Research Article

Theoretical Investigation of Thermodynamical and Structural Properties of 3d Liquid Transition Metals Using Different Reference Systems

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The present paper deals with the theoretical investigation of thermodynamical and structural properties like internal energy (E), entropy (S), Helmholtz free energy (F), isothermal compressibility (χ_T), specific Heat (C_V), structure factor $S(q)$, and long wave length limit $S(0)$ of structure factor of 3d liquid transition metals. To describe electron-ion interaction we have used our newly constructed parameter free model potential. To perform this task, we have used different reference systems like Percus Yevick Hard Sphere (PYHS), One Component Plasma (OCP), and Charged Hard Sphere (CHS) reference systems. We have also seen the influence of different local field correction functions like Hartree (HR), Taylor (TR), and Sarkar et al. (SR) on thermodynamical properties of 3d liquid transition metals. Finally we conclude that the proper choice of the model potential along with reference system plays a vital role in the study of thermodynamical and structural properties of 3d liquid transition metals.

1. Introduction

The structure and thermodynamics of liquid metals have been widely studied with an increasing sophistication in the modelling of the interionic forces and in the classical statistical mechanics treatment of ionic correlations [1–48]. This study has drawn much theoretical attention both for its intrinsic interest and for the relevance to an understanding of electronic properties. The calculations of the atomic interactions in bonded metals have mainly been based on the density dependent pairwise potentials derived from electron-ion pseudopotential with the linear response theory and second order perturbation theory. The statistical mechanics side of the problem has been calculated with perturbation theory integral equations and computer simulations [1–10]. Although a lot of work has been done on both the structure and thermodynamics, still some questions await a definite answer. The limitations of linear response theory based interactions are well known. It is also possible to consider the interactions based on second order perturbation theory as effective pairwise potentials [11, 12]. However, in such case one would expect that a combined study of the structural and thermodynamic consequences of the interaction could illuminate in a quantitative way the relevance of such effective model interactions for the explanation of the physical and chemical properties of the liquid metals. We believe that only a combined analysis of structural and thermodynamic data should be able to assess the quality of any model for the interionic forces. However, only a few studies have been made addressing simultaneously these two problems.

In all these attempts the use of pseudopotential approach is found a remarkable success. But many existing studies have been limited to local model potentials with empirically determined parameters [13–15]. Also it is found in our literature survey [1–50] that some abinitio pseudopotentials suitable for the perturbation theory of the ionic interactions were generated. In general, the pseudopotentials like Ashcroft empty core model (AS) [16–19], Heine-Abarenkov

model (HA) [17, 20, 21], harmonic model potential (HMP) [17, 20, 21], generalized nonlocal model potential (GNMP) [22–24], energy independent nonlocal model potential (EINMP) [25, 26] and so forth. have been applied to study the structure and thermodynamics of liquids.

On the other side of the treatment of the atomic correlations, computer simulation has a precision limited only by numerical errors. However, when focusing on trends of thermodynamic quantities, approximate but reliable theories aimed at modelling the free energy are still very useful tools. The simplest of such method is Gibbs-Bogoliubov (GB) approach [24, 27, 28].

The general idea underlying the GB [24, 27, 28] inequality is that the true Helmholtz free energy of a liquid metal is bounded from above by the free energy of a suitably chosen reference system plus the difference in average potential energy between the actual and the reference system, calculated using the distribution functions of the reference systems. Thus the choice of the reference system is clearly very important. Ideally the basis for choosing the best reference system is that one expects it to give the lowest free energy and the expressions required for the thermodynamic and structure can be expressed possibly in an analytic form. People have applied popular reference system like Percus-Yevick Hard Sphere (PYHS) [23, 29–38], One Component Plasma (OCP) [37–44], Charged Hard Sphere (CHS) [29, 30, 45–48], Hard Sphere Yukawa (HSY) [49, 50], Optimized Random Phase Approximation (ORPA) [24], and Soft Sphere (SS) systems [23].

Thus it is highly desirable to search a better reference system which gives good explanation of various properties when it is used with a particular model potential. Hence proper combination of a model potential and a reference system is one of the basic requirement in explaining various structure and thermodynamics of liquid metals. So, we thought it worthwhile to study the structure and thermodynamics of liquid transition metals using our own model potential using different reference systems.

In the last two decades, the considerable efforts have been made to understand the structure and thermodynamics of several simple liquid metals, liquid transition metals, liquid rare-earth metals, and their alloys [1–50]. The interatomic potentials of simple metals [24, 37–39, 45–49, 51–55] have been fully investigated and their thermodynamic properties could be derived with sufficient accuracy, but in the case of transition metals the hybridization of d electron with s electron makes the things complex. Computer experiments are always intended to propose a plausible interpretation of experimental results in some cases to give the solution to an experimentally inaccessible problem. Despite the success of the theory in the solid state, results for the structure factor of liquid transition metals using molecular dynamics and other complicated liquid state theories have not been so reliable [1–10]. The reliability of the predicted values, however, entirely depends on the validity of a given interatomic potential and the model used. Compare to simple liquid metals only a few attempts are made on liquid transition metals [2–10, 50, 55–58]. Therefore, the present paper deals with the computation of thermodynamical and structural

properties like internal energy (E), entropy (S), Helmholtz free energy (F), isothermal compressibility (χ_T), specific heat (C_V), structure factor $S(q)$, and long wave length limit of structure factor $S(0)$ of 3d liquid transition metals using our newly constructed parameter free model potential [43, 59, 60] with different reference systems like Percus-Yevick Hard Sphere (PYHS) [23, 29–38], One Component Plasma (OCP) [37–44], and Charged Hard Sphere (CHS) [29, 30, 45–48] systems.

An important application of pseudopotential is the calculation of structural properties of disordered materials such as liquid, amorphous, and their alloys. The problem with model pseudopotential is that of their transferability, because still there is no accurate method to obtain the form factor by which all the properties of liquid metals may be successfully investigated. It is found that a particular pseudopotential may be suitable for some properties of some metals and unsuitable for other properties of other metals. The usefulness of any model potential depends on how many number of parameters it involves. Generally, the potential involving less number of parameters is considered to be, comparatively a better one than that involving more number of parameters because it avoids more complexities in the calculation. It has been observed that a unique method of the determination of the potential parameter has not been pointed out so far. A number of investigators have used fitting procedure in which the potential parameters are fitted in such a way that a good agreement with experimental findings is to be obtained. Such a procedure will generally give good results for a certain property, but the same set of parameters will not give good results for other properties. Hence, we thought it worthwhile to construct a parameter free model potential which, by employing, explains the physical as well as chemical properties of condensed matter.

A pseudopotential method employing a simple model of a solid composed of atomic cores and valence electrons can predict the existence and properties of new solids and their properties [61]. By implementing this idea we have constructed a new model potential which is splitted into three regions [43, 59, 60],

$$
W_B(r) = \begin{cases} 0, & r < r_i, \\ -\left(\dfrac{Ze^2}{r_a}\right)\left\{2 - \exp\left(\dfrac{r}{r_a} - 1\right)\right\}, & r_i \leq r \leq r_a, \\ -\left(\dfrac{Ze^2}{r}\right), & r > r_a. \end{cases}
$$

$$(1)$$

Basically, this is the modified version of the Ashcroft's empty core model [62]. Here we have considered actual core of an ion as an empty core rather than pseudizing it. The whole effective region is splitted into three parts. The effective weak potential felt by an electron is sandwiched between empty core and long range coulomb potential which is continuous at $r = r_a$ and is considered between the ionic radius (r_i) and atomic radius (r_a).

