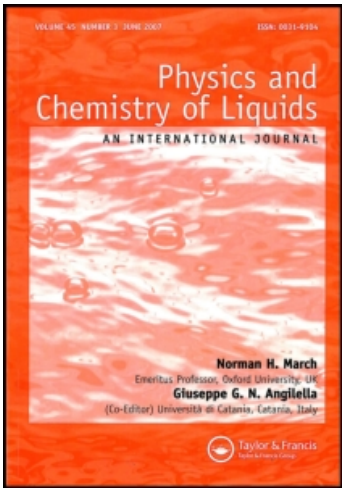

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Sound velocity of liquid metals and metalloids at the melting temperature

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In this article, we report a re-examination of the inter-relationship of the parameter $(RT_m/M)^{0.5}$ and the velocity of sound c_m at the melting temperature T_m for 41 liquid metals and metalloids. Sound velocities correlate with the equation $c_m = 7.5642(RT_m/M)^{0.5}$. Unknown sound velocities are estimated for as yet unmeasured liquid transition and lanthanide elements.

Keywords: Sound velocity; Liquid metals; Density; Surface tension

1. Introduction

Recently, Iida *et al*. [1] have introduced a new parameter ξ which gives an indication of an atom's hardness or softness. A linear relation was shown to exist between ξ and the repulsive exponent n of the intermolecular pair potential $\phi(r)$ for condensed systems. The new parameter is also useful in discussions of anharmonic effects of atomic motion in liquid metals and was applied to the prediction of the viscosities of several liquid transition metals as well as the Group IIA metals, strontium and barium. Interpolated $\xi^{0.5}$ based on the periodic variation of $\xi^{0.5}$ and atomic number were used for this purpose. Values of $\xi^{0.5}$ can be calculated from measured velocities of sound in liquid metals and metalloids at their respective melting temperatures. The present article further examines the periodic variation of $\xi^{0.5}$ with atomic number using additional sound velocity data as well as the inter-relationship of the parameter $(RT_m/M)^{0.5}$ and the velocity of sound c_m at the melting temperature T_m. Sound velocities for several as yet unmeasured liquid transition and lanthanide metals are also estimated.

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2. Formulation

According to Einstein [2], the velocity of sound c in a solid is related to the mean frequency of atomic vibrations ν and atomic volume V;

$$c \propto \nu V \tag{1}$$

Using the concept of the vibrational instability of crystal lattices, Lindemann [3] related ν to the melting temperature T_m and atomic weight M

$$\nu \propto \left(\frac{T_m}{MV^{2/3}}\right)^{0.5} \tag{2}$$

From equations (1) and (2) the velocity of sound c_m at the melting temperature gives

$$c_m \propto \left(\frac{RT_m}{M}\right)^{0.5} \tag{3}$$

in which R is the gas constant. A similar correlation is observed in liquid metals at the melting temperature [4]. For the liquid state the thermodynamic result;

$$S(0) = \rho k_B T K_T \tag{4}$$

relates the long-wavelength limit of the static structure factor to the average particle density $\rho = N_o/V$, temperature T and isothermal compressibility K_T. N_o and k_B are the Avogadro number and Boltzmann constant, respectively. Equation (4) is readily expressed in the alternate form

$$c_m = \left\{\gamma k_B N_o S(0)\right\}^{0.5}\left(\frac{T_m}{M}\right)^{0.5} \tag{5}$$

where γ is the ratio of the isobaric and isochoric heat capacities. With $\{\gamma/S(0)\}^{0.5}$ constant, equation (5) indicates that c_m for liquid metals and metalloids should linearly correlate with the quantity $(RT_m/M)^{0.5}$. Figure 1 shows this correlation for 41 liquid metals and metalloids for which c_m values are available in the literature, table 1. For purposes of clarity, individual data points for the elements are not labelled in figure 1. For a forced line fit through the origin one obtains

$$c_m = 7.5642\left(\frac{RT_m}{M}\right)^{0.5}\left(\mathrm{m\,s^{-1}}\right) \tag{6}$$

Iida *et al.* [5] and Kasama *et al.* [6] indicate that the Lindemann expression for the average vibrational frequency requires correction

$$\nu_{\text{corrected}} = \beta\nu \tag{7}$$

The correction factor β is given in terms of the liquid surface tension σ_m, atomic volume V_m and packing fraction η_m at the melting temperature

$$\beta = 1.1 \times 10^3 \left\{\frac{V_m^{1/3}}{\left(1.97\eta_m^{1/3} - 1\right)}\right\}\left(\frac{\sigma_m}{RT_m}\right)^{0.5} \tag{8}$$

