Thermodynamic properties of some liquid metals using pseudopotential theory

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Thermodynamic properties of some liquid metals using pseudopotential theory

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The Gibbs–Bogoliubov (GB) inequality is used to evaluate the Helmholtz free energy of some liquid metals. The structural contribution to the Helmholtz free energy is investigated by adopting a Percus–Yevick (PY) hard sphere fluid. A well known single parametric empty core (EMC) local pseudopotential of Ashcroft is applied to describe the electron-ion interaction along with five different local field correction functions viz Hartree (HR), Taylor (TY), Ichimaru–Utsumi (IU), Farid *et al*. (FR) and Sarkar *et al*. (SR). 2.18 to 28% of the influence on the Helmholtz free energy is concluded as due to these local field correction functions with respect to the static HR dielectric function. A qualitative agreement with experimental or theoretical results is achieved.

Keywords: thermodynamic properties; pseudopotential theory; PY hard sphere model; 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 thermodynamic properties with some success [1–25]. This advance has been made possible due to the combination of the pseudopotential with thermodynamic perturbation theories. The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and structure factor. 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 approximation [26]. A link between both theories is provided by a variational technique based on the Gibbs–Bogoliubov inequality [1–25]. This Gibbs–Bogoliubov inequality states that when the Hamiltonian of a given system is regarded as the Hamiltonian of a reference 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 minimise the free energy.

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Hafner [4] has reported the internal energy of liquid alkali metals at their melting temperature using optimised pseudopotential. The results reported differ in the order of 3–4% from the experimental findings. In the computation of the entropy and the internal energy of Na, K, Rb and Cs, Singh and Singh [5] have employed Ashcroft's empty core (EMC) [27], Heine–Abarenkov [5] and harmonic model potentials [5]. They conclude that the thermodynamic properties of the alkali metals are very sensitive to the details of the potential inside the core region. In their study the local field correction due to Hubbard and Sham [5] was adopted. The temperature-dependent thermodynamic properties of liquid Na, K, Rb and Cs were investigated by Singh and Singh [7] on the bases of Heine–Abarenkov model potential [7]. They have concluded that the internal energy depends very little on the temperature above the melting point. The application of generalised nonlocal model potential (GNMP) [8] and energy independent nonlocal model potential (EINMP) [9] have produced quite consistent results regarding the internal energy of liquid alkali metals. In all of the above studies, the PY theory [26] was adopted as a reference system for structural description. Ono *et al.* [10] have reported the use of a one component plasma (OCP) system in the study of Helmholtz free energy of liquid alkali metals. The soft sphere (SS) reference system was used by Akinlade [12]. Also, Akinlade *et al.* [13,14] have reported their results using a modified generalised nonlocal model potential (MGNMP) with a charged hard sphere (CHS) reference system [13,14]. Recently, Thakor *et al.* [15–18] have reported temperature-dependent thermodynamic properties of some liquid metals using model potential formalism. Very recently, Baria [19] has reported thermodynamic properties of some d- and f-shell liquid metals using a variational approach.

A literature survey reveals that though local pseudopotentials have proved to be very good for explaining various electronic, transport, static and vibrational properties of liquid metals, the local pseudopotentials have not so far been rigorously applied to study the thermodynamics of the large number of liquid metals so far. The influence of various exchanges and correlations on the thermodynamic is also not investigated from the aforesaid study. Hence, we thought it worthwhile to apply well-known Ashcroft EMC model potential [27] in a detailed 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 the influence of exchange and correlation effects, we have used five different types of the local field correction functions due to Hartree (HR) [28], Taylor (TY) [29], Ichimaru–Utsumi (IU) [30], Farid *et al.* (FR) [31] and Sarkar *et al.* (SR) [32]. The structural contribution to the Helmholtz free energy is accounted for by adopting a PY-hard sphere [26] reference system.

2. Computational methodology

The well known EMC model potential of Ashcroft [27] used to explain electron-ion interaction in the liquid metals is of the following form (in Ryd. units)

$$W_{\rm B}(q) = \frac{-4\pi Z e^2}{\Omega_0 \, q^2} \cos(q r_C). \tag{1}$$

Here Z, e, Ω_0, q and r_C are the valence, charge of the electron, atomic volume, wave vector and parameter of the model potential, respectively [3–5,15–19].

