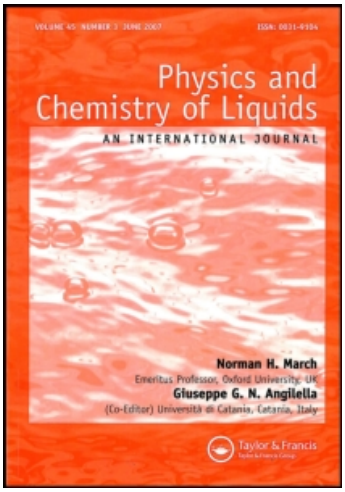

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Calculation of Sound Velocities of Liquid Metals at their Melting Point via the Percus-Yevick Theory of Melting

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In this brief note, we utilize the 3N collective coordinate theory of liquids of Percus and Yevick[1], as applied to the phenomenon of melting by Omini[2], to calculate the sound velocities in various simple liquid metals at their melting temperatures. We perform this calculation by taking derivatives of Omini's[2] calculated Percus-Yevick dispersion relations for their "liquid phonon" collective coordinate elementary excitations of the liquid. We compare these calculated sound velocities with experimental data, where possible, to ascertain the validity of the liquid phonon dispersion relation as a source of sound velocities.

Omini[2] has calculated the melting entropy of a group of simple metals using the Percus-Yevick[1] collective coordinate description of the elementary excitations of a liquid as a collection of liquid phonon bosons. Basically, Percus and Yevick[1] replaced the potential energy

$$V = 1/2 \sum_{i \neq j} (\underline{x}_i - \underline{x}_j) = 1/2 \sum_{i \neq j} (1/(2\pi^3)) \int d^3k \, e^{i\underline{k} \cdot (\underline{x}_i - \underline{x}_j)} \, \tilde{V}(k) \quad (1)$$

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by

$$V^{PY} = 1/2 \sum_{i \neq j} \sum_{\{\underline{k}\}} \nu_{\underline{k}} \, e^{i\underline{k} \cdot (\underline{x}_i - \underline{x}_J)} \tag{2}$$

where the $\{\underline{k}\}$ is an optimally chosen set of wavevectors. Defining 3N collective coordinates

$$q_{\underline{k}}^{PY} = \sum_i e^{i\underline{k} \cdot \underline{x}_i} \tag{3}$$

V^{PY} becomes

$$V^{PY} = 1/2 \sum_{\{\underline{k}\}} \nu_{\underline{k}} \, (q_{\underline{k}} \, q_{-\underline{k}} - N) \tag{4}$$

where $\nu_{\underline{k}}$ are $\underline{k}$ dependent coefficients, the potential energy of an assembly of 3N harmonic oscillators with frequencies

$$\omega_{\underline{k}}^{PY^2} = \underline{k}^2 \, k_B T/m \, (1 + \nu_{\underline{k}}/k_B T) \tag{5}$$

with a maximum cut-off frequency of at maximum wavevector $Q=(18\pi^2 \rho/m)^{1/3}$, where m is the atomic mass of the particles of the liquid and ρ is the liquid density. Ascarelli, Harrison and Paskin[3] have related the long wavelength part of the liquid structure factor to the set of coefficients, ν_k via

$$S(0) = k_B T/ \, (k_B T + \nu_{\underline{k}}) \tag{6}$$

so that the Percus-Yevick[1] liquid phonon dispersion relation, at the melting temperature, becomes

$$\omega_{\underline{k}}^{PY^2} \, (T_M) = k^2 \, k_B \, T_M / m \, S(0) \tag{7}$$

For light metals: Li, Na, K, Rb, Cs, Mg, Al, Zn, and Ga S(0) is determined from the theoretical liquid structure factors of Ashcroft and Lekner[4], which are based on a packing fraction η of 0.45, giving S(0) = 0.025. For the heavier metals: Pb, Tl and Sn, a value of η is chosen such that S(0) = 0.009 for Pb and S(0) = 0.008 for Tl and Sn.

