Velocity of Sound in Liquid Simple Metals near the Melting Point

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In this paper we report comparisons between theoretical and experimental values of the velocity of sound in twenty liquid simple metals near the melting point. We used three model theories, namely, (1) an improved Rosenfeld's approach, (2) Ascarelli's approach and (3) a modified Ascarelli's approach. For alkali metals, the three model theories give much the same predictions in the velocity of sound. For polyvalent metals, electrons play an important role when the valency is increased. For noble metals, the degree of agreement between theory and experiment is improved by taking into account the effects of the ionic core due to the *s-d* hybridization.

1. Introduction

The velocity of sound is one of the most basic thermodynamic properties. Nevertheless, only a few theoretical studies have been made of this phenomenon since the pioneering work of Ascarelli.[1] Recently, however, Yokoyama[2] has modified the Rosenfeld formula[3] of the velocity of sound and successfully explained the temperature dependence of the velocity of sound in liquid alkali metals up to quite high temperatures. In the subsequent work Yokoyama[4] has shown that a hard-sphere model immersed in a uniform background potential is capable of describing the velocity of sound in liquid 3*d* transition metals near the melting point. An interesting point presented in Ref. 4) is that the effects caused by electrons are relatively small but still important for yielding predictions in good agreement with the experimental data. Therefore, it seems necessary to perform a systematic study on the role of electrons in any theory of the velocity of sound.

The purpose of the present paper is to investigate the velocity of sound in liquid alkali, noble and polyvalent metals by means of both an improved Rosenfeld's approach and two model theories incorporating effects caused by the electrons, and to report the effects caused by the electrons in the theory of the velocity of sound. In the next section, we mention the three model theories and approximations to be employed. Results of the numerical calculations are presented and compared with available experimental data in Section 3. Discussion will be made regarding the effects of the ionic core due to the *s-d* hybridization for noble metals in comparison with observed data. Conclusions drawn from the present work will be presented in the last section.

2. Model Theories

2.1 Improved Rosenfeld's approach (hard-sphere model)

The velocity of sound, *c*, is defined by[2,3]

$$Mc^2 = (\partial p/\partial \rho)_S = (\partial p/\partial \rho)_T + T[(\partial p/\partial T)_V]^2/(\rho^2 C_V/N),$$
(1)

where M is the atomic mass, V the volume, T the absolute temperature, N the total number of ions and ρ the number density of ions. p and S, respectively, denote the pressure

and the entropy. C_V stands for the heat capacity at constant volume which is purely kinetic, $C_V = (3/2)Nk_B$ with k_B being the Boltzmann constant, for a classical system of hard spheres. Then the velocity of sound, *c*, is given by

$$c = s(\xi)^{new}(k_B T/M)^{1/2},$$
(2)

where ξ is the packing fraction defined by

$$\xi = \pi \rho \sigma^3/6,$$
(3)

and

$$s(\xi)^{new} = (p(\xi) + \xi p'(\xi) + (2/3)(3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V + p(\xi))^2)^{1/2}.$$
(4)

In eq. (3), σ is a hard-sphere diameter. $p(\xi)$ and $p'(\xi)$ are given by the Carnahan-Starling expression[5] as

$$p(\xi) = (1 + \xi + \xi^2 - \xi^3)/(1 - \xi)^3,$$
(5)

and

$$p'(\xi) \equiv dp(\xi)/d\xi = 2(2 + 2\xi - \xi^2)/(1 - \xi)^4.$$
(6)

The temperature dependence of σ is estimated by the use of the empirical formula proposed by Protopapas *et al.*[6]:

$$\sigma(T) = 1.12\sigma_m[1 - 0.112(T/T_m)^{1/2}],$$
(7)

in which σ_m is the value of σ at the melting point, T_m. From eq. (7),

$$(\partial \ln \sigma/\partial \ln T)_V = -(0.056\sigma_0/\sigma(T))(T/T_m)^{1/2},$$
(8)

in which σ_0 is given by $\sigma_0 = 1.0878(\rho_m)^{-1/3}$ with ρ_m being the number density of ions at T_m and $\sigma_m = 0.888\sigma_0$. As explained in Ref. 7), we can extract the value of ξ through eq. (9) of Ref. 8). The value of ξ is 0.463 for liquid metals near the melting point. With $\xi = 0.463$, as shown in Ref. 8), we can account for the structural, thermodynamic, transport, and surface properties of the liquid metals near the melting point on the basis of a hard-sphere model.

