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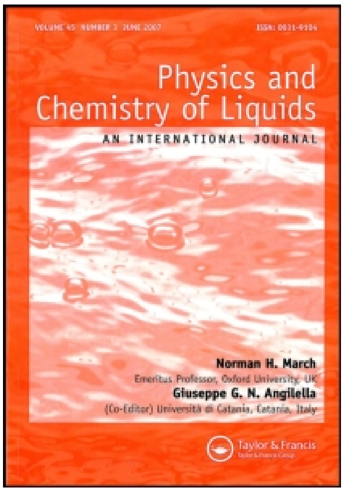

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Thermodynamics of liquid d- and f-shell metals: a variational approach

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Thermodynamics of liquid d- and f-shell metals: a variational approach

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The Gibbs–Bogoliubov variational method is applied to investigate the thermodynamic properties of some d- and f-shell metals in liquid phase namely; Rh, Ir, Cu, Ag, Ni, Pd, Pt, Au, La, Yb, Ce, and Th using pseudopotential theory. For description of the structure, Percus-Yevick hard sphere model is used as a reference system. Ashcroft's well-known empty core model potential is used to describe the electron-ion interaction. The local field correction function proposed by Hartree, Taylor, Ichimaru–Utsumi, Farid *et al*., and Sarkar *et al*. are applied to introduce the exchange and correlation effects in the study of thermodynamics of these metals. The comparison with available experimental or theoretical findings is found in qualitative agreement and establishes the use of the local field correction functions in such study.

Keywords: Thermodynamic properties; Pseudopotential theory; PY hard sphere model; d- and f-shell liquid metals

1. Introduction

The theoretical basis for an understanding of the thermodynamics of simple liquid metals has been forged in recent years to a point where it can be used to calculate the thermodynamics properties with some success [1–24]. This advance has been made possible due to the combination of the pseudopotential with thermodynamics perturbation theories. The pseudopotential theory, enables one to formulate the energy in terms of the pseudopotential and of the structure factor. On the other side, it is possible to write down closed form expressions for the thermodynamic quantities of hard sphere systems, including the structure factor, in the Percus-Yevick (PY) approximation [25]. A link between both theories is provided by a variational technique based on the Gibbs–Bogoliubov (GB) inequality [1–24]. This GB inequality states that when the Hamiltonian of a given system is regarded as the Hamiltonian of a reference

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system plus a perturbation, the free energy of the system will always be smaller than that of the reference system plus the expectation values of the perturbation (calculated with the structure factors of the reference system). In our case, the reference system is one of the hard spheres, and the hard sphere diameters will be chosen to minimize the free energy.

Also, in the previous two decades, considerable efforts have been made to the understanding of structure and thermodynamic properties of several liquid noble, transition, and rare-earth metals [4–16]. A large number of experimental measurements on various properties of these metals are now available in the literature [17,18]. The interatomic potentials of the simple liquid metals [26–28] 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. Despite the success of the theory in the solid state, results for the structure factor of liquid 3d-transition metals using molecular dynamics and other complicated liquid state theories have not been so reliable [22,23]. Wills and Harrison [29] have derived the interatomic potentials for transition metals and obtained thermodynamic properties reasonably good. The WH-potentials [29] have also been used for the determination of the surface properties of noble metals [6] and thermodynamic properties of 3d-transition metals in the liquid state [11,14]. The variational technique with a hard sphere fluid as a reference system have been used by Bretonnet and Derouiche [14] for the calculation of Helmholtz free energy of a series of liquid transition metals. The potentials of Wills–Harrison [29] and Bretonnet–Derouiche [14] are also successfully exploited for the computation of several equilibrium properties. A number of theoretical calculations based on the atomistic model and the use of interatomic potentials have been used for the study of the liquid metals [26–28]. 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. The reliability of the predicted values, however, is entirely depends on the validity of a given interatomic potential and the model used. Very recently, Baria [5] has reported thermodynamic properties of some d- and f-shell liquid metals using a variational approach using model potential formalism.

