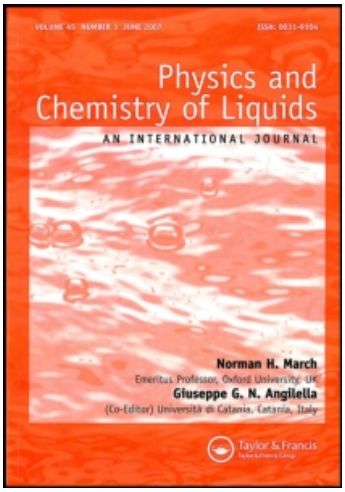

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Letter

Sound Velocities and Entropies of Non-Simple Liquid Metals Based on the Percus–Yevick Phonon Description

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Recently, Yokoyama, Ohkoshi and Young[1] (hereafter I) reported calculations of "phonon dispersion curves" and sound velocities of liquid Na, K, Rb and Pb by invoking a perturbation theory based on a zeroth order system of independent density fluctuations having wave indices between 0 and $k_0 = 3^{1/3}k_D$. They suggested that sound velocities of liquid metals can be well predicted by the phonon perturbation approach, the details of the temperature dependence of the structure factor at constant volume being important for this. With the increased availability of structure-factor data within the phonon region in **k** space,[2] it has now become possible to extend the calculations of I to a variety of non-simple liquid metals for evaluation of sound velocities. The aim of this short communication is to present such results which suggest the efficacy of the phonon method in this respect. The overall success of the calculations lend further credibility to the form of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ proposed in I. This function is necessary input information into the calculations but, unfortunately, has not been measured with accuracy; a form applicable to all liquid metals near their melting points is suggested in Figure 1 of I.

The dispersion relation, to first order of phonon perturbation, is given by (Eq. (17) in I)

$$\omega_k \approx \omega_k^0\left[1 + \frac{1}{2N}\sum_{\mathbf{k}'(\neq\mathbf{k})}\left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2\left\{\frac{\partial \ln a(\mathbf{k}-\mathbf{k}')}{\partial \ln T}\right\}_\Omega a(\mathbf{k}-\mathbf{k}')\right] \tag{1}$$

Here ω_k^0 is the independent-phonon frequency, given by

$$\frac{Mk_BT}{\hbar^2k^2}\,a(k)x^2 = \frac{x}{e^x - 1} + \tfrac{1}{2}x + a(k);\; x = \frac{\hbar\omega_k^0}{k_BT} \tag{2}$$

or, more simply, by the Egelstaff formula[3,4]

$$\omega_k^0 = k\left[\frac{k_BT}{Ma(k)}\right]^{1/2}, \tag{3}$$

Equation (3) following from Eq. (2) by a very accurate first-order expansion in x. In the above equations, $a(k)$ is the static structure factor and M the mass of an ion. In the subsequent numerical processing of these equations, we use the observed $a(k)$ where it appears in Eqs. (1) and (3), but we adopt the stratagem referred to in the previous paragraph when using the expression in the curly brackets in Eq. (1).

Since

$$v_S = \left(\frac{d\omega}{dk}\right)_{k=0} \tag{4}$$

is defined as the sound velocity, the slope of the phonon dispersion curve at sufficiently small k should give the velocity of sound at the fixed temperature and density. Proceedings in this way (for algebraic details, see I), we obtained the results shown in Table I for alkaline earth, noble and transition metals, respectively. From the table, it is seen that theory is in good agreement with experiment. The calculated velocities of sound are within 5% of the measured values except for Ba and Au. For Au, however, a marked discrepancy between the two is found and we do not know at present why this is so. The calculated velocities of sound are very susceptible to the accuracy of $a(k)$ at low k, so that they have the uncertainties shown in the table. We quote the Egelstaff values in parentheses so as to show the degree of progress we have made in the present work.

Next we consider the entropies. The total entropy[9] is expressed as

$$S = S_0 + S_1' + S_1'' + S_{\text{elec}} \tag{5}$$

TABLE I

Comparison of calculated and measured velocities of sound in non-simple liquid metals

	T (K)	v_s (ms^{-1}) calc.	v_s (ms^{-1}) expt.	$\frac{v_s \text{ (calc)}}{v_s \text{ (expt)}}$
Mg	953	3943 (3611)	4049 ± 1.5[a]	0.97 (0.89)
Ca	1123	3040 ± 30 (2580)	2972 ± 3[a]	1.02 (0.87)
Sr	1053	1950 ± 20 (1795)	1898 ± 1.5[a]	1.03 (0.95)
Ba	1003	1470 ± 20 (1299)	1328 ± 2[a]	1.10 (0.98)
Cu	1573	3230 ± 10 (2929)	3360[b]	0.96 (0.87)
Ag	1273	2610 ± 40 (2273)	2694[b]	0.97 (0.84)
Au	1423	1730 ± 20 (1582)	2518 ± 23[c]	0.69 (0.63)
Fe	1833	3980 ± 40 (3622)	3959 ± 27[d]	1.01 (0.91)
Co	1823	4020 ± 20 (3660)	4002 ± 20[d] [4056 ± 34][c]	1.00 (0.91)
Ni	1773	3870 ± 20 (3553)	4020 ± 5[d]	0.96 (0.88)

[a] McAlister *et al.*[5]

[b] Webber and Stephens.[6]

[c] Bek and Steeb.[7]

[d] Tsu and Takano:[8] the observed temperature coefficients of the velocities of sound in $ms^{-1}\,K^{-1}$ are -1.00 for Fe, -0.53 for Co and -0.35 for Ni, respectively.