2.2 Ascarelli's approach

Ascarelli[1] used a model of hard spheres immersed in a uniform (without gradients) potential which provides the cohesion that the hard-sphere gas otherwise lacks. This approach

is supported by the well-known form of writing the total binding energy E (per atom) of a metal, which when calculated to the second order in a perturbation scheme can be conveniently separated into two terms[9,10]

$$NE = NE_0 + (1/2) \sum_{\substack{i,j \\ i \neq j}} V(r_{ij}),\qquad (9)$$

where E_0 is a quantity dependent on the volume of the system but independent of the positions of the ions, and $V(r)$ is an effective pair interaction energy. As the structure of liquid metals is largely determined by the short-range repulsive forces, we approximate $V(r)$ by a simple hard-sphere potential. The total binding energy E of a metal is completely determined by E_0, which while supplying the cohesion to the hard-sphere system, does not change the equilibrium configurations of the ions.

We now approximate E_0 by the sum of two terms: the kinetic energy of a free-electron gas, and a negative energy term, $-B/V^{1/3}$, which contains the energy of the interaction of valence electrons with the ion, and the energy of the interaction of valence electrons with themselves. B is a constant to be determined by considering the pressure of the system to be zero at the melting point. For simplicity in the following, we write B in terms of a dimensionless constant A defined by

$$B = 3A(V_m)^{1/3} k_B T_m.\qquad (10)$$

We then write the pressure as[1]

$$pV/(Nk_BT) \equiv p/\rho k_BT = (2/5)(zE_F/k_BT)$$
$$- A(V_m/V)^{1/3}(k_BT_m/k_BT) + p_hV/Nk_BT,\qquad (11)$$

where z is the number of valence electrons per atom(valency), V_m is the volume at the melting point and E_F is the Fermi energy. p_h is the pressure of the hard-sphere system, which is well described by the Carnahan-Starling equation of states given in eq. (5), namely,

$$p_hV/Nk_BT = p_h/\rho k_BT = p(\xi)$$
$$= (1 + \xi + \xi^2 - \xi^3)/(1 - \xi)^3.\qquad (5)$$

Now assuming the total pressure $pV/Nk_BT \fallingdotseq 0$ under normal conditions at the melting point in eq. (11), we find

$$A = p_h/\rho_m k_B T_m + (2/5)(zE_F(T_m)/k_B T_m)$$
$$= (1 + \xi_m + \xi_m^2 - \xi_m^3)/(1 - \xi_m)^3$$
$$+ (2/5)(zE_F(T_m)/k_BT_m),\qquad (12)$$

where ξ_m is the packing fraction at the melting point which is 0.463 as mentioned in the previous subsection. A is a constant which is independent of ρ and T in the following calculations. We can then write, after a simple differentiation of the pressure with respect to the volume and the temperature,

$$(\partial p/\partial \rho)_T/k_BT = (2/3)(zE_F/k_BT)$$
$$- (4/3)A(\rho/\rho_m)^{1/3}(k_BT_m/k_BT)$$
$$+ p(\xi) + \xi p'(\xi),\qquad (13)$$

$$(\partial p/\partial T)_V/\rho k_B = p(\xi) + 3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V.\qquad (14)$$

In the derivation of eq. (13), we assumed $(\partial \sigma/\partial \rho)_T \fallingdotseq 0$. Then, substituting eqs. (13) and (14) into eq. (1), we obtain

$$c/(k_BT/M)^{1/2} = [(2/3)(zE_F/k_BT)$$
$$- (4/3)A(\rho/\rho_m)^{1/3}(k_BT_m/k_BT)$$
$$+ p(\xi) + \xi p'(\xi) + (2/3)\{p(\xi)$$
$$+ 3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V\}^2]^{1/2}.\qquad (15)$$

There are four differences between Ascarelli's original approach and the present approach, which are as follows:
(1) A different ξ_m was used (Ascarelli used 0.45, while we used 0.463),
(2) A different equation of states was used (Ascarelli used Reiss et al.'s[1] but we used the Carnahan-Starling equation of states),
(3) The temperature dependence of σ was differently treated from Ascarelli,
(4) We did not assume that $C_p/C_V = 1.15$ for all metals employed by Ascarelli.

