

## Structural Properties of Some Liquid 3d Transition Metals

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### Abstract

The numerical results of the static structure factors,  $S(q)$ , its equivalent pair distribution function,  $g(r)$  which yields by Fourier inversion of the earlier, for some liquid 3d transition metals are presented sequentially in this study. The effective interionic (ion-ion) interaction is a crucial factor for the theoretical studies of the above properties. A model pseudopotential which connects the  $sp$  and  $d$ -band contributions is employed to derive the effective interionic interactions deduced from an inverse scattering method. The liquid structure is calculated using the linearised version of the Weeks-chandler-Andersen (LWCA) thermodynamic perturbation theory of liquids. The resulting  $S(q)$ s and  $g(r)$ s agree plausibly well with the observed X-ray diffraction data.

**Keywords:** Transition metals, Static structure factors, Pair correlation functions, LWCA theory

### I. Introduction

Most of the elements lying in the 3d transition metal series namely the SC, Ti, V and Cr have incompletely filled  $d$  bands along with filled  $s$ -bands except Cr following the Ar based electronic structure. Their physical properties are significantly influenced by the  $d$ -bands via  $sd$  mixing (sometimes termed as  $sd$  hybridization). This is the basis to call these elements as the transition metals. Therefore, a complete description of these systems requires a model that can take into account both  $sp$ -and  $d$ -band effects in the interionic interactions. Liquid structure of the above 3d transition metals using a simple effective pair interaction<sup>[1]</sup> in accord with the linearised version of the Weeks-chandler-Andersen (LWCA) thermodynamic perturbation theory of liquids<sup>[2,3]</sup> has been presented.

Lately Bretonnet and Silbert (BS)<sup>[1]</sup> proposed a model to describe effective interionic (ion-ion) interactions, initially, for liquid transition metals, which deals  $sp$  and  $d$ -bands separately within the well recognized pseudopotential formalism. The  $sp$ -band is expressed via the empty core model; the  $d$ -band contribution is resulting from the  $d$ -band scattering phase shift by using the inverse scattering approach inside the core region. The ensuing model pseudopotential hence reduces to a simple local form. The BS model is easy to handle numerically. Besides, the local form allows developing this model to other liquid metals for which effects of  $sd$  hybridization are significant. Previous works in concurrence with the thermodynamically self-consistent VMHNC integral equation theory by Bhuiyan et al.<sup>[4]</sup> encouraged us to inspect the structures of some liquid 3d transition metals by LWCA liquid state theory for which experimental  $S(q)$  and  $g(r)$  data are available in ref.<sup>[5]</sup>. The liquid structures reveal the detailed configurations of the

respective ions and  $S(q) \sim 1$  denotes no correlation among the observed X-ray diffraction data.

The knowledge of static structure factor,  $S(q)$  or its Fourier inversion,  $g(r)$  is the essential precondition in the theory of liquid metals for a complete description of static as well as transport properties. In this work static structure factors and their inversion functions are inspected in the vicinity of the slightly above melting temperatures. A separate LWCA<sup>[2,3]</sup> liquid state theory is used to carry out the structural calculations.

The concerned transition metals are much important both in metallurgical and technological point of view, few of its applications are as follows. Scandium used for high intensity lighting and as a tracing agent for crude oil. Titanium used in desalination plants for converting sea water into fresh water. Vanadium is used in producing rust resistant and high-speed tools steels. Chromium is used to harden steel, to manufacture stainless steel, and to form many useful alloys and also widely used as a catalyst.

The outline of this article is as follows: in section II the essential formalisms are briefed, in section III the results and discussion have been presented succeeding by concluding comments in section IV.

### II. Theories

#### (a) Bretonnet-Silbert Model Potential

The proposed Bretonnet-Silbert model potential uses the empty-core model to explain the nearly free electron  $sp$ -band and  $d$ -band contributions presumed from an inverse scattering method. The merely position reliant pseudopotential may be formed by the superposition of the  $sp$  and  $d$ -band contributions via inverse scattering approach within the core region for metallic system as:

$$W(r) = \begin{cases} \sum_{m=1}^2 B_m \exp\left(\frac{-r}{ma}\right) & \text{for } r < R_c \\ -\frac{Ze^2}{r} & \text{for } r > R_c \end{cases} \quad (1)$$

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The term inside the core reduces exponentially. The unscreened (un-shield) form factor has the analytical form as

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

Where  $n$  denotes the ionic number density

$$J_m = 2 - \exp\left(\frac{R_c}{ma}\right) \left\{ \left[ \frac{R_c(1+m^2 a^2 q^2)}{ma} + (1-m^2 a^2 q^2) \right] \frac{\sin(qR_c)}{maq} + \left[ 2 + \frac{R_c(1+m^2 a^2 q^2)}{ma} \right] \cos(qR_c) \right\} \quad (3)$$