In the reciprocal space, the corresponding bare-ion form factor of the present model potential is given by [43, 59, 60]

$$W_B(q) = \frac{-4\pi Z e^2}{q^3 r_a \Omega (1 + q^2 r_a^2)^2} \left[\begin{array}{l} 2(1 + 2q^2 r_a^2) \sin(qr_a) - qr_a(1 + 3q^2 r_a^2) \cos(qr_a) + 2(1 + q^2 r_a^2)^2 \\[4pt] \times \{qr_i \cos(qr_i) - \sin(qr_i)\} - \exp\left(\frac{r_i}{r_a} - 1\right) \\[4pt] \times \left\{ \begin{array}{l} (-2q^3 r_a^3 + q^3 r_a^2 r_i + q^5 r_a^4 r_i) \cos(qr_i) \\[2pt] -(-q^2 r_a^2 + q^4 r_a^4 + q^4 r_a^3 r_i + q^2 r_a r_i) \sin(qr_i) \end{array} \right\} \end{array} \right]. \tag{2}$$

Here Z, e, Ω, q, r_i, and r_a are the valency, electronic charge, atomic volume, wave vector, ionic radius, and atomic radius, respectively. The local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] have been applied to see the influence of exchange and correlation effect on thermodynamical properties of liquid transition metals.

2. Theory

The Helmholtz free energy (F) lies at the heart of the pseudopotential perturbation scheme to calculate the thermodynamical properties of liquid metals. The Helmholtz free energy of the system is defined by the use of the GB inequality as follow:

$$F \le F_0 + \langle H - H^0 \rangle, \tag{3}$$

where F_0 is the Helmholtz free energy (per ion) of the reference system, H and H^0 denote the Hamiltonians of the real and reference system, respectively.

Again,

$$F = E - TS \tag{4}$$

with E, S, and T are internal energy, entropy, and absolute temperature respectively.

The internal energy of reference system is given by

$$E = \frac{3}{2} k_B T + F_1 + F_{EG} + F_{BS} + F_M. \tag{5}$$

F_1 is the first order electronic term arising from the average interaction of the valence electron with noncoulombic part of the bare ion pseudopotential. One has

$$F_1 = \lim_{q \to 0} \left\{ W_B(q) + \frac{4\pi Z}{q^2} \right\} \frac{Z}{\Omega}. \tag{6}$$

F_{EG} is the free energy of the electron gas. One has

$$F_{EG} = NZ \left\{ \frac{3}{10} k_F^2 - \frac{3}{4\pi} k_F - 0.0474 \right. $$
$$\left. - 0.0155 \ln k_F - \frac{1}{12} k_B^2 T^2 N(E_F) \right\}. \tag{7}$$

Here $N(E_F)$ is the density of the states per unit volume at Fermi energy. F_{BS} is the band structure energy and is given in terms of $F_N(q)$, the normalized energy wave number characteristic incorporating exchange and correlation corrections as,

$$F_{BS} = -\frac{z^2}{\pi} \int_0^\infty S(q) F_N(q) dq. \tag{8}$$

Here $S(q)$ is the structure factor of reference system. $F_N(q)$ is the normalized energy wave number characteristic. It is expressed as

$$F_N(q) = \left(\frac{q^2}{4\pi Z^2 e^2}\right)^2 \left[1 - \frac{1}{\varepsilon(q)}\right] \left[\frac{1}{1 - f(q)}\right] |W_B(q)|^2. \tag{9}$$

Here $\varepsilon(q)$ is called the modified dielectric function. It includes exchange and correlation effect in the screening through local field correction function $f(q)$. $W_B(q)$ is the unscreened form factor. It depends on the core-ion pseudopotential and hence allows us to investigate its effect on the thermodynamics function. Here $\varepsilon(q)$ is the modified Hartree dielectric screening function which takes into account the conduction electron interaction

$$\varepsilon(q) = 1 + [1 + \varepsilon_H(q)][1 - f(q)] \tag{10}$$

$\varepsilon_H(q)$ is the static dielectric function and $f(q)$ is the correction factor for the exchange and correlated motion of the conduction electrons. F_M is the Madelung energy and it can be written as follows.

For PYHS systems

$$F_M = \frac{Z^2 \pi \sigma^2}{(1 + 2\eta)\Omega} \left(1 - \frac{\eta}{5} + \frac{\eta^2}{10}\right). \tag{11}$$

For OCP system

$$F_M = k_B t \left(\frac{\Gamma^* - \Gamma}{\Gamma}\right) \left(A\Gamma + B\Gamma^{1/4} + B\Gamma^{-1/4} + D\right). \tag{12}$$

The constants A, B, C, and D are -0.89752, 0.94544, 0.17954, and -0.80049, respectively. Γ^* is effective plasma parameter, $\Gamma^* = Z^2 e^2 \beta / r_s$, r_s is the radius of the atomic sphere, $r_s = (3\Omega/4\pi)^3$. $\beta = k_B t$, where k_B and t are Boltzmann constant and absolute temperature, respectively.

For CHS systems

$$F_M = k_B t \left(\frac{\Gamma^* - \Gamma}{2\eta^{1/3}}\right)$$
$$\times \left(1 + \eta - \frac{\eta^2}{5} - \frac{1 + 2\eta}{k}\left\{\sqrt{1 + 2k\xi} - 1\right\}\right), \tag{13}$$

where $\zeta = (1 - \eta)^3/(1 + 2\eta)^2$ and $k = (12\eta^{2/3}\Gamma)^{1/2}$.

TABLE 1: The input parameters used in the present computations.

Metal	Z	T (K) [65, 66]	Density n (gm/cm³) [65, 66]	r_i (Å)	r_a (Å)
Sc	1.50	1833	2.92	0.81	1.61
Ti	1.50	1973	4.15	0.68	1.45
V	1.50	2173	5.36	0.59	1.31
Cr	1.50	2173	6.26	0.64	1.25
Mn	1.50	1533	5.96	0.80	1.37
Fe	1.50	1823	7.00	0.64	1.24
Co	1.50	1823	7.71	0.74	1.25
Ni	1.50	1773	7.71	0.72	1.25
Cu	1.50	1423	7.96	0.72	1.28

The computation of the entropy is more straight forward and computed using $S = S_{\text{gas}} + S_{\text{elec}} + S_i$ with,

$$S_{\text{gas}} = \frac{5}{2}k_B + k_B \ln\left\{\Omega\left(\frac{k_B T}{4\pi}\right)^{1/2}\right\}, \qquad S_{\text{elec}} = \left(\frac{\pi^2 k_B^2 T}{k_F^2}\right), \tag{14}$$

where S_i term represents the contribution from the different reference system.

For PYHS system

$$S_{\text{PYHS}} = \frac{k_B \eta (3\eta - 4)}{(1-\eta)^2}. \tag{15}$$

For OCP system

$$S_{\text{OCP}} = -3B\Gamma^{1/4} + 5C\Gamma^{-1/4} - D\ln\Gamma \\ + D[A + 4(B - C)] + 0.420. \tag{16}$$

For CHS system

$$S_{\text{CHS}} = \frac{(1+2\eta)k_B}{72\xi\eta} \\ \times \left\{3k\xi\left[\sqrt{1+2k\zeta}+1\right] - 2\left[(1+2k\zeta)^{3/2}-1\right]\right\} \\ - k_B\left[\frac{6\eta}{1-\eta} + 2\ln(1-\eta)\right]. \tag{17}$$

For a given number density ρ, packing fraction η (HS, CHS, and SS reference systems) and plasma parameter Γ (OCP reference system) are varied to obtain a minimum variational upper bound for the Helmholtz free energy (F).

The long wave length limit of structure factor $S(q)$ is defined as follows.