2.3 Modified Ascarelli's approach

The Helmholtz free energy of a liquid metal is assumed to be written as[11,12]

$$F = F_R + U_g(V, T),\qquad (16)$$

where F_R is the Helmholtz free energy of a model reference liquid capable of describing the structure-dependent part of the system of interest and $U_g(V, T)$ is a function of the volume V and the absolute temperature T representing the difference in the free energies of the reference and the real liquid. If a hard-sphere model is employed as a reference liquid, we may write from Shimoji[13]

$$F_R = F_H = Nk_BT[-\ln \Lambda^3 - \ln(1/\rho) + (3 - 2\xi)$$
$$/(1 - \xi)^2 - 4].\qquad (17)$$

Here F_H denotes the Helmholtz free energy of a hard-sphere liquid, and Λ is the thermal de Broglie wavelength. We used the Carnahan-Starling equation of states in eq. (17). The contribution from the non-reference liquid part is given as

$$U_{g,H}(V, T)/N = u_{eg} - (1.8z^2B_H)/a\qquad (18)$$

in Ryd. Here z is the valency and a is the Wigner-Seitz radius given by $a = (3/4\pi\rho)^{1/3}$. In eq. (18), the first term u_{eg} stands for the electron-gas energy derived from kinetic, exchange and correlation energies[14]:

$$u_{eg} = 2.2z^{5/3}/a^2 - 0.916z^{4/3}/a$$
$$+ z(0.031 \ln az^{-1/3} - 0.115).\qquad (19)$$

The second term denotes the electrostatic energy in the point-ion model and the coefficient B_H can be determined by the zero-pressure condition at the melting point

$$p = -(\partial F/\partial V)_T \fallingdotseq 0,\qquad (20)$$

as stated in Subsection 2.2. The explicit expression for B_H is given as follows:

$$B_{\mathrm{H}} = (a(T_{\mathrm{m}})^2/(1.8z^2))[-0.031z/a(T_{\mathrm{m}})$$
$$- 0.916z^{4/3}/a(T_{\mathrm{m}})^2 + 4.42z^{5/3}/a(T_{\mathrm{m}})^3$$
$$+ ((1 + \xi_{\mathrm{m}} + \xi_{\mathrm{m}}^2 - \xi_{\mathrm{m}}^3)/(1 - \xi_{\mathrm{m}})^3)$$
$$\times (3k_{\mathrm{B}}T_{\mathrm{m}}/a(T_{\mathrm{m}}))], \tag{21}$$

where T_{m} denotes the melting temperature and $a(T_{\mathrm{m}}) = (3/(4\pi\rho_{\mathrm{m}}))^{1/3}$ with ρ_{m} being the number density of ions at the melting point. Then, the pressure is expressed as

$$pV/(Nk_{\mathrm{B}}T) = -(a/3k_{\mathrm{B}}T)[0.031z/a + (0.916z^{4/3}$$
$$+ 1.8z^2B_{\mathrm{H}})/a^2 - 4.42z^{5/3}/a^3] + p(\xi), \tag{22}$$

where B_{H} is treated as a constant which is indepentent of the temperature and density. From eq. (22), assuming $(\partial\sigma/\partial\rho)_{\mathrm{T}} \coloneqq 0$, the density derivative of the pressure at constant temperature is given as

$$(\partial p/\partial\rho)_{\mathrm{T}}/k_{\mathrm{B}}T = (1/k_{\mathrm{B}}T)[-0.031z/3$$
$$- 4(0.916z^{4/3} + 1.8z^2B_{\mathrm{H}})/(9a)$$
$$+ (22.1z^{5/3})/(9a^2)] + p(\xi) + \xi p'(\xi). \tag{23}$$