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From the literature survey, it reveals that though the local pseudopotentials are proved very good for explaining various electronic, transport, static, and vibrational properties of liquid metals, the local pseudopotentials are not rigorously applied to study the thermodynamics of large number of the liquid metals so far. The influence of various exchange and correlations on the thermodynamic is also not investigated from the aforesaid study. Hence, we thought it worthwhile to apply well-known Ashcroft's empty core (EMC) model potential [30] in the detail investigation of Helmholtz free energy of some liquid metals of the different groups of the periodic table.

The local field correction function is a very important factor for establishing a well local pseudopotential and for the proper reproduction of the property under investigation. To investigate influence of exchange and correlation effects, we have used five different types of the local field correction functions due to Hartree (HR) [31], Taylor (TY) [32], Ichimaru–Utsumi (IU) [33], Farid *et al.* (FR) [34], and Sarkar *et al.* (SR) [35]. The structural contribution to the Helmholtz free energy is accounted by adopting PY-hard sphere [25] reference system.

2. Computational methodology

Well-known EMC model potential of Ashcroft's [30] used to explain electron–ion interaction in the liquid metals is of the following form (in Ryd. units)

$$W_{\mathrm{B}}(q) = \frac{-4\pi Z e^2}{\Omega_{\mathrm{o}} q^2} \cos(q r_{\mathrm{C}}). \tag{1}$$

Here Z, e, Ω_0, q, and r_{c} are the valence, charge of the electron, atomic volume, wave vector, parameter of the model potential, respectively.

A successful method for the theoretical calculation of thermodynamic properties in metallic systems has been discussed by GB equation [17]. In this formulation, the Helmholtz free energy (F) of the system is written in the form [5,17]

$$F = U - TS, \tag{2}$$

with U is the internal energy and S the entropy of the system at a temperature T.

The internal energy U can be expressed as [5,17]

$$U = U_{\mathrm{elec}} + U_{\mathrm{ion}} + U_{\mathrm{elec-ion}}, \tag{3}$$

where,

$$U_{\mathrm{elec}} = NZ\left\{\left(\frac{3}{10}\right)k_{\mathrm{F}}^2 - \left(\frac{3}{4\pi}\right)k_{\mathrm{F}} - 0.0474 - 0.0155\ \ln\ k_{\mathrm{F}} - \left(\frac{1}{2}\right)\left(\frac{\pi k_{\mathrm{B}}}{k_{\mathrm{F}}}\right)^2 T^2\right\}, \tag{4}$$

$$U_{\mathrm{ion}} = \frac{3}{2} K_{\mathrm{B}} T + \left(\frac{Z^2}{\pi}\right) \int_0^{\infty} \left\{a(q) - 1\right\} \mathrm{d}q, \tag{5}$$

and

$$U_{\mathrm{elec-ion}} = \lim_{q\to 0}\left\{V^0(q) + \frac{8\pi Z}{q^2}\right\}\left(\frac{Z}{\Omega}\right) + \frac{1}{16\pi^3}\int_0^{\infty}\left\{V^0(q)\right\}^2 a(q)\left\{\frac{1}{\varepsilon(q)} - 1\right\} q^4 \mathrm{d}q. \tag{6}$$

Here, k_{F}, N, $a(q)$, $W_{\mathrm{B}}(q)$, and $\varepsilon(q)$ are the Fermi wave vector, total number of atoms, structure factor, bare ion pseudopotential [30], and the modified HR dielectric function [31], respectively.

The modified HR dielectric function $\varepsilon(q)$, which takes into account of the conduction electrons interaction, is of the form [31],

$$\varepsilon(q) = 1 + \left\{\varepsilon_{\mathrm{H}}(q) - 1\right\}\left\{1 + f(q)\right\}. \tag{7}$$

In this expression, $\varepsilon_{\mathrm{H}}(q)$ is the static HR dielectric function [31] and $f(q)$ the correction factor for the exchange and correlated motion of the conduction electrons. In the present study we consider the local field correction due to Hartree [31], Taylor [32], Ichimaru–Utsumi [33], Farid *et al.* [34], and Sarkar *et al.* [35] to investigate the relative influence of exchange and correlation effects.

