Analysis of Thermodynamics of Liquid d- and f-Shell Metals with the Variational Approach

J. K. Baria

V. P. & R. P. T. P. Science College, