Static Properties of Liquid Cu and Zn

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Abstract

Positional aspects of ions are revealed from static properties. The effective interionic interaction is a significant factor for theoretically studying of it. A model pseudopotential is used for such type of calculation which combines the sp- and d-band contributions to deduce the effective interionic interactions. The liquid structure is calculated using the linearised Weeks-Chandler-Andersen (LWCA) thermodynamic perturbation theory of liquids. Calculated results of the static structure factors, S(q) and the corresponding pair correlation function, g(r) that attained by Fourier transform of the former, for liquid Cu and Zn are presented in this article. The theoretical results of S(q) and g(r) concur well with the experimental X-ray diffraction data.

1. Introduction

The elements in the 3d transition metals series namely the Cu and Zn have completely filled d- bands along with filled s-bands except Cu following the Ar-based electronic structure. Their physical properties are greatly influenced by the strong d-band scattering or via sd transition or sd hybridization. For this basic reason, these elements are known as transition metals. They are also known as polyvalent liquid metals. A complete description of these elemental systems entails a model to tackle into account both sp-and d-band effects in the interionic interactions. Liquid state structures of the above transition metals using a simple effective pair interaction in concurrence with the linearised Weeks-Chandler-Andersen (LWCA) thermodynamic perturbation theory of liquids[1,2] has been presented.

A model pseudopotential was proposed by Bretonnet and Silbert (BS) [3] to describe effective interionic interactions, primarily, for liquid transition metals. This model treats orbital sp- and d-bands separately within the presumed effective pair potential formalism. The sp-band is articulated via the empty core model; the d-band contribution is resulting from the d-band scattering phase shift by using the inverse scattering approach within the core region. The resultant model pseudopotential thus takes a simple local form which is easy to handle computationally. Moreover, the local form allows one to develop this model to other liquid metals for which the effects of sd hybridization are significant. Some previous works in concurrence with the thermodynamically self-consistent VMHNC integral equation theory by Bhuiyan et al. [4] encouraged me to investigate of static structures of liquid Cu and Zn by LWCA liquid state theory for which experimental S(q) data are available in ref. [5]. The problem was tackled by VMHNC theory, but the present attempt is solely confined on treating it by hard sphere (HS) theory. The interionic positional features at liquid state has been depicted via the liquid structures which ascribes the detailed configurations and correlations of respective ions and S(q)~1

indicates un-correlation among the experimental X-ray diffraction data.

Regarding of liquid static aspects i.e. static structure factor, S(q), or its Fourier transform, g(r), is the essential requirement in the formulations of liquid metals for a complete depiction of static or dynamic structure, thermodynamic and transport properties. This article comprises hard sphere (HS) diameters, packing densities, static structure factors and their inversion functions that are inspected both at melting and at the vicinity of slightly above melting temperatures. A thermodynamic perturbative LWCA [1, 2] liquid state theory is used to calculate the hard sphere diameters and other related parameters and one component structural formula is used to calculate the structures of the liquid metals.

The plan of this article is as follows: in sections to come the underlying formalisms are briefly articulated, and mechanisms of parameterization are presented followed by several concluding remarks with ending citations.

2. Theories

A. Effective pair potentials

The effective pairwise model potential uses the sp- and d-band contributions presumed from an inverse scattering method within the core region. The bare position dependent effective potential can be constructed by the superposition of the sp- and d-band contributions for metallic system which might be applied to liquid transition metals as:

$$W(r) = \begin{cases} \sum_{m=1}^{2} B_m \exp(\dfrac{-r}{ma}) & for \quad r < R_C \\ -\dfrac{Ze^2}{r} & for \quad r > R_C \end{cases} \quad (1)$$

The potential portrayed that inside the core region it varies exponentially and outside the core it falls inversely with r. The term outside the core is purely the Coulomb interaction

between an electron and an ion. The non-screened form factor associated with the potential parameters has the analytical form as:

$$W(q) = 4\pi n a^3 \left| \frac{B_1 J_1}{(1+a^2 q^2)^2} + \frac{8B_2 J_2}{(1+4a^2 q^2)^2} \right| - \frac{4\pi Zn}{q^2}\cos(qR_c)$$

(2)

Where n denotes the ionic number density and q is the momentum transfer. The coefficients B_m is a function of a, R_c and Z, whereupon J_m is a function of a and R_c and its nature is harmonic.

