

## Velocity of Sound and Compressibility in Liquid Metals\*†

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A model of hard spheres immersed in a uniform background potential, which has been successfully applied to the calculation of atomic self-diffusion in liquid metals, is shown to give a quantitative description of the velocity of sound, the compressibility, and their temperature dependences in liquid metals of widely different masses, valences, densities, and melting points.

### INTRODUCTION

Recently the pseudopotential method has been suggested to describe metals, but the actual calculation of properties depending on rearrangement of the atoms—the atomic properties—has not been so far very successful.<sup>1,2</sup> The difficulty is mainly due to the critical dependence of the atomic properties on the detailed behavior of the “screening,” which awaits a better understanding of exchange and correlation among valence electrons at electron densities found in normal metals.<sup>3,4</sup>

However the pseudopotential formulation is consistent with a pair-wise interaction as a valid representation of the interaction energy between electronically screened ions. The justification for this concept may be found in a perturbation expansion of a total energy of a metal, which to the second order can be written as the sum of two terms, one *independent* and one *dependent* on the distance between ions.<sup>5</sup>

Lacking at the moment, for the above reasons and because of the additional difficulty of treating the liquid structure itself, an accurate calculation of the compressibility and velocity of sound in liquid metals, we describe here a simple approach based on a model, which although semiphenomenological in character has yet provided a successful quantitative description of atomic self-diffusion.<sup>6</sup>

### THE MODEL

The structures of all simple liquids, metallic and nonmetallic, are very similar near their melting points. This shows that the atomic distribution in the liquid is rather insensitive to the details of the potential,<sup>7</sup> to the extent that with a good approximation it can be understood as a result of packing of hard spheres.<sup>8</sup> Recent molecular-dynamics calculations have further substantiated the preceding observation.<sup>7</sup> This suggests also that the structure of liquid metals is largely determined by the short-range repulsive forces.

We accordingly describe the basic entities composing a liquid metal system to be hard-sphere-like; we imagine them, apart from some subtleties, as the Ziman neutral pseudo-atoms,<sup>2,9</sup> and we think of them as essentially free particles immersed in a uniform (without gradients) potential which will provide the cohesion that the hard-sphere gas otherwise lacks.

This picture is supported by the well-known form of writing the total binding energy  $E$  (per atom) of a metal,<sup>5</sup> which when calculated to the second order in a perturbation scheme can be con-

veniently separated into two terms

$$NE = NE_0 + \frac{1}{2} \sum_{i,j(i \neq j)} V(r_{ij}) \quad (1)$$

where  $E_0$  is a quantity dependent on the volume of the system but independent of the positions of the ions,  $V(r)$  is an effective pair interaction energy, and  $N$  is the number of the atoms in the system. The effective pair interaction  $V(r)$  results from the sum of a direct Coulomb interaction between the ions and an indirect pair interaction through the electrons, the so-called band structure energy. Although the general form of  $V(r)$  has been shown to be characterized by a very strong repulsion of very short range and by a much weaker and much longer-ranged component at large  $r$ , its detailed behavior has not yet been established reliably, because of the difficulty of evaluating bare ion potentials and an accurate form of the “screening.”<sup>3,4</sup> It should be remembered, of course, that because of the free-electron-like nature of liquid metals, the contribution to the energy from the atom-position-dependent terms is very small with respect to the large contribution of the volume-dependent terms contained in  $E_0$ , which are primarily responsible for the cohesion. Since the pair interaction terms provide a negligible contribution to the total energy, and having before recognized the prevailing role of the short-range repulsive interatomic forces in determining the structure of a liquid metal, we feel justified in approximating the effective pair interaction  $V(r)$  by a simple hard-sphere potential. This is positive and infinite for distances less than  $2\sigma$  and zero otherwise. We consider  $\sigma$  as an approximate measure of the radius of a pseudo-atom.

We are then assuming that the total binding energy  $E$  of our system is completely determined by  $E_0$ , which will supply the cohesive energy that our hard-sphere fluid otherwise lacks. Because the term  $E_0$  is not dependent on the ion separation, it leads to no forces on any particle; thus, while supplying the cohesion to the hard-sphere system, it does not change the equilibrium configurations of the particles. These are identical to what they would be in a fluid of hard spheres at the same density but without the  $E_0$  energy term.