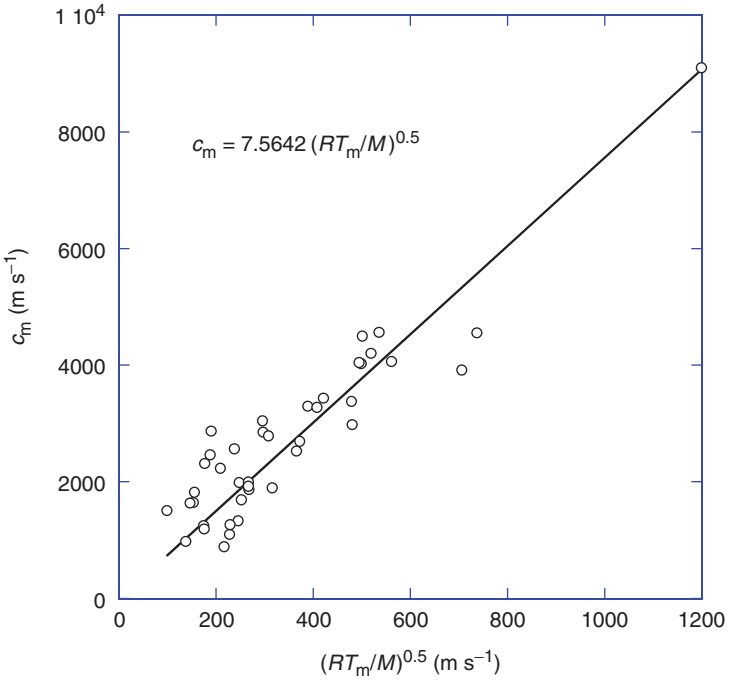

Figure 1. Velocity of sound of liquid metals and metalloids c_m at their melting temperature T_m as a function of the parameter $(RT_m/M)^{0.5}$.

A packing fraction $\eta_m = 0.468$ is a good approximation for all liquid metals. Using β values calculated from equation (8), the correlation of c_m with $\beta(RT_m/M)^{0.5}$ was examined, figure 2. For a forced line fit through the origin the following result is obtained

$$c_m = 17.793\beta\left(\frac{RT_m}{M}\right)^{0.5}\left(\mathrm{m\,s^{-1}}\right) \tag{9}$$

Equations (8) and (9) may be used together with liquid surface tension, density and melting temperatures to estimate unknown sound velocities at the melting temperature. Following Iida *et al.* [1], equation (6) may also be written in the form

$$c_m = 7.5642\left(\frac{\xi RT_m}{M}\right)^{0.5}\left(\mathrm{m\,s^{-1}}\right) \tag{10}$$

in which ξ is a correction factor. Using equation (10), values of ξ may be calculated from measured sound velocities. The calculated values of ξ are listed in table 1.

3. Results and discussion

The slope of figure 1, 7.5642 in SI units on the basis of 41 liquid metals and metalloids may be compared with a value of 9 suggested by Iida and Guthrie [7] on the basis of

Table 1. Measured sound velocities c_m, ξ parameter, Grüneisen constant γ_G and repulsive exponent n at the melting temperature T_m for liquid metals and metalloids.