The HR [31] dielectric function does not include any exchange and correlation effect among the conduction electrons. Hence, it is purely a static dielectric function, which is given by

$$f_{\mathrm{H}}(q) = 0. \tag{8}$$

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The screening function of Taylor [32] is best justified at high densities. It covers the overall features of the various local field corrections function proposed before 1972. The correction factor of Taylor [46] is expressed as

$$f_{\mathrm{T}}(q) = \left(\frac{q^2}{4k_{\mathrm{F}}^2}\right)\left[1 + \frac{0.1534}{\pi k_{\mathrm{F}}}\right]. \tag{9}$$

The correction function of Ichimaru–Utsumi [33] is a fitting formula for the dielectric screening function of degenerate electron liquids at metallic and lower densities. It reproduces accurately the Monte Carlo results as well as those of microscopic calculations, which also satisfies self-consistency conditions in the compressibility sum rule and short range correlations. This function involves the logarithmic singularity at $q = 2k_{\mathrm{F}}$ and the accompanying peak at $q = 1.94k_{\mathrm{F}}$. It can be expressed as

$$f_{\mathrm{IU}}(X) = AX^4 + BX^2 + C + \left[AX^4 + \left(B + \frac{8A}{3}\right)X^2 - C\right]\left[\left(\frac{4 - X^4}{4X}\right)\ln\left|\frac{2+X}{2-X}\right|\right]. \tag{10}$$

The correction function of Farid *et al.* [34] satisfies the exact asymptotic results for the short and long wavelength limits as determined in terms of some exact frequency moments of the density–density correlation function. The major ingredient of it is the quantum-Monte Carlo results of Ceperley and Alder for the correlation energy in the paramagnetic state of the uniform electron gas. The equation is given by,

$$f_{\mathrm{F}}(X) = AX^4 + BX^2 + C + \left[AX^4 + DX^2 - C\right]\left[\left(\frac{4 - X^4}{4X}\right)\ln\left|\frac{2+X}{2-X}\right|\right]. \tag{11}$$

The screening function of Sarkar *et al.* [35] is latest one, which is derived in the same fashion as that of the Ichimaru–Utsumi [33] and Farid *et al.* [34], is given by,

$$f_{\mathrm{S}}(X) = A[1 - (1 + BX^4)]\exp\left(-CX^2\right). \tag{12}$$

In Equations. (10)–(12), $X = q/k_F$. The constants A, B, C, and D involve in the above expressions are well defined in the respective references [33–35].

The second most essential part in the computation of the Helmholtz free energy (F) is to calculate the entropy (S).

The total entropy (S) is given by [5, 17]

$$S = S_{\mathrm{gas}} + S_{\eta} + S_{\mathrm{elec}}, \tag{13}$$

with

$$S_{\mathrm{gas}} = \left(\frac{5}{2}\right)k_{\mathrm{B}} + k_{\mathrm{B}}\ln\left\{\Omega\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{\frac{1}{2}}\right\}, \tag{14}$$

$$S_{\eta} = k_{\mathrm{B}}\eta(3\eta - 4)(1 - \eta)^{-2}, \tag{15}$$

and

$$S_{\mathrm{elec}} = \left(\frac{\pi^2 {k_{\mathrm{B}}}^2 T}{{k_{\mathrm{F}}}^2}\right). \tag{16}$$

Table 1. The input parameters and constants used in the present calculations.

Metals	Z	T	Ω_O (au)	η	r_c (au)
Rh	1.5	2236.0	95.60	0.45	0.71
Ir	1.5	2720.0	99.80	0.45	0.72
Cu	1.5	1423.0	119.60	0.46	0.69
Ag	1.5	1273.0	173.06	0.45	0.94
Ni	1.5	1773.0	85.21	0.45	0.59
Pd	1.5	1853.0	113.87	0.47	0.68
Pt	1.5	2053.0	120.31	0.47	0.68
Au	2.0	1423.0	228.46	0.46	0.74
La	2.0	1243.0	216.63	0.43	0.84
Yb	2.0	1123.0	312.75	0.43	0.80
Ce	2.0	1143.0	265.24	0.42	0.81
Th	2.0	2031.0	222.98	0.42	0.88

Table 2. U_{elec} and U_{ion} (in 10^{-3} au) of liquid metals.