For PYHS

$$S(0) = \frac{(1-\eta)^4}{(1+2\eta)^2}. \tag{18}$$

For OCP system

$$S(0) = \lim_{q \to 0} S(q)$$

$$= \left[1 - \frac{\Gamma}{20\alpha_2^2}(5\alpha_2^4 + \alpha_1^4) \\ + 4\pi Z^2 e^2 \beta\rho \left\{ \begin{array}{l} \frac{5}{3}r_a^2 + \frac{4}{3}\frac{r_i^3}{r_a} \\ -2\exp\left(\frac{r_i}{r_a}-1\right) \\ \times(2r_a^2 - 2r_a r_i + r_i^2) \\ + \frac{\pi}{4k_F} - \frac{\gamma_0}{k_F^2} \end{array} \right\} \right]^{-1}. \tag{19}$$

For CHS system

$$S(0) = \lim_{q \to 0} S(q)$$

$$= \left[4\pi\rho a\Gamma \left\{ \begin{array}{l} \frac{5}{3}r_a^2 + \frac{4}{3}\frac{r_i^3}{r_a} \\ -2\exp\left(\frac{r_i}{r_a}-1\right) \\ \times(2r_a^2 - 2r_a r_i + r_i^2) \\ - \frac{\sigma^2(\alpha-1)}{12\eta^{2/3}\Gamma} + \frac{\pi}{4k_F} + \frac{\gamma_0}{k_F^2} \end{array} \right\} \right]^{-1}. \tag{20}$$

The isothermal compressibility χ_T and specific heat C_V at constant volume can be expressed as

$$\chi_T = \frac{S(0)}{\rho k_B T}, \qquad \frac{C_V}{k_B} = \frac{t}{k_B}\frac{\partial S}{\partial t}. \tag{21}$$

3. Results and Discussion

The thermodynamical variational properties of 3d series of liquid transition metals elements have been investigated without any adjustable parameter. Table 1 represents the input parameters used in the present computation. Self-consistent calculations by Moriarty [73] indicate that elements whose properties are affected by d bands, the valency

TABLE 2: Calculated variational parameter (packing fraction η and plasma parameter Γ) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of 3d liquid transition metals.

Metal	$S(q)$	Packing fraction (η)					Plasma parameter (Γ)			
		HR [63]	TR [64]	SR [65]	Others [34, 45, 48, 50]	Expt. [67]	HR [63]	TR [64]	SR [65]	Others [44, 45, 56]
Sc	PYHS	0.4395	0.4295	0.4292	0.353, 0.330, 0.325, 0.430	0.43	66	68	68	—
	CHS	0.4302	0.4294	0.4299						
Ti	PYHS	0.4323	0.4317	0.4314	0.415, 0.415, 0.418, 0.362	0.44	70	72	72	110, 105
	CHS	0.4330	0.4348	0.4337						
V	PYHS	0.4442	0.4338	0.4335	0.418, 0.420, 0.425, 0.374	0.44	64	64	64	110, 105
	CHS	0.4312	0.4291	0.4316						
Cr	PYHS	0.4406	0.4389	0.4394	0.443, 0.445, 0.445, 0.380	0.45	68	68	66	110, 105
	CHS	0.4347	0.4365	0.4349						
Mn	PYHS	0.4662	0.4665	0.4658	0.500, 0.508, 0.515, 0.404	0.45	96	96	96	110, 105
	CHS	0.4648	0.4619	0.4630						
Fe	PYHS	0.4551	0.4549	0.4553	0.435, 0.430, 0.389, 0.411	0.44	86	86	88	110, 105
	CHS	0.4585	0.4581	0.4569						
Co	PYHS	0.4547	0.4548	0.4540	0.420, 0.405, 0.400, 0.370	0.45	74	74	72	110, 105
	CHS	0.4582	0.4606	0.4630						
Ni	PYHS	0.4572	0.4562	0.4566	0.405, 0.380, 0.373, 0.351	0.45	88	88	88	110, 105
	CHS	0.4614	0.4631	0.4619						
Cu	PYHS	0.4764	0.4766	0.4758	0.418, 0.383, 0.370, 0.450	0.46	106	106	106	—
	CHS	0.4842	0.4840	0.4845						

(Z) lie in a narrow range $1.1 < Z < 1.7$. By implementing this concept, we have taken $Z = 1.5$ for 3d liquid transition metals, respectively. Therefore the number of d electrons, which do not participate to conduction, is fixed since $Z_s + Z_d$ is constant. We have displaced in Table 2 the values of the variational parameter with Hartree (HR) [63], Taylor (TR) [64] and Sarkar et al. (SR) [65] local field correction functions using Percus-Yevick Hard Sphere (PYHS) [23, 29–38], One Component Plasma (OCP) [37–44], and Charged Hard Sphere (CHS) [29, 30, 45–48] reference systems for 3d liquid transition metals. The present results of variational parameter η are quite good in agreement with experimental data [67] as well as other theoretical data [36, 45, 48, 50] whereas in the case of plasma parameter (Γ) the experimental data is not available, but with other theoretical data [44, 45, 56] it is reasonable because we have taken actual plasma parameter (Γ) rather than fitting it as done by others [45]. We have noticed that the effect of local field correction function on variational parameters (η and Γ) is very small. It is also found that the largest values of variational parameter (η and Γ) are obtained when the d band is filled to a large extent, while lowest values are obtained when the d band is nearly empty in the case of 3d liquid transition metal. This is clearly related to the strongest bonding which occurs when only the bonding but not the antibonding states are occupied. Figure 1 represents the variational parameters (η and Γ) with Hartree (HR) [63] local field correction for 3d liquid transition metals using different reference systems.

Figure 2 represents the Helmholtz free energy versus variational parameter of Cu liquid transition metals due
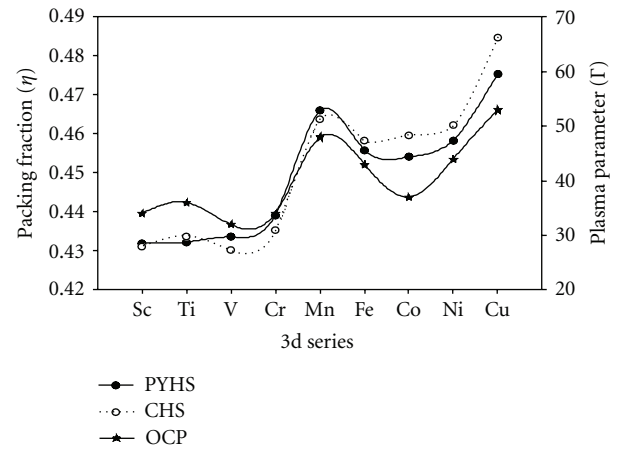

FIGURE 1: Packing fraction (η) and plasma parameter (Γ) obtained from the variational method for 3d liquid transition metals.

to Sarkar et al. (SR) [65] local field correction function. The OCP system gives the lowest Helmholtz free energy compared to other reference systems. Figure 2 represents Helmholtz free energy versus variational parameter of liquid Cu for different local field correction function due to CHS system, which indicates that Taylor (TR) [64] local field correction function gives the lowest Helmholtz free energy, while Hartree (HR) [63] gives maximum Helmholtz free energy.
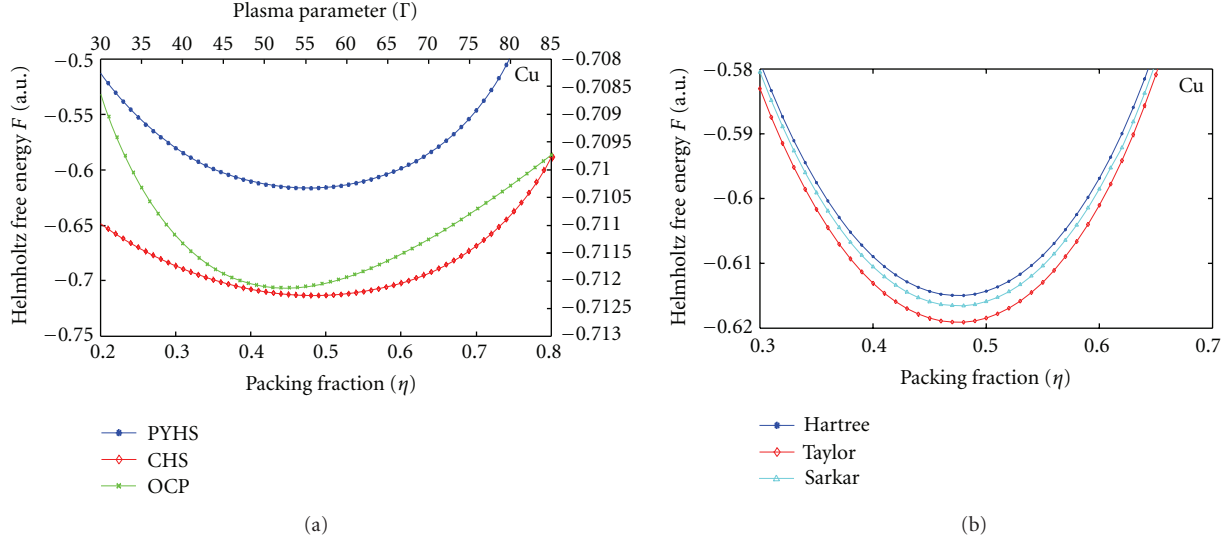
(a)