A successful method for the theoretical calculation of thermodynamic properties in metallic systems has been discussed by Gibbs–Bogoliubov equation [20]. In this formulation, the Helmholtz free energy (F) of the system is written in the form [3–5,15–19]

$$F = U - TS, \qquad (2)$$

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

The internal energy U can be expressed as [3–5,15–19]

$$U = U_{elec} + U_{ion} + U_{elec-ion}, \qquad (3)$$

where,

$$U_{elec} = NZ\left\{\left(\frac{3}{10}\right)k_F^2 - \left(\frac{3}{4\pi}\right)k_F - 0.0474 - 0.0155\ln k_F - \left(\frac{1}{2}\right)\left(\frac{\pi k_B}{k_F}\right)^2 T^2\right\}, \qquad (4)$$

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

and

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

Here, k_F, N, $a(q)$ and $\varepsilon(q)$ are the Fermi wave vector, total number of atoms, structure factor [27] and the modified Hartree dielectric function [28].

The modified Hartree dielectric function $\varepsilon(q)$, which takes into account interaction of the conduction electrons, is of the form [28],

$$\varepsilon(q) = 1 + \{\varepsilon_H(q) - 1\}\{1 + f(q)\}. \qquad (7)$$

In this expression $\varepsilon_H(q)$ is the static Hartree dielectric function [28] 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 corrections due to HR [28], TY [29], IU [30], FR [31] and SR [32] to investigate the relative influence of exchange and correlation effects.

The HR [28] 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

$$f_H(q) = 0. \qquad (8)$$

The screening function of TY [29] 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 TY [29] is expressed as

$$f_T(q) = \left(\frac{q^2}{4k_F^2}\right)\left[1 + \frac{0.1534}{\pi k_F}\right]. \qquad (9)$$

The correction function of IU [30] 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 $q = 2k_F$ and the accompanying peak at $q = 1.94k_F$. It can be expressed as

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

The correction function of FR [31] 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 this 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,

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

The screening function of Sarkar *et al.* SR [32] is the latest one, which is derived in the same fashion as that of IU [30] and FR [31], is given by,

$$f_S(X) = A \left[1 - \left(1 + BX^4 \right) \right] \exp \left(-CX^2 \right). \quad (12)$$

In Equations (10)–(12), $X = q/k_F$. The constants A, B, C and D involved in the above expressions are well-defined in the respective references [30–31].

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 [3–5,15–19]

$$S = S_{gas} + S_\eta + S_{elec}, \quad (13)$$

with

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

$$S_\eta = k_B \eta (3\eta - 4)(1 - \eta)^{-2}, \quad (15)$$

and

$$S_{elec} = \left(\frac{\pi^2 k_B^2 T}{k_F^2} \right), \quad (16)$$

where k_B, m and h are the Boltzmann constant, atomic mass and 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 [20].

$$\eta(T) = A_W \exp(-B_W T), \quad (17)$$

where T is the absolute temperature. The parameters A_W and B_W are given by Waseda [20].

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}, $U_{elec-ion}$, U, various contributions to the entropy, S and F are tabulated in Tables 2–7.

From Tables 2 and 3, it can be seen that the values of U_{elec} and U_{ion} are negative, while $U_{elec-ion}$ has a positive contribution to the internal energy. The present results of U_{elec} and U_{ion} are found to be in qualitative agreement with the theoretical results of others [17,18] and experimental data [21]. There are large variations found in the presently computed results and others because the U_{elec} and U_{ion} terms are dependent on the model potential and the structure factor of the liquid metals.

It can be seen from Table 4 that the local field correction functions affect the total internal energy (U) through U_{ion} and $U_{elec-ion}$. The effect is more visible on $U_{elec-ion}$ which involves the first and second order band structure energies. The presently computed results of the total internal energy (U) from FR-screening function have been found to be lower, while those from HR-screening function have been found to be higher than the other local field correction functions. Comparisons of computed

