the former is depicted in Figure 8. Because of the presence of the factor  $(k/k_0)^2$  in the integrand in

†  $\rho \partial S(q)/\partial \rho$  for  $\phi_{hs}(r)$  (—) in Figure 3 in the paper of Egelstaff *et al.*<sup>11</sup> corresponds to the present curve with  $\eta = 0.40$ . Semiquantitative agreement is found between the two. Interested readers can find this using the value of  $k_0 = 1.225 \text{ \AA}^{-1}$  for Rb. We evaluated  $n\{\partial a_{HS}(k/k_0)/\partial n\}_T$  analytically under the assumption  $(\partial \sigma/\partial n)_T = 0$ . Any curve of Egelstaff *et al.* can not give a correct description of  $\gamma_V$ .

TABLE II

Details of the calculated entropies (in units of  $Nk_B$ ) and the thermal pressure coefficients (in units of  $\text{bar} \cdot \text{K}^{-1}$ ) for simple liquid metals. All entries are corresponding to the temperatures and the packing fractions given in Table I.

	$S_0$	$S_1'$	$S_1''$	$S_{elec}$	$S$ (calc)	$\gamma_V^0$	$\gamma_V^{1'}$	$\gamma_V^{1''}$	$\gamma_V^{elec}$	$\gamma_V$ (calc)
Na	7.25	0.47	0.03	0.05	7.80	18.48	0.35	0.02	0.12	18.97
K	8.48	0.47	0.03	0.07	9.05	9.96	0.18	0.01	0.08	10.23
Rb	9.67	0.47	0.03	0.08	10.25	8.39	0.15	0.01	0.07	8.62
Cs	10.50	0.47	0.04	0.09	11.10	6.72	0.12	0.01	0.07	6.92
Cu	9.41	0.47	0.03	0.17	10.08	61.77	1.12	0.09	1.18	64.16
Ag	10.23	0.46	0.03	0.20	10.92	45.80	0.79	0.08	0.95	47.62
Mg	8.28	0.47	0.02	0.12	8.89	29.15	0.56	0.02	0.43	30.16
Zn	8.47	0.46	0.02	0.10	9.05	53.63	0.92	0.06	0.54	55.15
Cd	9.19	0.46	0.01	0.10	9.76	40.60	0.66	0.05	0.41	41.72
Al	7.97	0.47	0.02	0.11	8.58	42.29	0.78	0.03	0.54	43.64
Ga	6.70	0.45	0.01	0.04	7.20	57.93	0.84	0.04	0.21	59.02
In	8.53	0.45	0.02	0.08	9.08	38.68	0.58	0.07	0.26	39.59
Tl	10.36	0.46	0.01	0.11	10.94	30.53	0.51	0.03	0.34	31.41
Sn	9.09	0.46	0.01	0.09	9.65	35.00	0.55	0.04	0.28	35.87
Pb	10.52	0.46	0.02	0.11	11.11	28.73	0.48	0.04	0.32	29.57
Sb	11.10	0.48	0.02	0.15	11.75	21.41	0.43	0.00	0.45	22.29
Bi	10.68	0.47	0.01	0.10	11.26	24.66	0.43	0.01	0.26	25.36

$(\partial\eta/\partial T)_V$  are from Table I of Yokoyama *et al.*<sup>3</sup> and for Cu, Ag, Zn, Cd, Ga, Tl, Sn, Sb and Bi from Table 1.3 of Shimoji<sup>24</sup> (see Eq. (15) in the text).