(b)

FIGURE 2: Helmhotz free energy versus variational parameters (packing fraction (η) and Plasma parameter (Γ)) for different reference systems due to Sarkar et al. (SR) [65] local field correction function and for different local field correction function due to CHS system of Cu liquid metals.
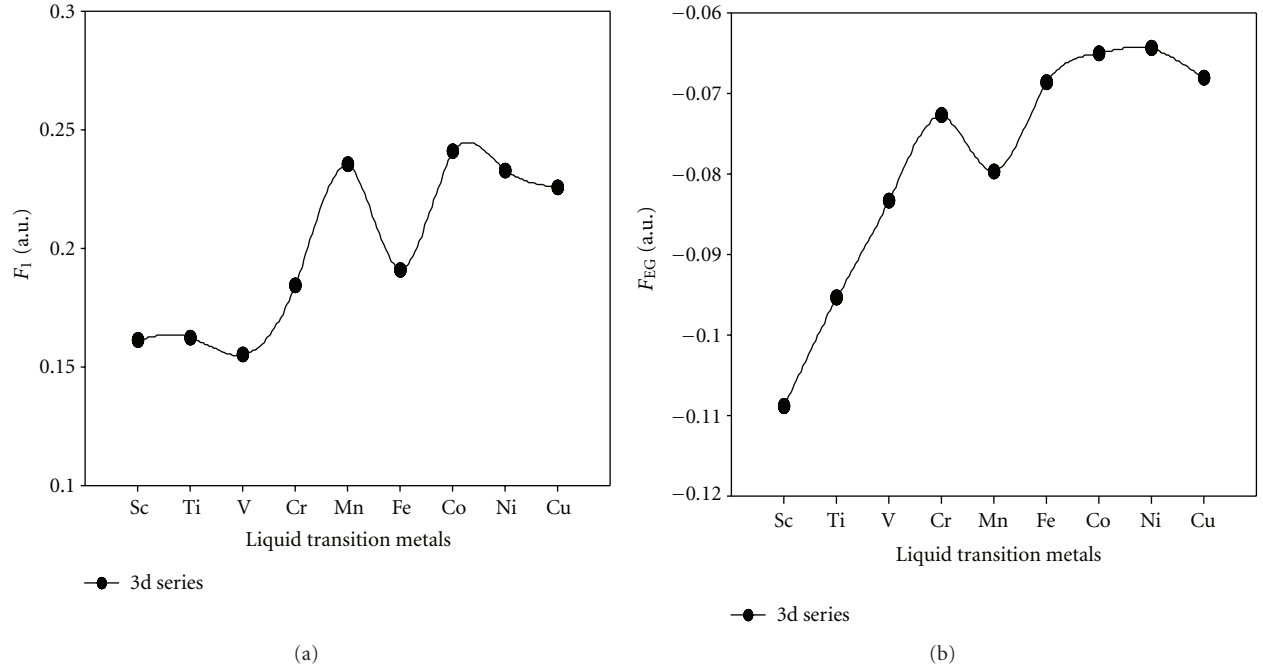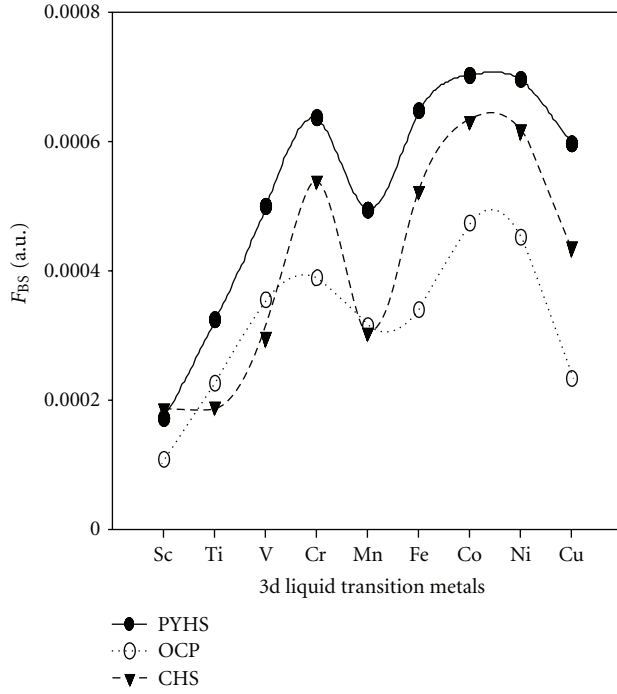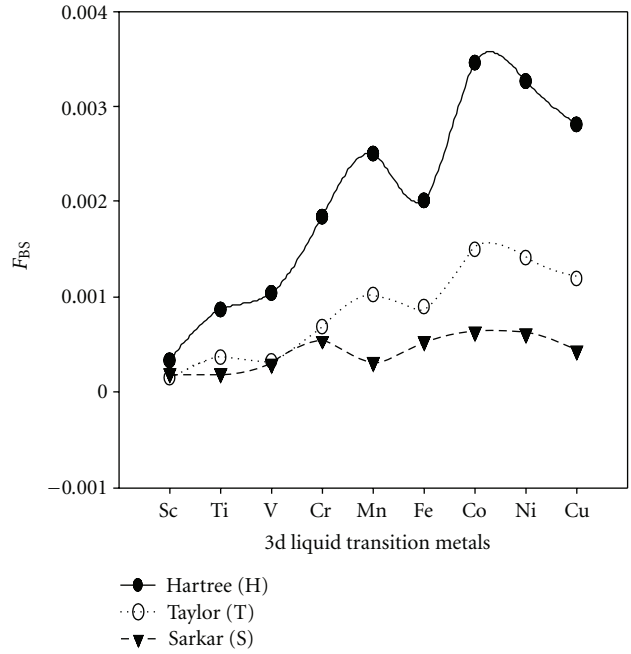

(a)

(b)

FIGURE 3: Calculated first order electronic energy (F_1) and free energy of the electron gas (F_{EG}) of liquid transition metals.

Figure 3 shows calculated F_1 and F_{EG} terms of 3d liquid transition metals. F_1 and F_{EG} terms are independent of the reference system and influence of local field correction function so that they remain constant for each system. Figure 4 represents Band structure energy F_{BS} and the effect of local field correction on F_{BS} term of 3d liquid transition metals. F_{BS} depends upon both reference system and local field correction functions. The OCP system gives the lowest

value of Band structure energy. The maximum value of F_{BS} is obtained for 3d series for liquid Co. The deviation of local field correction on F_B is going on increasing from Sc to Cu as the d shell is going to fill up (or atomic number is going on increasing). The Taylor (TR) [64] shows less deviation of F_{BS} while Sarkar et al. (SR) [65] shows much deviation from Hartree (HR) [63] for CHS system. Figure 5 represents calculated value of Madelung energy F_M term

