Thermodynamics and Structure of Simple Liquid Metals Calculated Using an Analytic Pair Potential

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Abstract

The analytic interatomic pair potential for simple metals is derived from first principles using second order pseudopotential theory by Pettifor and Ward . It is developed using the Heine-Abarenkov pseudopotential for simple metals and applied to the calculations of the structural and thermodynamic properties of liquid metals. The corresponding liquid metal structure is calculated using the random phase approximation and the hypernetted-chain formulation. The long-wavelength limit $S(0)$ of the structure factor of liquid metals using the hard-sphere system as reference is also investigated. The calculated thermodynamic and structural properties using the real space formalism are in better agreement with experimental results than the results of earlier calculations using the same approach.

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1. Introduction

Second order pseudopotential theory provides a convenient framework to calculate interatomic pair potential. But the method has the well known disadvantage of being slowly convergent due to a logaritmic singularity in the Linhard response function. Pettifor and Ward (PW) [1] derived an analytic expression for the interatomic pair potential by replacing the Linhard function with a rational polynomial. This led to an analytic expression for the pair potential in the form of a three exponentially damped oscillatory terms. This form proved successful in explaining the structural phase transitions of crystalline Na, Mg and Al under pressure.

Khajil and Tomak (KT)[2-3] have recently used this formalism to study the thermodynamic properties of liquid simple metals with reasonable success. KT employed the simplest Ashcroft empty core (EC) pseudopotential and the hard sphere description of the liquid metal structure. It is of considerable interest therefore to determine the effects of using better electron-ion pseudopotentials and a better description of the structure on the thermodynamic properties of liquid metals, in a systematic manner.

In this work, we show a better agreement with experimental results by the use of the Heine-Abarenkov pseudopotential (LHA) and random phase approximation (RPA) of the structure [4]. We are also concerned with an investigation of the long-wavelength (LW) limit S(0) of the structure factor. In order to investigate the effect of the electron-ion interaction, we compare the results obtained using LHA to the EC model potential and experiments. We show that the analytic expression of the RPA structure factor in the limit $q \rightarrow 0$ which is derived from the analytic pair potential gives better results than the previous calculations in the same approach.

The layout of the present paper is as follows: In section II we summarize the analytical approach for the pair potential. In section III we give a brief review of the theory of RPA in the liquid structure. It is applied to the LW limit of the structure factor of liquid metals using the hard-sphere (HS) reference system. The real space formalism of the thermodynamic properties is given in section IV. The results and discussion are given in section V.

2. Pair Potentials

The pair potential is the interaction between an ion and a second ion and its screening cloud of electrons in a metallic liquid environment. It is given by

$$\Phi(R; r_s) = \frac{2Z^2}{R} \left[1 - \frac{2}{\pi} \int_0^\infty M^2(q) \frac{\varepsilon(q, r_s) - 1}{\varepsilon(q, r_s)} \frac{\sin(qR)}{q} dq \right], \tag{1}$$

where Z is the valence and $M(q)$ is a normalized bare electron-ion interaction given by

$$V_b(q) = \frac{8\pi Z}{\Omega_0 q} M(q), \tag{2}$$

with the atomic volume Ω_0 which is related to the electron-density parameters r_s by $\Omega_0 = Z(4\pi/3)r_s^3$ and

$$M(q) = (1 - A)\cos qR_M + \frac{A}{qR_M}\sin qR_M, \tag{3}$$

for the LHA pseudopotential. $\varepsilon(q, r_s)$ is the dielectric function. PW fit the actual dielectric function by the analytic form,

$$\varepsilon^{-1}(q) = \sum_{n=1}^{6} \frac{D_n q^2}{q^2 - q_n^2}, \tag{4}$$

and thus obtain an analytic pair potential

$$\Phi(R, r_s) = \frac{2Z^2}{R} \sum_{n=1}^{3} A_n \cos(k_n R + \alpha_n) \exp(-\kappa_n R), \tag{5}$$

where the amplitude A_n is given by

$$A_n = 2d|M(q_n)|^2, \tag{6}$$

and the phase α_n is given by

$$\alpha_n = \delta_n + 2arg\left[M(q_n)\right]. \tag{7}$$

The relation between these parameters and the weights D_n and poles q_n are as follows:

$$D_n = d_n \exp(i\delta_n) \tag{8}$$
$$q_n = k_n + i\kappa_n \tag{9}$$

It is important to note that D_n and q_n depend only on the density of the free electron gas and not upon the particular atom or pseudopotential being used. A_n and α_n, on the other hand, depend on the choice of pseudopotential as well as the density of the free electron gas appropriate for the liquid metal under consideration.

