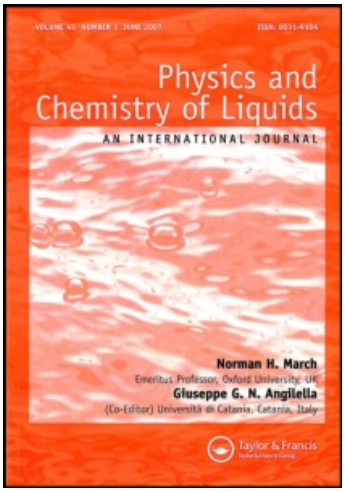

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I. Yokoyama[a]; I. Ohkoshi[a]; W. H. Young[b]
[a] Department of Mathematics and Physics, National Defense Academy, Yokosuka, Japan [b] School of Mathematics and Physics, University of East Anglia, Norwich, UK

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Letter

Specific Heats of Liquid Metals Based on the Percus–Yevick Phonon Description

I. YOKOYAMA,† I. OHKOSHI,† and W. H. YOUNG‡

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

‡*School of Mathematics and Physics, University of East Anglia, Norwich, NR4 7TJ, UK*

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The Percus–Yevick phonon theory is compatible, in general, with our somewhat limited knowledge of the specific heat of liquid metals at constant volume. Exceptions, however, appear to be the lighter alkalis.

In a previous paper by Ohkoshi, Yokoyama, Waseda and Young[1] (hereafter I) we reported calculations of entropies of liquid metals using the Percus–Yevick (PY) phonon theory in which the elementary excitations are density fluctuations up to a maximum wave number $k_0 = 3^{1/3}k_D$. The total entropy is expressed as

$$S = S_0 + S_1' + S_1'' + S_{\text{elec}}, \tag{1}$$

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

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

$$S_1' = \frac{k_B}{4N} \sum_{\mathbf{k},\mathbf{k}'}{}' \left(\frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 a(\mathbf{k} - \mathbf{k}'), \tag{3}$$

$$S_1'' = \frac{k_B}{4N} \sum_{\mathbf{k},\mathbf{k}'}{}' \left(\frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 \left\{ \frac{\partial \ln a(\mathbf{k} - \mathbf{k}')}{\partial \ln T} \right\}_V a(\mathbf{k} - \mathbf{k}'), \tag{4}$$

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

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

The dashes on the summations indicate that all terms $\mathbf{k} = \mathbf{k}'$ are omitted. The first term S_0 describes the independent phonon result[2] and S_1' and S_1'', which include the structure factor $a(\mathbf{k} - \mathbf{k}')$, are due to the phonon-phonon interaction. S_{elec} arises from thermal excitation of the conduction electrons; it is small for simple metals and is adequately approximated by its Sommerfeld form.

In I, we neglected S_1'' partly because $\{\partial \ln a(k)/\partial \ln T\}_V$ was not known experimentally for any liquid metal and partly because it was expected to be numerically smaller than S_1' The latter expectation is based on a discussion by Gray *et al.*[3] who estimated S_1'' to be $\sim 0.1\ \mathrm{Nk}_B$ for Na. They pointed out that this small value arose because $\{\partial \ln a(k)/\partial \ln T\}_V$ oscillates with amplitude less than unity in the important region $k_0 \leq k \leq 2k_0$ and that this behaviour is likely to be general.

In the present letter we estimate S_1'' using a hard-sphere structure factor $a_{\text{HS}}(k)$ (the only route known to us at the present time) and confirm the general proposition above. Once this is done, we may further differentiate with respect to T and thereby test the ability of the PY method to predict specific heats C_V at constant volume. The effective hard sphere diameters vary with T and V (although in the present application V is generally held constant for any given system). In this way, a reasonably good average description of the structure factors of most liquid metals is afforded over the range $(k_0, 2k_0)$ and this should be adequate for calculating S_1''. Wherever necessary below we use the diameter variations of Harder *et al.*[4] for simple metals and of Tamaki and Waseda[5] for transition metals.

For illustrative purposes $\{\partial \ln a_{\text{HS}}(k/k_0)/\partial \ln T\}_V$ for Rb is shown in Figure 1 together with $\{\Delta \ln a(k/k_0)/\Delta \ln T\}_P$ for Na, a curve obtained in chord approximation from observed data at 100°C and 200°C (Gray *et al.*, Figure 2). The similarity of the profiles should be noted. Of course, $\{\partial \ln a_{\text{HS}}(k/k_0)/\partial \ln T\}_V$ varies slightly from metal to metal depending upon the variation of packing fraction η with T at constant volume, but qualitatively it is much the same for all metals.