FIGURE 4: Calculated band structure energy (F_{BS}) of 3d liquid transition metals for different reference system with Sarkar et al. (SR) [65] local field correction function and for different local field correction functions along with charged hard sphere (CHS) reference system.
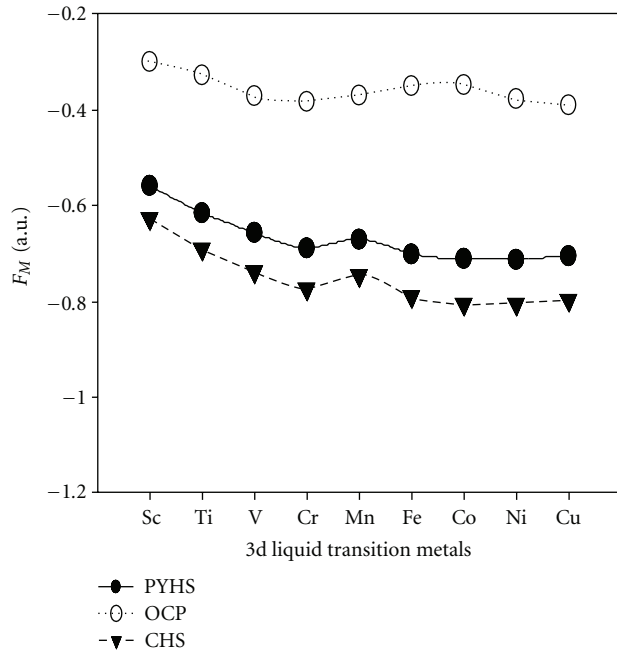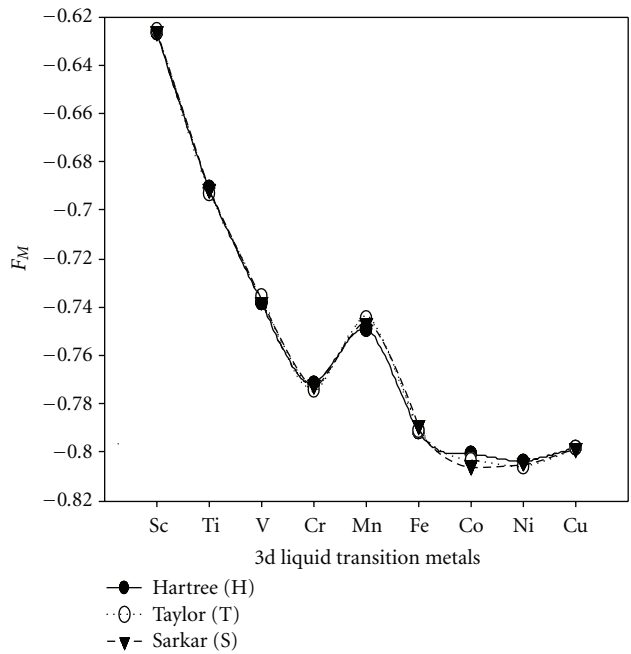

FIGURE 5: Calculated Madelung energy (F_M) of 3d liquid transition metals for different reference system with Sarkar et al. (SR) [65] local field correction function and for different local field correction functions along with charged hard sphere (CHS) reference system.

TABLE 3: Calculated internal energy (E) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of 3d liquid transition metals.

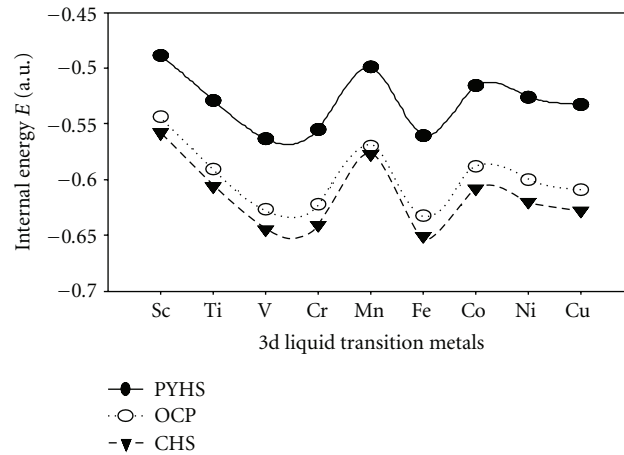| Metal	$S(q)$	Internal energy (E) in au			
		HR [63]	TR [64]	SR [65]	Other [10, 35]
Sc	PYHS	−0.4897	−0.4887	−0.4886	
	OCP	−0.5433	−0.5437	−0.5436	−0.7180
	CHS	−0.5570	−0.5548	−0.5580	
Ti	PYHS	−0.5286	−0.5299	−0.5290	
	OCP	−0.5906	−0.5909	−0.5906	−0.7247, −0.6593
	CHS	−0.6053	−0.6064	−0.6063	
V	PYHS	−0.5653	−0.5645	−0.5634	
	OCP	−0.6268	−0.6271	−0.6267	−0.7638, −0.7193
	CHS	−0.6458	−0.6439	−0.6445	
Cr	PYHS	−0.5544	−0.5570	−0.5550	
	OCP	−0.6219	−0.6223	−0.6221	−0.7841, −0.7162
	CHS	−0.6397	−0.6409	−0.6408	
Mn	PYHS	−0.4976	−0.5010	−0.4989	
	OCP	−0.5699	−0.5702	−0.5700	−0.7305, −0.6717
	CHS	−0.5790	−0.5781	−0.5772	
Fe	PYHS	−0.5594	−0.5627	−0.5606	
	OCP	−0.6313	−0.6349	−0.6324	−0.7284, −0.7088
	CHS	−0.6501	−0.6528	−0.6508	
Co	PYHS	−0.5138	−0.5187	−0.5156	
	OCP	−0.4866	−0.4865	−0.4867	−0.6649, −0.7134
	CHS	−0.6042	−0.6114	−0.6078	
Ni	PYHS	−0.5241	−0.5289	−0.5261	
	OCP	−0.5983	−0.6031	−0.6001	−0.7971, −0.7257, −0.812
	CHS	−0.6190	−0.6198	−0.6200	
Cu	PYHS	−0.5312	−0.5353	−0.5327	
	OCP	−0.6088	−0.6094	−0.6091	−0.3779
	CHS	−0.6273	−0.6281	−0.6281	

FIGURE 6: Calculated internal energy (E) of 3d liquid transition metals for different reference system with Sarkar et al. (SR) [65] local field correction function.

TABLE 4: Calculated entropy (S/k_B) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of liquid transition metals.

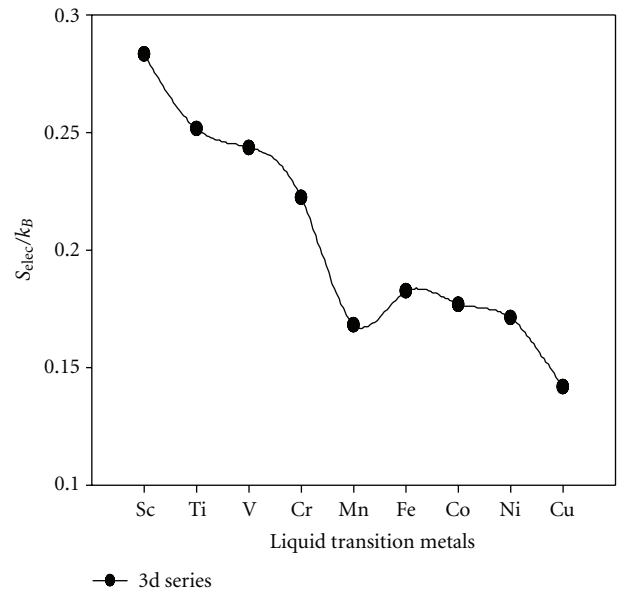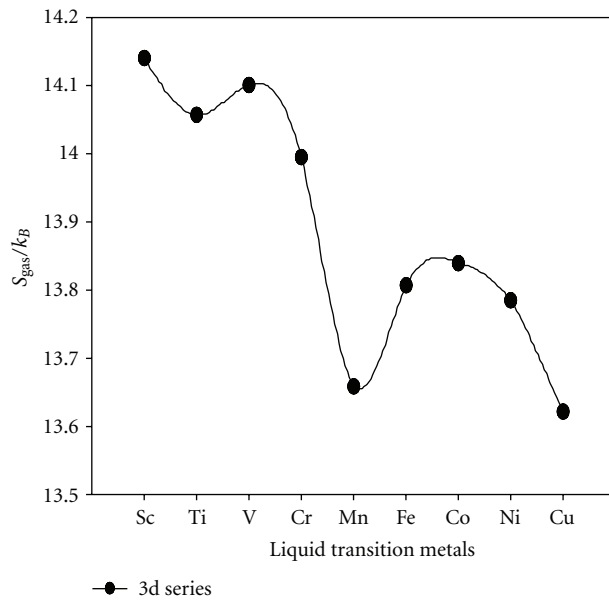| Metal	$S(q)$	Entropy (S/k_B) in au				
		HR [63]	TR [64]	SR [65]	Other [8, 10, 35, 45, 56]	Expt. [50, 68]
Sc	PYHS	10.67	10.85	10.81		
	OCP	12.75	12.72	12.72	11.48,11.56, 11.87	12.05
	CHS	11.02	11.04	11.00		
Ti	PYHS	10.68	10.67	10.68		
	OCP	12.44	12.41	12.41	12.42, 12.04, 11.28, 11.55, 11.06	12.01
	CHS	10.86	10.85	10.85		
V	PYHS	10.51	10.70	10.70		
	OCP	12.57	12.57	12.57	12.15, 12.06, 11.35, 11.61, 11.24	12.08
	CHS	10.92	10.95	10.94		
Cr	PYHS	10.45	10.47	10.47		
	OCP	12.38	12.41	12.38	12.00, 11.94, 11.13, 11.34, 10.95	11.58
	CHS	10.74	10.73	10.73		
Mn	PYHS	9.57	9.58	9.58		
	OCP	11.62	11.62	11.62	11.14, 11.37, 10.65, 10.87, 10.41	12.05
	CHS	9.86	9.87	9.88		
Fe	PYHS	9.95	9.94	9.94		
	OCP	11.90	11.88	11.90	11.93, 11.84, 11.11, 11.39, 10.98	12.11
	CHS	10.14	10.15	10.14		
Co	PYHS	9.99	9.98	10.00		
	OCP	12.09	12.12	12.09	12.44, 11.98, 11.19, 11.49, 10.98	12.08
	CHS	10.17	10.14	10.14		
Ni	PYHS	9.88	9.87	9.86		
	OCP	11.85	11.85	11.85	12.76, 12.06, 11.27, 11.56, 11.08, 11.21	11.69
	CHS	10.05	10.04	10.04		
Cu	PYHS	9.30	9.31	9.32		
	OCP	11.44	11.44	11.44	12.06, 11.08, 10.04, 10.26, 9.68, 10.21	10.27
	CHS	9.45	9.45	9.45		