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

$$U(r, n) = \frac{Z}{r} \left[ 1 - \frac{2}{\pi} \int_0^\infty dq F_N(q) \sin(qr) / q \right] \quad (4)$$

The ionic potential is oscillatory. Where  $F_N(q)$  is the normalized energy wave number characteristic:

$$F_N(q) = \left[ \frac{q^2 w(q)^2}{4\pi Zn} \right]^2 \left[ 1 - \frac{1}{\varepsilon(q)} \right] \left[ \frac{1}{1-G(q)} \right] \quad (5)$$

Here,  $\varepsilon(q)$  and  $G(q)$  denote the dielectric function and the local field correction, respectively. From the expression (4) the effective pair potential,  $u(r, n)$  is obtained by the usual techniques, using a dielectric function of the Ichimaru and Utsumi form ref. [6]. Moreover, it requires that both  $w(r)$  and its first derivative be continuous at the core. As a result, the coefficients  $B_1$  and  $B_2$  may be written in terms of the three parameters which characterize  $w(r)$ , namely the empty-core radius,  $R_c$ , the softness parameter,  $a$ , and the effective  $s$  electrons occupancy number,  $Z_s$ . The term outside the core is simply the Coulomb interaction between an electron and an ion.

### (b) Static Structure Factor (One-Component System)

One component structure factor  $S(q)$  (e.g. Ashcroft and Lekner, 1966) is calculated from the following relation between the structure factor and the corresponding pair distribution function:

$$S(q) = 1 + \rho_o \int [g(r) - 1] \exp(-i\vec{q}\cdot\vec{r}) d\vec{r} \quad (6)$$

The essential constituents in calculating the structure factors are the hard sphere (HS) diameters. The values of HS diameters are determined by using the linearized version of the Weeks–Chandler–Andersen (LWCA) thermodynamic perturbation theory [2, 3]. The corresponding pair distribution function may be obtained by the Fourier inversion of  $S(q)$  as:

$$g(r) = 1 + \frac{1}{(2\pi)^3} \int (S(q) - 1) \times \exp(i\vec{q}\cdot\vec{r}) d^3 q \quad (7)$$

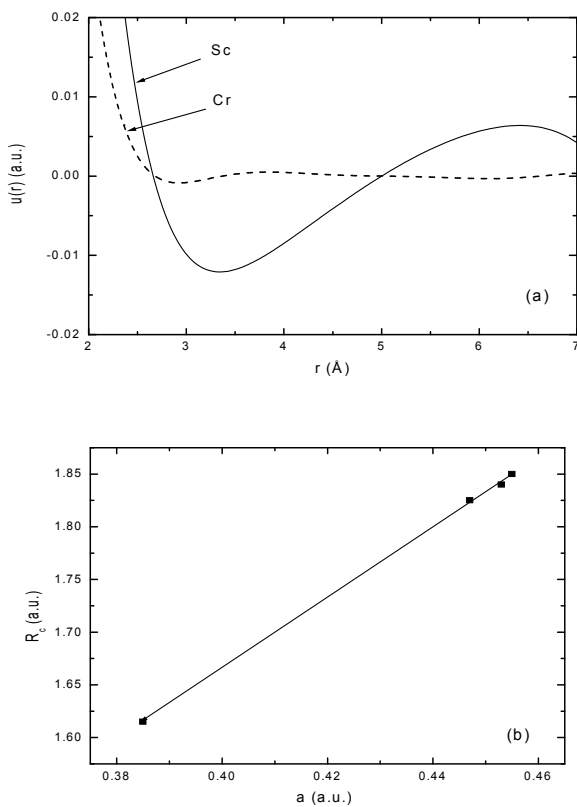
### III. Results and Discussion

The stated effective pair potential contains three parameters,  $R_c$ ,  $Z_s$  and  $a$ , whose choice are required to reproduce the observed structural properties of the concerned 3d transition liquid metals. Since the used potential describe the nearly free electron sp-band by the empty core model, a procedure similar to that discussed in refs. [7, 8] has been followed 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. Larger values of ‘ $a$ ’ result in a softer repulsive potential. The self-consistent calculations by Moriarty [9] pointed out 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  $Z_s = 1.4$ , but with the elements at the beginning of the 3d series taking on larger values. In this study, we have chosen the typical value  $Z_s = 1.4$ , except for Sc and Ti for which we have taken the top most value within the range  $Z_s = 1.7$  for the earlier and  $Z_s = 1.5$  for the later. Contained by the constraint  $R_c/a$  noted above, we pick for the value of the softness parameter ‘ $a$ ’ which best accounts for the damping of the oscillations of  $S(q)$  for each metal. Noted that, plotting  $R_c$  against  $a$ , shows a linear pattern, that treats a smaller values of the parameter  $a$  are a measure of the hardening of the repulsive core [10-12] by attributing the filling 3d band across the 3d series as shown in fig. 1 (b).