S_1'' is conveniently given, for numerical calculations, by

$$S_1''/\mathrm{Nk}_B = \frac{T}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_V \left\{\frac{81}{32}\int_0^1 \frac{d(k/k_0)}{(k/k_0)}\int_0^1 \frac{d(k'/k_0)}{(k'/k_0)}\left[\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}^2 \xi_1 - 2\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}\xi_3 + \xi_5\right]\right\} \quad (6)$$

where

$$\xi_\alpha = \int_{|k-k'|/k_0}^{(k+k')/k_0} \left(\frac{q}{k_0}\right)^\alpha \left\{\frac{\partial \ln a_{\text{HS}}(q/k_0)}{\partial \ln \eta}\right\} a_{\text{HS}}\left(\frac{q}{k_0}\right) d\left(\frac{q}{k_0}\right), \quad \alpha = 1, 3, 5 \quad (7)$$

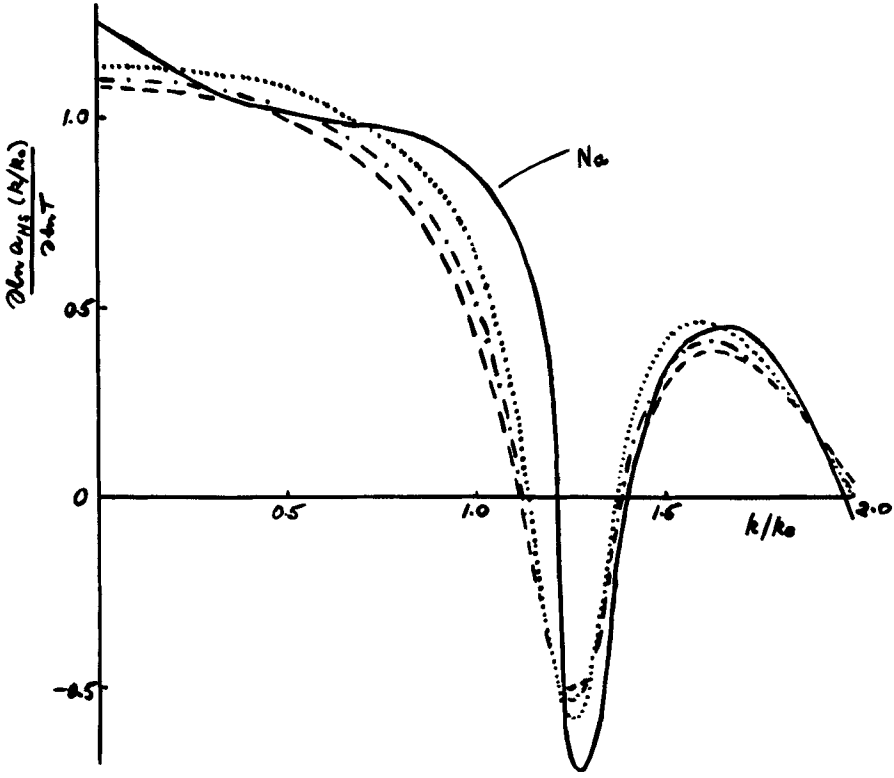

FIGURE 1 $\{\partial \ln a_{HS}(k/k_0)/\ln T\}_V$ for liquid Rb at 313 K: (----), $\eta = 0.40$; (-.-.-), $\eta = 0.42$; (···, $\eta = 0.45$, compared with $\{\Delta \ln a(k/k_0)\Delta \ln T\}_P$ for liquid Na using the measurements of Greenfield *et al.*[6] at 373 K and 473 K. The profiles are similar in the most significant part for anharmonicity (around the positive jump).

In Eq. (6), $T/\eta(\partial n/\partial T)_V$ is negative for all metals, and if the big brace of Eq. (6) (a function of η only) is negative, S_1''/Nk_B is positive. We evaluated the big brace to be -0.038, -0.040, -0.043 for $\eta = 0.40$, 0.42 and 0.45, respectively.

These packing fractions cover most applications and certainly those below and it is sufficient for our purpose to regard the big brace value as being -0.04 and independent of η. These results are incorporated into Table 1 together with data from I. Surprisingly, the values of S_1''/Nk_B are around 0.03 for all metals studied, implying in particular that the proposition of Gray *et al.* is correct. The factor $(T/\eta)(\partial\eta/\partial T)_V$ is responsible for this constancy of S_1''/Nk_B; in general, for simple metals $(\partial\eta/\partial T)_V$ is rather big, but the melting temperature is low, while for transition metals the situation is roughly reversed.

TABLE I

Entropies and specific heats (in units of Nk_B) of liquid metals near the melting points

	$T(K)$	S_0	S_1'	S_{elec}	$(\partial\eta/\partial T)_V$ $(10^{-4}K^{-1})$	S_1''	S (calc)	S (expt)	C_V (calc)	C_V (expt)
Na	378	6.92	0.46	0.05	−3.13	0.03	7.46	7.84	3.08	3.48
K	343	8.28	0.46	0.07	−3.32	0.03	8.84	9.14	3.10	3.44
Rb	313	9.23	0.48	0.08	−3.87	0.03	9.82	10.26	3.11	3.30
Cs	303	10.29	0.46	0.09	−3.78	0.04	10.88	11.13	3.13	3.21
Mg	953	8.38	0.45	0.12	−0.906	0.02	8.97	9.01	3.14	2.96
Al	943	8.05	0.47	0.11	−0.949	0.02	8.65	8.62	3.13	3.11
In	433	8.20	0.43	0.07	−1.79	0.02	8.72	9.13	3.09	3.16
Pb	613	10.50	0.48	0.12	−1.34	0.02	11.12	11.19	3.14	3.14
Ti	1973	10.17	0.45	0.87	−0.56	0.03	11.52	11.88	(3.90)	4.5–?
V	2173	10.42	0.47	1.01	−0.49	0.03	11.93	12.07	(4.04)	5.0–?
Cr	2173	9.38	0.44	1.57	−0.50	0.03	11.42	11.57	(4.60)	4.7–?
Mn	1533	9.72	0.47	1.12	−0.70	0.03	11.34	12.05	(4.15)	5.5–?
Fe	1833	9.51	0.46	1.39	−0.58	0.03	11.39	12.07	(4.42)	5.5–?
Co	1823	9.85	0.45	1.47	−0.58	0.03	11.80	12.05	(4.50)	4.9–?
Ni	1773	9.58	0.45	1.43	−0.60	0.03	11.49	11.72	(4.46)	5.2–?

Experimental data are from Hultgren *et al.*[7] S_0, S_1' and S_{elec} are from I except for the transition metals. For simple metals S_{elec} is evaluated in Sommerfeld approximation, while for transition metals it is estimated by using the theoretically obtained $N(E_F)$ of Asano and Yonezawa[8] (see also Figure 4 in I). $(\partial\eta/\partial T)_V$ for simpe metals are from Table I of Harder *et al.*,[4] and for transition metals from Table II of Tamaki and Waseda.[5]

The total entropy may now be recorded with more certainty than hitherto and the agreement with experiment is seen to be good (Table I).

We are now able to discuss C_V. Differentiation of Eqs. (1)–(5) gives

$$C_V = T\left(\frac{\partial S_0}{\partial T}\right)_V + T\left(\frac{\partial S_1'}{\partial T}\right)_V + T\left(\frac{\partial S_1''}{\partial T}\right)_V + T\left(\frac{\partial S_{elec}}{\partial T}\right)_V. \tag{8}$$

The term $T(\partial S_1''/\partial T)_V$ should be much smaller than the preceding two in view of the smallness of S_1''. Thus C_V is moderately well described by

$$C_V \approx C_{0_V} + \frac{k_B}{4N}\sum_{\mathbf{k},\mathbf{k}'}{}' \left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2 \left\{\frac{\partial \ln a(\mathbf{k}-\mathbf{k}')}{\partial \ln T}\right\}_V a(\mathbf{k}-\mathbf{k}') + S_{elec}\left\{1 + \frac{T}{N(E_F)}\left(\frac{\partial N(E_F)}{\partial T}\right)_V\right\}, \tag{9}$$

(cf. Figure 1 in I and the discussion thereon). Hence

$$C_V/NK_B \approx 3 + S_1''/Nk_B + (S_{elec}/Nk_B)\left\{1 + \frac{T}{N(E_F)}\left(\frac{\partial N(E_F)}{\partial T}\right)\right\}_V. \tag{10}$$

The derivative in this equation should be negligible for simple metals[9] and we make the same assumption for transition metals. Specific heats are

then easily found from the entropy data already calculated and these are shown in Table I. Those for the transition metals are recorded in parentheses because of their sensitivity to the above assumption.

On comparing the calculated and observed specific heats, we see that the magnitudes (relative to 3) for simple polyvalent metals are adequately described (if not the detailed variation from case to case). The results for the alkalis, however, are not satisfactory. Also, unfortunately, reliable experimental data are not available for the transition metals. The trouble appears to be in the uncertainty of the thermodynamic parameters used to reduce the observed C_P's to obtain C_V's. We have, therefore, recorded the measured C_P's in the manner indicated; clearly theory and experiment could well be completely compatible.

In summary, we can now say that the PY phonon theory can account very well for the entropies of liquid metals and is not incompatible with our somewhat limited knowledge of the specific heats, except possibly in the cases of the lighter alkalis.

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