3. The Structure

We need the pair correlation function g(R) to calculate the thermodynamic properties of liquid metals. For this, we follow the simplest route from the pair potential $\Phi(R)$ to $g(R)$. The direct correlation function is decomposed as

$$c(R) = c_0(R) + c_1(R), \tag{10}$$

where $c_0(R)$ is determined by the repulsive forces alone. The use of Weeks-Chandler and Anderson (WCA) expansion [5-7],

$$\Phi(R) = \Phi_0(R) + \Phi_1(R), \tag{11}$$

along with $g_0(R) = y_\alpha(R) \exp[\beta\Phi_0(R)]$ the Ornstein-Zernike (OZ) equation and subtraction of the repulsive couplings yield a residual OZ-equation.

$$h_1(q) = \frac{S_\sigma^2(q)c_1(q)}{1 - \rho_0 c_1(q)S_\sigma(q)} \tag{12}$$

The simplest possible choice for a closure relation needed for the residual OZ-equation is

$$c_1(R) = -\beta\Phi_1(R), \tag{13}$$

which is known as the random phase approximation (RPA).

The $\Phi_0(R)$ part may be replaced by Percus-Yevick (PY) hard-sphere model. Several different forms for the tail of effective potential $\Phi_1(R)$ is used to find anaytical expressions for the structure factor S(q). Here we will use the potential which is calculated by using the LHA and EC electron-ion pseudopotentials.

The resulting structure factor has the form,

$$S(q) = [1 - \rho_0\,(c_{HS}(q) + c_1(q))]^{-1} \tag{14}$$

where $\rho_0 = \frac{N}{\Omega_0}$ is the number density and $c_{HS}(q)$ is the PY-HS direct correlation function, which is calculated by using the effective HS diameter σ_{WCA}. Within the WCA method, one may take [8],

$$\Phi(\sigma_{WCA} - \Phi_1(R_0) \cong k_B T. \tag{15}$$

The LW limit of the structure factor $S(q)$ is given by [9],

$$S_{RPA}^{-1}(0) = S_{HS}^{-1} + \rho_0\Phi_1(0)/k_B T, \tag{16}$$

where $\Phi_1(0) = \int_0^\infty \Phi_1(R)4\pi R^2 dR$ is the limit of the tail part of the pair potential. We also calculate the HNC structure factors using Zerah's method [10].

4. The Thermodynamic Quantities

The total energy of the liquid metal can now be calculated using completely analytic expression in real space. The total energy per ion U is given by,

$$U = \frac{3}{2}k_B T + u(n_0) + 2\pi\rho_0 \int_0^\infty R^2\Phi(R; n_0)g(R)dR, \tag{17}$$

where $n_0 = NZ/\Omega_0$ is the average conduction electron density. $u(n_0)$ is given by

$$u(n_0) = u_{egas} + \frac{1}{2}\Phi(R = 0; n_0), \tag{18}$$

where the electron-gas term in the second-order approximation is

$$\frac{u_{egas}}{Z} = \frac{0.982}{r_s^2} - \frac{0.712}{r_s} - (0.110 - 0.031\ln r_s). \tag{19}$$

The pressure is the volume derivative of the free energy and is given by,

$$
\begin{aligned}
P & = \rho_0 k_B T + \rho_0 n_0 \frac{du(n_0)}{dn_0} - \frac{2}{3}\pi\rho_0^2 \int_0^\infty dR R^3 \frac{\partial\phi(R;n_0)}{\partial R} g(R) \\
& + 2\pi\rho_0^2 \int_0^\infty dR R^2 n_0 \frac{\partial\phi(R;n_0)}{\partial R} g(R).
\end{aligned}
\tag{20}
$$

