The structure and effective pair potential of liquid manganese near the melting point

Takashi Arai, Seiichi Naito and Isao Yokoyama

Department of Mathematics and Physics, National Defense Academy, Yokosuka 239, Japan

The simple-metal theory can describe, in some favorable cases, the structures of liquid 3d transition metals when the pseudopotential parameters are chosen appropriately. This is shown, using the Percus–Yevick integral equation, for liquid manganese which has a half-filled d band and is claimed to be difficult to handle theoretically. The Ashcroft empty-core form for the s-electron pseudopotential is employed. The value of core radius is determined from the density of liquid manganese at 1533 K and the effective valence, Z_s, is determined by the value of the plasma parameter with which the liquid structures and thermodynamic properties are well described by the one-component plasma (OCP) model. The validity of the value of Z_s is supported by the Gibbs–Bogoliubov method using the OCP reference system.

1. Introduction

Recently Hausleitner and co-workers [1,2] have presented, quite successful, ab initio calculations of the structures and thermodynamic properties of liquid transition metals, based on effective pair interactions calculated within a hybridized nearly free-electron tight-binding theory and on a thermodynamic variational method with a hard-sphere Yukawa reference system.

Naito et al. [3], on the other hand, have reported that the simple-metal theory with the help of the one-component plasma (OCP) model can achieve, in some favorable cases, a good description of the structures of liquid 3d transition metals when the pseudopotential parameters are chosen appropriately. The aim of this work is to show this description for liquid manganese (with a half-filled d band) which is claimed to be theoretically difficult. We use the Percus–Yevick integral equation, which has been successfully applied to expanded liquid rubidium [4,5], to calcu-

late the liquid structure factor and the pair distribution function. The results are compared with experimental data.

2. Calculation procedure

We have assumed that, as a first approximation to the electronic structure of a transition metal with Z valence electrons per ion, Z_d electrons are incorporated in the non-overlapping ion core, the remaining $Z_s = Z - Z_d$ electrons per ion are in the free-electron-like states, and their coupling is considered to be weak. This idea of the separation between the core and conduction electron states corresponds to the proposal by Wills and Harrison [6], although the contribution by the d-electron is not explicitly taken into account here. Thus the calculation in this work is based on a straightforward application of the simple-metal theory.

We view a liquid metal as a collection of ions with potential energy described by a structure-independent term, $u_0(n)$ and a pairwise interaction, $u(r, n)$: both terms depend in principle on n, the number density of the ions. The interatomic pair potential, $u(r, n)$, using a standard pseudopoten-

Correspondence to: Dr T. Arai, Department of Mathematics and Physics, National Defense Academy, Yokosuka 239, Japan. Tel: +81-468 41 3810. Telefax: +81-468 44 5902.

tial formalism [7,8] can be, in atomic units, written as

$$u(r, n) = \frac{Z_s^2}{r}\left(1 - \frac{2}{\pi}\int_0^\infty \frac{F_N(k, n)}{k}\sin kr \, dk\right),$$
(1)

where Z_s is the effective valence and

$$F_N(k, n) = \left(\frac{k^2 v(k)}{4\pi Z_s}\right)^2\left(1 - \frac{1}{\epsilon(k, n)}\right)$$
(2)

is the normalized energy–wavenumber characteristic. Here $v(k)$ is the local pseudopotential and $\epsilon(k, n)$ is the dielectric screening function which may be written as

$$\epsilon(k, n) = 1 + (4\pi/k^2)\Pi(k, n),$$
(3)

where $\Pi(k, n)$ is the electron-gas polarization function

$$\Pi(k, n) = \frac{(k_F/\pi^2)f(x)}{1 - (4k_F/\pi k^2)G(x)f(x)}.$$
(4)

k_F is the Fermi wavenumber,

$$f(x) = \frac{1}{2} + \frac{x^2 - 1}{4x}\ln\left|\frac{1 - x}{1 + x}\right|, \quad x = k/2k_F,$$
(5)

and $G(x)$ incorporates the effects of exchange and correlation in the electron gas.

In the present work we have used the Ashcroft empty-core form [9],

$$v(k) = -(4\pi Z_s/k^2)\cos kr_c,$$
(6)

for the pseudopotential, where r_c is the core radius, and the Geldart–Vosko expression [10] is used to describe the electron gas.