$B_1 = (Ze^2/R_c) (1-2a/R_c) \exp(R_c/a)$,

$B_2 = (2Ze^2/R_c) (a/R_c -1) \exp(0.5R_c/a)$

$$J_m = 2 - \exp\left(\frac{R_c}{ma}\right)\left\{\left[\frac{R_c(1+m^2 a^2 q^2)}{ma} + (1-m^2 a^2 q^2)\right]\right.$$

$$\left.\frac{\sin(qR_c)}{maq} + \left[2 + \frac{R_c(1+m^2 a^2 q^2)}{ma}\right]\cos(qR_c)\right\};$$

3

The effective interionic (ion-ion) potential may be written as

$$u(r,n) = Z^2/r\ [1-2/\pi \int_0^\infty dq\ F_N(q)\ \text{Sin}(qr)/q\ ]$$

(4)

The ionic potential indeed varies harmonically, where $F_N(q)$ is the normalized energy wave number characteristic:

$$F_N(q) = (q^2/4\pi n Ze^2)^2\ W^2(q)\ [1- 1/\varepsilon(q)]\ [1- G(q)]^{-1}$$

(5)

Here, $\varepsilon(q)$ and $G(q)$ indicate the dielectric function and the local field correction, respectively. From the expression (4) the effective pair potential, u(r,n), is obtained by following the usual techniques of Ichimaru and Utsumi form ref. [6] because these forms satisfy the compressibility sum rule and the short range correlation conditions in addition to applicability over a wide range of metallic densities. Furthermore, it requires that both W(r) and its first derivative be continuous at the core. As a result, the coefficients B_1 and B_2 are written in terms of the above three parameters which characterize W(r), namely the empty-core radius, R_c the softness parameter, a, and the effective s electrons occupancy number, Z_s.

B. Static structure factor

For elemental system (single component) the static structure factors S(q) are calculated from the following relation between the structure factor and the pair distribution function:

$$S(q) = 1 + \rho_0 \int [g(r) -1]\ \exp(-i\vec{q}.\vec{r})dr$$

(6)

The essential ingredients in calculating the structure factors are the HS diameters. The values of HS diameters are determined by using the linearized Weeks–Chandler–Andersen (LWCA) thermodynamic perturbation theory [1, 2]. The corresponding pair correlation function may be obtained by the Fourier transform of S(q) in the following way:

$$g(r) = 1 + \frac{1}{(2\pi)^3} \int (S(q) - 1)\times \exp(i\vec{q}.\vec{r})d^3 q$$

(7)

3. Results and Discussion

The proper values of the parameters R_c, Z_s and a of the effective pair potential is selected in this section. The choice of parameterization is required to reproduce the observed structural properties of 3d transition liquid metals. Since the used potential describe the nearly free electron sp-band by the empty core model, we follow a procedure similar to that discussed in refs. [7] to fit the core radius R_c; the values chosen are shown in table-1. The values of a are restricted to the range $4<R_c/a<5$, so that u(r,n) has both a short-range repulsive part and an attractive tail, otherwise it becomes purely repulsive. Greater values of a produce softer repulsive potential as shown in fig.1 (a). The self-consistent calculations by Moriarty [8] noted that, at normal densities, the effective number of nearly sp electrons take on values in the narrow range $1.1\leq Z_s \leq 1.7$, with a typical value of $Z_s = 1.3$. In this article, the chosen typical values are $Z_s =1.3$ for Zn and 1.5 for Cu in accordance with the fitting of structural data. Accordingly, the constraint R_c/a noted above, the value of the softness parameter, a was selected which best report for the damping of the oscillations of S(q) for each metal. Noted that, the values of R_c, a and σ show an upward trend with rising atomic number, whereas Z and η show a downward trend compare to the earlier. Alternatively, smaller values of the parameter a are a measure of the hardening of the repulsive core [9, 10] by attributing the filling 3d band across the concerned systems. The lower values of σ for Cu than Zn might be attributed of its higher temperature that may causes reduction of Cu hard sphere (HS) size by some scattering mechanisms of charge transfer.

Table 1: Input values of T_m (melting) and T temperature; n_m & n are ionic number densities; R_c, core radius; a, softness parameter; Zs, effective number of s-electrons; $σ_s$, effective hard sphere diameters, and $η_s$ are packing fractions.