The bulk modulus is defined by

$$
\begin{aligned}
B & = -\Omega_0 \left(\frac{\partial P}{\partial\Omega_0}\right)_T \\
& = \rho_0 k_B T - \frac{4}{9}\pi\rho_0^2 \int_0^\infty R^3 g(R)\frac{\partial\Phi}{\partial R}dR + \frac{2}{9}\pi\rho_0^2 \int_0^\infty R^4 g(R)\frac{\partial^2\Phi}{\partial R^2}dR
\end{aligned}
\tag{21}
$$

in the long wavelength limit.

The advantage of this real space formalism is that the total energy is a sum of only two terms one of which contains all the structure dependent contribution. The main contribution to total energy comes from the $\Phi_{bs}(R=0)$ term

5. Results and Conclusion

The input parameters used in our calculations are given in Table 1. All the reported r_s and r_c values are taken from Ref.[9]. r_c=1.12 a.u. for Al is taken from Ref.[11]. LHA model potential radius R_M in our calculations are from Ref.[12] except Al. R_M and A values for Al are calculated by using the first zero $V_b(q_0) = 0$ of the LHA model potential as given in Ref.[13]. The remaining values of A are determined by fitting the first zero q_0 and $V_b^{\max}(q)$ to the values given [13]. The values of q_0 used in this work are also listed in Table 1.

Table 1. Input Parameters

Metals	Li	Na	K	Rb	Cs	Al
T($^\circ$K)	453.	371.	337.	312.	302.	933.
r_s(a.u.)	3.309	4.048	5.026	5.372	5.792	2.163
r_c(a.u.)	1.28	1.70	2.25	2.45	2.67	1.12
A	1.183	1.119	1.060	1.062	1.025	1.245
R_M(a.u.)	2.80	3.40	4.20	4.60	4.80	2.80
q_0(a.u.)	1.31	1.03	0.79	0.72	0.66	1.35

The resulting pair potentials using LHA model potential for Li, Na, K, Rb, Cs are shown in Figure 1, as illustrative cases. All the calculated pair potential parameters are given in Table 2.

In Figure 2, the Al pair potential using LHA is plotted together with EC model potential result.

Table 2. Calculated Pair Potential Parameters

Metals	n	$k_n/2k_f$	$\kappa_n/2k_f$	A_n	α_n/π
Li	1	0.264	0.869	1.978	-0.282
	2	0.688	0.656	1.705	-0.752
	3	0.958	0.274	0.015	-0.791
Na	1	0.292	0.899	2.230	-0.336
	2	0.717	0.639	0.684	-0.813
	3	0.958	0.271	0.014	-0.874
K	1	0.317	0.929	2.499	-0.394
	2	0.753	0.626	0.666	-0.885
	3	0.959	0.267	0.015	-0.969
Rb	1	0.325	0.937	2.619	-0.412
	2	0.765	0.623	0.675	-0.914
	3	0.959	0.265	0.016	0.982
Cs	1	0.332	0.947	2.626	-0.427
	2	0.777	0.618	0.650	-0.922
	3	0.959	0.263	0.016	0.986
Al	1	0.171	0.800	5.036	-0.215
	2	0.648	0.694	2.832	-1.187
	3	0.958	0.279	0.021	0.200
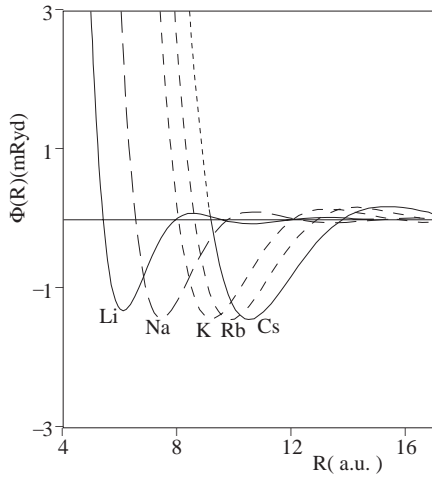
Figure 1. The pair potentials for Li, Na, K, Rb, Cs
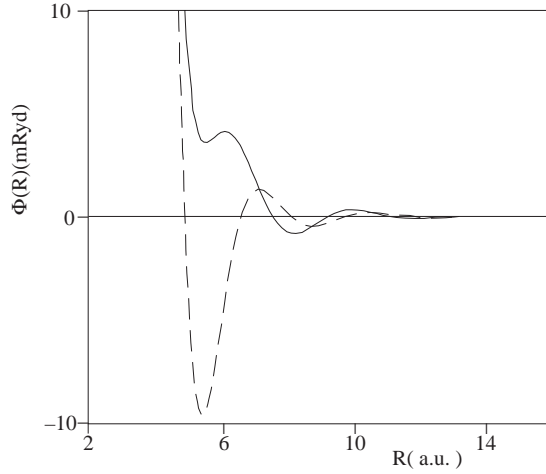
Figure 2. Calculated pair potentials for Al. The EC and LHA model potentials are denoted by the full and dashed curves, respecively

