

STRUCTURAL ANALYSIS OF LIQUID 3D TRANSITION METALS USING CHARGED HARD SPHERE REFERENCE SYSTEM

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Abstract. *The Charged Hard Sphere (CHS) reference system is applied to study the structural analysis of liquid 3d transition metals. Here we report the structure factor $S(q)$, pair distribution function $g(r)$, interatomic distance r_1 of nearest neighbour atoms and coordination number n_1 for liquid 3d transition metals viz: Ti, V, Cr, Mn, Fe, Co, Ni and Cu. To describe electron-ion interaction our own model potential is employed alongwith the local field correction due to Sarkar et al (SS). The present results of $S(q)$ and $g(r)$ are in good agreement with experimental findings. The maximum discrepancy obtained from the experimental data for the coordination number is 4.22% in the case of Ti while the lowest is 0.31% for Cu. Thus CHS is capable of explaining the structural information of a nearly empty d-shell, nearly filled d-shell and fully filled d-shell elements.*

I. INTRODUCTION

The Charged Hard Sphere (CHS) model is extremely useful in the evaluation of structure factor of simple metals in liquid state. In spite of simplicity, the model yields quite satisfactory results and has been utilized to study the structures of liquid metals by various authors [1-8].

Singh and Holz [4] studied the structure factor of liquid alkali metals by adopting CHS as a reference system and they concluded that the alkali metals at different temperatures are in excellent agreement with experimental data. Structural studies of some rare earth metals through CHS model has been carried out by Gopal Rao and Bandyopadhyaya [5] and very good agreement has been achieved with experimental results. We have also produced structural information for liquid alkali metals as well as rare earth metals by adopting CHS method, successfully [7, 8].

Though the CHS method [1-7] is proved very useful for explaining structural properties of liquid metals, the study of liquid 3d transition metals using CHS is not found in our literature survey. One of the most interesting points in the field of liquid state physics is whether the liquid structure of transition metals having the incomplete d shell differs from that of simple metals such as aluminum. The above two facts have motivated us to study the structural analysis of liquid 3d transition metals like Ti, V, Cr, Mn, Fe, Co, Ni and Cu.

Here we report the structure factor $S(q)$, pair distribution function $g(r)$, interatomic distance r_1 of nearest neighbour atoms and coordination number n_1 for liquid 3d transition metals using CHS reference system [1-8].

II. THEORY

CHS reference system is essentially made up of positively charged identical hard spheres interacting via Coulomb potential embedded in a non-responding back ground of conduction electrons. The positively charged hard spheres are assumed to occupy certain finite dimension in space. This system has been solved exactly by Palmer and Weeks [3] within a mean spherical approximation inside the core and outside the core, a perturbation in the form of Coulomb interaction is assumed to act.

According to Palmer and Weeks [3], the direct correlation function of the system of CHS in a uniform background of electron is given by

$$C_0(x) = \begin{cases} A + Bx + Cx^2 + Dx^3 + Ex^5, & x < 1 \\ -\frac{\gamma}{x}, & x > 1 \end{cases} \quad (1)$$

Here $x = \frac{r}{\sigma}$ with σ being the effective hard-core diameter of the charged spheres and $\gamma = \beta \frac{(Ze)^2}{\varepsilon_0 \sigma}$ is the ion-ion coupling strength. Further $\beta = \frac{1}{k_B T}$, k_B is the Boltzmann constant, T is the absolute temperature of the system, Ze is the ionic charge and ε_0 is the static dielectric constant of the system. Since the electron background is uniform, its dielectric constant is unity. The coefficients A, B, C, D and E in equation (1) are well defined in [3-8].

Within a linear screening approximation [3-8], the static structure factor of a liquid metal is given by [3-8]

$$S(q) = \frac{S_0(q)}{1 + \rho \beta \bar{V}(q) S_0(q)} \quad (2)$$

Here $S_0(q)$ is the static structure factor of the CHS reference system. By taking the Fourier transform of $C_0(x)$, the simple analytical expression of $S_0(q)$ is obtained as

$$S_0(q) = \frac{1}{1 - \rho C_0(q)} \quad (3)$$

with

$$\begin{aligned} \rho C_0(q) = & \left(\frac{24\eta}{q^6} \right) \left[Aq^3 (\sin q - q \cos q) \right. \\ & + Bq^2 \{ 2q \sin q - (q^2 - 2) \cos q - 2 \} \\ & + Cq \{ (3q^2 - 6) \sin q - (q^2 - 6) \} \\ & + D \{ (4q^2 - 24) q \sin q - (q^4 - 12q^2 + 24) \cos q + 24 \} \\ & \left. + \frac{E}{q^2} \left\{ \frac{6(q^4 - 20q^2 + 120)}{(q^6 - 30q^4 + 360q^2 - 720)} q \sin q - \right. \right. \\ & \left. \left. (q^6 - 30q^4 + 360q^2 - 720) \cos q - 720 \right\} - \gamma q^4 \cos q \right] \end{aligned} \quad (4)$$

Here q is expressed in units of σ^{-1} .

In equation (2) $\bar{V}(q)$ is the attractive screening correlation to the direct ion-ion potential of the form

$$\bar{V}(q) = \left[\frac{W_B^2(q)}{\phi(q)} \right] \left[\frac{1}{\varepsilon(q)} - 1 \right] \quad (5)$$

Where $W_B(q)$ is the bare ion pseudopotential, $\phi(q) = \frac{4\pi e^2}{q^2}$ is the Fourier transforms of bare Coulombic interaction between two electrons and $\varepsilon(q)$ be the modified dielectric function. In the present study we have used the most recent dielectric function due to Sarkar et al (SS)[9].

To describe electron-ion interaction, model potential used is of the form (in real space) [6-8, 10-14]

$$W_B(r) = \begin{cases} 0; & r < r_c, \\ -\left(\frac{Ze^2}{r}\right) \left[1 - \exp\left(-\frac{r}{r_c}\right)\right]; & r \geq r_c. \end{cases} \quad (6)$$

This model potential is continuous in $\mathbf{r}$ - space and it is the modified version of the Ashcroft's empty core model. In comparison with Ashcroft empty core model potential, we have introduced $\frac{Ze^2}{r} \exp\left(-\frac{r}{r_c}\right)$ as a repulsive part outside the core which vanishes faster than only Coulomb potential $-\frac{Ze^2}{r}$ as $r \rightarrow \infty$. In the reciprocal space, the corresponding bare-ion form factor of present model potential is given by [6-8, 10-14],

$$W_B(q) = \left(\frac{-4\pi Ze^2}{\Omega_0 q^2}\right) \left[\cos(qr_c) - \left\{ \frac{(qr_c) \exp(-1)}{1 + q^2 r_c^2} \right\} \{ \sin(qr_c) + qr_c \cos(qr_c) \} \right]. \quad (7)$$

Here Z , Ω , q and r_c are the valency, atomic volume, wave vector and the parameter of the potential, respectively. The potential contains only single parameter r_c , which is estimated by employing the relation $r_c = 0.51(z^{-1/3})R_a$, where R_a is the atomic radius [15].

The description of the atomic distribution in non-crystalline materials frequently employs the concept of the distribution function. In particular, the pair distribution function $g(r)$, which corresponds to the probability of finding another atom at a distant r from the origin atom (at the point, $r = 0$) is used.

The expression for the pair distribution function $g(r)$ is given by [3-8]

$$g(r) = 1 + \left(\frac{1}{2\pi^2 \rho r}\right) \int_0^\infty q \{S(q) - 1\} \sin(qr) dq. \quad (8)$$

Using this pair distribution function we obtain the inter atomic distance r_1 of the first nearest neighbor atoms from the first maxima of $g(r)$ curve.

Another function $4\pi r^2 \rho g(r)$ obtained from $g(r)$ is used in the discussion of the structure of non-crystalline systems. This has been called the radial distribution function

(RDF). This function corresponds to the number of atoms in the spherical shell between R and $R + dR$. Thus the coordination number is obtained from the relation [16]

$$n_1 = \int_{r_0}^{r_m} 4\pi\rho r^2 g(r) dr \quad (9)$$

Where, r_0 is the left-hand edge of the first peak and r_m corresponds to the first minimum on the right-hand side of the first peak in RDF.

III. RESULTS AND DISCUSSION

The constants and parameters used in the present computations are tabulated in Table 1. Figures (1)-(8) represent the generated $S(q)$ and $g(r)$ of Ti, V, Cr, Mn, Fe, Co, Ni and Cu, respectively, along with the experimental results [16]. Tables 2 and 3 represent the first and second peak position and related magnitude in $S(q)$ and $g(r)$, respectively.