(a)

(b)

FIGURE 7: Calculated S_{gas} and S_{elec} of liquid transition metals.

TABLE 5: Calculated Helmholtz free energy (F) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of liquid transition metals.

Metal	$S(q)$	Helmholtz free energy (F) in au			
		HR [63]	TR [64]	SR [65]	Others [24, 34, 50]
Sc	PYHS	−0.6136	−0.6145	−0.6140	
	OCP	−0.6913	−0.6914	−0.6913	−0.735, −0.755, −0.756
	CHS	−0.6848	−0.6830	−0.6857	
Ti	PYHS	−0.6620	−0.6632	−0.6624	
	OCP	−0.7460	−0.7460	−0.7457	−0.704, −0.730, −0.734, −0.733, −0.731
	CHS	−0.7409	−0.7419	−0.7418	
V	PYHS	−0.7098	−0.7117	−0.7106	
	OCP	−0.7997	−0.8000	−0.7996	−0.765, −0.798, −0.803, −0.768, −0.765
	CHS	−0.7961	−0.7945	−0.7950	
Cr	PYHS	−0.6982	−0.7011	−0.6992	
	OCP	−0.7922	−0.7931	−0.7924	−0.757, −0.794, −0.799, −0.786, −0.783
	CHS	−0.7875	−0.7886	−0.7885	
Mn	PYHS	−0.5905	−0.5940	−0.5919	
	OCP	−0.6827	−0.6830	−0.6828	−0.686, −0.721, −0.726, −0.736, −0.735
	CHS	−0.6747	−0.6739	−0.6732	
Fe	PYHS	−0.6749	−0.6781	−0.6760	
	OCP	−0.7695	−0.7728	−0.7706	−0.743, −0.776, −0.778, −0.755, −0.754
	CHS	−0.7678	−0.7706	−0.7684	
Co	PYHS	−0.6290	−0.6340	−0.6310	
	OCP	−0.6262	−0.6264	−0.6263	−0.752, −0.785, −0.785, −0.757, −0.756
	CHS	−0.7215	−0.7284	−0.7249	
Ni	PYHS	−0.6350	−0.6397	−0.6368	
	OCP	−0.7313	−0.7361	−0.7331	−0.756, −0.790, −0.791, −0.751, −0.750
	CHS	−0.7318	−0.7325	−0.7327	
Cu	PYHS	−0.6150	−0.6192	−0.6166	
	OCP	−0.7119	−0.7125	−0.7121	−0.746, −0.780, −0.783, −0.730, −0.726
	CHS	−0.7125	−0.7132	−0.7132	

and effect of local field correction functions on 3d liquid transition metals for CHS system. The CHS system gives the lowest value of F_M term while OCP system gives the highest values of F_M term for liquid transition metals. From Figure 5, it is clear that F_M term is not much sensitive to the choice of local field correction function. The calculated value of internal energy (E) of 3d liquid transition metals is tabulated in Table 3 along with other available data [10, 35] and also plotted in Figure 6 for Sarkar et al. (SR) [65] local field correction function. From these, it is clear that CHS system gives a lower internal energy (E) compares to other systems for all liquid transition metals. It is also noticed that the value of internal energy has not been much affected by the influence of local field correction functions. The F_M and F_{EG} give negative contribution to internal energy (E) while F_1 and F_{BS} give positive contribution to internal energy (E). F_1 term includes the electron-ion interaction through model potential. In this calculation major contribution comes from the term F_M while contribution of F_{BS} is very small.

The calculated entropy of liquid transition metals is presented in Table 4. The minimum numerical values have been obtained due to the PYHS system while the maximum due to the OCP system. From the present results, we have observed that the OCP system gives excellent agreement with present results and experimental data [50, 68] for entropy compared to other reference system for 3d liquid transition metals (except Cu). A good agreement has been found with experimental data [50, 68] for liquid Ti, V, and Mn due to Sarkar et al. (SR) [65] local field correction function for OCP system while for liquid Fe, Co, and Ni due to Hartree (HR) [63] local field correction function for OCP system. The different contributions of entropy (S), are plotted in Figures 7–9 along with Sarkar et al. (SR) [65] local field correction function of 3d liquid transition metals.

TABLE 6: Calculated long wave length limit of structure factor $S(0)$ due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of 3d liquid transition metals.

Metal	$S(q)$	Long wave length limit of structure factor $S(0)$				
		HR [63]	TR [64]	SR [65]	Other [69, 70]	Expt. [71, 72]
Sc	PYHS	0.0280	0.0307	0.0300		
	OCP	0.0252	0.0362	0.0340	—	0.036
	CHS	0.0346	0.0349	0.0341		
Ti	PYHS	0.0299	0.0297	0.0299		
	OCP	0.0264	0.0386	0.0363	0.0226, 0.0236, 0.0228	0.020
	CHS	0.0337	0.0331	0.0332		
V	PYHS	0.0268	0.0295	0.0295		
	OCP	0.0283	0.0410	0.0387	0.0234, 0.0243, 0.0236	0.025
	CHS	0.0342	0.0344	0.0343		
Cr	PYHS	0.0277	0.0280	0.0281		
	OCP	0.0236	0.0316	0.0308	0.0205, 0.0212, 0.0207	0.021
	CHS	0.0329	0.0325	0.0325		
Mn	PYHS	0.0217	0.0218	0.0218		
	OCP	0.0136	0.0173	0.0167	0.0231, 0.0242, 0.0233	0.024
	CHS	0.0245	0.0244	0.0245		
Fe	PYHS	0.0242	0.0240	0.0240		
	OCP	0.0197	0.0273	0.0257	0.0202, 0.0210, 0.0204	0.020
	CHS	0.0265	0.0265	0.0264		
Co	PYHS	0.0243	0.0242	0.0244		
	OCP	0.0146	0.0180	0.0177	0.0199, 0.0207, 0.0201	0.019
	CHS	0.0264	0.0257	0.0259		
Ni	PYHS	0.0237	0.0236	0.0234		
	OCP	0.0154	0.0197	0.0191	0.0199, 0.0207, 0.0201	0.020
	CHS	0.0256	0.0253	0.0253		
Cu	PYHS	0.0197	0.0198	0.0199		
	OCP	0.0128	0.0165	0.0159	0.0172, 0.0179, 0.0173	0.018
	CHS	0.0207	0.0205	0.0205		

Among three contributions, only S_i depends on structure and potential terms while S_{gas} and S_{elec} depend only on density and are independent of reference system and local field correction functions. The numerical value of S_{gas} is much larger than S_i. The S_{gas} increases the absolute value of entropy whereas S_i tends to decrease the total entropy of system. From Figures 7–9, it is clear that PYHS system gives the lowest value of S_i term while OCP system gives the highest numerical value of S_i term of liquid transition metals. It is also noticed that S_i term is not much sensitive to the use of different local field correction function. We have compared our results with available theoretical data [10, 35]. The minimum numerical values of entropy (S) have been obtained due to the PYHS system while the maximum due to the OCP system.