Then, substituting eqs. (14) and (23) into eq. (1), we obtain

$$c^2/(k_{\mathrm{B}}T/M) = (1/k_{\mathrm{B}}T)[-0.031z/3$$
$$- 4(0.916z^{4/3} + 1.8z^2B_{\mathrm{H}})/(9a)$$
$$+ (22.1z^{5/3})/(9a^2)] + [p(\xi) + \xi p'(\xi)$$
$$+ (2/3)\{p(\xi) + 3\xi p'(\xi)(\partial\ln\sigma/\partial\ln T)_V\}^2], \tag{24}$$

where the formula for $(\partial\ln\sigma/\partial\ln T)_V$ is given in eq. (8).

3. Results

Using eqs. (2), (15) and (24), we calculated the velocity of sound of twenty simple metals. The results are summarized in Table 1, together with input data and experimental data, and are graphically shown in Figs. 1, 2 and 3. Generally speaking, our theoretical results are in reasonable agreement with the experimental data. As seen from the table, the role of the electrons generally gives beneficial increases in the velocity of sound through the structure-independent term. The main features of our results are summarized as follows.

(1) There is no essential difference between Ascarelli's approach and the modified Ascarelli's approach.

(2) Despite having included effects caused by the electrons, no improvement can be seen over the hard-sphere model for liquid alkali metals.The Fermi energy part is almost cancelled by the electron-ion interaction part, i.e., $(2/3)zE_{\mathrm{F}}/(k_{\mathrm{B}}T) - (4/3)A(\rho/\rho_{\mathrm{m}})^{1/3}(k_{\mathrm{B}}T_{\mathrm{m}}/k_{\mathrm{B}}T) \coloneqq 0$, so that the velocity of sound, c, can be determined largely from the hard-sphere model (see, eqs. (2), (4) and (15)).

(3) For noble metals, no improvement can be seen over the hard-sphere model in spite of having included effects caused by the electrons. The reason for this appears to be
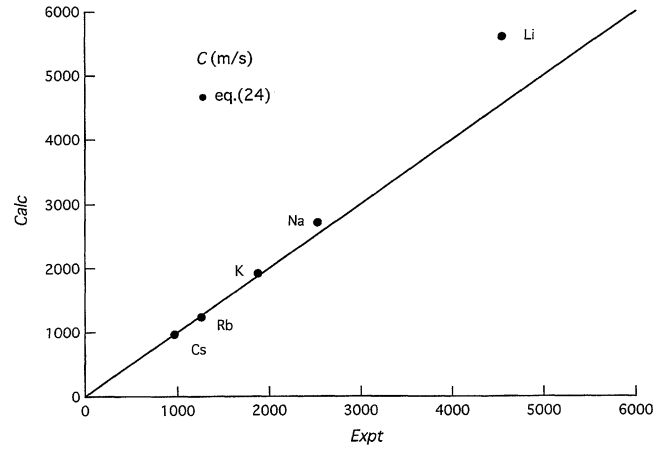

Fig. 1 Comparison between theory and experiment for the velocity of sound in liquid alkali metals near the melting point. The solid line denotes the 45° axis.
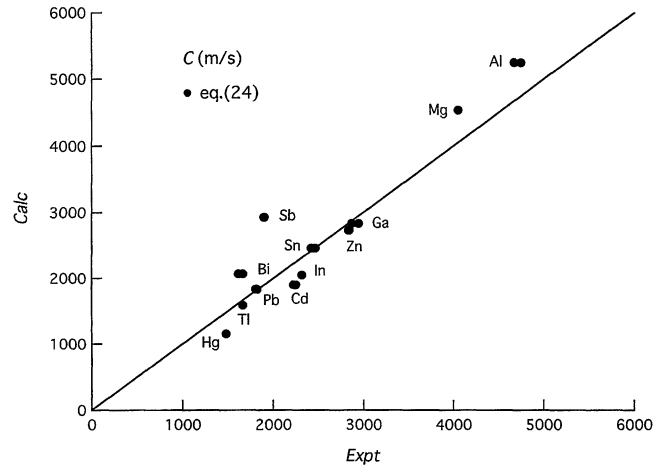