From Tables 2 and 3, it is found that the first and second peak position and related magnitude in $S(q)$ and $g(r)$ are in good agreement with the experimental data [16]. From the figures (1) – (8), it is seen that as the atomic number increases from Ti to Cu, the oscillations of the structure factor systematically increase in amplitude. A noticeable discrepancy between present results and experimental data [16] has been found in Ti and V. From the careful analysis of the figures, it is found that a discrepancy between present results and experimental data [16] go on decreasing as the atomic number increases from Ti to Cu. The excellent agreement has been obtained for Cu. This characteristic must be related to the incomplete 3d shell of these elements because the structural information experimentally obtained seems to be affected more or less by the electronic structure of outer shell for these elements. These results give qualitative support for the suggestion that a partial overlap of one atom with another for the elements having a nearly empty d shell such as Ti, is larger than that for the elements having a nearly filled d shell such as Ni. While in the case of Cu, d shell is fully filled up.

Table 1. *Parameters and constants used in present computation*

Metal	$T(K)$	$\rho(gm/cm^3)$	Z	η	$k_F(\text{\AA}^{-1})$	$r_c(\text{\AA})$
Ti	1973	4.15	1.5	0.44	0.3705	0.6461
V	2173	5.36	1.5	0.44	0.3954	0.6055
Cr	2173	6.27	1.5	0.45	0.4137	0.5787
Mn	1533	5.97	1.5	0.45	0.3995	0.5993
Fe	1823	7.01	1.5	0.44	0.4193	0.5710
Co	1823	7.70	1.5	0.45	0.4249	0.5634
Ni	1773	7.72	1.5	0.45	0.4258	0.5622
Cu	1423	7.97	1.5	0.46	0.4192	0.5711

Table 2. *First and second peak position and related magnitude in $S(q)$*

Metal	First Peak position and Related magnitude in $S(q)$				Second Peak position and Related magnitude in $S(q)$			
	Peak position Q_1 in ($\text{\AA}^{-1}$)		Related magnitude		Peak position Q_2 ($\text{\AA}^{-1}$)		Related magnitude	
	Present	Expt.	Present	Expt.	Present	Expt.	Present	Expt.
Ti	2.6334	2.45	2.4593	2.367	4.9890	4.40	1.2587	1.258
V	2.8098	2.70	2.4553	2.359	5.3232	5.00	1.2593	1.223
Cr	2.9404	3.00	2.5701	2.452	5.5409	5.40	1.2799	1.220
Mn	2.8250	2.85	2.6188	2.495	5.3362	5.20	1.2742	1.225
Fe	2.9800	2.95	2.4883	2.382	5.6455	5.40	1.2550	1.254
Co	3.0202	3.00	2.5985	2.437	5.6913	5.70	1.2763	1.189
Ni	3.0266	3.10	2.6032	2.419	5.7034	5.70	1.2757	1.210
Cu	2.9644	3.00	2.7623	2.587	5.5694	5.40	1.2951	1.288

Table 3. *First and second peak position and related magnitude in $g(r)$*

Metal	First peak position and related magnitude in $g(r)$				Second peak position and related magnitude in $g(r)$			
	Peak position r_1 in ($\text{\AA}$)		Related magnitude		Peak position r_2 in ($\text{\AA}$)		Related magnitude	
	Present	Expt.	Present	Expt.	Present	Expt.	Present	Expt.
Ti	2.7993	3.20	2.3714	2.239	5.3024	5.80	1.2331	1.161
V	2.6300	2.80	2.3655	2.287	4.8790	5.10	1.2234	1.179
Cr	2.5400	2.50	2.3745	2.453	4.6409	4.60	1.2794	1.271
Mn	2.6247	2.60	2.4081	2.333	4.8420	4.90	1.2493	1.232
Fe	2.5083	2.60	2.2838	2.537	4.5933	4.70	1.2701	1.214
Co	2.4818	2.50	2.3226	2.373	4.5562	4.70	1.2982	1.228
Ni	2.4765	2.50	2.3184	2.361	4.5509	4.40	1.2992	1.241
Cu	2.5294	2.50	2.4081	2.755	4.6197	4.70	1.3110	1.274

The interatomic distance r_1 of the nearest neighbour atoms and coordination number n_1 are also calculated and represented alongwith the experimental data [16] in Table 4.

Good agreements have been found between the present results and experimental data [16] in both the cases i.e. interatomic distance r_1 and coordination number n_1 . The deviations from the experimental data [16] in the case of coordination number n_1 are found highest 4.22% for Ti while lowest 0.31% for Cu.