3. Results

3.1. Effective pair potential

The pair potential $u(r, n)$ is shown in fig. 1 using the values of r_c and Z_s given in table 1. The value of r_c is determined through the relation $k_0 r_c = \pi/2$. Here k_0 denotes the position of the first node of the Ashcroft pseudopotential in
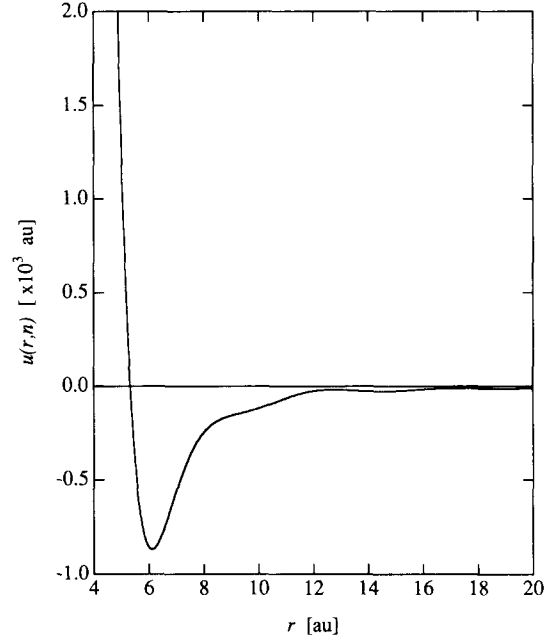

Fig. 1. Effective pair potential for liquid Mn at 1533 K.

k-space and is chosen to get the correct number of degrees of freedom, i.e., $k_0 = (18\pi^2 n)^{1/3}$, in the same way as in the method suggested by Yokoyama [11] for describing the long-wavelength limit of the structure factor of liquid alkali metals. The value of r_c given in table 1 is comparable to those given in table 2 of Hausleitner et al. [2]. On the other hand, the value of Z_s is determined from the plasma parameter $\Gamma = 110$ with which the liquid structures and thermodynamic properties are moderately well described

Table 1
$s(0)$ of liquid Mn at 1533 K

T (K)	ρ (g cm^{-3})	Γ	Z_s	r_c (a.u.)	$S(0)$ eq. (7)	PY [a]	Exp. [b]
		100	1.19		0.023		
Mn 1533	5.97			1.31		0.024	0.024
		110	1.25		0.021		

ρ is the mass density, r_c the core radius, Γ the plasma parameter and $Z_s = \sqrt{\Gamma a k_B T}$ the effective valence with $a = (3/4\pi n)^{1/3}$.
[a] From the Percus–Yevick integral equation.
[b] From Waseda and Ueno [16].

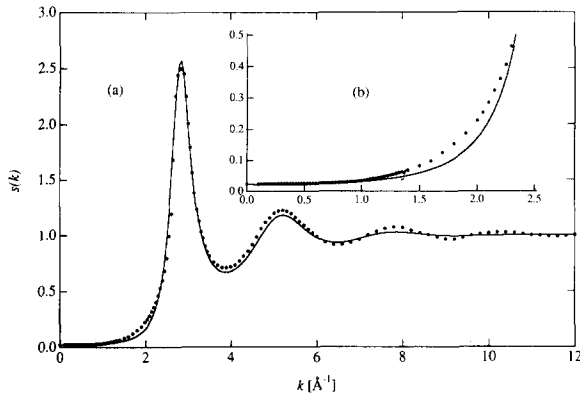Fig. 2. Structure factors for (a) the high-k region and (b) the low-k region: ————, Percus–Yevick integral equation; ●, experimental data [15,16].

by the classical one-component plasma (OCP) model [3,12–14].

The pair potential, $u(r, n)$, is quite different, in the position and depth of the first minimum, from the interatomic potential derived from first principles (see fig. 2 of ref. [1]).

3.2. Structure factor and pair distribution function

The Percus–Yevick integral equation is employed to calculate the liquid structure factor, $s(k)$, and the pair distribution function, $g(r)$, using the pair potential shown in fig. 1. The calculated results are displayed in figs. 2 and 3 and compared with the experimental data [15,16]. As can be seen from these figures, both the
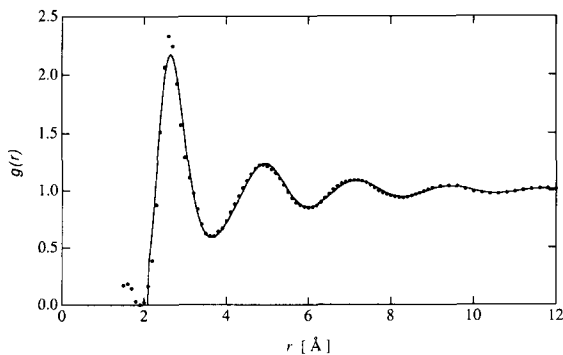

Fig. 3. Pair distribution functions: ————, Percus–Yevick integral equation; ●, experimental data [15].

observed $s(k)$ and the $g(r)$ are rather well described by this pair potential and the quality of description seems to be better than that of ref. [2]. However, the calculated $s(k)$ damps more quickly than the experimental $s(k)$ in the higher-k region and is lower than the experimental $s(k)$ over the k-region between 1 and 2.3 $\overset{\circ}{\text{A}}^{-1}$.

