Velocity of Sound in Liquid 3d Transition Metals near the Melting Point

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A hard-sphere model, which has been successfully applied to the calculations of excess entropy, self-diffusion coefficient, shear viscosity coefficient and surface tension, is shown to give a quantitative description of the velocity of sound in liquid 3d transition metals if a uniform background potential is properly taken into account.

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1. Introduction

In 1968, Ascarelli¹⁾ presented a model theory on the velocity of sound in liquid metals. He used a model of hard spheres immersed in a uniform background potential. Since then, more than 30 years have passed. The velocity of sound is one of the most basic thermodynamic properties. Nevertheless, only a few studies have been made of this quantity. Theoretical and semi-empirical equations for the velocity of sound in liquid metals, including purely empirical methods, are well reviewed by the works^{2,3)} of Iida and Guthrie.

Recently, using a hard-sphere model, Rosenfeld⁴⁾ has shown that the velocity of sound divided by the thermal velocity has about the same value (typically ~ 10 , with a spread of values between ~ 6 and ~ 12) for many liquid metals near the melting point. Taking account of the temperature dependence of a hard-sphere diameter, Yokoyama⁵⁾ has modified Rosenfeld's formula and successfully explained the temperature dependence of the velocity of sound as well as the self-diffusion coefficient in liquid alkali metals up to quite high temperatures. However, both Rosenfeld and Yokoyama do not take into account effects caused by the electrons.

The purpose of the present paper is to investigate the velocity of sound in the liquid 3d transition metals in terms of the improved Rosenfeld's approach incorporating effects caused by the electrons. No theoretical approaches, to the best of our knowledge, have yet been successful in predicting values of the velocity of sound in the liquid 3d metals. The present work can be interpreted as a refined version of the model theory first developed by Ascarelli. Ascarelli assumed, to a good approximation, the specific heat ratio $C_p/C_v = 1.15$ for all liquid metals in his model theory, but we did not use this assumption in our formalism.

2. Model Theory

The Helmholtz free energy of a liquid transition metal is assumed to be written as^{6,7)}

$$F = F_R + U_g(V, T), \quad (1)$$

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 volume V and 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 Shimoji⁸⁾

$$\begin{aligned} F_R &= F_H \\ &= Nk_B T [-\ln \Lambda^3 - \ln(1/n) + (3 - 2\xi)/(1 - \xi)^2 - 4]. \end{aligned} \quad (2)$$

Here F_H denotes the Helmholtz free energy of a hard-sphere liquid, and Λ is the thermal de Broglie wavelength, n is number density of ions, k_B is the Boltzmann constant and ξ is the packing fraction. We used Carnahan-Starling equation of states in eq. (2).⁸⁾ We take the same form as Itami and Shimoji⁶⁾ for the contribution from the non-reference liquid part:

$$\begin{aligned} U_{g,H}(V, T)/N &= u_{eg} - (1.8z^2)/a + B_H/a^6 \\ &\quad - (1/6)\pi^2 k_B^2 T^2 v_a N(E_F) \end{aligned} \quad (3)$$

in Ryd. Here z is the valency, a is the Wigner-Seitz radius given by $a = (3v_a/4\pi)^{1/3}$, $v_a = V/N$ and $N(E_F)$ the density of states per unit volume at the Fermi energy. In eq. (3), the last term arises from thermal excitation of the conduction electron; this is important in the calculation of the entropy of liquid transition metals because of the large values of $N(E_F)$ due to d bands and high melting temperatures. The first term u_{eg} stands for the electron-gas energy derived from kinetic, exchange and correlation energies:^{9,10)}

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

The second term in eq. (3) denotes the electrostatic energy in the point-ion model. The third term represents the contribution from the remaining effects of ionic core due to the s - d hybridization; the coefficient B_H can be determined by the zero-pressure condition near the melting point

$$p = -(\partial F/\partial V)_T = 0. \quad (5)$$

The explicit expression for B_H is given as follows:

$$\begin{aligned} B_H &= (a(T_m)^7/6)[0.031z/a(T_m) \\ &\quad + (0.916z^{4/3} + 1.8z^2)/a(T_m)^2 - 4.42z^{5/3}/a(T_m)^3 \\ &\quad - ((1 + \xi_m + \xi_m^2 - \xi_m^3)/(1 - \xi_m)^3) \times (3k_B T_m/a(T_m))], \end{aligned} \quad (6)$$

where T_m denotes the melting temperature and $a(T_m) = (3/(4\pi n_m))^{1/3}$ with n_m being the number density of ions at the melting point. In the derivation of eq. (6), we used the rectangular model of the density of states for evaluation of the last term of eq. (3) (for details, see Refs. 6), 7)). Then, the pressure is expressed as

$$pV/(Nk_B T) = -(a/3k_B T)[0.031z/a + (0.916z^{4/3} + 1.8z^2)/a^2 - 4.42z^{5/3}/a^3 - 6B_H/a^7] + (1 + \xi + \xi^2 - \xi^3)/(1 - \xi)^3, \quad (7)$$

where B_H is treated as a constant which is independent of the temperature and density. From eq. (7), assuming $(\partial\sigma/\partial n)_T = 0$ with σ being a hard-sphere diameter, the density derivative of the pressure at constant temperature is given as

$$\begin{aligned} (\partial p/\partial n)_T/k_B T &= (1/k_B T)[-0.031z/3 - 4(0.916z^{4/3} + 1.8z^2)/(9a) \\ &\quad + (22.1z^{5/3})/(9a^2) + 6B_H/a^6] + p(\xi) + \xi p'(\xi), \end{aligned} \quad (8)$$

where $p(\xi) \equiv (1 + \xi + \xi^2 - \xi^3)/(1 - \xi)^3$ and $p'(\xi) \equiv dp(\xi)/d\xi = 2(2 + 2\xi - \xi^2)/(1 - \xi)^4$. The temperature derivative of the pressure at constant volume is simply given by

$$(\partial p/\partial T)_V/nk_B = p(\xi) + 3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V. \quad (9)$$

