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THERMODYNAMIC PROPERTIES OF LIQUID METALS USING PERCUS–YEVICK (PY) HARD SPHERE REFERENCE SYSTEM

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The Gibbs–Bogoliubov inequality is used to evaluate the Helmholtz free energy of some liquid metals. The structural contribution to this energy is investigated by adopting the Percus–Yevick (PY) hard sphere fluid. The well-known single parametric empty core local pseudopotential of Ashcroft is applied to describe the electron–ion interaction along with five different local field correction functions, viz, Hartree, Taylor, Ichimaru–Utsumi, Farid et al., and Sarkar et al. The difference of 2.18 to 28.00% in the influence on the Helmholtz free energy is due to these local field correction functions with respect to the static Hartree dielectric function. A qualitative agreement with experimental or theoretical results is achieved.

Keywords: *Thermodynamic properties; pseudopotential theory; PY hard sphere model; liquid metals.*

Introduction. The theoretical basis for understanding the thermodynamics of simple liquid metals has been forged in recent years to the point where it can be used to calculate the thermodynamic properties with some success [1–25]. This advance has become possible due to the combination of the pseudopotential and thermodynamics perturbation theories. The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and structure factor. On the other hand, it is possible to write closed-form expressions for the thermodynamic quantities of hard sphere systems, including the structure factor, in the Percus–Yevick (PY) approximation [26]. A link between both theories is provided by a variational technique based on the Gibbs–Bogoliubov inequality [1–25]. This 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 consisting of the hard spheres, and the hard sphere diameters will be chosen to minimize the free energy.

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

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The literature survey reveals that although local pseudopotentials proved to be very useful for explaining various electronic, transport, static, and vibrational properties of liquid metals, they are not rigorously applied to study the thermodynamics of a large number of liquid metals so far. The influence of various exchange and correlations on the thermodynamics is also not investigated in the aforesaid studies. Hence it is worthwhile to apply the wellknown Ashcroft empty core (EMC) model potential [27] in the detailed investigation of the Helmholtz free energy of some liquid metals of different groups of the periodic table.

The local field correction function is a very important factor for establishing a local pseudopotential and for the proper reproduction of the property under investigation. To investigate the influence of the exchange and correlation effects, we have used five different types of local field correction functions of 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 the PY hard sphere reference system [26].

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

$$W_{\mathrm{B}}(q) = -\frac{4\pi Z e^2}{\Omega_0 q^2}\cos(q r_{\mathrm{C}}) . \tag{1}$$

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

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

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

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

where

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

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

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

Here, $V^0(q)$ and $\varepsilon(q)$ are the bare ion pseudopotential [27] and the modified Hartree dielectric function [28]. The latter quantity with account for the interaction of conduction electrons is of the form [28]

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

Here, $\varepsilon_{\mathrm{HR}}(q)$ is the static Hartree dielectric function [28]. In the present study we consider the five above-mentioned correction functions to investigate the relative influence of exchange and correlation effects.

The Hartree [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

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

The screening function of Taylor [29] is most justified at high densities. It covers the overall features of various local field correction functions proposed before 1972. The correction factor of Taylor [29] is expressed as

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

The correction function of Ichimaru–Utsumi [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 $q = 2k_{\mathrm{F}}$ as well as the accompanying peak at $q = 1.94k_{\mathrm{F}}$ and can be expressed as

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

The correction function of Farid et al. [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 the latter is represented by the quantum-Monte Carlo results of Ceperley and Alder for the correlation energy in the paramagnetic state of a uniform electron gas. The equation is given by

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

The screening function of Sarkar et al. [32] is the latest one, which is derived in the same fashion as those of Ichimaru–Utsumi [30] and Farid et al. [31]; it is given by the equation

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

In Eqs. (10)–(12) $X = q/k_{\mathrm{F}}$, the constants A, B, C, and D are well defined in [30, 31].