Element	c_m (m s^{-1})	ξ	γ_G	n
Li	4554	0.667	1.091	1.091(2.83)
Na	2526	0.832	1.086	4.516(4.33)
K	1876	0.859	1.247	5.485(4.50)
Rb	1251	0.899	1.198	5.191(5.90)
Cs	983	0.895	1.232	5.395(5.04)
Be	9104	1.006	1.788	8.731
Mg	4065	0.916	2.058	10.351(10.0)
Ca	2978	0.672	1.206	5.239(6.78)
Sr	1902	0.635	1.092	4.550(7.19)
Ba	1331	0.510	0.502	1.011
Al	4561	1.263	2.925	15.549(6.74)
Si	3920	0.539	2.192	11.154
Mn	3381	0.870	2.203	11.221(4.70)
Fe	4200	1.145	2.593	13.557(8.60)
Co	4031	1.138	2.902	15.412
Ni	4047	1.171	2.802	14.811(8.60)
Cu	3440	1.164	2.672	14.035(8.27)
Zn	2850	1.613	2.455	12.728(12.70)
Ga	2873	3.996	2.076	10.458(7.45)
Ge	2693	0.914	1.687	8.120
Se	1100	0.407	0.718	2.308
Mo	4502	1.411	3.930	21.580
Ag	2790	1.430	2.826	14.957(10.8)
Cd	2237	1.991	2.890	15.340(16.2)
In	2320	3.024	2.499	12.992(8.08)
Sn	2464	3.000	2.480	12.880(8.8)
Sb	1988	1.119	1.636	7.819
Te	889	0.294	0.358	0.147
La	2002	0.980	1.666	7.998
Ce	1693	0.788	1.138	4.831
Pr	1925	0.912	1.739	8.432
Yb	1274	0.539	3.693	20.160
Ta	3303	1.263	3.084	16.507
W	3279	1.128	3.717	20.301
Pt	3053	1.869	7.982	45.892
Au	2568	2.042	4.116	22.698(14.5)
Hg	1511	4.109	2.808	14.848(18.5)
Tl	1650	2.028	2.402	12.413(10.2)
Pb	1821	2.406	2.586	13.514(12.0)
Bi	1640	2.170	2.273	11.641
Pu	1195	0.803	0.761	2.566

25 liquid metals and metalloids. The slope of figure 2, 17.793 in SI units may be compared with a value of 18 obtained by the latter workers for the same 25 elements. A simple linear correlation was also suggested between ξ and the repulsive exponent n of the following pair potential of condensed systems

$$\phi(r) = \varepsilon\left(\frac{a}{r}\right)^n - b\delta^3 \exp(-\delta r) \tag{11}$$

where r is the radial distance between atoms and the parameters $\varepsilon > 0$, $a > 0$, $n > 3$, $b \geq 0$ and $\delta > 0$. Matsuda and Hiwatari [8] used measured values of the bulk modulus at 0 K to obtain values for the repulsive exponent of 19 elements.

$$\xi = 0.15n \tag{12}$$

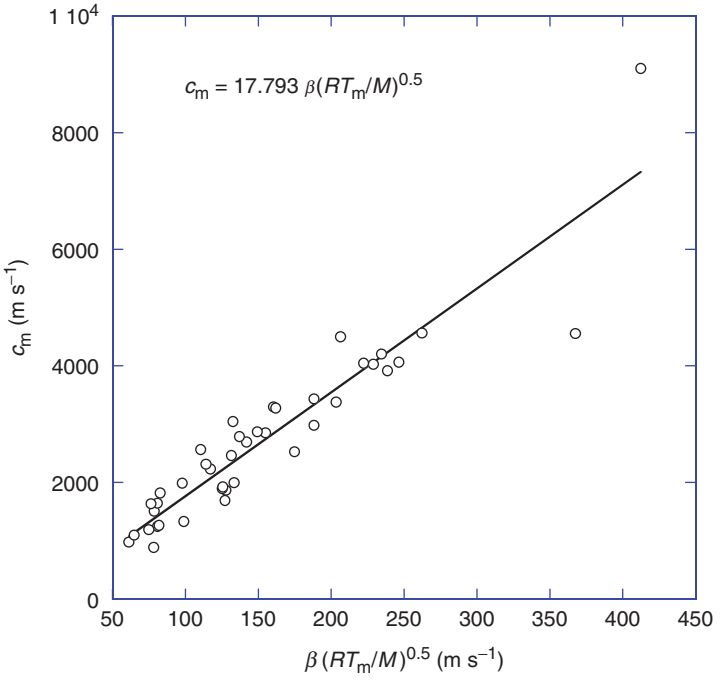

Figure 2. Velocity of sound of liquid metals and metalloids c_m at their melting temperature as a function of the parameter $(\beta RT_m/M)^{0.5}$.

The repulsive exponent n may also be obtained from the Grüneisen constant γ_G using the relation [8]

$$n = 6\gamma_G - 2 \tag{13}$$

γ_G values have been calculated from measured sound velocities for the 41 liquid elements examined in the present study using the relation

$$\gamma_G = \frac{\alpha c_m^2 M}{C_P} \tag{14}$$

where α is the melt expansivity and C_P the isobaric heat capacity. Melt expansivities were taken from [9–12] and heat capacities from [13]. On the basis of equations (13) and (14) the calculated values of γ_G and n are listed in table 1.

