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ENTHALPY, ENTROPY AND HELMHOLTZ FREE ENERGY OF TRANSITION AND RARE EARTH LIQUID METALS

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Recently proposed model potential of Baria and Jani is used to calculate Enthalpy, Entropy and Helmholtz free energy of liquid transition and rare earth metals with the variational approach. The parameter of the potential is determined with the standard zero pressure condition along with well established Sarkar et al screening function for exchange and correlation effect. Here we strongly emphasize that the parameter of the potential is independent of any fitting procedure either with any experimental data or with any theoretical values of any physical properties. The structure factor derived by Percus-Yevick solution for hard sphere fluids, which is characterized by hard sphere diameter, is used. A good agreement between theoretical investigations and experimental findings has confirmed the ability of the model potential to the liquid d and f – shell metals.

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In the last two decades, the considerable efforts have been made to the understanding of structure and thermodynamic properties of several liquid noble, transition and rare-earth metals [1-13]. A large number of experimental measurements on various properties of these metals are now available in the literature [14-15]. The interatomic potentials of simple metals [16-18] 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 that reliable. [3, 19].

Wills and Harrison [20] have derived the interatomic potentials for transition metals and obtained thermodynamic properties reasonably good. The potentials of Wills and Harrison have also been used for the determination of the surface properties of noble metals [21] and thermodynamic properties of 3d transition metals in the liquid state [3, 11]. The variational technique with a hard sphere fluid as a reference system have been used by Bretonnet and Deroache [11] for the calculation of Helmholtz free energy of a series of liquid transition metals. The potentials of Wills and Harrison [20] and Bretonnet and Deroache [11] 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 liquid metals [22-24]. 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.

Recently Baria and Jani [25-27] have proposed a model potential, using this potential they have reported large number of physical properties of d and f-shell metals successfully [25-27].

For the investigation of thermodynamic properties of liquid metals, the Helmholtz free energy, F, lies at the heart of the pseudopotential perturbation scheme. The standard thermodynamic relation for the free energy is [28, 29]

$$F = E - T S \tag{1}$$

where, E is the internal energy i.e. Enthalpy and S is the entropy of the system at a temperature T. Under the usual perturbation theory the internal energy E can be expressed as [28, 29]

$$E = E_{ion} + E_{elec} + E_{elec-ion}. \tag{2}$$

Here the first term E_{ion} is composed of kinetic energy $\{(3/2)\ k_B T\}$ of ions plus the contribution due to ion-ion interactions, usually known as Madelung contribution. Thus, we write [28, 29],

$$E_{ion} = \left(\frac{3}{2}\right) k_B T + \left(\frac{Z^2}{\pi}\right) \int_0^\infty \{a(q) - 1\} dq \tag{3}$$

where Z is the valency and a(q) is the structure factor. For the structure dependent contribution, the structure factor, a(q), for liquid metals is calculated from the Percus-Yevick solution for HS fluids which is characterized by the HS diameter (σ) or, equivalently, by the packing fraction $\eta = (\pi\sigma^3/6\Omega)$.

The term E_{elec} in equation (2) is the energy of the homogeneous electron gas, which is the sum of kinetic energy of electrons, exchange energy, correlation energy, and the low temperature specific heat contribution for the electron gas. Hence the expression for E_{elec} becomes [28, 29]

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

with k_F is the Fermi wave vector and N is the total number of atoms.

In the framework of pseudopotential second ordered perturbation theory $E_{elec\text{-}ion}$ has been obtained by [28, 29],

$$\begin{aligned} E_{elec-ion} = & \lim_{q \to 0} \left\{ W_B(q) + \frac{8\pi Z}{q^2} \right\} \left(\frac{Z}{\Omega}\right) + \\ & \frac{1}{16\pi^3} \int_0^\infty \{ W_B(q) \}^2 a(q) \frac{\varepsilon_H(q)}{\{1 + [\varepsilon_H(q) - 1][1 - G(q)]\}} q^4 \, dq \end{aligned} \tag{5}$$

Where, the first term on right hand side represents the first order energy and the second is the band structure energy. Here, $W_B(q)$ is bare ion pseudopotential, of Baria and Jani [25-27], its q-space form (in Ryd. Unit) is given by,

$$W_B(q) = -\frac{8\pi Z}{\Omega_0 q^2} \left\{ \begin{aligned} & \frac{4(\cos(q r_c) - 1)}{q^2 r_c^2} + \frac{4\sin(q r_c)}{q r_c} + \frac{\sin(q r_c)}{(1 + q^2 r_c^2)^3} \left[5 q r_c - 4 q^3 r_c^3 - q^5 r_c^5 \right] \\ & + \frac{\cos(q r_c)}{(1 + q^2 r_c^2)^3} \left[11 q^2 r_c^2 + 4 q^4 r_c^4 + q^6 r_c^6 \right] + \frac{2 e q^2 r_c^2 (q^2 r_c^2 - 3)}{(1 + q^2 r_c^2)^3} - \cos(q r_c) \end{aligned} \right\} \tag{6}$$

Where r_c is the parameter of the potential and e is the base of natural logarithm. $\varepsilon_H(q)$ is the modified Hartree dielectric function and G (q) is the exchange and correlation function due to Sarkar et al [30]. Using zero pressure condition we have evaluated the parameter of the potential r_c which is shown in Table 1. The necessary parameters used in the calculations are also displayed in table 1.