In Table I we reproduce Omini's[2] dispersion relations and their derivatives with respect to dimensionless wavevector (y = k/Q), the distance to the upper limit of the wavevector set, Q, expressed as a fraction, as estimated from Omini's[2] data, the slopes being averages over a wavevector interval taken from Omini's Table I. Since

$$v_s \, (T_M) = (d\omega(k)/dk)_{T_M} = (k_B \, T_M / m \, S(0))^{1/2} \tag{8}$$

is defined as the sound velocity, the latter part of the equation being valid in the long wavelength limit only, the slopes should be the sound velocities in

each wavevector, or wavelength, interval, at the melting temperature. Also, since $Q(T_M) = (18\pi^2 \rho(T_M)/m)^{1/3}$, and

$$\rho(T_M) = m/V(T_M) \tag{9}$$

we see that

$$Q(T_M) = (18\pi^2 / V(T_M))^{1/3} \tag{10}$$

Thus, the volume per atom at the melting temperature is easily calculated as a function of frequency, and is also represented, since its cube root is the minimum wavelength at which a sound wave will propagate in the liquid (i.e. the Percus-Yevick maximum wavevector cut-off)

$$V(T_M) = 18\pi^2 / Q^3(T_M) \tag{11}$$

and since

$$(4/3)\pi \lambda^3(T_M) = V(T_M) \tag{12}$$

we see that the minimum wavelength for propagation at the melting point is

$$(\lambda(T_M))_{MIN} = (13.5\pi)^{1/3} / Q(T_M) \tag{13}$$

and

$$(k(T_M))_{MAX} = 2\pi Q(T_M) / (13.5\pi)^{1/3} \tag{14}$$

In Figure 1 we illustrate Omini's[2] Percus-Yevick liquid phonon dispersion relations for all the liquid metals treated. These dispersion relations peak

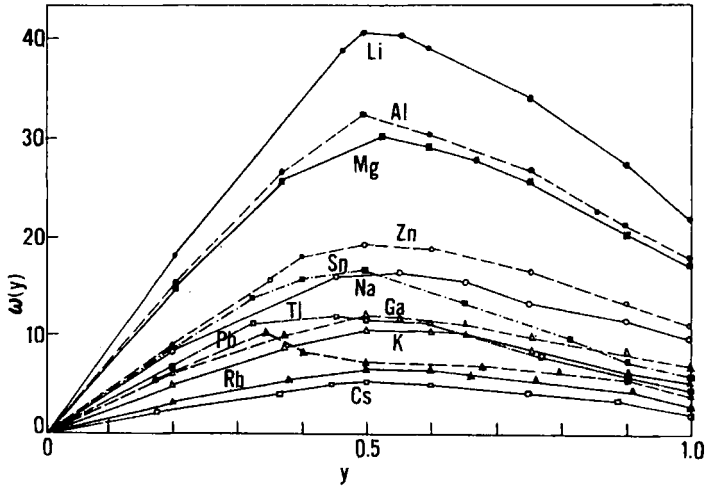

FIGURE 1 Omini's liquid phonon dispersion relations for a variety of simple metals at their melting temperatures.

below Q, so that the sound velocities can only be calculated up to the peak in each dispersion relation. The negative values for sound velocities beyond each peak are taken as an indication that sound will not propagate for k (or y) values above the peak. Thus, the k_{Max} and λ_{MIN} values estimates above are in error because the dispersion relations are not increasing monatonic. We must not forget that this is not a solid with long range order, and the cooked up collective coordinate description of the liquid by Percus and Yevick[1] need not follow the trends we are accustomed to in solids, so the maximum in the liquid phonon dispersion relations should not come as a surprise. Thus, equations (10) through (13), predicated on the view that the dispersion relation would be increasing monatonic, are all wrong by a factor of about 2, and in Pb by a factor of about 3.