Fig. 2 Same as Fig. 1, but for liquid polyvalent metals.
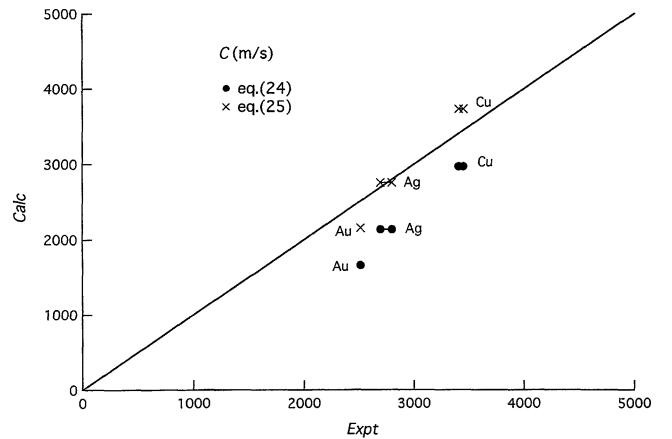
Fig. 3 Same as Fig. 1, but for liquid noble metals. The values of z_Γ are determined from $\Gamma = 120$ and used in eq. (25).

quite different from that for alkali metals, which will be discussed in the next section.

(4) The degree of progress made by including effects of the electrons tends to increase in the sequence divalent $\rightarrow$ trivalent $\rightarrow$ tetravalent $\rightarrow$ pentavalent when the number of valence electrons is increased. Much improvement

Table 1   Velocity of sound calculated from the three model theories. Experimental data are taken from Iida and Guthrie.[16] Experimental value of liquid Li is taken from Ref. 2) which is measured at 470 K.

	T (K)	ρ (10^3 kgm^{-3})	ξ	c_{calc} (ms^{-1}) eq. (2)	eq. (15)	eq. (24)	c_{expt} ms^{-1}	eq. (24)/eq. (2)	eq. (24)/eq. (15)	eq. (24)/c_{expt}
Li	463	0.512	0.463	5435	5540	5599	4544	1.02	1.01	1.23
Na	378	0.928	0.463	2698	2677	2714	2527	1.01	1.01	1.07
K	343	0.826	0.463	1971	1887	1918	1877	0.97	1.02	1.02
Rb	313	1.476	0.463	1273	1212	1234	1260	0.97	1.02	0.98
Cs	303	1.836	0.463	1005	947	965	967	0.96	1.02	1.00
Cu	1423	7.947	0.463	3149	2961	2973	3407~3450	0.94	1.00	0.87~0.86
Ag	1273	9.311	0.463	2286	2125	2136	2694~2797	0.93	1.01	0.79~0.76
Au	1423	17.23	0.463	1789	1655	1662	2512	0.93	1.00	0.66
Mg	953	1.58	0.463	4167	4497	4539	4051	1.09	1.01	1.12
Zn	723	6.55	0.463	2213	2702	2729	2831~2839	1.23	1.01	0.96~0.96
Cd	623	7.99	0.463	1567	1878	1901	2223~2248	1.21	1.01	0.86~0.85
Hg	238	13.68	0.463	725	1135	1156	1478	1.59	1.02	0.78
Al	943	2.383	0.463	3934	5198	5246	4668~4745	1.33	1.01	1.12~1.11
Ga	323	6.08	0.463	1432	2794	2830	2868~2944	1.98	1.01	0.99~0.96
In	433	7.02	0.463	1292	2023	2052	2313	1.59	1.01	0.89
Tl	588	11.26	0.463	1129	1569	1590	1662	1.41	1.01	0.96
Sn	523	6.99	0.463	1397	2430	2462	2416~2462	1.76	1.01	1.02~1.00
Pb	613	10.68	0.463	1145	1810	1834	1805~1821	1.60	1.01	1.02~1.01
Sb	933	6.46	0.463	1842	2896	2929	1895~1900	1.59	1.01	1.55~1.54
Bi	573	10.03	0.463	1102	2040	2067	1614~1664	1.88	1.01	1.28~1.24

is achieved for Hg, Ga, Tl, Sn and Pb.