We 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 interaction of the valence electrons with the ion, and the energy of interaction of the valence electrons with themselves.  $B$  is a con-

stant to be defined later and  $V$  is the atomic volume of the system. This simplified form for the binding energy can be understood on the basis of the Wigner and Seitz (WS) calculation<sup>10</sup> as extended to polyvalent metals.<sup>11</sup> The WS method, which approximates the atomic cell with a sphere of equal volume, seems in fact even more suitable for the description of liquid metals,<sup>2</sup> which have average spherical symmetry, than to solid metals. Here we make two additional approximations: (a) the ions are considered as point ions. This approximation follows from the observation that the volume of the WS sphere is large with respect to the ionic core volume, this being even more so at liquid densities. Accordingly we may neglect the positive repulsive term contained in the energy of the lowest state of the valence electrons; (b) the correlation energy per atom of a free-electron gas is approximated by the well-known semiempirical formula<sup>11</sup>  $(0.284Z^{4/3}e^2/V^{1/3})^{1/2}(\frac{4}{3}\pi)^{1/3}$ . Here  $Z$  is the number of valence electrons per atom and  $e$  is the electronic charge.

This form of the correlation energy is as accurate as the several existing formulas, which on account of the difficulty of the calculation for electron densities as found in metals, have been derived by interpolation.

With these assumptions, all contributions to the binding energy (i. e., Coulomb, exchange, correlation, and the energy of the lowest state of the valence electrons), except the Fermi energy, show a negative  $\frac{1}{3}$  power in the volume dependence, and they indeed add to a negative term.

The constant  $B$  could accordingly be estimated; however, for the calculation of the compressibility and velocity of sound in liquid metals, we determine  $B$  by the more accurate procedure of considering the pressure of our 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

$$B = 3A(V_m)^{1/3}KT_m.$$

We then write the energy and pressure of our system as:

$$\frac{NE}{KT} = N\frac{3ZE_F}{5KT} - 3NA\left(\frac{V_m}{V}\right)^{1/3}\frac{KT_m}{KT}, \quad (2)$$

$$\frac{PV}{NKT} = \frac{2ZE_F}{5KT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{KT_m}{KT} + \frac{P_hV}{NKT}. \quad (3)$$

Here  $N$  is the number of atoms in the system;  
 $K$  is the Boltzman constant;

$T$  is the temperature ( $^{\circ}$ K) and  $T_m$  that at the melting point;

$A$  is an adimensional constant;

$Z$  is the number of valence electrons per atom;

$E$  is the total binding energy per atom;

$E_F$  is the Fermi energy;

$V_m$  is the volume of the system at the melting point;

$V$  is the volume of the system;

$P$  is the pressure;

$P_h$  is the pressure of a hard sphere.

We consider the pressure of the hard sphere to be well described by the Reiss, Frisch, and

Lebowitz formulation,<sup>12</sup> which is known to be quite accurate also at high density, namely,

$$P_hV/NKT = (1 + \eta + \eta^2)/(1 - \eta)^3, \quad (4)$$

where  $\eta$  is the packing fraction defined as  $\eta = \frac{4}{3}\pi\sigma^3 \times N/V$ , where  $\sigma$  is the hard-sphere radius.

It is worthwhile to notice that such a hard-sphere radius is expected to be temperature-dependent. This is not surprising as the hard-sphere radius is essentially some average of the repulsive part of the pair interaction.

We assume that all simple metallic liquids at their melting point shows the same packing fraction  $\eta(T_m) = 0.45$ , since this value has been shown to fit the diffraction data of a number of different liquid metals.<sup>8</sup>

We can derive the temperature dependence of the hard-sphere radius, and then of the packing fraction, by the variation of the total pressure with temperature at constant volume. This has been measured for alkali metals,<sup>13</sup> and recently the range of the data has been extended for sodium.<sup>14</sup>

We here assume that the temperature variation of the hard-sphere radius is the same for all metals; this can be shown to be true to a good approximation for alkali metals, where data at constant volume exist.

By using Eqs. (3) and (4) and considering the volume to remain constant at the value  $V_m$  at normal pressure, we obtain from the data

$$\frac{1 + \eta_V(T) + \eta_V^2(T)}{[1 - \eta_V(T)]^3} = 3.7 + 6.3 \frac{T_m}{T}, \quad (5)$$

where  $T_m$  is the melting temperature at normal pressure in degrees Kelvin, and  $\eta_V$  is the packing fraction at constant volume. The variation of the packing fraction  $\eta_V$  with temperature is plotted in Fig. 1. The packing fraction  $\eta$  at normal pressure is then found by the following simple relation:

$$\eta = \eta_V(T)V_m/V. \quad (6)$$

Assuming  $PV/NKT \sim 0$  under normal conditions at the melting point in Eq. (2) and recalling that  $\eta = 0.45$ , we find