In Figure 2 we plot out the calculated $v_s(T_M)$ values as a function of y(=k/Q), with the experimental points as indicated. The calculated $v_s(T_M)$ values, except for the long wavelength limit result at y=0, are averages over some incremental y interval, since Omini's[2] dispersion relations were only

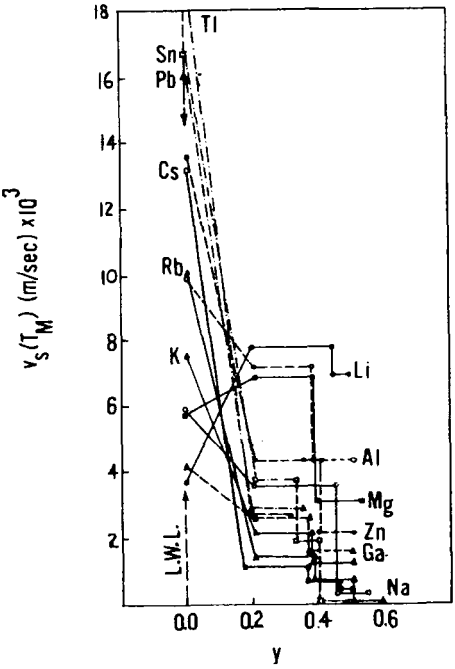

FIGURE 2 Sound velocities at the melting temperature for k=0 and k>0 for a variety of simple liquid metals.

TABLE I

Estimated sound velocities at the melting temperature from the Percus-Yevick dispersion relations for liquid phonons, for $k > 0$, and exact sound velocities in the long wavelength limit, $k = 0$

Metal	y	ω (y)	$T_{M(^{\circ}K.)}$	$S_{T_M}(0)$	$Q(T_M)$	k (=yQ)	$\lambda (=2\pi/k)$	v_s (T_M) Thy. (m/sec)	$v_s(T_M)$ Exp. (m/sec)
Li	0.000	0.00	479.4	0.025	1.975	0.000	L.W.L.	3,600.	–
	0.200	18.24				0.395	15.906	7,710.	–
	0.469	38.98				0.926	6.785	6,390.	–
	0.500	40.96				0.988	6.359		
Na	0.000	0.00	397.8	0.025	1.625	0.000	L.W.L.	5,970.	2531.
	0.200	7.49				0.325	19.322	3,380.	–
	0.450	15.93				0.731	8.595	0,360.	–
	0.550	16.29				0.894	7.028		
K	0.000	0.00	363.	0.025	1.307	0.000	L.W.L.	7,440.	1880.
	0.200	4.41				0.261	24.073	2,220.	–
	0.375	8.29				0.490	12.822	1,290.	–
	0.500	9.90				0.654	9.607		
Rb	0.000	0.00	338.9	0.025	1.223	0.000	L.W.L.	10,620.	1260.
	0.200	2.68				0.245	25.645	1,340.	–
	0.380	5.09				0.465	13.512	0.780.	–
	0.500	6.02				0.612	10.266	0.020.	–
	0.600	6.00				0.734	8.560		

TABLE I (*Continued*)

Metal	y	ω (y)	T_M (°K.)	$S_{T_M}(0)$	$Q(T_M)$	k(=2π/k)	λ (= 2π/k)	$v_s(T_M)$ Thy.(m/sec)	$v_s(T_M)$ Exp.(m/sec)
Cs	0.000	0.00	328.4	0.025	1.138	0.000	L.W.L.	13,010.	967.
	0.175	3.65				0.199	31.573	0.980.	–
	0.371	4.09				0.422	14.889	0.650.	–
	0.439	4.35				0.500	12.566	0.390.	–
	0.500	4.17				0.569	11.042		
Mg	0.000	0.00	924.0	0.025	1.901	0.000	L.W.L.	5,740.	–
	0.210	14.18				0.399	15.747	6,740.	–
	0.375	25.30				0.713	8.812	3,080.	–
	0.526	29.95				1.000	6.283		
Al	0.000	0.00	960.0	0.025	2.108	0.000	L.W.L.	10,060.	4673.-4730.
	0.200	14.25				0.422	14.889	7,100.	–
	0.375	26.68				0.791	7.943	4,220.	–
	0.500	31.95				1.054	5.961		
Zn	0.000	0.00	719.5	0.025	2.240	0.000	L.W.L.	13,530.	2850.
	0.200	8.38				0.448	14.025	4,190.	–
	0.350	14.67				0.784	8.014	4,180.	–
	0.400	16.76				0.0.896	7.012	2,050.	–
	0.500	18.81				1.120	5.610		