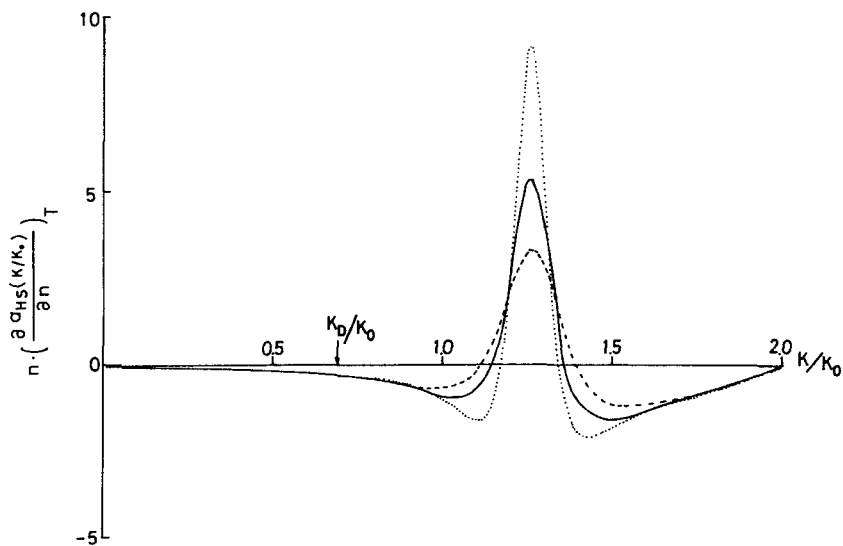


FIGURE 7  $n\{\partial\alpha_{HS}(k/k_0)/\partial n\}_T$  for three packing fractions: (—),  $\eta = 0.40$ ; (---),  $\eta = 0.45$ ; (·····),  $\eta = 0.50$ , respectively.



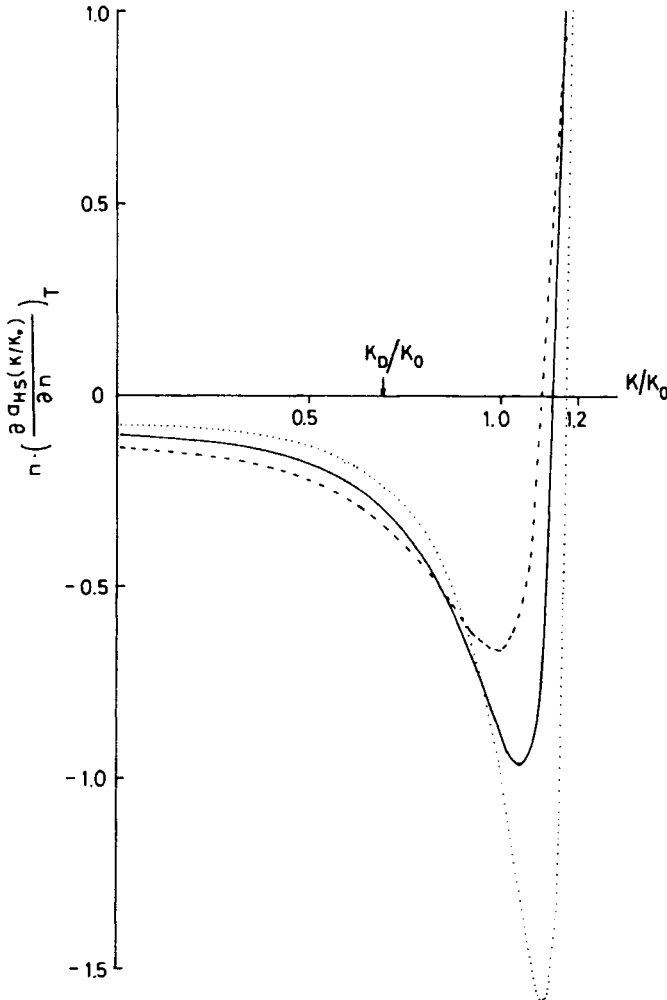


FIGURE 8 As Figure 7, drawn to a large scale.

Eq. (8) the very low  $k$  region up to about  $k_D/k_0$  is not so significant and most of the integral value arises from the region  $(k_D/k_0, 1)$  which is peculiar to liquids (see Figure 3 of Gray *et al.*<sup>27</sup> for an entropy discussion).

In the present study, however, the  $\gamma_V$  are obtained under the assumption  $(\partial\sigma/\partial n)_T = 0$ . Now we estimate a probable effect from this source on the present results in terms of ab initio calculations. As is well known the Gibbs-Bogoliubov method tells us how to approximate given interatomic forces at specified density and temperature by 'best' hard-sphere interactions. The

description of the hard-sphere reference system and the associated variational principle are believed to be the most reliable aspects of the method,<sup>24,28,29</sup> so it is of interest to see if we can calculate interatomic forces well enough that  $\gamma_V$  of Table I can be reproduced.