Lastly, we conclude that CHS reference system with our own model potential is capable of explaining the structural information of a nearly empty d-shell, nearly filled d-shell and fully filled d-shell liquid 3d transition metals, successfully.

Table 4. *Interatomic distance r_1 and Coordination number n_1*

Metal	Interatomic distance r_1 in ($\text{\AA}$)			Coordination n_1		
	Present	Expt.	% deviation from Expt.	Present	Expt.	% deviation from Expt.
Ti	2.7993	3.20	12.5218	10.4396	10.9	4.2238
V	2.6300	2.80	6.0714	10.6105	11.0	3.5409
Cr	2.5400	2.50	1.6000	10.9102	11.2	2.5875
Mn	2.6247	2.60	0.9500	10.8079	10.9	0.8449
Fe	2.5083	2.60	3.5269	10.7607	10.6	1.5160
Co	2.4818	2.50	0.7280	11.2978	11.4	0.8964
Ni	2.4765	2.50	0.9400	11.3189	11.6	2.4232
Cu	2.5294	2.50	1.1760	11.3353	11.3	0.3123

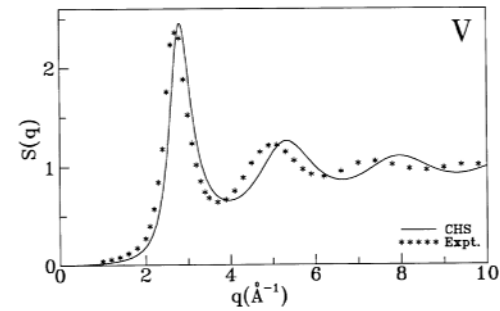
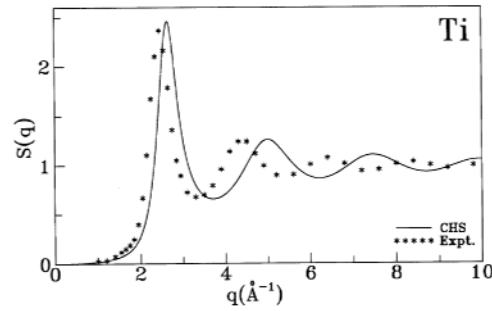
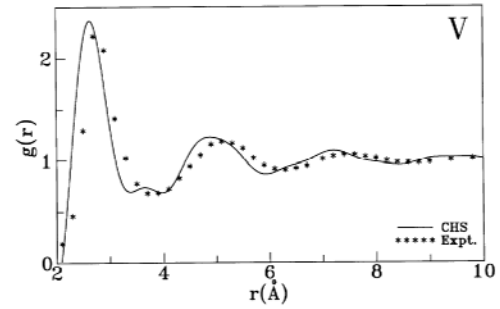
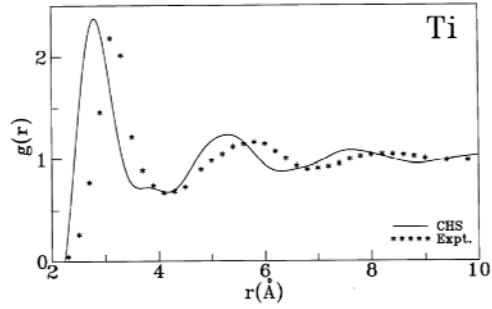


Fig. 1. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Ti at 1973K

Fig. 2. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for V at 2173K

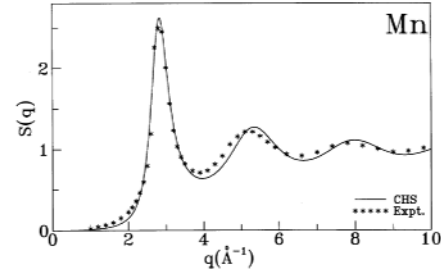
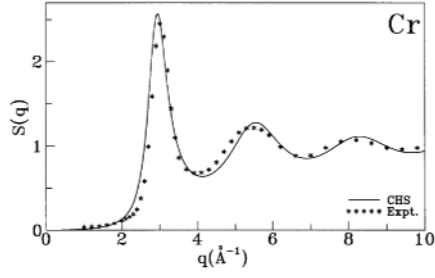
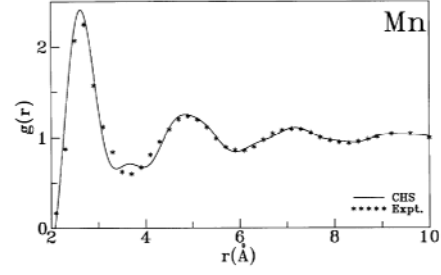
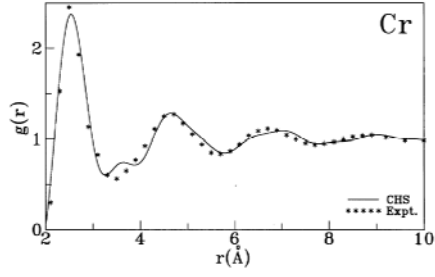