Liquid	T_m(K)	T(K)	n_m(Å^{-3})	n (Å^{-3})	R_c(a.u.)	a (a.u.)	Z_s	$σ_m$(Å)	σ (Å)	$η_m$	η
Cu	1358	1423	0.0791	0.0755	1.17	0.245	1.5	2.41	2.40	0.58	0.55
Zn	693	723	0.0665	0.0637	1.27	0.285	1.3	2.47	2.46	0.52	0.50

Some sort of similar parameterization was used in ref. [11] but a different parameterization was used in a preceding work of ref. [1] where the choice of $R_c = r_0/2$, where r_0 is the Wigner-Seitz radius. The values of a are fitted to pleasing the small q-behavior of S(q) such as of $R_c/a > 5$ for the 3d liquid metals. Here, only the imposed constraint $4 < R_c/a < 5$ allows the essential interaction between the repulsive and attractive contributions to the potential which is the more precise prescription of R_c used. Note that, regardless of the parameterization chosen, the LWCA theory in combination with the effective pair potential always converges to a solution. The effective hard sphere diameters, σ_s, and the corresponding packing fractions both at melting and above melting temperatures, using the relation $\eta = \pi n\sigma^3/6$, are calculated by the LWCA [1, 2] theory as shown in table-1. It shows that the values of HS diameters and packing fractions are slightly larger at melting rather than above melting. This trend also noticed at ionic number density data.

One component static structure factors and the corresponding Fourier transforms are computed using the stated expressions (6) and (7) respectively where the results of the effective BS potential and LWCA liquid state theory were employed. At enactment of the numerical calculations the input thermodynamics data used such as the temperature, T, and ionic number density, n both at melting and just above the melting point, are taken from ref. [5] as shown in table-1. The numerical results obtained for the liquid structure factors, S(q) and the corresponding pair correlations, g(r) of liquid Cu and Zn are shown in figs.1 & 2. To reproduce the results theoretically the calculated values are compared with the available experimental X-ray diffraction data [5].
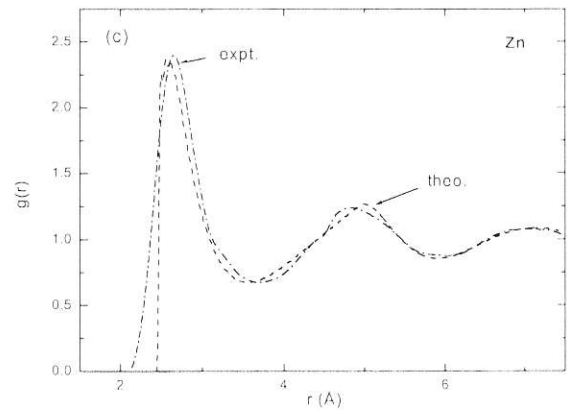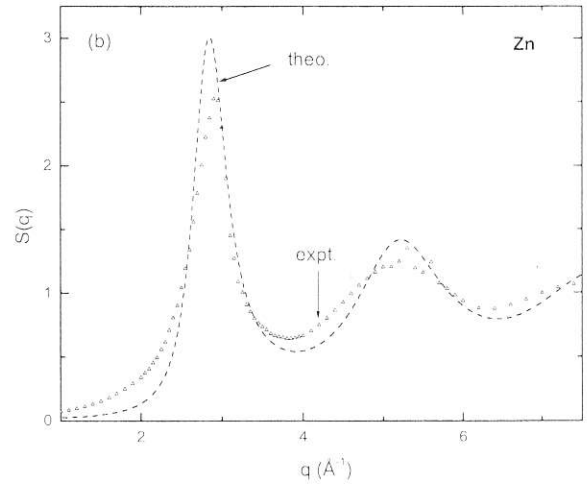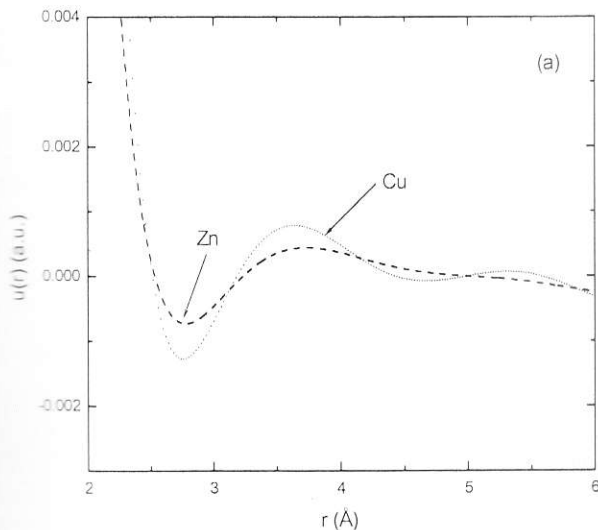

Fig. 1: (a) Potential profiles of liquid Cu & Zn, (b) static structure factor, S(q) at q range, (c) the equivalent Fourier inversion, g(r) of liquid Zn

The potential profiles of Cu & Zn are shown in fig.1 (a) that shows a repulsive hard core part and an attractive tail part repeatedly oscillating with gradually decaying amplitudes. It is seen that for Zn the potential well is shallower than Cu. It is also seen that the value of the position r of the first minimum is mostly same, and oscillations are almost in phase relative to the potentials of the Cu. Therefore, we observe a harmonic feature between the potentials. The tail part oscillations of the potentials may be understood by the Friedel oscillations contributed by the conduction electrons.