We have chosen the Ashcroft empty-core radii with parameters given in Table 4 of Yokoyama *et al.*<sup>30</sup> which are approximately consistent with a variety of experimental data related to structure factors and entropies (the latter both for pure metals and alloys). Then we have used the Geldart-Vosko<sup>31</sup> screening function so as to calculate interatomic forces from which, using Eq. (6), we found the results shown in Table III. The calculations have been confined to the metals indicated partly because Yokoyama *et al.* do not list core parameters for other metals and partly because we believe these eleven cases suffice for comparison with those in Table I. By comparison of Table I with Table III we can deduce the role of  $(\partial\sigma/\partial n)_T$  which reduces the present results by about 10% or more for polyvalent metals and 20% or more for alkalis. Exceptions are found for Mg, Cd and Al. For Al, the rate of reduction is only 2% or so, whereas for Mg and Cd, a reversed trend is found. But the trouble here for the latter is not significant. To scrutinize this let us return again to Figure 3. If we want to get  $\gamma_V^{GB}$  for Mg we find  $\eta_{ph}$  to be 0.443 which gives the calculated entropy of 8.65. This is only lower by 2.7% than the observed one. As for Cd,  $\gamma_V^{GB}$  corresponds to  $\eta_{ph}$  of 0.488 which gives the calculated entropy of 9.66, and this undershoots the experiment only by 1%. Therefore if we admit only a small allowance for the entropies the difficulty raised here is able to be removed. So we may say from the discussions above

TABLE III

Packing fractions  $\eta_{GB}$  and thermal pressure coefficients  $\gamma_V^{GB}$ , at the melting points, obtained by ab initio calculations using the Ashcroft empty-core pseudopotentials with the screening function of Geldart-Vosko.

	$T$ (K)	$r_c$ (au)	$\eta_{GB}$	$\gamma_V^{GB}(\text{calc})$ (bar · K <sup>-1</sup> )	$\gamma_V(\text{expt})$ (bar · K <sup>-1</sup> )	$\gamma_V^{GB}(\text{calc})/\gamma_V(\text{expt})$
Na	373	1.66	0.431	15.6	13.0	1.20
K	337	2.20	0.435	8.50	7.59	1.12
Mg	923	1.31	0.446	32.9	33.9	0.97
Zn	700	1.04	0.462	49.1	56.0	0.88
Cd	594	1.25	0.485	43.2	44.8	0.96
Al	933	1.08	0.456	42.5	47.7	0.89
In	429	1.15	0.434	33.3	39.2	0.85
Tl	576	1.225	0.417	27.5	33.9	0.81
Sn	505	1.31	0.451	29.2	40.2	0.73
Pb	600	1.44	0.452	26.3	33.5	0.78
Bi	544	1.50	0.421	20.6	29.2	0.70

The 'experimental' values  $\gamma_V(\text{expt})$  are transferred from Table I.

that the effect of  $(\partial\sigma/\partial n)_T$  on  $\gamma_V$  is fairly small for Mg, Cd and Al which provide probably the best hard-sphere systems in the present context. The quality of the prediction of ab initio calculations is, on the whole, poorer than those of the original method for polyvalent metals. A definite answer to this problem requires a more detailed analysis than can be given here. Nevertheless the whole story presented in this study still remains unchanged. As far as Na and K are concerned, however,  $\gamma_V^{GB}$  are still larger by 10%-20% than the experiments. This tells us that  $a_{HS}(k/k_0)$  will not provide accurate density-derivatives of structure factor (especially in the range between  $k_D$  and  $k_0$ ), and is inadequate for a correct description of  $\gamma_V$ . More suitable structure factors as well as their density-derivatives are highly needed in this respect; for example, the structure factors based on the one-component-plasma which are said to be rather good, particularly for liquid alkali metals (see the most recent review of Shimoji and Young<sup>32</sup>).

#### 4 CONCLUSIONS

It has been shown that the PY phonon theory of liquids appears to be applicable for predicting thermal pressure coefficients of simple liquid metals at the melting points. Harmonic effects are dominant in the description of the thermal pressure coefficients as well as the entropies. Agreement between theory and experiment is rather good for polyvalent metals, but poor for lighter alkali metals. However the ab initio calculations suggest to us that the present results are very susceptible to the approximations adopted. For a completely quantitative exploration of the present approach, accurate density-derivatives of structure factors in the phonon region, particularly the range ( $k_D$ ,  $k_0$ ) are highly desirable.

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