Fig. 3. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Cr at 2173K

Fig. 4. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Mn at 1533K

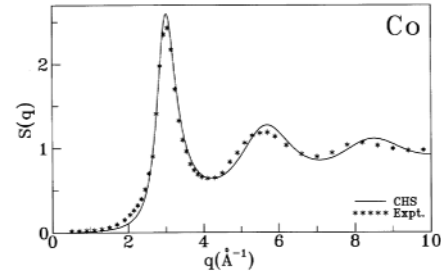
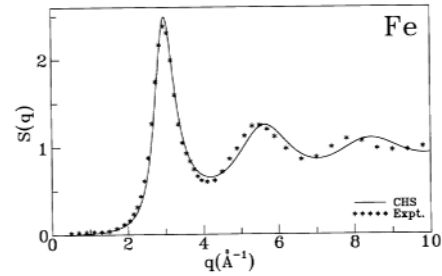
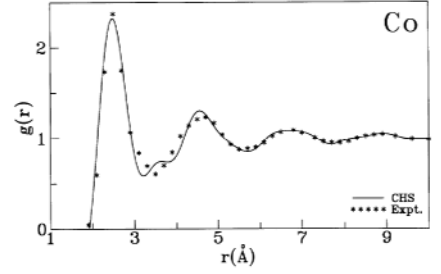
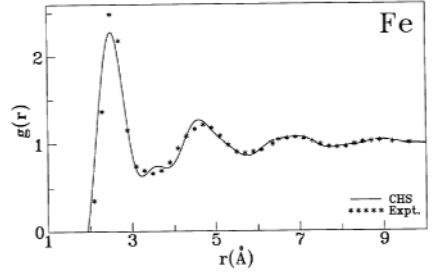


Fig. 5. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Fe at 1823K

Fig. 6. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Co at 1823K

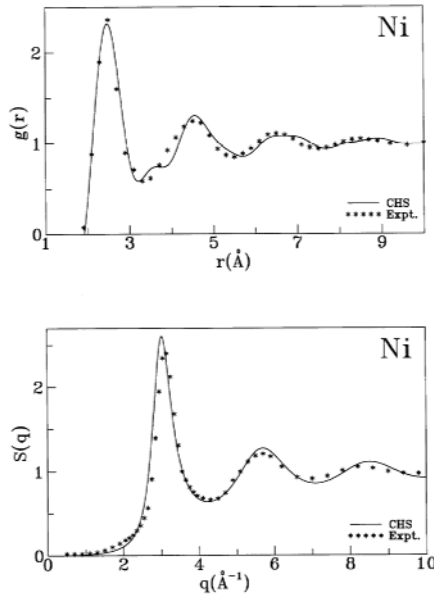


Fig. 7. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Ni at 1773K

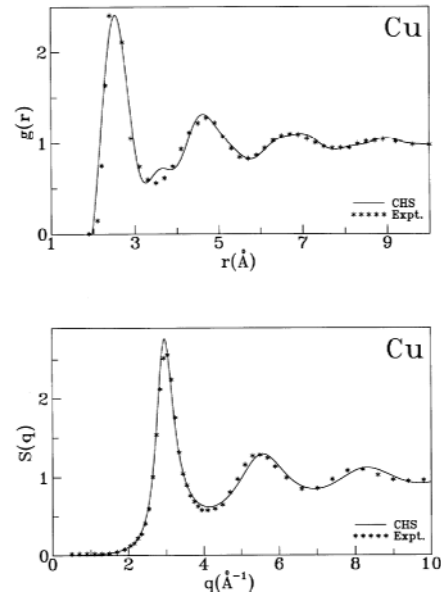


Fig. 8. Structure factor, $S(q)$ and pair distribution function, $g(r)$ for Cu at 1423K

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