Table 5 represents Helmholtz free energy of 3d liquid transition metals. Figure 10 represents calculated Helmholtz free energy F of 3d liquid transition metals due to Sarkar et al.

(SR) [65] local field correction function. The OCP system gives minimum Helmholtz free energy compared to other reference system for liquid transition metals (except Co and Cu). For Co and Cu, the CHS system gives the minimum Helmholtz free energy. The values of Helmholtz free energy have not been much affected by the influence of local field correction functions. Hence we say that structure and potential are responsible to lower the free energy of the system. Therefore OCP and CHS systems show a lower Helmholtz free energy than PYHS. Among them OCP gives a lower Helmholtz free energy than other systems.

In our previous [60] attempt, we have thermodynamical properties like entropy (S), internal energy (E), and Helmholtz free energy (F) of 3d liquid transition metals using variational principle based on the Gibbs-Bogolyubov inequality with Percus-Yevick hard sphere reference system. But, here we have used three different reference systems
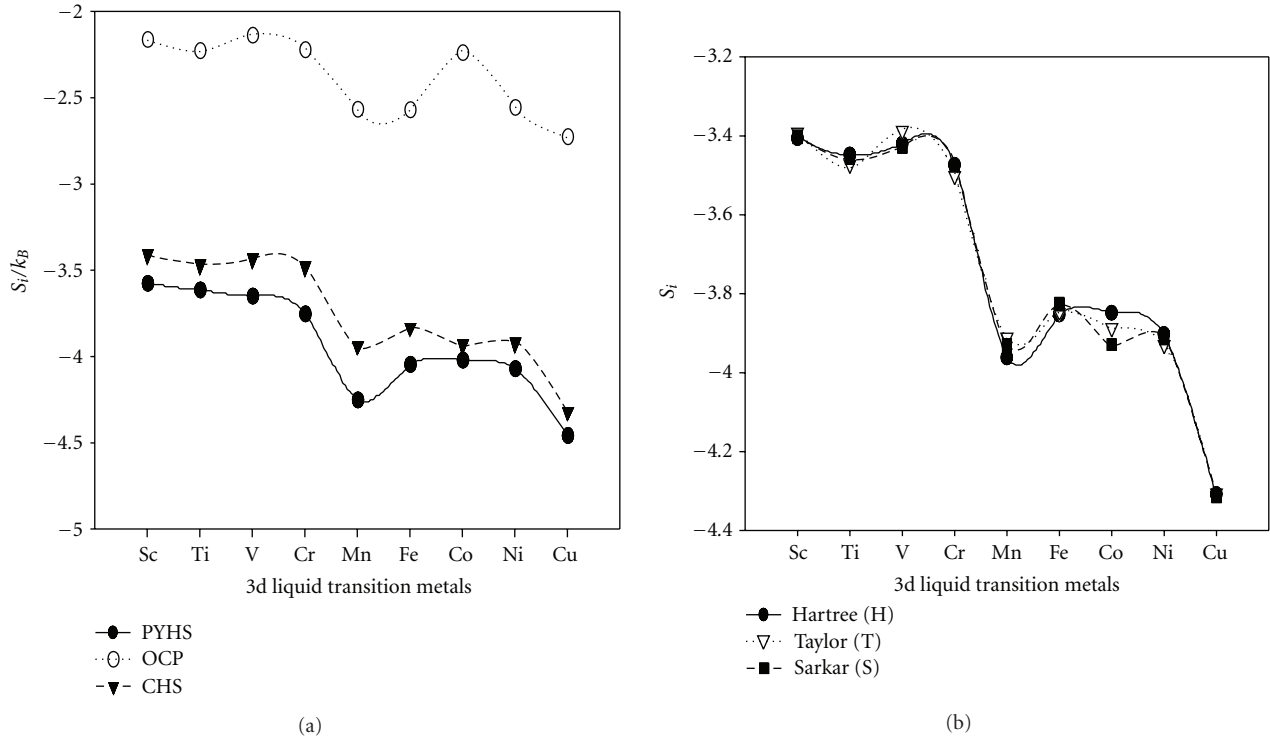
(a)

(b)

FIGURE 8: Calculated S_i of 3d liquid transition metals for different reference systems with Sarkar et al. (SR) [65] local field correction function and for charged hard sphere (CHS) reference systems with different local field correction functions.

TABLE 7: Calculated isothermal compressibility (χ_T) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of 3d liquid transition metals.

Metal	$S(q)$	Isothermal compressibility $\chi_T \times 10^{-12}$ cm²/dyne				
		HR [63]	TR [64]	SR [65]	Others [45]	Expt. [45, 71]
Sc	PYHS	2.83	3.10	3.03		
	OCP	2.55	3.66	3.44	2.25, 2.31, 1.91	3.64
	CHS	3.50	3.53	3.45		
Ti	PYHS	2.10	2.09	2.11		
	OCP	1.86	2.72	2.56	1.56, 1.28	1.48, 1.40
	CHS	2.37	2.33	2.34		
V	PYHS	1.41	1.56	1.55		
	OCP	1.49	2.16	2.04	1.25, 1.23, 1.01	1.10, 1.31
	CHS	1.80	1.81	1.80		
Cr	PYHS	1.27	1.29	1.29		
	OCP	1.09	1.45	1.41	1.07, 1.01, 0.82	1.06, 1.10
	CHS	1.51	1.49	1.49		
Mn	PYHS	1.57	1.57	1.57		
	OCP	0.98	1.25	1.21	1.63, 1.52, 1.23	1.73
	CHS	1.77	1.76	1.77		
Fe	PYHS	1.26	1.26	1.26		
	OCP	1.03	1.43	1.34	1.29, 1.26, 1.02	1.04, 1.05
	CHS	1.38	1.38	1.38		
Co	PYHS	1.23	1.23	1.23		
	OCP	0.74	0.91	0.89	1.29, 1.23, 0.98	0.97, 0.96
	CHS	1.33	1.30	1.31		
Ni	PYHS	1.22	1.22	1.21		
	OCP	0.80	1.02	0.99	1.21, 1.26, 1.00	0.98, 1.03
	CHS	1.32	1.31	1.30		
Cu	PYHS	1.33	1.34	1.34		
	OCP	0.86	1.11	1.07	1.58	1.51, 1.45
	CHS	1.39	1.38	1.38		

TABLE 8: Calculated specific heat (C_V/k_B) due to different local field correction functions like Hartree (HR) [63], Taylor (TR) [64], and Sarkar et al. (SR) [65] of 3d liquid transition metals.