The second most essential part in the computation of the Helmholtz free energy F is calculation of the entropy S, which is given by [3–5, 15–19]

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

where

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

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

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

Using the information on packing fraction η, we calculated the entropy. In the present study we have calculated η as a function of temperature [20]:

$$\eta(T) = A_{\mathrm{W}}\exp(-B_{\mathrm{W}}T) . \tag{17}$$

TABLE 1. The Input Parameters and Constants Used in the Present Calculations

Metals	Z	T, K	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. Values of U_{elec} and U_{ion} for Liquid Metals

Metals	$-U_{\text{elec}}\cdot 10^3$, au		$-U_{\text{ion}}\cdot 10^3$, au	
	Present results	Other results [17, 18]	Present results	Other results [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. Values of $U_{\text{elec–ion}}\cdot 10^3$ (au) for Liquid Metals

Metals	Present results					Other results [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	–
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	–

TABLE 4. Values of $-U\cdot 10^3$ (au) for Liquid Metals

Metals	Present results					Experimental results [33]	Others results [17, 18]
	HR	TY	IU	FR	SR		
Li	395.37	384.86	383.47	382.97	389.53	254	236.63, 251.80, 251.55, 265.55, 306.94
Na	305.60	303.38	302.97	302.92	304.21	226	157.69, 178.99, 179.30, 193.59, 232.08
K	261.46	259.87	259.57	259.54	260.46	194	126.11, 148.95, 149.11, 162.82, 195.61
Rb	251.68	248.76	248.25	248.17	249.94	180	131.39, 154.54, 154.58, 169.66, 204.11
Cs	244.91	240.79	240.15	239.99	242.56	170	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	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
Cd	1172.56	1116.64	1106.91	1104.98	1141.98	1000	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	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	2096.20
Tl	2257.85	2070.48	2050.11	2038.48	2168.83	2145	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
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	$S_{\mathrm{gas}}/k_{\mathrm{B}}$		S_{η}/k_{B}		$S_{\mathrm{elec}}/k_{\mathrm{B}}$	
	Present results	Other results [17, 18]	Present results	Other result s[17, 18]	Present results	Other results [17, 18]
Li	8.7848	8.82	–4.1331	–3.78	0.0411	0.0431
Na	11.1784	11.22	–4.1331	–4.18	0.0511	0.0525
K	12.5668	12.66	–4.1331	–3.59	0.0688	0.0734
Rb	14.0055	14.04	–3.5866	–3.61	0.0749	0.0766
Cs	14.8804	14.92	–3.5866	–3.60	0.0891	0.0925
Be	8.1929	–	–3.9421	–	0.0464	–
Mg	10.7390	–	–4.1331	–	0.0633	–
Ca	12.1083	–	–4.1331	–	0.1110	–
Sr	13.5448	–	–4.1331	–	0.1248	–
Ba	14.3343	–	–4.1331	–	0.1289	–
Zn	11.7997	–	–4.1331	–	0.0373	–
Cd	12.9558	–	–3.9421	–	0.0412	–
Hg	13.9045	–	–3.9421	–	0.0236	–
Al	10.5484	–	–3.9421	–	0.0379	–
Ga	12.1419	–	–3.5866	–	0.0172	–
In	13.1770	–	–3.9421	–	0.0263	–
Tl	14.1398	–	–3.9421	–	0.0362	–
Gd	14.0198	–	–3.5866	–	0.1075	–
Si	10.6949	–	–2.8273	–	0.0551	–
Ge	12.3046	–	–2.8273	–	0.0451	–
Sn	13.2545	–	–3.5866	–	0.0258	–
Pb	14.2099	–	–4.1331	–	0.0320	–
Sb	13.4193	–	–3.1111	–	0.0351	–
Bi	14.3800	–	–3.1111	–	0.0234	–

TABLE 6. Total Entropy S/k_{B} of Liquid Metals

Metals	Present results	Other results [17, 18]	Experimental results [33]
Li	4.6928	5.08	5.74
Na	7.0965	7.10	7.84
K	8.5025	9.15	9.14
Rb	10.4938	10.51	10.27
Cs	11.3828	11.40	11.14
Be	4.2971	–	–
Mg	6.6691	6.7856	9.02
Ca	8.0863	–	–
Sr	9.5365	–	–
Ba	10.3301	–	–
Zn	7.7040	–	9.18
Cd	9.0548	9.1354	9.94
Hg	9.9860	–	–
Al	6.6442	6.7787	8.63
Ga	8.5725	–	–
In	9.2612	9.2965	9.13
Tl	10.2339	10.2760	11.00
Gd	10.5407	–	–
Si	7.9228	–	–
Ge	9.5224	–	–
Sn	9.6937	–	–
Pb	10.1089	10.1718	11.13
Sb	10.3433	–	–
Bi	11.2923	–	–

TABLE 7. Values of $-F{\cdot}10^3$ (au) of Liquid Metals

Metals	Present results					Other values [17, 18]	Experimental results [33]
	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	–	–

The parameters A_W and B_W are given by Waseda [20].