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

Metals	Z	T	Ω_0 (au)	η	r_c (au)
Li	1.0	453.0	146.46	0.46	0.97
Na	1.0	378.0	266.08	0.46	1.60
K	1.0	343.0	480.84	0.46	2.00
Rb	1.0	313.0	627.15	0.43	2.05
Cs	1.0	323.0	775.73	0.43	2.07
Be	2.0	1562.0	54.78	0.45	0.75
Mg	2.0	1053.0	157.68	0.46	1.36
Ca	2.0	1223.0	292.93	0.46	1.61
Sr	2.0	1153.0	381.17	0.46	1.87
Ba	2.0	1103.0	427.80	0.46	2.38
Zn	2.0	823.0	103.27	0.46	1.28
Cd	2.0	723.0	145.55	0.45	1.01
Hg	2.0	393.0	157.68	0.45	1.57
Al	3.0	1043.0	111.46	0.45	1.12
Ga	3.0	423.0	131.99	0.43	1.17
In	3.0	533.0	175.90	0.45	1.28
Tl	3.0	688.0	194.00	0.45	1.45
Gd	3.0	1703.0	254.93	0.43	0.79
Si	4.0	1733.0	121.48	0.38	0.97
Ge	4.0	1253.0	146.25	0.38	1.01
Sn	4.0	623.0	180.85	0.43	1.04
Pb	4.0	713.0	203.86	0.46	1.41
Sb	5.0	903.9	205.26	0.40	1.33
Bi	5.0	544.6	238.56	0.40	1.40

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

Metals	U_{elec}		U_{ion}	
	Present results	Others [17,18]	Present results	Others [17,18]
Li	−76.03	−76.63	−324.75	−262.37, −262.38, −262.39
Na	−81.60	−81.71	−266.08	−215.45, −215.46
K	−80.64	−80.07	−218.14	−172.07
Rb	−78.87	−78.61	−194.64	−161.03
Cs	−77.08	−76.66	−181.02	−149.38
Be	45.43	−	−1306.87	−
Mg	−117.68	−	−911.08	−
Ca	−153.55	−	−737.65	−
Sr	−160.66	−	−675.35	−
Ba	−162.60	−	−649.92	−
Zn	−71.99	−	−1052.81	−
Cd	−110.24	−	−947.40	−
Hg	−116.96	−	−925.41	−
Al	−29.83	−	−2259.14	−
Ga	−72.67	−	−2139.14	−
In	−131.48	−	−1943.86	−
Tl	−147.92	−	−1879.79	−
Gd	−187.66	−	−1704.74	−
Si	41.49	−	−4028.37	−
Ge	−34.19	−	−3790.31	−
Sn	−105.58	−	−3642.35	−
Pb	−140.26	−	−3558.29	−
Sb	−93.66	−	−5657.06	−
Bi	−151.91	−	−5383.54	−

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

Metals	Present results					Others [17,18]
	HR	TY	IU	FR	SR	
Li	5.41	15.93	17.32	17.81	11.25	32.07, 73.47, 87.12, 87.22, 102.40
Na	42.08	44.30	44.71	44.76	43.48	65.07, 103.51, 117.87, 118.17, 139.48
K	37.32	38.91	39.21	39.24	38.32	56.67, 89.32, 103.03, 103.19, 126.03
Rb	21.83	24.75	25.26	25.34	23.57	35.52, 69.98, 85.05, 85.09, 108.24
Cs	13.20	17.32	17.95	18.11	15.54	18.42, 53.01, 68.73, 68.94, 91.50
Be	−96.31	−44.20	−35.44	−33.71	−73.72	−
Mg	23.71	62.53	65.05	67.76	42.76	−
Ca	12.19	36.28	38.02	39.50	25.15	−
Sr	3.46	50.32	53.29	56.55	27.58	−
Ba	−142.03	89.33	109.69	125.20	−23.77	−

Table 3. Continued.

Metals	Present results					Others [17,18]
	HR	TY	IU	FR	SR	
Zn	16.91	106.69	112.76	119.57	55.62	–
Cd	−114.92	−59.00	−49.27	−47.33	−84.34	–
Hg	−38.76	103.66	114.60	124.86	28.34	–
Al	−173.07	−71.29	−61.69	−55.30	−129.61	–
Ga	−222.43	−127.23	−118.23	−112.54	−178.34	–
In	−165.17	−82.33	−74.24	−69.42	−124.15	–
Tl	−230.14	−42.77	−22.40	−10.77	−141.12	–
Gd	−1509.34	−856.14	−736.78	−714.33	−1150.94	–
Si	−1184.49	−1002.46	−976.75	−971.98	−1089.08	–
Ge	−1220.03	−1032.95	−1003.70	−999.93	−1114.73	–
Sn	−1005.46	−799.71	−762.22	−759.11	−885.75	–
Pb	−570.31	−227.87	−188.59	−168.08	−413.81	–
Sb	−1569.92	−974.45	−912.37	−875.43	−1312.17	–
Bi	−1533.04	−941.50	−879.08	−842.85	−1264.90	–

values with available theoretical [17,18] and experimental [21] data are highly encouraging and have been found to be in qualitative agreement. The temperature-dependent η is incorporated in the calculation of the structure factor $a(q)$. This $a(q)$ is then used in the computation of U_{ion} and $U_{elec-ion}$ for temperature dependency. It is also observed that the magnitude of the internal energy increases with temperature.