(5)   Disagreement between theory and experiment can be found for Li, Cu, Ag, Au, Hg, Sb and Bi. Among the liquid metals studied here, the quantum correction might be needed for Li, while Sb and Bi are classified as anomalous metals having a change in the electronic state when they melt from a crystal semimetal to a liquid metal.[15] Hg is the obvious exception.

4. Discussion

For noble metals, the predictions in terms of the genuine hard-sphere model appear to be better than those based on both Ascarelli's and the modified Ascarelli's approach. The reason for this is discussed here. For noble metals, it seems necessary to carefully take into account the effects of the over-lap of electron shells of neighbouring ions because of the large sizes of their ion cores. With this situation in mind, we tried to calculate the velocity of sound using the following

formula (see, eq. (11) of Ref. 4))

$$c^2/(k_B T/M) = (1/k_B T)[-0.031z/3 - 4(0.916z^{4/3} + 1.8z^2)$$
$$/(9a) + (22.1z^{5/3})/(9a^2) + 6B_H/a^6]$$
$$+ [p(\xi) + \xi p'(\xi) + (2/3)\{p(\xi)$$
$$+ 3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V\}^2]. \qquad (25)$$

The last term of the first square bracket represents the contribution arising from effects of the ionic core due to the s-d hybridization; the coefficient B_H can be determind by the zero-pressure condition at the melting point. The explicit expression for B_H is given as follows:

$$B_H = (a(T_m)^7/6)[0.031z/a(T_m) + (0.916z^{4/3} + 1.8z^2)$$
$$/a(T_m)^2 - 4.42z^{5/3}/a(T_m)^3 - ((1 + \xi_m + \xi_m^2 - \xi_m^3)$$
$$/(1 - \xi_m)^3) \times (3k_B T_m/a(T_m))]. \qquad (26)$$

As mentioned in Ref. 4), the effective valence, z_Γ, is determined from the value of a plasma parameter Γ. As suggested by Itami and Shimoji,[11] we employ $\Gamma = 120$ for noble metals. The values of the velocity of sound calculated from $\Gamma = 120$ are summarized in Table 2, together with the values of z_Γ. As seen from the table, our theoretical results

Table 2 Velocity of sound in liquid noble metals calculated from eq. (25). z_Γ is the effective valence calculated from the plasma parameter $\Gamma = 120.$[11] $T/T_\mathrm{m} = 1.049$, 1.032 and 1.065 for Cu, Ag and Au, respectively, and ρ has been taken equal to ρ_m (mass density at the melting point). $(\partial \ln \sigma / \partial \ln T)_\mathrm{V} = -0.064$ for Cu, Ag and Au.

	T (K)	ρ ($10^3\,\mathrm{kgm^{-3}}$)	ξ	z_Γ	c_calc ($\mathrm{ms^{-1}}$)	c_expt ($\mathrm{ms^{-1}}$)	eq. (25)/eq. (2)	eq. (25)/eq. (15)	eq.(25)/c_expt
Cu	1423	7.947	0.463	1.22	3731	3407 ~ 3450	1.18	1.26	1.08 ~ 1.10
Ag	1273	9.311	0.463	1.21	2758	2694 ~ 2797	1.21	1.30	0.99 ~ 1.02
Au	1423	17.23	0.463	1.26	2155	2512	1.20	1.30	0.86

agree reasonably well with the experimental data. A graphic comparison of the calculated with the experimental values is shown in Fig. 3 for demonstrative purposes.

5. Conclusion

We have shown that a hard-sphere model immersed in a uniform background potential is capable of describing the velocity of sound in liquid metals near the melting point. The degree of progress made by including the effects of the electrons generally increases when the number of valence electrons is increased. For liquid alkai metals, however, the Fermi energy part is almost cancelled by the electron-ion interaction part so that the velocity of sound can be well described by a hard-sphere model. As for noble metals, the s-d hybridization effect must be taken into account in order to yield predictions in better agreement with the experimental data.

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