For the expanded data set of 41 liquid elements considered in the present study, a modified linear correlation between ξ and n is obtained, figure 3

$$\xi = 0.093n \tag{15}$$

With the exception of lithium, barium, selenium, tellurium and plutonium, all the other liquid elements satisfy the condition that $n > 3$. For comparison purposes, values of n obtained from low temperature bulk moduli are shown in parentheses in table 1.

Equations (8) and (9) were used to calculate sound velocity values c_m for as yet unmeasured transition and lanthanide elements. Liquid densities used for this purpose were taken from [9–12], surface tensions from [10,14] and melting temperatures

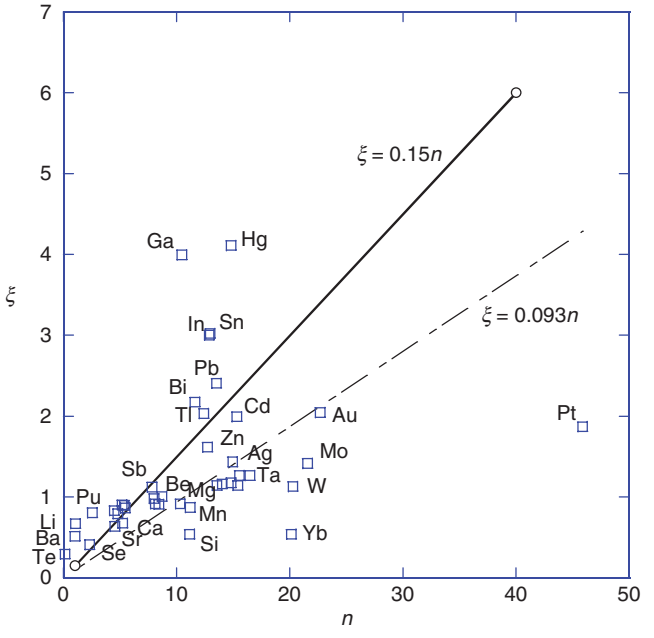

Figure 3. Relationship of the parameter ξ to the repulsive exponent n of the intermolecular pair potential. For purposes of clarity data points for several elements are unlabelled.

from [13]. On the basis of equations (8) and (9), calculated values of c_m are listed in table 2. These values may be used together with estimates of the temperature coefficient of sound velocity [15] to determine sound velocity values at other temperatures.

Also included in table 2 for comparison are the sound velocities of the rare earth elements calculated by Yokoyama *et al.* [16] using the Percus–Yevick phonon model of the liquid state together with low angle diffraction data. Recently [17], the present author has shown that the surface tension, density and sound velocity of liquid metals and metalloids may be correlated by the relation

$$\log c_m = 0.5226 \log\left(\frac{\sigma_m}{\rho}\right) + 5.4364. \tag{16}$$

Equation (16) gives the velocity in $m\,s^{-1}$ when the surface tension is expressed in Nm^{-1} and the density in $kg\,m^{-3}$, respectively. Sound velocities calculated from equation (16) are also shown in table 2 for comparison.

In figure 4, the periodicity of c_m with atomic number for the liquid rare earth elements is examined. Figure 4 includes both experimental values (La, Ce, Pr, Yb) and values estimated from equations (8) and (9). The divalent lanthanides Eu and Yb occur at the minima of the double periodicity displayed in figure 4.

Surface tension, expansivity, and binding energy have been observed to display an analogous periodicity for the liquid rare earth elements [10]. Measured c_m values together with values estimated from equations (8) and (9) were used with equation (10) to calculate $\xi^{0.5}$. Values of $\xi^{0.5}$ vary periodically with atomic number, figure 5, with the group IIIA elements (excluding Tl) occupying the major peaks and the group VIA elements the major valleys of the plot.

Table 2. Calculated sound velocities c_m at the melting temperature T_m for liquid transition and rare earth elements.