In comparison with the presently computed results of the total internal energy (U) from static HR-function, the percentile influences for Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Al, Ga, In, Tl, Gd, Si, Ge, Sn, Pb, Sb and Bi liquid metals of TY, IU, FR and SR-functions are of the order of 1.48–3.14%, 0.45–0.88%, 0.38–0.73%, 0.69–1.39%, 0.96–2.01%, 4.20–9.28%, 3.11–7.08%, 3.01–6.98%, 2.76–6.25%, 2.85–6.57%, 3.46–8.25%, 1.66–4.61%, 1.90–4.38%, 11.30–25.70%, 8.49–19.10%, 11.50–25.50%, 10.15–22.57%, 7.82–17.43%, 9.89–21.65%, 1.77–4.78%, 1.81–4.51%, 1.83–4.27%, 3.94–9.72%, 10.54–23.37%, 2.35–5.30%, 1.84–4.11%, 2.09–4.36%, 2.52–5.18%, 3.67–9.42%, 3.52–9.49% and 3.79–9.76%, respectively.

The calculated results of the total internal energy (U) for Li, Na, K, Rb, Cs, Mg, Zn, Cd, Al, In and Tl liquid metals deviate in the range of 33.76–55.66%, 25.41–35.22%, 25.26–34.77%, 27.49–39.82%, 29.21–44.06%, 8.79–14.34%, 0.15–9.30%, 9.66–17.26%, 13.43–20.98%, 5.56–10.37% and 1.11–5.26% from the experimental data [21], respectively.

The various contributions to the entropy are given in Table 5. Among the three contributions, only S_η is structure-dependent whereas the 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 to be in fair agreement with those of others [17,18]. The present results of the total entropy (S) are given in Table 6. The comparison of the calculated total entropy (S) with the available experimental finding [21] shows that, as the temperature of the liquid

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

Metals	Present results					Exp. [21]	Others [17,18]
	HR	TY	IU	FR	SR		
Li	−395.37	−384.86	−383.47	−382.97	−389.53	−254.00	−236.63, −251.80, −251.55, −265.55, −306.94
Na	−305.60	−303.38	−302.97	−302.92	−304.21	−226.00	−157.69, −178.99, −179.30, −193.59, −232.08
K	−261.46	−259.87	−259.57	−259.54	−260.46	−194.00	−126.11, −148.95, −149.11, −162.82, −195.61
Rb	−251.68	−248.76	−248.25	−248.17	−249.94	−180.00	−131.39, −154.54, −154.58, −169.66, −204.11
Cs	−244.91	−240.79	−240.15	−239.99	−242.56	−170.00	−134.54, −157.10, −157.31, −173.03, −207.62
Be	−1357.74	−1305.63	−1296.87	−1295.14	−1335.15	−	−
Mg	−1005.05	−966.23	−963.71	−961.00	−986.00	−879.00	−646.6
Ca	−879.01	−854.92	−853.18	−851.70	−866.05	−	−
Sr	−832.55	−785.69	−782.72	−779.46	−808.43	−	−
Ba	−954.55	−723.19	−702.83	−687.33	−836.30	−	−
Zn	−1107.89	−1018.11	−1012.04	−1005.23	−1069.18	−1013.6	−1064.00
Cd	−1172.56	−1116.64	−1106.91	−1104.98	−1141.98	−1000.00	−715.1
Hg	−1081.13	−938.71	−927.77	−917.51	−1014.02	−	−
Al	−2462.03	−2360.26	−2350.66	−2344.27	−2418.57	−2035.00	−1646.10
Ga	−2434.24	−2339.04	−2330.04	−2324.35	−2390.15	−	−
In	−2240.51	−2157.67	−2149.57	−2144.76	−2199.49	−2030.00	−2096.20
Tl	−2257.85	−2070.48	−2050.11	−2038.48	−2168.83	−2145.00	−1942.40
Gd	−3401.75	−2748.55	−2629.19	−2606.74	−3043.34	−	−
Si	−5171.37	−4989.34	−4963.63	−4958.86	−5075.96	−	−
Ge	−5044.53	−4857.45	−4828.20	−4824.43	−4939.23	−	−
Sn	−4753.39	−4547.63	−4510.15	−4507.04	−4633.67	−	−
Pb	−4268.87	−3926.42	−3887.15	−3866.63	−4112.36	−	−3733.00
Sb	−7320.64	−6725.17	−6663.09	−6626.15	−7062.89	−	−
Bi	−7068.48	−6476.95	−6414.52	−6378.29	−6800.34	−	−