Results and Discussion. The input parameters and constants used in the present investigation of the thermodynamic properties of liquid metals are presented in Table 1. The computed values of the thermodynamic properties (U_{elec}, U_{ion}, $U_{\text{elec–ion}}$, U, as well as various contributions to the entropy S, and the Helmholtz free energy F) are given in Tables 2–7.

From Tables 2 and 3 it is seen that the values of U_{elec} and U_{ion} are negative, while $U_{\text{elec–ion}}$ can make a positive contribution to the internal energy. The present results for U_{elec} and U_{ion} are found to be in qualitative agreement with other theoretical results [17, 18] and experimental data [33]. However, there are large differences in the presently computed results and other ones because U_{elec} and U_{ion} are dependent on the model potential and the structure factor of 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 to be lower, while those from HR-screening function are higher than for other local field correction functions. The comparison of computed results with available theoretical [17, 18] and experimental [33] data is highly encouraging and reveals qualitative agreement. The temperature dependent fraction η is incorporated in the calculation of structure factor $a(q)$ and then $a(q)$ is 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.

In comparison with the presently computed results of the total internal energy U from static HR-function, the 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 in the cases of TY, IU, FR, and SR-functions are (in percent) of the order of 1.48–3.14, 0.4–0.88, 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 percent) 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, respectively, from the experimental data [33].

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 thus are independent of the model pseudopotential. The major contribution to the total entropy comes from the term S_{gas}. The present results for various contributions to the entropy are found to be in fair agreement with other ones [17, 18]. Present results for the total entropy *S* are given in Table 6. The comparison of the calculated total entropy *S* with the available experimental values [33] shows that, as the temperature of the liquid metals changes, the deviation from experimental data of [33] increases. In general, the deviation is within 2.18–28.00%.

Finally, using the total internal energy *U* and total entropy *S*, we have generated the Helmholtz free energy *F*, whose values are given in Table 7. From this table it is seen that the present results for the Helmholtz free energy of liquid metals are found to be in qualitative agreement with the available experimental [33] and theoretical [17, 18] findings. Moreover, it is noted that among the five employed local field correction functions, the function for HR (without exchange and correlation) gives the maximum numerical value of *F*, while the function for FR gives the minimum value.

The influence of the static HR-function on the Helmholtz free energy *F* 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 at various local field correction functions are found to be (in percent) 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 the Helmholtz free energy *F* is predicted. The computed findings of the Helmholtz free energy for Li, Na, K, Rb, Cs, Zn, Cd, Al, In, Tl, and Pb liquid metals deviate (in percent) in the ranges: 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, respectively, from the experimental data [33].

Thus, Tables 2–7 enable one to conclude that the presently calculated values of the total internal energy *U* and total entropy *S* are in fair agreement with the experimental data [33] 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 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. It should be noted that the theoretical or experimental data of only 12 liquid metals among 24 ones are available in the literature for comparison.

The numerical values of the thermodynamic properties of liquid metals are found to be quite sensitive to a selection of the local field correction function and are shown to vary significantly with a change in the function. Thus, the calculation of the thermodynamic properties is 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 cited studies, the present study spans the metallic elements of different groups of the Periodic Table on a common platform of the model potential and common criteria for evaluating the parameter of the model potential. This is critical for obtaining concrete conclusions.

Conclusions. We conclude that a proper choice of the local field correction function plays a vital role in predicting the thermodynamic properties of liquid metals. In comparison with the earlier reported investigation of the thermodynamics of some liquid metals of different groups of the periodic table, the present results are superior both qualitatively and quantitatively.

NOTATION

a, structure factor; *e*, charge of electron; *f*, correction factor for the exchange and correlated motion of the conduction electrons; *h*, Planck constant; k_B, Boltzmann constant; k_F, Fermi wave vector; *m*, atomic mass; *N*, total number of atoms; q, wave vector; r_C, parameter of the model potential; S, entropy of the system; T, temperature; U, internal energy; V^0, bare ion pseudopotential; W_B, EMC model potential of Ashcroft; Z, valence; ε and ε_{HR}, modified and static Hartree dielectric functions; η, packing fraction; Ω_0 atomic volume. Subscripts: elec, electron; gas, gas; ion, ion; HR, TY, IU, FR, and SR relate to the use of the correction functions of Hartree, Taylor, Ichimaru–Utsumi, Farid et al., and Sarkar et al., respectively.

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