Element	c_m (m s^{-1})	c_m (m s^{-1}) [16]	c_m (m s^{-1}) [17]
Sc	4237		4272
Ti	4546		4309
V	4683		4255
Cr	4116		3663
Y	3143		3258
Zr	3666		3648
Nb	3593		3385
Ru	3563		3214
Rh	3283		2950
Pd	2926		2657
Hf	2631		2559
Re	2943		2665
Os	2777		2487
Ir	2643		2416
Nd	2176	2200	2212
Sm	1672		1670
Eu	1477	1860	1568
Gd	2027	2240	2041
Tb	2009	2120	2014
Dy	1944	2130	1941
Ho	1926	2560	1919
Er	1882	2450	1867
Lu	2198	2380	2176

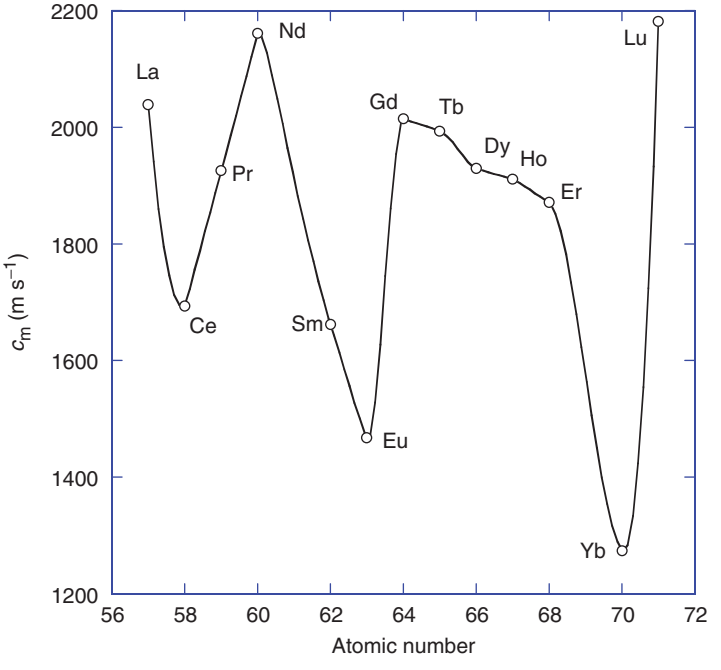

Figure 4. Periodicity of experimental and calculated sound velocities c_m at the melting temperature T_m for the liquid rare earth metals.

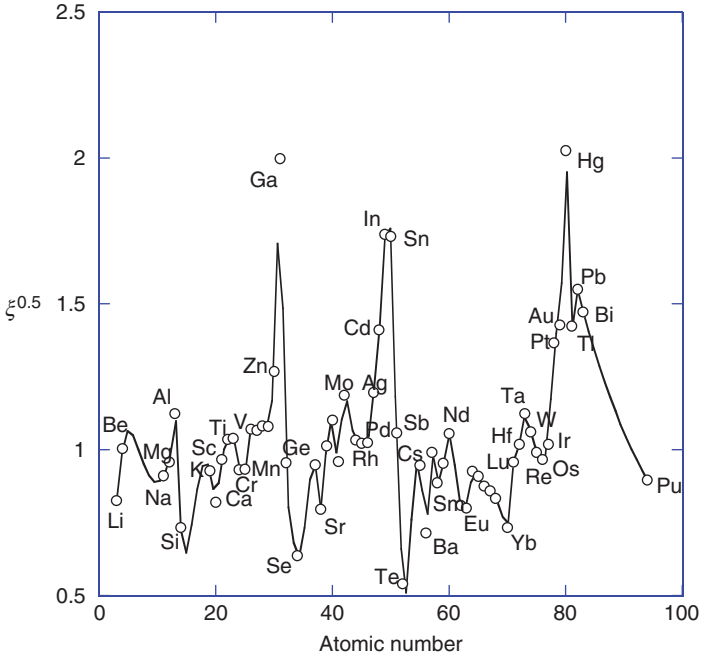

Figure 5. Periodicity of the parameter $\xi^{0.5}$ with atomic number for liquid metals and metalloids. For purposes of clarity individual data points for several elements are unlabelled.

4. Conclusions

The correlation of measured sound velocities at the respective melting temperatures with the parameter $(RT_m/M)^{0.5}$ has been re-examined for 41 liquid metals and metalloids. Measured surface tensions and melt densities have been used to estimate velocities of sound at the melting temperature for several as yet unmeasured liquid transition and lanthanide metals. The estimated sound velocities show good agreement with other estimates of c_m. The periodicity of the parameter ξ, representative of the repulsive energy of the interatomic pair potential has also been examined

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