The calculated RPA structure factor for Na is shown in Figure 3, again as an illustrative case. The results, obtained by using the EC pseudopotentials are given for the purposes of comparison. The experimental values given in this figure are taken from Waseda [14]. It is easily seen that the LHA results is superior.

Table 3 shows our results for $S(0)$ using LHA model potential in RPA. The calculated $S_{RPA}(0)$ results by using EC model are not good. For example, the WCA effective HS diameter $\sigma_{Al} = 5.169$ a.u. and the corresponding packing fraction $\eta_{Al} = 0.57$ comes out to be unacceptably large. The effect of the electron-ion interection is apparent in these results. We note that better agreement with experiment can be obtained by LHA model potential. The experimental $S(0)$ values in Table 3 are taken from [9].

Table 3. Calculated S(0) values for simple metals using LHA model potential

Metals	σ(a.u.)	η	$S_{HS}(0)$	$S_{RPA}(0)$	$S_{exp}(0)$
Li	5.112	0.461	0.0229	0.0269	0.0260
Na	6.299	0.471	0.0200	0.0236	0.0240
K	7.814	0.469	0.0210	0.0249	0.0240
Rb	8.413	0.480	0.0190	0.0216	0.0220
Cs	8.987	0.467	0.0160	0.0166	0.0170

The calculated RPA and HNC structure factors $S(q)$ are shown in figure 4 for Al using LHA model potential. The experimental $S(q)$ also is shown in the same figure. The problem with HNC is the unacceptable $S(q)$ values for small q.
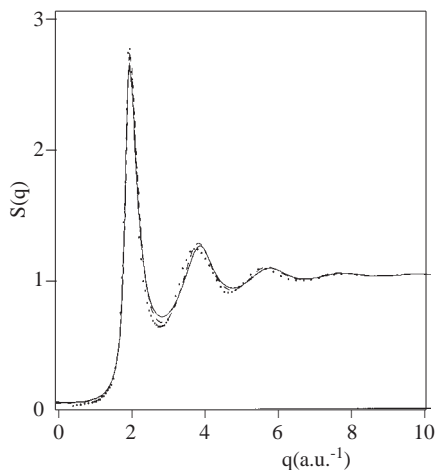

Figure 3. The calculated RPA and HNC structure factors for Na at 371K.: full curve (HNC-EC) , dashed curve (HNC-LHA) and dotted curve (experiment).
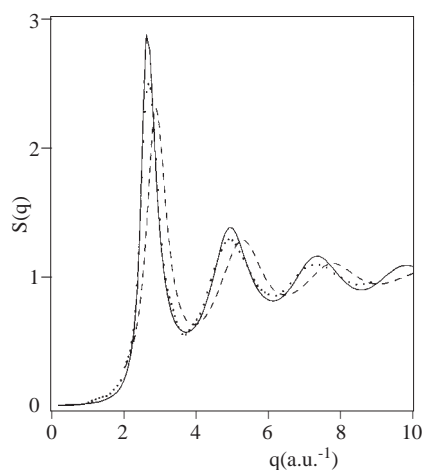
Figure 4. The structure factors calculated using LHA model potential for liquid Al: full curve (RPA-LHA), dashed curve (HNC-LHA) and dotted curve (experiment).1

