*Reprinted from*

PHYSICAL REVIEW Volume 173, Number 1 5 September 1968

# Velocity of Sound and Compressibility in Liquid Metals*†

P. Ascarelli

*Brookhaven National Laboratory, Upton, New York and Army Materials and Mechanics Research Center, Watertown, Massachusetts*

( Received 28 December 1967, revised manuscript received 19 April 1968)

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.[1,2] 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.[3,4]

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.[5]

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.[6]

## 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,[7] to the extent that with a good approximation it can be understood as a result of packing of hard spheres.[8] Recent molecular-dynamics calculations have further substantiated the preceding observation.[7] 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,[2,9] 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,[5] which when calculated to the second order in a perturbation scheme can be conveniently separated into two terms

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

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."[3,4] 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[10] as extended to polyvalent metals.[11] 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,[2] which have average spherical symmetry, than to solid metals. Here we make two additonal 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[11] $(0.284Z^{4/3}e^2/V^{1/3})\frac{1}{2}(\frac{4}{3}\pi)^{1/3}$. 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:

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

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

Here $N$ is the number of atoms in the system;

$K$ is the Boltzman constant;

$T$ is the temperature (°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,[12] which is known to be quite accurate also at high density, namely,

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

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.[8]

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,[13] and recently the range of the data has been extended for sodium.[14]

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

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

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:

$$\eta = \eta_V(T)V_m/V. \tag{6}$$

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

$$A = 10 + \tfrac{2}{5}ZE_F(T_m)/KT_m. \tag{7}$$

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

$$a(0) = KT\chi_T\frac{N}{V} = \left[\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{2}{3}\frac{ZE_F}{KT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{4}{3}\frac{KT_m}{KT}\right]^{-1} \tag{8}$$

$$S = \left\{\frac{1}{M}\frac{C_P}{C_V}KT\left[\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{2}{3}\frac{ZE_F}{KT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{4}{3}\frac{KT_m}{KT}\right]\right\}^{1/2}, \tag{9}$$

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-