Metal	$S(q)$	Specific heat (C_V/k_B)				
		HR [63]	TR [64]	SR [65]	Others [45]	Expt. [45]
Sc	PYHS	3.63	3.55	3.57		
	OCP	2.78	2.79	2.79	3.72, 3.91, 4.75	4.39
	CHS	3.84	3.80	3.83		
Ti	PYHS	3.57	3.58	3.57		
	OCP	2.77	2.79	2.79	3.56, 3.85, 4.90	3.53
	CHS	3.86	3.84	3.85		
V	PYHS	3.67	3.58	3.58		
	OCP	2.73	2.73	2.73	3.59, 3.87, 5.17	4.15
	CHS	3.84	3.80	3.81		
Cr	PYHS	3.64	3.63	3.62		
	OCP	2.74	2.72	2.74	3.46, 3.88, 5.26	3.90
	CHS	3.85	3.84	3.84		
Mn	PYHS	3.86	3.85	3.85		
	OCP	2.82	2.82	2.82	3.27, 3.75, 4.33	4.56
	CHS	4.11	4.07	4.07		
Fe	PYHS	3.76	3.76	3.76		
	OCP	2.79	2.80	2.79	3.63, 3.94, 4.84	4.38
	CHS	4.09	4.06	4.07		
Co	PYHS	3.75	3.75	3.75		
	OCP	2.72	2.71	2.72	3.61. 4.01, 4.93	4.00
	CHS	4.07	4.07	4.07		
Ni	PYHS	3.78	3.78	3.79		
	OCP	2.79	2.79	2.79	3.76, 4.13, 4.99	4.46
	CHS	4.10	4.09	4.10		
Cu	PYHS	3.95	3.95	3.94		
	OCP	2.84	2.84	2.84	2.67, 3.18, 3.58	3.04
	CHS	4.36	4.35	4.36		

like Percus-Yevick Hard Sphere (PYHS) [23, 29–38], One Component Plasma (OCP) [37–44], and Charged Hard Sphere (CHS) [29, 30, 45–48]. Our present results for thermodynamical properties are improved compared to our previous attempt [60]. Thus in present investigation, we have seen the influence of structure factor $S(q)$ and different local field correction functions on thermodynamical and structural properties of 3d liquid transition metals. It plays much more crucial role in the study of thermodynamical and structural properties of 3d liquid transition metals compare to our previous studies [60].

The structure factor $S(q)$ obtained from the variational parameter (η and Γ) is illustrated in Figure 11. It is observed that in most of the cases overestimated the magnitude of the first peak, although in those cases the locations of the maxima and minima are reasonable predicted. We have explained the slight overestimation of our $S(q)$ value when compared with experiment in cases where they occur, as being that in those cases where η is greater than 0.45 (which is

the value expected from liquid state theory). The implication of this is that effective hard sphere diameter is too large and by interference, the repulsive part of the pair potential in polyvalent metals extends too far [30]. CHS systems gives better results for structure factor $S(q)$ compared to OCP system. OCP system gives much high peak in the structure factor compare to CHS system.

Table 6 represents calculated long wave length limit of structure factor $S(0)$ of 3d liquid transition metals using our obtained variation parameters. The present results of long wave length limit $S(0)$ is also compared with available experimental [71, 72] as well as other data [69, 70]. The present results are in a good agreement with available experimental data [71, 72] for Ti, V, Cr, Fe, and Cu liquid metals due to PYHS system, whereas for Sc and Mn due to CHS system and for Co and Ni liquid metals it is due to OCP system. Tables 7 and 8 show the calculated isothermal compressibility, (χ_T) and specific heat (C_V) of 3d liquid transition metals, respectively, along with available
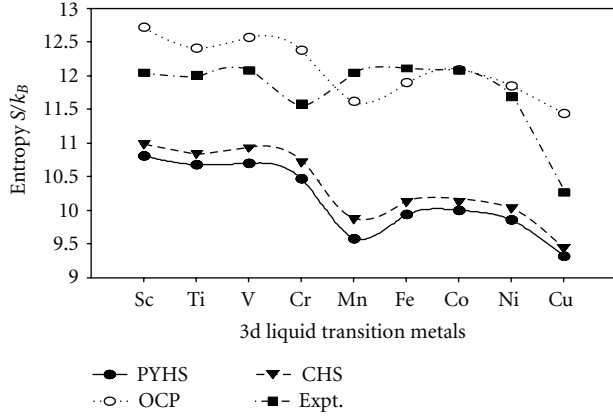
FIGURE 9: Calculated Entropy (*S*) of 3d liquid transition metals for different reference systems with Sarkar et al. (SR) [65] local field correction function.
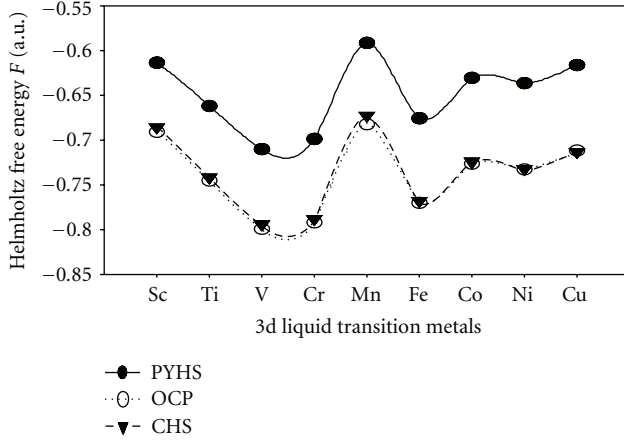

FIGURE 10: Calculated Hemlholtz free energy (*F*) of 3d liquid transition metals for different reference systems with Sarkar et al. (SR) [65] local field correction function.

FIGURE 11: Structure factor $S(q)$ of 3d liquid transition metals for Sarkar et al. (SR) [65] local field correction function.

experimental data [45, 71] and other theoretical data [45]. The good agreement with available experimental data [45, 71] has been obtained for isothermal compressibility (χ_T) due to CHS for Mn and Cu liquid metals, OCP for Sc, Co, and Ni liquid metals and PYHS for V and Cr liquid metals. It is found that good agreement with available experimental data [45] have been achieved for specific heat (C_V) of Sc, V, Cr, Fe, Co, Ni liquid metals due to CHS system, whereas for Ti and Cu liquid metals it is due to PYHS and OCP systems respectively. So that overall CHS system is best suitable for calculating structural and thermodynamical properties of liquid transition metals along with our model potential compared to other reference system. This combination can be used to calculate other properties like electronic, magnetic, transport, and vibrational properties of liquid metals.
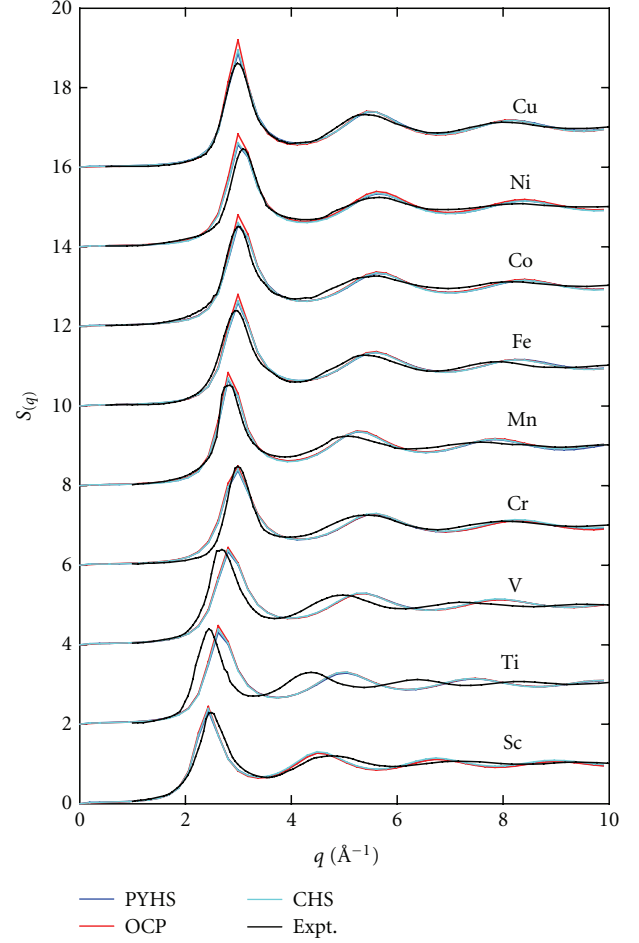
4. Summary and Conclusions

(i) The thermodynamical and structural properties of liquid transition metals have been successfully investigated along with our newly constructed parameter free model potential.

(ii) These properties are very sensitive to the choice of reference systems. The good qualitative and quantitative data of the thermodynamical and structural properties of liquid transition metals have been obtained and would be beneficial to the other theoreticians as well as experimentalists working in the same field.

(iii) These properties of liquid metals are not sensitive to the use of the different local field correction functions.

(iv) Thus the application of our newly proposed model potential in the present study definitely adds new contribution to understand the thermodynamical and structural properties of transition metals in liquid state.

(v) Thus the proper choice of the model potential along with the reference system plays a vital role in the study of the thermodynamical and structural properties of 3d liquid transition metals.

Acknowledgment

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