The calculated pressure P and bulk modulus B values along with the experimental B are given in Table 4 at the melting temparature of liquid metals. Also given in Table 4 are the calculated P and B values using the EC model potential with the parameters given in [3]. The theoretical results which are calculated by other workers are listed in the same table. Comparision shows that LHA pseudopotential results in improved thermodynamic values.

These calculations are repeated for HS model to check the effectiveness of RPA. We find considerable improvement over the HS values especially for B if RPA description is used. Although there is certainly some room for improvement over the RPA description, we find the LHA pseudopotential to be the best among the model pseudopotentials.

Table 4. Calculated Energy U(Ryd), Pressure $P(10^{10} \text{ dyn/cm}^2)$ and Bulk Modulus $B(10^{10} \text{ dyn/}cm^2)$ values

Metals	Li	Na	K	Rb	Cs	Al
$-U^a$	0.581	0.474	0.387	0.366	0.342	6.843
$-U^b_{exp.}$	0.518	0.464	0.388	0.372	0.347	4.176
$-P^a$	4.384	2.181	1.043	0.844	0.646	59.036
B^a	11.179	4.840	1.998	1.583	1.042	90.899
$B^b_{exp.}$	11.500	5.380	2.600	2.000	1.400	41.322
$-P^c$	15.301	2.695	2.402	1.573	1.437	61.143
B^c	31.897	9.217	5.098	2.719	2.749	151.587
$-U^d$	0.552	0.473	0.393	0.362	0.390	4.312
$-P^d$	1.660	1.340	1.050	0.640	0.890	26.300
B^d	-	9.740	2.930	-	-	-
B^e	7.850	5.870	2.490	1.560	1.630	56.200

a These values are calculated using LHA model potential.
b Reference 15.
c These values are calculated using EC model potential, reference 3.
d Reference 16.
e Reference 17.

References

[1] G. Pettifor and M.A.Ward, *Solid State Commun.,* **49** (1984) 291.

[2] T. M. A. Khajil and M. Tomak, *Phys. Rev.,* **A38** (1988) 5437.

[3] T. M. A.Khajil and M.Tomak, *Il Nuovo Cimento.,* **D13,** N5 (1991) 597.

[4] J. Hafner, From Hamiltonians to Phase Diagrams Springer-Verlag, Berlin, 1987

[5] J. D. Weeks, D. Chandler, *Phys. Rev. Lett.,* **25** (1970) 149.

[6] J. D. Weeks, D. Chandler, and H.C.Anderson, *J. Chem.Phys.,* **54** (1971) 5237.

[7] J. D. Weeks, D. Chandler, and H.C.Anderson, *J.Chem.Phys.,* **55** (1971) 5422.

[8] A. Meyer, M.Silbert and W.H. Young, *Chem. Phys.,* **49** (1980) 147.

[9] R. Evans and W. Schirmacher, *J. Phys. C.,* **11,** (1978) 2437.

[10] G. Zerah, *J. Comput. Phys.,* **61** (1985) 280.

[11] J.Chihara and S. Kambayashi, *J. Phys.: Condens. Matter* **6** (1994) 10221.

[12] A. E. O. Animalu and V. Heine, *Phil. Mag.,* **12** (1965) 1249.

[13] M.L. Cohen and V. Heine, *Solid State Phys.,* **24** (1970) 37.

[14] Y. Waseda, The Structure of Non-Crystalline Materials (New York, Mc Graw-Hill, 1980).

[15] M. Smihoji, Liquid Metals, (Academic Press, New York ,1970).

[16] R.Kumaravadivel, *J. Phys.,* **F13** (1983) 1607.

[17] M. Hassegawa and M. Watabe, *J. Phys. Soc. Japan* **32** (1972) 14.