	U_{elec}		U_{ion}	
Metals	Present results	Others [5]	Present results	Others [5]
Rh	−75.05	157.27	−731.99	−835.67
Ir	−79.69	161.04	−716.67	−776.99
Cu	−89.49	60.46	−686.33	−379.17
Ag	−107.59	72.89	−605.94	−327.09
Ni	−64.23	125.13	−765.84	−887.28
Pd	−87.13	166.10	−694.46	−841.07
Pt	−91.12	169.31	−679.62	−831.77
Au	−143.33	81.39	−800.47	−328.28
La	−140.00	433.21	−837.37	−1081.46
Yb	−155.45	434.97	−740.68	−1145.82
Ce	−149.55	415.03	−788.58	−1084.30
Th	−144.06	391.45	−827.75	−1113.29

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where, k_B, m, and h are the Boltzmann constant, the atomic mass, and the Planck's constant, respectively. Using the information of packing fraction η, the entropy has been calculated. In the present study, we have calculated η as a function of temperature [17].

$$\eta(T) = A_W \exp(-B_w T) \tag{17}$$

where T is the absolute temperature. The parameters A_w and B_w are given by Waseda [17].

3. Results and discussion

The input parameters and constants used in the present investigation of the thermodynamic properties of the liquid metals are tabulated in table 1. The computed values of the thermodynamic properties such as U_{elec}, U_{ion}, $U_{\text{elec–ion}}$, U, various contributions to the entropy, S and F are tabulated in tables 2–7.

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Table 3. $U_{\text{elec-ion}}$ of liquid metals.

	Present results					
Metals	HR	TY	IU	FR	SR	Others [5]
Rh	−126.16	−46.58	−37.74	−33.08	−87.46	−72.41
Ir	−125.78	−46.46	−37.63	−33.01	−86.91	−76.16
Cu	−154.64	−54.34	−44.07	−37.93	−104.88	−59.22
Ag	−87.18	−30.25	−23.38	−20.33	−57.00	−74.59
Ni	−184.71	−71.12	−59.48	−52.40	−131.64	−49.76
Pd	−147.39	−47.47	−37.63	−31.36	−98.42	−77.29
Pt	−153.08	−49.61	−39.49	−32.99	−102.03	−79.44
Au	−517.72	−201.37	−159.03	−142.14	−352.60	−74.45
La	−423.52	−199.02	−167.06	−155.98	−304.52	−147.64
Yb	−541.62	−233.00	−190.83	−174.96	−376.25	−141.31
Ce	−511.23	−236.30	−197.96	−184.17	−364.10	−143.47
Th	−399.59	−199.27	−170.09	−160.53	−292.34	−143.79

Table 4. Total internal energy (U) of liquid metals.

	Present results					
Metals	HR	TY	IU	FR	SR	Others [5]
Rh	−933.20	−853.62	−844.78	−840.12	−894.50	−750.11
Ir	−922.14	−842.83	−834.00	−829.37	−883.27	−692.10
Cu	−930.46	−830.16	−819.89	−813.75	−880.70	−377.93
Ag	−800.71	−743.78	−736.92	−733.86	−770.53	−328.79
Ni	−1014.78	−901.19	−889.55	−882.47	−961.71	−811.91
Pd	−928.98	−829.06	−819.21	−812.94	−880.01	−752.25
Pt	−923.82	−820.35	−810.23	−803.73	−872.77	−744.90
Au	−1461.53	−1145.18	−1102.83	−1085.94	−1296.41	−321.35
La	−1400.89	−1176.40	−1144.44	−1133.35	−1281.89	−795.88
Yb	−1437.75	−1129.13	−1086.96	−1071.09	−1272.37	−852.17
Ce	−1449.36	−1174.43	−1136.09	−1122.30	−1302.23	−812.73
Th	−1371.40	−1171.08	−1141.90	−1132.34	−1264.15	−865.63

From the tables 2 and 3, it is seen that the values of the U_{elec} and U_{ion} are negative while the $U_{\text{elec–ion}}$ has positive contribution to the internal energy. The present results of the U_{elec} and U_{ion} are found in qualitative agreement with those of theoretical results of the others [5] and experimental data [24]. There are large variations found in the presently computed results and others because U_{elec} and U_{ion} terms are depended on the model potential and the structure factor of the liquid metals.