3.3. Long-wavelength limit of structure factor

According to Chaturvedi et al. [17], the long-wavelength limit of the structure factor $s(0)$ for liquid metals can be written as

$$s(0) = \left(k_{DH}^2/k_e^2 + k_{DH}^2/k_i^2 + k_{DH}^2 r_c^2 \right)^{-1}, \quad (7)$$

where

$$k_{DH} = \left(4\pi n Z_s^2/k_B T \right)^{1/2}$$

is the Debye–Hückel inverse screening length and k_i is the 'inverse screening length' of the OCP given by

$$k_{DH}^2/k_i^2 = 1 - 0.398415\Gamma$$
$$+ 0.31122\Gamma^{1/4} - 0.1850. \quad (8)$$

The quantity k_e in eq. (7) is the inverse screening length of the electron gas and is related to $\epsilon(k, n)$ as

$$\lim_{k \to 0} \epsilon(k, n) = 1 + k_e^2/k^2, \quad (9)$$

where

$$k_e^2 = \frac{4\pi k_F^3}{(\pi k_F)^2 - \pi k_F - 0.153} \quad (10)$$

for the Geldart–Vosko [10] expression. In table 1, the calculated values of $s(0)$ are summarized together with the parameters used in this work. The agreement between the calculated and the experimental $s(0)$ is good, although affected by the value of the plasma parameter used.

4. Discussion

The value of Γ used in this work is 110 with which the OCP model can account well for the experimental structure factor, the observed en-

tropy, the isothermal compressibility, the specific heats and the ratio of specific heats of liquid Mn at 1533 K. We wisk to study why this is so using the Gibbs–Bogoliubov variational method with the OCP reference system [7,8]. The Helmholtz free energy of the system can be written as

$$F = F_{id} + u_0(n) - T\,\Delta S_0 + \tfrac{1}{2}nu(0,\,n)$$

$$+ \tfrac{1}{2}\int \frac{dk}{(2\pi)^3} u(k,\,n)\big(s_{OCP}(ka,\,\Gamma) - 1\big),$$

$$(11)$$

where F_{id} is the free energy of an ideal gas, $u_0(n)$ the volume energy, $a = (3/4\pi n)^{1/3}$, and ΔS_0 is the excess entropy:

$$\Delta S_0/k_B = -2.83632\Gamma^{1/4} + 0.89770\Gamma^{-1/4}$$

$$+ 0.80049 \ln \Gamma + 1.78559. \quad (12)$$

$u(k,\,n)$ is the Fourier transform of $u(r,\,n)$, $u(0,\,n)$ is the $k = 0$ limit, and $s_{OCP}(ka,\,\Gamma)$ is the OCP structure factor. The right-hand side of eq. (11) is minimized with respect to Γ. Detailed expressions of the formalism are given in ref. [8]. Here we use the OCP structure factor developed by
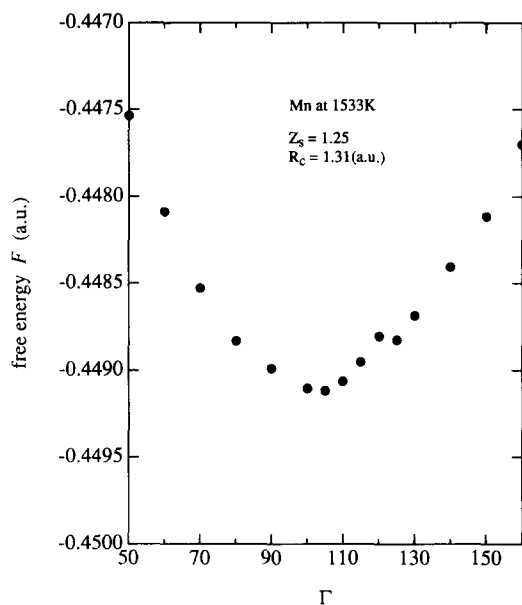
Chaturvedi et al. [18]. In fig. 4, the calculated Helmholtz free energy is plotted against Γ for liquid Mn at 1533 K. As can be seen from the figure, the position of the minimum of the free energy is found around $\Gamma = 105$. However, this value of Γ is close to 110. Thus we can say that the validity of the value of Z_s used in this work is well supported by the thermodynamic variational method based on the OCP reference system.

5. Conclusion

The simple-metal theory can describe the structure of liquid manganese near the melting point when the pseudopotential parameters are chosen appropriately. We showed this using the Percus–Yevick integral equation.

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Fig. 4. Helmholtz free energy (in atomic units) versus plasma parameter, Γ. The position of the minimum of the free energy is found around $\Gamma = 105$.