The values calculated by the Egelstaff formula, Eq. (3) are in parentheses.

where

$$S_0 = k_B \sum_{\mathbf{k}} \left\{ \frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right\}, \tag{6}$$

$$S_1' = \frac{k_B}{4N} \sum_{\mathbf{k},\mathbf{k}'}' \left(\frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 a(\mathbf{k} - \mathbf{k}'), \tag{7}$$

$$S_1'' = \frac{k_B}{4N} \sum_{\mathbf{k},\mathbf{k}'}' \left(\frac{\mathbf{k} \cdot \mathbf{k}'}{kk'} \right)^2 \left\{ \frac{\partial \ln a(\mathbf{k} - \mathbf{k}')}{\partial \ln T} \right\}_\Omega a(\mathbf{k} - \mathbf{k}'), \tag{8}$$

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

$$S_{\text{elec}} = \tfrac{1}{3}\pi^2 N(E_F) N k_B^2 T. \tag{9}$$

We are interested in the contribution of S_1'' to the total entropy because this is also sensitive to the details of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ over the k-range of interest.

The numerical results for the entropies are summarized in Table II for a variety of metals. Agreement between theory and experiment is satisfactory for the alkaline earths and noble metals, and excellent for the transition

TABLE II

Input data and entropies (in units of Nk_B) of non-simple liquid metals

	T (K)	ρ (g · cm^{-3})	k_0 (Å^{-1})	S_0	S_1'	S_1''	Selec	S (Calc)	S (expt)
Mg	953	1.545	1.895	8.38	0.45	0.13	0.12	9.08	9.01
Ca	1123	1.370	1.541	9.56	0.46	0.13	0.22	10.37	10.95
Sr	1053	2.380	1.427	11.06	0.46	0.14	0.24	11.90	—
Ba	1003	3.320	1.373	11.65	0.47	0.13	0.25	12.50	14.03
Cu	1573	7.86	2.365	9.14	0.45	0.12	0.10	9.81	10.66
Ag	1273	9.27	2.095	10.13	0.44	0.13	0.11	10.81	11.06
Au	1423	17.20	2.106	11.68	0.45	0.13	0.12	12.38	12.01
Sc	1833	2.92	1.908	10.38	0.50	0.15	0.72	11.75	12.10
Ti	1973	4.15	2.101	10.17	0.45	0.17	0.87	11.66	11.88
V	2173	5.36	2.241	10.42	0.47	0.17	1.01	12.07	12.07
Cr	2173	6.27	2.345	9.38	0.44	0.11	1.57	11.50	11.57
Mn	1533	5.97	2.265	9.72	0.47	0.14	1.12	11.45	12.05
Fe	1833	7.01	2.377	9.51	0.46	0.14	1.39	11.50	12,07
Co	1823	7.70	2.409	9.95	0.45	0.14	1.47	11.91	12.05
Ni	1773	7.72	2.414	9.58	0.45	0.12	1.43	11.58	11.72

The experimental values are taken from Hultgren *et al.*[11] The S_0, S_1' and Selec for Mg and the transition metals are from Yokoyama *et al.*[9] except for Ca, Sr, Ba, Cu, Ag, Au and Sc. For the alkaline earth and noble metals Selec is evaluated in the Sommerfeld approximation, while for transition metals it is estimated by using the *theoretically* obtained $N(E_F)$ of Asano and Yonezawa[12] (see also Figure 4 of Ohkoshi *et al.*[13]).

metals. Attention should be paid to the values of S_1'' for the transition metals. Yokoyama, Ohkoshi and Young[9] used a hard-sphere structure factor in their specific heat calculations for the evaluation of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$. The values of S_1'' thus found are around 0.03 for all metals studied. Clearly, the present results give small but beneficial increases in total entropies through the role of S_1'', bringing theory into excellent agreement with experiment for transition metals. For Au, the entropy seems to be well described by the present approach though seriously wrong for the velocity of sound. A possible reason for this could come from the fact that entropies, in general, are dominated by the correct description of $a(k)$ over the range between k_D and k_0, but are rather insensitive to the accuracy of $a(k)$ in the lower k region. As for Ba, we find that the agreement is not as good as could be desired. One possibility is that S_{elec} is evaluated in the Sommerfeld approximation in this case. The mean free path in Ba, however, is close to the nearest neighbour distance which casts doubt on a nearly free electron approach. Ratti and Evans[10] have suggested that Ba behaves in a manner similar to the transition metals with the large observed electrical resistivities being due to d scattering at the Fermi energy. If this is the case, we can expect

$N(E_F)$ to be considerably larger than the free electron value. This means the value of S_{elec} could be as large as that of a transition metal and therefore a considerable improvement over the present entropy result would be expected.

In summary, we have shown that the phonon perturbation approach, together with the proposed form of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ developed in I, is able to describe successfully the sound velocities as well as the entropies in non-simple liquid metals.

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