It is seen from table 4 that, the local field correction functions affect the total internal energy (U) through U_{ion} and $U_{\text{elec–ion}}$. The effect is more visible on $U_{\text{elec–ion}}$ which involves the first and second order band structure energies. Presently computed results of the total internal energy (U) from FR-screening function are found lower while those from HR-screening function are found higher than the other local field correction functions. The comparisons of computed yielding with available theoretical [5] and experimental [24] data are highly encouraging and found qualitative agreement. The temperature dependent η is incorporated in the calculation of structure factor $a(q)$. This $a(q)$ is then used in the computation of U_{ion} and $U_{\text{elec–ion}}$ for temperature dependency. It is also observed that the magnitude of the internal energy increases with temperature.

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Table 5. Various contributions to the entropy of liquid metals.

	$S_{\mathrm{gas}}/k_{\mathrm{B}}$		S_{η}/k_{B}		$S_{\mathrm{elec}}/k_{\mathrm{B}}$	
Metals	Present results	Others [5]	Present results	Others [5]	Present results	Others [5]
Rh	12.3884	15.82	−3.9421	−3.94	0.1166	0.114
Ir	13.3832	17.80	−3.9421	−3.94	0.1459	0.141
Cu	11.9039	14.26	−4.1331	−4.133	0.0861	0.085
Ag	13.0671	15.39	−3.9421	−5.000	0.0986	0.106
Ni	11.4458	14.40	−3.9421	−3.262	0.0856	0.077
Pd	12.6279	15.66	−4.3336	−4.333	0.1085	0.099
Pt	13.5923	16.74	−4.3336	−4.333	0.1248	0.111
Au	14.2480	16.44	−4.1331	−4.133	0.1095	0.118
La	13.6710	16.40	−3.5866	−3.586	0.0923	0.102
Yb	14.3677	16.44	−3.5866	−3.586	0.1065	0.084
Ce	13.8864	16.19	−3.4209	−2.966	0.0971	0.088
Th	14.4695	17.77	−3.4209	−3.586	0.1537	0.153

Table 6. Total entropy (S/k_{B}) of liquid metals.

Metals	Present results	Others [5]	Expt. [24]
Rh	8.5628	11.99	–
Ir	9.5870	13.27	–
Cu	7.8570	9.87, 10.21	10.28
Ag	9.2235	10.49, 10.84	10.96
Ni	7.5893	11.21, 11.69, 12.76	10.02
Pd	8.4029	11.43, 12.11	11.50
Pt	9.3835	12.52, 12.93	12.46
Au	10.2244	12.04, 12.43	12.00
La	10.1766	12.90, 13	12.87
Yb	10.8876	12.94	–
Ce	10.5626	13.32, 14.4	14.67
Th	11.2023	14.33	–

In comparison with the presently computed results of the total internal energy (U) from static HR-function, the percentile influences for Rh, Ir, Cu, Ag, Ni, Pd, Pt, Au, La, Yb, Ce, and Th liquid metals of TY, IU, FR, and SR-functions are of the order of 4.15–9.97%, 4.22–10.06%, 5.35–12.54%, 3.77–8.35%, 5.23–13.04%, 5.27–12.49%, 5.53–13.00%, 1.47–3.11%, 2.90–6.38%, 12.39–27.99%, 3.49–9.27%, and 2.61–5.76%, respectively.

The calculated results of the total internal energy (U) for Rh, Ir, Cu, Ag, Ni, Pd, Pt, Au, La, Yb, Ce, and Th liquid metals deviate in the range of 11.21–24.41%, 17.01–33.24%, 53.90–146.20%, 55.38–143.53%, 8.73–24.99%, 8.07–23.49%, 7.90–24.02%, 70.86–354.81%, 30.46–76.02%, 21.60–68.72%, 28.46–78.33%, and 24.19–58.43% from the experimental data [24], respectively.