$$A = 10 + \frac{2}{3}ZE_F(T_m)/KT_m. \quad (7)$$

We can then write, after a simple differentiation of the pressure with respect to the volume,

$$\begin{aligned} a(0) &= KT\chi_T\frac{N}{V} \\ &= \left[ \frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{2ZE_F}{3KT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{4KT_m}{3KT} \right]^{-1} \\ S &= \left\{ \frac{1}{M} \frac{C_P}{C_V} KT \left[ \frac{(1+2\eta)^2}{(1-\eta)^4} \right. \right. \\ &\quad \left. \left. + \frac{2ZE_F}{3KT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{4KT_m}{3KT} \right] \right\}^{1/2}, \quad (9) \end{aligned}$$

where  $\chi_T$  is the isothermal compressibility defined by  $\chi_T = -(1/V)(\partial V/\partial P)_T$ ,  $A$  is defined by Eq. (7), and the temperature dependence of the pack-

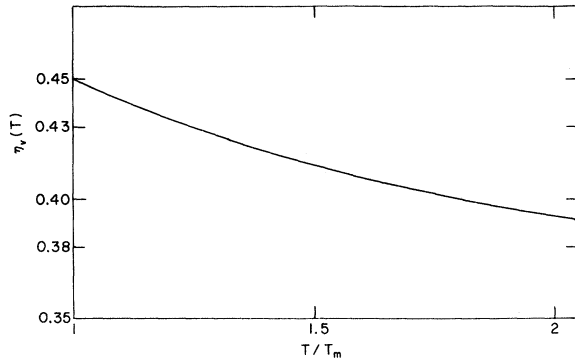


FIG. 1. The temperature dependence of the packing fraction  $\eta_V$  at constant volume as derived by solving Eq. (5) is plotted. The temperature  $T$  is taken in  $^{\circ}\text{K}$ .

ing fraction and then of the hard-sphere radius is determined at each temperature by solving Eqs. (5) and (6). In particular, at the melting point we obtain:

$$a(0) = (27 + \frac{1}{5} \times \frac{2}{3} Z E_F / K T_m)^{-1}, \quad (10)$$

and for the velocity of sound,

$$s_m = \left\{ \frac{1}{M} \frac{C_P}{C_V} K T_m \left[ 27 + \frac{1}{5} \left( \frac{2}{3} \frac{Z E_F}{K T_m} \right) \right] \right\}^{1/2}. \quad (11)$$

In Table I we compare  $s_m$  calculated by Eq. (11) with the experimental values taken from Smith *et al.*<sup>15</sup> for a number of metals, we assume to a

good approximation,<sup>16</sup>  $C_P/C_V = 1.15$  for all metals, the velocity of sound  $S_{BS} = (\frac{2}{3} Z E_F / M)^{1/2}$  calculated by Bohm and Staver<sup>17</sup> is also shown. Their result, although obtained in a more sophisticated way, can be interpreted as deriving only from the compressibility of a free noninteracting electron gas.<sup>18</sup>

The agreement of  $s_m$  from Eq. (11) with experimental data<sup>15,19</sup> seems to be very good; the trend in each valence group is also obtained. The improvement over the BS result is noticeable especially for polyvalent metals.

Discrepancies are found, as expected, for Ag and Cu, where an extra correction to the energy due to overlap of electron shells of neighboring atoms is probably needed; and for the "semimetals" Bi and Sb, which have been found to undergo structural changes in the liquid range.<sup>19</sup> Sb shows also an anomalous temperature dependence of the velocity of sound, which increases above the melting point up to a maximum.<sup>19</sup>

In Fig. 2 the temperature dependences of the velocity of sound for Rb, Zn, In, and Sn are shown as derived by Eq. (10), and experimental values are also indicated.

The agreement is very good considering the simplicity of the model and the sensitivity of temperature coefficient of sound velocity as a probe.

#### CONCLUSION

We have shown that a simple model of hard spheres in a uniform background potential is able to describe successfully the compressibility, the velocity of sound, and their temperature dependences in normal liquid metal of widely different masses, densities, and melting points.