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

Metals	S_{gas}/k_B		S_{η}/k_B		S_{elec}/k_B	
	Present results	Others [17,18]	Present results	Others [17,18]	Present results	Others [17,18]
Li	8.78	8.82	−4.13	−3.78	0.04	0.04
Na	11.18	11.22	−4.13	−4.18	0.05	0.05
K	12.57	12.66	−4.13	−3.59	0.07	0.07
Rb	14.01	14.04	−3.59	−3.61	0.07	0.08
Cs	14.88	14.92	−3.59	−3.60	0.09	0.09
Be	8.19	–	−3.94	–	0.05	–
Mg	10.74	–	−4.13	–	0.06	–
Ca	12.11	–	−4.13	–	0.11	–
Sr	13.54	–	−4.13	–	0.12	–
Ba	14.33	–	−4.13	–	0.13	–
Zn	11.80	–	−4.13	–	0.04	–
Cd	12.96	–	−3.94	–	0.04	–
Hg	13.90	–	−3.94	–	0.02	–
Al	10.55	–	−3.94	–	0.04	–
Ga	12.14	–	−3.59	–	0.02	–
In	13.18	–	−3.94	–	0.03	–
Tl	14.14	–	−3.94	–	0.04	–
Gd	14.02	–	−3.59	–	0.11	–
Si	10.69	–	−2.83	–	0.06	–
Ge	12.30	–	−2.83	–	0.05	–
Sn	13.25	–	−3.59	–	0.03	–
Pb	14.21	–	−4.13	–	0.03	–
Sb	13.42	–	−3.11	–	0.04	–
Bi	14.38	–	−3.11	–	0.02	–

Table 6. Total entropy (S/k_B) of liquid metals.

Metals	Present results	Others [17,18]	Exp. [21]
Li	4.69	5.08	5.74
Na	7.10	7.10	7.84
K	8.50	9.15	9.14
Rb	10.49	10.51	10.27
Cs	11.38	11.40	11.14
Be	4.30	–	–
Mg	6.67	6.79	9.02
Ca	8.09	–	–
Sr	9.54	–	–
Ba	10.33	–	–
Zn	7.70	–	9.18
Cd	9.05	9.14	9.94
Hg	9.99	–	–
Al	6.64	6.78	8.63
Ga	8.57	–	–
In	9.26	9.30	9.13
Tl	10.23	10.28	11.00

Table 6. Continued.

Metals	Present results	Others [17,18]	Exp. [21]
Gd	10.54	–	–
Si	7.92	–	–
Ge	9.52	–	–
Sn	9.69	–	–
Pb	10.11	10.17	11.13
Sb	10.34	–	–
Bi	11.29	–	–

metals changes, the deviation with experimental observation [21] also increases. In general, the deviation is in the range of 2.18–28.00%.

Finally, using the total internal energy (U) and total entropy (S) we have generated the Helmholtz free energy (F) values which are shown in Table 7. From Table 7 it can be noted that the present results of Helmholtz free energy of liquid metals are in qualitative agreement with the available experimental [21] and theoretical [17,18] findings in the literature. Also, it is noted that, among the five local filed correction functions employed, the local field correction function due to HR (without exchange and correlation) gives the maximum numerical value of Helmholtz free energy, while the local field correction function due to FR gives the minimum value.