The velocity of sound, c , on the other hand, is defined by

$$\begin{aligned} Mc^2 &= (\partial p/\partial n)_S \\ &= (\partial p/\partial n)_T + T[(\partial p/\partial T)_V]^2/(n^2 C_V/N), \end{aligned} \quad (10)$$

where M is the atomic mass and S is the entropy. C_V denotes the heat capacity at constant volume which is purely kinetic, $C_V = (3/2)Nk_B$ for a classical system of hard spheres. Therefore, substituting eqs. (8) and (9) into eq. (10), we obtain

$$\begin{aligned} c^2/(k_B T/M) &= (1/k_B T)[-0.031z/3 - 4(0.916z^{4/3} + 1.8z^2)/(9a) \\ &\quad + (22.1z^{5/3})/(9a^2) + 6B_H/a^6] \\ &\quad + [p(\xi) + \xi p'(\xi) + (2/3)\{p(\xi) \\ &\quad + 3\xi p'(\xi)(\partial \ln \sigma/\partial \ln T)_V\}^2], \end{aligned} \quad (11)$$

where the formula for $(\partial \ln \sigma/\partial \ln T)_V$ is given in Ref. 5).

3. Results

Before presenting numerical results, the problem regarding the valency of the transition metals must be mentioned. In this work, we employ the effective valence determined from the one-component plasma (OCP) model (for details, see Refs. 6), 7), 12) and references therein). The OCP is characterized by an ion-sphere radius $a = (3/(4\pi n))^{1/3}$ and a plasma parameter $\Gamma = (ze)^2/(ak_B T)$, where z is the valence and e is the electronic charge. The effective valence, z_Γ , is determined from $\Gamma = 110$, with which the OCP structure factors can well reproduce the experimental structure factors (see Table 1 and Fig. 1 of Ref. 12)). The values of z_Γ determined from Γ are evidently larger than unity, which could be due to some effect of the s - d hybridization.

Using eq. (11) we can now calculate the velocity of sound in the liquid 3d transition metals. The results are summarized in Table 1, together with input data and experimental data available. As seen from the table, our theoretical results

Table 1 Comparison of the velocity of sound in the liquid 3d transition metals near the melting point. z_Γ is the effective valence calculated from the plasma parameter $\Gamma = 110$.¹²⁾ $\rho^{16)}$ has been taken equal to ρ_m (mass density at the melting point) for all metals. Experimental values of the velocity of sound for Fe, Co and Ni are taken from TABLE 4.7 of Ref. 2). According to Ashcroft and Mermin,¹⁷⁾ the melting temperatures T_m of Ti, V and Cr are 1933 K, 2163 K and 2130 K, respectively. These values are different from those given in TABLE 1.1 of Ref. 18) but seem to be reasonable in the light of the temperatures given in this table.

	T (K)	ρ (10^3 kg m^{-3})	ξ	z_Γ	$(\partial \ln \sigma/\partial \ln T)_V$	$c/(k_B T/M)^{1/2}$	c_{calc} (m/s)	c_{expt} (m/s)	$c_{\text{calc}}/c_{\text{expt}}$
Ti	1973	4.15	0.463	1.47	-0.064	8.48	4960 (4282)	5230*	0.95 (0.82)
V	2173	5.36	0.463	1.49	-0.064	8.33	4959 (4358)	5150*	0.96 (0.85)
Cr	2173	6.27	0.463	1.46	-0.064	8.25	4864 (4313)	4520*	1.08 (0.95)
Mn	1533	5.97	0.463	1.25	-0.064	8.40	4044 (3524)	3710*	1.09 (0.95)
Fe	1833	7.01	0.463	1.33	-0.064	8.25	4307 (3822)	4375 3958	0.98 1.09 (0.87)
Co	1823	7.70	0.463	1.32	-0.064	8.23	4172 (3711)	4060 4002	1.03 1.04 (0.93)
Ni	1773	7.72	0.463	1.30	-0.064	8.23	4122 (3667)	4029 4020	1.02 1.03 (0.91)

*Estimated values taken from Ref. 3). The values calculated by the hard-sphere term only are in parentheses.

Fig. 1 Comparison between theory and experiment for the velocity of sound in the liquid 3d transition metals near the melting point. The values of z_F are determined from $\Gamma = 110$ for all metals. The solid line denotes the 45° axis.

agree reasonably well with the liquid transition metals data. Comparison of the calculated with the experimental values is graphically made in Fig. 1 for demonstrative purposes.

4. Discussion

In the last few years there has been considerable progress in understanding of the structural, thermodynamic, transport and surface properties of liquid metals using a hard-sphere model.^{5,13–15} The present calculations appear to confirm the usefulness of this hard-sphere approach developed so far. From the table, the calculated values of the velocity of sound are in good agreement with the experimental values within 5–6%, except for Cr and Mn. We quoted the genuine hard-sphere values in parentheses so as to show the degree of progress we have made by including the effects of the electrons. Clearly, the role of the electrons gives

beneficial increases in the velocity of sound through the structure-independent term.

5. Conclusion

For the first time we have shown that a hard-sphere model immersed in the uniform background potential is capable of describing the velocity of sound in the liquid 3d transition metals near the melting point. The effects caused by the electrons are relatively small, but yield predictions in better agreement with the experimental data.

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