The second most essential part to investigate the free energy is the entropy, S, of the HS fluids. Using the information of HS diameter (σ) or packing fraction η, one can evaluate the entropy, S, as [28, 29].

$$S = S_{gas} + S_{\eta} + S_{elec} \tag{6}$$

with

$$S_{gas} = \left(\frac{5}{2}\right) k_B + k_B \ln\left\{\Omega\left(\frac{k_B T}{4\pi}\right)^{\frac{1}{2}}\right\} \tag{7}$$

$$S_{\eta} = k_B\, \eta\,(3\eta - 4)(1-\eta)^{-2} \tag{8}$$

$$S_{elec} = \left(\frac{\pi^2 {k_B}^2 T}{{k_F}^2}\right) \tag{9}$$

We have calculated the various contributions to the internal energy i. e., enthalpy, entropy and Helmholtz free energy of some d and f-shell metals at melting temperature. In expressions (3) and (5), the integration has been carried out up to $40k_F$ to avoid any artificial cutoff in the calculation and to achieve proper convergence. The input parameters used in present calculation are shown in Table 1.

The presently calculated values of internal energy i. e., enthalpy, entropy and Helmholtz free energy are displayed in table 2 to 4 and were ever possible we have either compared it with experimental data or with others such theoretical findings.

Thus it gets confirmed from Tables 3 and 4 that the presently calculated values of entropy are in good agreement with experimental data and are comparable to the other reported data [9, 10, 31]. This confirms the applicability of our model potential in the investigation of thermodynamic properties of liquid d and f-shell metals. So, present model potential is equally useful in the calculation of various properties of liquid metals without any modification.

Table 1. Input parameters used in the present calculations.

Metal	Temperature in (K)	r_c (au)	Z	η	Ω_0 (au)
Cu	1423	1.12609	1.0	0.46	79.4
Ag	1273	1.53714	1.0	0.45	115.4
Au	1423	1.57667	1.0	0.46	114.6
Ni	1773	1.04924	2.0	0.45	73.6
Pd	1853	1.36692	2.0	0.47	99.3
Pt	2053	1.39280	2.0	0.47	101.6
Rh	2236	1.29288	3.0	0.45	92.6
Ir	2720	1.32486	4.0	0.46	95.5
La	1194	2.58257	2.0	0.43	252.2
Yb	1098	2.42841	2.0	0.43	222.98
Ce	1072	2.40225	2.0	0.53	233.22
Th	2031	2.25595	2.0	0.45	222.98

Table 2. Enthalpy of liquid transition and rare earth metals.

Metal	Various contributions to the Enthalpy x 10^{-3} (au/atom)			Total Enthalpy (H) x 10^{-3} (au/atom)
	H_{elec}	H_{ion}	$H_{elec-ion}$	
Cu	-59.223	-379.169	60.458	-377.933
Ag	-74.590	-327.092	72.891	-328.792
Au	-74.453	-328.284	81.392	-321.345
Ni	-49.759	-887.275	125.128	-811.905
Pd	-77.285	-841.067	166.101	-752.250
Pt	-79.442	-834.769	169.309	-744.902
Rh	-72.412	-835.669	157.270	-750.811
Ir	-76.155	-776.987	161.044	-692.098
La	-147.637	-1081.456	433.211	-795.882
Yb	-141.314	-1145.821	434.972	-852.166
Ce	-143.467	-1084.297	415.030	-812.734
Th	-143.792	-1113.285	391.447	-865.630

Table 3. Entropy and helmholtz free energy of liquid transition and rare earth metals.

Metal	Various contributions to the Entropy			Total Entropy S / k_BT	Helmholtz free energy (F) x 10^{-3} (au/atom)
	S_{gas} / k_BT	$-S\eta / k_BT$	S_{elec} / k_BT		
Cu	14.248	-4.133	0.085	10.20	-14528.262
Ag	16.036	-5.000	0.106	10.93	-13358.153
Au	16.036	-4.133	0.118	12.02	-17681.906
Ni	14.395	-3.262	0.077	11.21	-19882.652
Pd	16.184	-4.333	0.099	11.95	-21172.984
Pt	16.742	-4.333	0.111	12.52	-25704.522
Rh	15.808	-3.942	0.114	11.98	-26810.249
Ir	17.071	-3.942	0.141	13.27	-36120.375
La	16.424	-3.586	0.102	12.94	-16041.556
Yb	16.412	-3.586	0.084	12.91	-14534.442
Ce	16.838	-2.966	0.088	13.96	-15221.914
Th	17.763	-3.586	0.153	14.33	-29111.626

Table 4. Entropy of the liquid transition and rare earth metals.

Metal	Entropy in unit of s/k_BT			
	Present	Expt. [31]	Others	
			[31]	[1]
Cu	10.20	10.28	9.87	
Ag	10.93	10.96	10.84	
Au	12.02	12.00	12.04	
Ni	11.21	11.69	10.02	12.76
Pd	11.95	12.11	11.50	
Pt	12.52	12.93	12.46	
Rh	11.98	-		
Ir	13.27	-		
La	12.94	13.0	12.87	
Yb	12.91	-		
Ce	13.96	14.4	14.67	
Th	14.33	-		

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