Table I. Comparison of the calculated and measured velocity of sound in liquid metals. The experimental data have been taken by R. T. Smith *et al.*, *Advan. Phys.* **16**, 515 (1967);  $S_m$  is the calculated velocity of sound at the melting point according to the formula

$$S_m = [(K T_m / M) (C_p / C_v) (27 + \frac{1}{5} \times \frac{2}{3} Z E_F / K T_m)]^{1/2}$$

$C_p/C_v$  has been taken equal to 1.15 for all metals,  $N/V$  is the mean atomic density,  $E_F$  the Fermi energy,  $\chi_T$  the isothermal compressibility,  $S_{BS} = (\frac{2}{3} Z E_F / M)^{1/2}$  is the Bohm and Staver result for the velocity of sound [D. Bohm and T. Staver, *Phys. Rev.* **143**, 36 (1966)],  $T_m$  is the melting temperature,  $M$  the atomic mass, and  $Z$  the valence. Velocities of sound are in units of m/sec.

	$T_m$	$M$	$Z$	$\frac{1}{5} \times \frac{2}{3} Z E_F / K T_m$	$S_{BS}$	$S_m$	$S_{exp}$	$S_{exp}/S_m$	$K T_m (N/V) \chi_T$
Na	373	23	1	13.2	2960	2500	2526	1.01	0.025
K	338	39.1	1	9.2	1810	1720	1890	1.1	0.028
Rb	313	85.48	1	8.6	1140	1103	1260	1.12	0.028
Cs	303	132.91	1	8.5	880	890	967	1.02	0.028
Cu	1356	63.54	1	8.2	2580	2700	3460	1.28	0.0285
Ag	1233	107.88	1	6.6	1740	1920	2710	1.4	0.0297
Zn	693	65.6	2	42.5	4180	2610	2712	1.02	0.014
Cd	594	112.41	2	40.5	2850	1840	2166	1.17	0.015
Hg	235	200.61	2	103	2100	1220	1478	1.2	0.008
Al	934	26.97	3	46	8750	4900	4670	0.96	0.014
Ga	303	69.72	3	168	5430	2850	2873	1.01	0.005
In	429	114.82	3	95	3760	2041	2315	1.11	0.008
Tl	575	204.4	3	66	2760	1580	1625	1.03	0.011
Sn	505	118.70	4	128	4630	2440	2464	1.02	0.006
Pb	601	201.21	4	100	3350	1900	1776	0.94	0.008
Sb	903	121.76	5	112	5340	3150	1893	0.6	0.006
Bi	544	209	5	146	3940	2080	1649	0.8	0.007

The consistency of the model with a previous description of the atomic self-diffusion in liquid metals and the possibility of correlating sound velocities with self-diffusion coefficients by the same hard-sphere radius give us some confidence in the basic correctness of the assumptions made. In order to improve the agreement between calculated and measured velocity of sound and then to reach

a detailed microscopic description of this quantity, a better understanding of the interatomic forces and their volume dependence in metals is probably needed.

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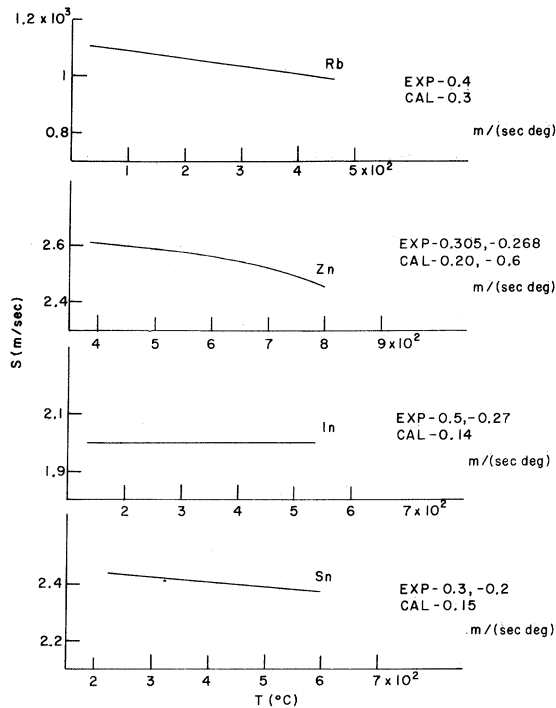


FIG. 2. Temperature dependence of the velocity of sound. The numbers to the right of the figure are the temperature coefficients of the velocities of sound in  $\text{m}/\text{sec deg}$ . The experimental ones indicated are the smallest and largest measured, reported by M. B. Gitis and I. G. Mikhailov (see Ref. 19). The calculated ones, when they are plotted in pairs, are the low-temperature and high-temperature values; this means that the temperature dependence is slightly nonlinear. The abscissas give the temperature in  $^{\circ}\text{C}$ , and the ordinates the velocity in  $\text{m}/\text{sec}$ . The plots begin at the melting points.

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