The percentile influences from static HR-function on Helmholtz free energy for Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Al, Ga, In, Tl, Gd, Tb, Si, Ge, Sn, Pb, Sb and Bi liquid metals of various local field correction functions are found to be of the order of 1.45–3.08%, 0.45–0.85%, 0.37–0.71%, 0.66–1.34%, 0.92–1.92%, 3.89–9.37%, 1.85–4.29%, 1.42–3.00%, 2.78–6.12%, 11.94–26.97%, 3.43–9.10%, 2.56–5.66%, 6.14–14.96%, 10.95–24.91%, 1.80–4.49%, 1.82–4.24%, 3.90–9.62%, 10.36–22.99%, 2.29–5.15%, 1.83–4.08%, 2.07–4.33%, 2.51–5.16%, 3.65–9.37%, 3.51–9.45% and 3.78–9.74%, respectively. Hence the strong influence of local field correction on Helmholtz free energy (F) is predicted. The computed findings of Helmholtz free energy for Li, Na, K, Rb, Cs, Zn, Cd, Al, In, Tl and Pb liquid metals deviate in the range of 32.09–51.74%, 24.23–33.09%, 24.85–34.01%, 26.54–37.94%, 27.72–40.97%, 0.49–5.41%, 9.55–16.99%, 14.23–22.06%, 5.80–10.49%, 1.21–5.32% and 6.39– 17.39% from the experimental data [21], respectively.

Thus, it is confirmed from Tables 2–7 that the presently calculated values of the total internal energy (U) and total entropy (S) are in fair agreement with experimental data [21] and other reported data [17,18]. 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. Out of 24 liquid metals the theoretical or experimental data of only 12 liquid metals are available in the literature for comparison.

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, calculation of the thermodynamic properties is one of the sensitive tests for proper assessment of the

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

Metals	Present results					Others [17,18]	Exp. [21]
	HR	TY	IU	FR	SR		
Li	−402.10	−391.59	−390.20	−389.71	−396.27	−244.09, −259.26, −259.36, −273.10, −314.40	−265
Na	−314.10	−311.88	−311.47	−311.42	−312.70	−166.19, −187.50, −187.80, −201.09, −240.58	−236
K	−270.70	−269.11	−268.81	−268.78	−269.70	−136.05, −158.90, −159.06, −172.76, −205.42	−202
Rb	−262.08	−259.16	−258.66	−258.57	−260.34	−141.81, −165.00, −165.27, −180.34, −214.84	−190
Cs	−256.56	−252.43	−251.80	−251.64	−254.21	−145.49, −168.05, −168.26, −183.98, −218.56	−182
Be	−1379.00	−1326.90	−1318.14	−1316.40	−1356.41	—	—
Mg	−1027.30	−988.48	−985.96	−983.25	−1008.25	−667.10	—
Ca	−910.34	−886.25	−884.51	−883.03	−897.38	—	—
Sr	−867.39	−820.53	−817.56	−814.30	−843.27	—	—
Ba	−990.65	−759.29	−738.93	−723.43	−872.40	—	—
Zn	−1127.98	−1038.20	−1032.12	−1025.32	−1089.26	−1032.70	−1084
Cd	−1193.30	−1137.39	−1127.65	−1125.72	−1162.72	−733.10	−1020
Hg	−1093.57	−951.15	−940.20	−929.94	−1026.46	—	
Al	−2483.99	−2382.22	−2372.61	−2366.22	−2440.53	−1666.40	−2035
Ga	−2445.73	−2350.53	−2341.52	−2335.84	−2401.64	—	—
In	−2256.15	−2173.31	−2165.21	−2160.40	−2215.13	−2108.90	−2042
Tl	−2280.16	−2092.78	−2072.42	−2060.79	−2191.14	−1915.50	−2165
Gd	−3458.62	−2805.42	−2686.06	−2663.61	−3100.22	—	—
Si	−5214.87	−5032.84	−5007.13	−5002.36	−5119.46	—	—
Ge	−5082.34	−4895.25	−4866.01	−4862.24	−4977.04	—	—
Sn	−4772.53	−4566.77	−4529.28	−4526.17	−4652.81	—	—
Pb	−4291.70	−3949.26	−3909.99	−3889.47	−4135.20	−3752.80	−3656
Sb	−7350.26	−6754.79	−6692.72	−6655.78	−7092.51	—	—
Bi	−7087.97	−6496.43	−6434.01	−6397.77	−6819.82	—	—

form factor of the model potential, and in the absence of experimental information such a calculation may be considered as one of the guidelines for further investigations either theoretical or experimental. In contrast with other reported studies, the present study spans the metallic elements from different groups of the periodic table on a common platform of the model potential and common criteria for evaluating the parameters 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 role in predicting thermodynamic properties of liquid metals. In comparison with the earlier reported investigation of thermodynamics of some liquid metals of different groups of the periodic table, the present results are superior in qualitative as well as quantitative ways.

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