The static structure, S(q) in addition to its Fourier transform, g(r) of the concerned liquid metals are mostly determined by the harsh repulsive part of the potential. The effects of the attractive part and the part of the Friedel oscillations on S(q) and g(r) are not significant. Since the tail part of potential is less significant to structure, so at large q it fits less well rather than the repulsive hard core part. On the other hand, since LWCA is a thermodynamic perturbation method and it does not deal with the full potential for numerical calculations, so this might be a possible reason for less fitting of structures at large q range. Both the qualitative and quantitative agreement of the numerical results with experiment is fine with a slight discrepancy in some cases, otherwise it is acceptable.
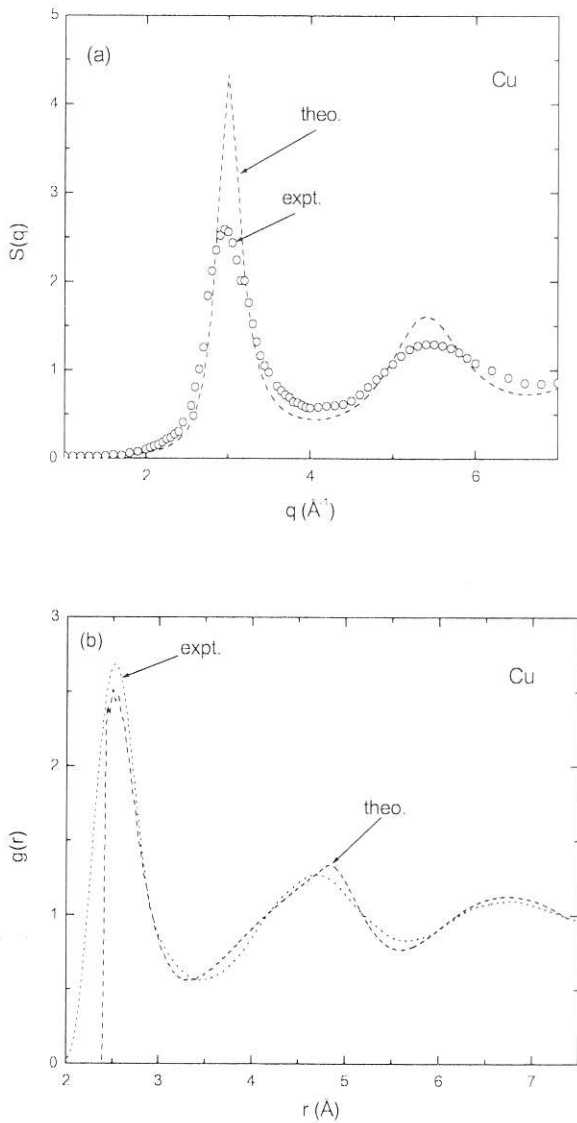
Fig.2: (a) Static structure factor, S(q) at q range, (b) the corresponding Fourier inversion, g(r) for liquid Cu

Lastly, perturbative treatment of LWCA theory shows a rather less agreement than the previous self-consistent calculations by VMHNC theory of liquids [13, 14] as it does not cover the full potential approach unlike the later one. This might be one possible reason for higher peaks shown in theoretical structural data as shown in figs.1 & 2. Such typical drawbacks may be overcome by employing the full potential approach.

Nonetheless, results show that both S(q) and g(r) are gradually converge for both the elements, the ions are highly correlated in a central zone and ionic correlation or interaction reduces in terms of rising q range with respect to the central zone and S(q)~1 and g(r)~1 termed as un-correlation among the configurationally sited ions.

4. Conclusion

The LWCA results fitted well with the available experimental data. This might be the reference system in HS treatments of liquid transition metals for advance research in this field to calculate the statics and transport properties of other liquid metals and their binary alloys. Consequently, LWCA theory is able to become a substitute of VMHNC theory and it can be recommended, like the VMHNC theory, for the calculation of liquid structures in spite of their crude form. Dynamic structures are yet another challenge to be tackled on the same gravity.

Acknowledgements

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