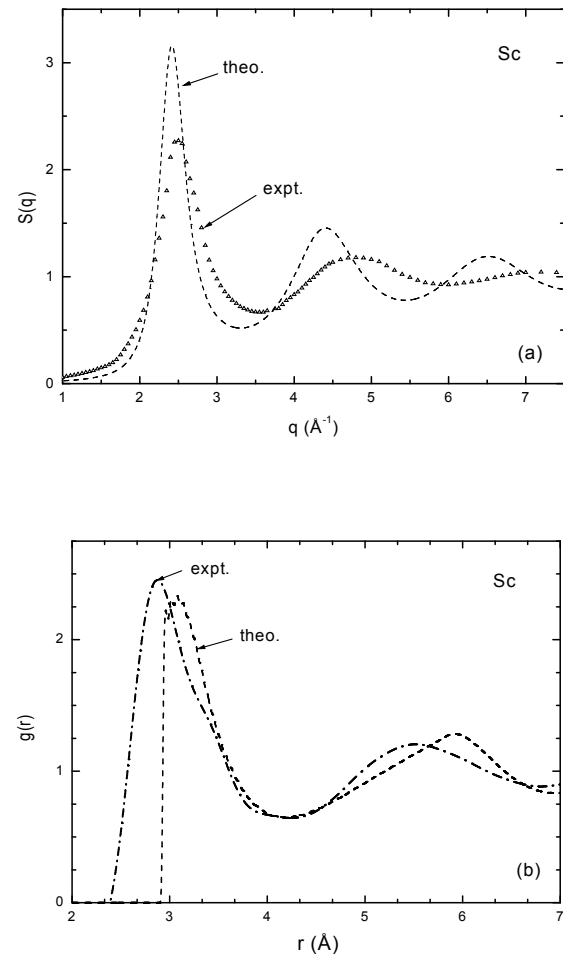
**Table-1. Input data: T, temperature; n, ionic number density;  $R_c$ , core radius; a, softness parameter;  $Z_s$ , effective number of s-electrons;  $\sigma_s$ , effective hard sphere diameters, and  $\eta_s$  are packing fractions.**

Liquid	T(K)	n ( $\text{\AA}^{-3}$ )	$R_c$ (a.u.)	a (a.u.)	$Z_s$	$\sigma_s$ ( $\text{\AA}$ )	$\eta_s$
Sc	1833	0.0391	1.850	0.455	1.7	2.92	0.51
Ti	1973	0.0522	1.840	0.453	1.5	2.64	0.50
V	2173	0.0633	1.825	0.447	1.4	2.56	0.56
Cr	2173	0.0726	1.615	0.385	1.4	2.44	0.55

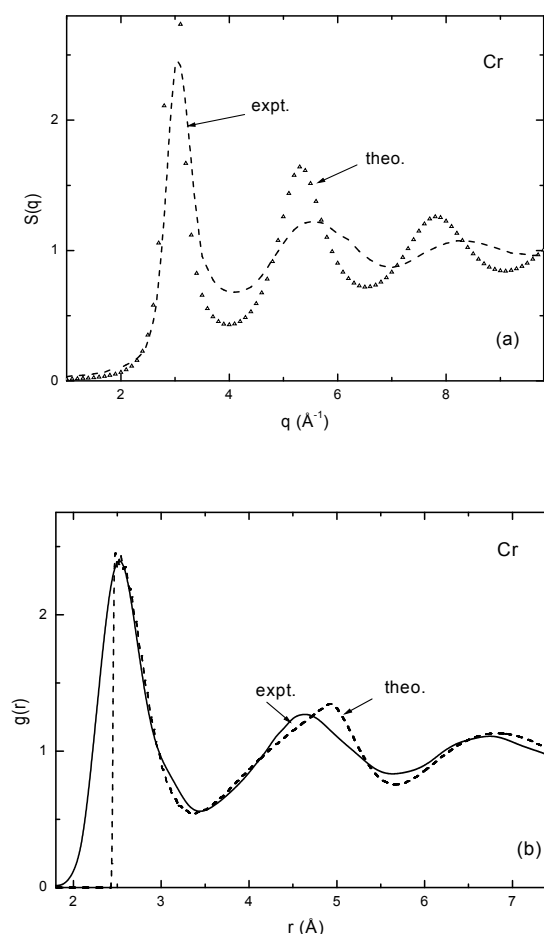
A different parameterization was used in a previous work<sup>[13]</sup> where the choice of  $R_c = r_0/2$ , where  $r_0$  is the Wigner-Seitz radius, and the fitting of a to the small q-behavior of  $S(q)$  gives a value of  $R_c/a > 5$  for the 3d liquid metals. In the present work, only the imposed 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 in this study. The parameter a is then adjusted such a way to follow the above prescription and pleasing this constraint also. Notice 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,  $\sigma_s$ , and the corresponding packing fractions, using the relation  $\eta = \pi n \sigma_s^3 / 6$ , where n is the ionic number density, are calculated by the LWCA<sup>[2, 3]</sup> liquid state theory as shown in table-1. In addition, data table depicts that the values of  $R_c$ , a, Z and  $\sigma$  are gradually decreases, whereas the values of n are gradually increases along with the concerned liquids temperature.