The various contributions to the entropy are given in table 5. Among the three contributions, only S_{η} is structure dependent while other two i.e., S_{gas} and S_{elec} depend only upon the density and are thus independent of the model pseudopotential. The major contribution to the total entropy comes from the term S_{gas}. The present results of various contributions of the entropy are found in fair agreement with the others [5]. Present results of the total entropy (S) are narrated in table 6. The comparison of the calculated total entropy (S) with the available experimental [24] finding shows that as

Table 7. Helmholtz free energy (F) of liquid metals.

	Present results					
Metals	HR	TY	IU	FR	SR	Others [5]
Rh	−993.86	−914.28	−905.44	−900.78	−955.16	−26810.25
Ir	−1004.76	−925.45	−916.62	−911.99	−965.89	−36120.38
Cu	−965.88	−865.58	−855.32	−849.17	−916.12	−14528.26
Ag	−837.91	−780.98	−774.12	−771.06	−807.74	−13358.15
Ni	−1057.41	−943.82	−932.18	−925.10	−1004.34	−19882.65
Pd	−978.31	−878.39	−868.55	−862.28	−929.34	−21172.98
Pt	−984.85	−881.39	−871.26	−864.77	−933.80	−25704.52
Au	−1507.62	−1191.27	−1148.93	−1132.04	−1342.50	−17681.91
La	−1440.97	−1216.48	−1184.51	−1173.43	−1321.97	−16041.56
Yb	−1476.49	−1167.87	−1125.70	−1109.83	−1311.11	−14534.44
Ce	−1487.61	−1212.68	−1174.34	−1160.55	−1340.48	−15221.91
Th	−1443.49	−1243.16	−1213.98	−1204.42	−1336.24	−29111.63

the temperature of the liquid metals changes the deviation with experimental observation [24] also increases. In general, the deviation is within 17.4–38.9%.

Finally, using the total internal energy (U) and total entropy (S) we have generated the Helmholtz free energy (F) which are shown in table 7. From the table 7 it is noticed that, the present results of the Helmholtz free energy (F) of liquid metals are found in qualitative agreement with the available experimental [24] or theoretical [5] findings in the literature. Also, it is noted that, among the five employed local filed correction functions, the local field correction function due to HR (without exchange and correlation) gives the maximum numerical value of the Helmholtz free energy (F), while the local field correction function due to FR gives the minimum value.

The percentile influences from static HR-function on the Helmholtz free energy (F) for Rh, Ir, Cu, Ag, Ni, Pd, Pt, Au, La, Yb, Ce, and Th liquid metals of various local field correction functions are found of the order of 3.89–9.37%, 3.87–9.23%, 5.15–12.08%, 3.60–7.98%, 5.02–12.51%, 5.01–11.86%, 5.18–12.19%, 10.95–24.91%, 8.26–18.57%, 11.20–24.83%, 9.89–21.99%, and 7.43–16.56%, respectively. Hence, the strong influence of local field correction on the Helmholtz free energy (F) is predicted.

Thus, it is confirmed from tables 2–7 that, the presently calculated values of total internal energy (U) and total entropy (S) are in fair agreement with the experimental data [24] and other reported data [5]. This confirms the applicability of the EMC model potential in the investigation of thermodynamic properties of liquid metals of the different groups of the periodic table. Therefore, the present EMC model potential is equally useful in the calculation of various properties of liquid metals without any modification.

The numerical values of the thermodynamic properties of liquid metals are found to be quite sensitive to the selection of the local field correction function and showing a significant variation with the change in the function. Thus, the calculations of the thermodynamic properties are one of the sensitive tests for the proper assessment of the form factor of the model potential and in the absence of experimental information such calculations may be considered as one of the guidelines for further investigations either theoretical or experimental. In contrast with the reported studies, the present study spans the d- and f-shell metallic elements of the different groups of the periodic table on a common platform of the model potential and common criteria for evaluating

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parameter of the model potential. This is very much essential for obtaining concrete conclusions.

4. Conclusions

Lastly we concluded that, proper choice of the local field correction function also plays a vital role in predicting thermodynamic properties of liquid metals. In comparison with the earlier reported investigation of thermodynamics of some liquid metals of the different groups of the periodic table, present results are superior in qualitative as well as quantitative ways.

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