TABLE I (*Continued*)

Metal	y	ω (y)	T_M (°K.)	S_{T_M} (0)	Q (T_M)	k (=yQ)	$\lambda(=2\pi/k)$	v_s (T_M) Thy.(m/sec)	v_s (T_M) Exp.(m/sec)
Ga	0.000	0.00	329.8	0.025	2.102	0.000	L.W.L.	4,110.	2873.
	0.200	5.04				0.420	14.960	2,510.	–
	0.370	9.30				0.778	8.076	1,550.	–
	0.500	11.31				1.051	5.978		
Pb	0.000	0.00	600.0	0.009	1.754	0.000	L.W.L.	16,150	1820.
	0.171	4.89				0.300	20.943	2,870.	–
	0.342	9.79				0.600	10.472		
Tl	0.000	0.00	576.0	0.008	1.805	0.000	L.W.L.	23,500.	1665.
	0.200	6.16				0.300	11.200	2,870.	–
	0.332	10.23				0.600	10.489		
Sn	0.000	0.00	505.0	0.008	1.845	0.000	L.W.L.	16,600.	2474.
	0.200	7.73				0.369	17.027	3.870.	–
	0.325	12.57				0.600	10.472	1,800,	–
	0.400	13.92				0.738	8.514	0.180.	–
	0.500	14.10				0.923	6.807		

given for eight y values between $y=0$ and $y=Q$. In Table I we list the $v_s(T_M)$ values as estimated from the slopes of the Omini[2] liquid phonon dispersion relations. Also listed is the exact value we calculate for the long wavelength limit of the sound velocity

$$v_s(T_M) = (k_B T_M / m S(0))^{1/2} \tag{15}$$

derived from the Ashcroft and Lekner[4] structure factors via the wavevector derivative of the Percus-Yevick[1] dispersion relation (7).

We notice in Figure 1 that $v_s(T_M)$ will decrease rapidly to zero as the wavevector, (frequency) increases, as seen in most cases in Figure 2. This is, of course, a general rule, the increases in $v_s(T_M)$ in some cases between the long wavelength limit value and the value beginning at $y=2$ being an indication that the liquid structure factor for K, Na and Tl and Cs is very steep at $y=0$, while that for Li, Sn, Pb, Zn, Rb, Al, Mg and Ga gets very shallow at $y=0$, so that $v_s(T_M)$ is lower than it is for any $y>0$.

Upon comparing our results with the limited experimental data available we find that the agreement is not as good as would be desired, but the order of magnitude of the predictions is correct. In Na, Cs, Al, Ga the calculated sound velocity is about a factor of two off, but in K, Rb, Zn, Pb, Tl and Sn the calculated sound velocity is a bit worse, being one half to one order of magnitude from the experimental values quoted in the literature.[5] Thus, we conclude that the Percus-Yevick treatment of liquids is not yet of sufficient modelling ability to exactly predict the experimental sound velocities in simple liquid metals, but neither is it so bad as to warrent its abandonment. Clearly, further refinement of the Percus-Yevick collective coordinate theory of liquids, and relation between the sound velocity and the long wavelength limit of the liquid structure factor, (15), is needed in order to calculate sound velocities more accurately in simple liquid metals.

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