**Fig.1.** (a) Potential profiles (e.g.) of the concerned liquid metals, (b) the softness parameter, a, versus core radius,  $R_c$ , pattern.

At numerical calculations, to reproduce the experimental X-ray diffraction values, the input thermodynamics data used such as the temperature, T, and ionic number density, n, just above the melting point, are taken from ref.<sup>[5]</sup> as shown in table-1. One component static structure formula is used to work out the liquids positional or configurational aspects at liquid state and therefore calculated the correlation exists among the distributed ions. In present calculation, almost half of the entire 3d series have been covered starting from Sc and ending by Cr. The numerically fitted values of  $S(q)$  and the corresponding  $g(r)$  have been computed by the earlier stated expressions (6) and (7) respectively.

**Fig.2.** (a) Static structure factor,  $S(q)$  at q vary, (b) the equivalent pair correlation function,  $g(r)$  for liquid Sc

The potential profiles of Sc & Cr are shown in fig.1 (a) that shows a repulsive hard core part of the falling potential and an attractive tail part repeatedly oscillating with gradually decaying amplitudes. Although, it is seen that for Cr the potential well is very shallow with lower acme in either way and the value of the position  $r$  of the first minimum is smaller than that of Sc, and the oscillations of it are almost out of phase relative to the potentials of the Sc, but both the potential profiles eventually diminish asymptotically. Thus, we assume that the root cause of discrepancy for Cr is due to the unusual features of its potential. But the results of  $S(q)$  and  $g(r)$  for Cr are in reasonable agreement. This may be understood in the following way. It is well known that the static structure of liquid metals is 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.



**Fig.3.** (a) Static structure factor,  $S(q)$  at  $q$  vary, (b) the corresponding Fourier inversion,  $g(r)$  for liquid Cr

The numerical results of the static structures,  $S(q)$  and the corresponding pair correlation functions,  $g(r)$  of the liquid 3d transition metals are presented in figs. 2 & 3, using effective pair interionic potentials and a thermodynamic perturbation theory of liquids. The reproducing results obtained in this work are of precisely comparable with the experimental X-ray diffraction data available in ref. [5]. Since the tail part of potential, mostly contributed by Friedel oscillations, is less significant to structure, so at large  $q$  it is

fitted less well than the hard part of the potential arising at small  $q$  range. After all, both the qualitative and quantitative agreements with experiment are fine with a few trivial discrepancies in some cases, or else it is in good concurrence.

Finally, the LWCA results reproduced a bit less well than that of the earlier VMHNC theory as the former one is a hard sphere theory as well as thermodynamic perturbation theory of liquids and it does not cover the full potential treatment unlike the self-consistent VMHNC theory of liquids [14, 15]. Results show that both  $S(q)$  and  $g(r)$  are converge for all elements with a slowly diminishing amplitudes, the ions are highly correlated in a centric zone and ionic correlation reduces in terms of rising  $q$  range with respect to the central zone and  $S(q) \sim 1$  and  $g(r) \sim 1$  termed as no correlation, which assumes very feeble interactions among the distributed ions.

#### IV. Conclusion

The depicted results by employing the HS model agreed well with the experimental values and it might be useful for further research in this manifestation to calculate the static and transport properties of other liquid metals and their binary alloys. HS model, like the VMHNC theory, is well suited as a reference liquid for the study of liquid state properties of transition metals. Thus LWCA theory can also be suggested for tackling the dynamic structures of liquids on the same or other effective pair potential footing.

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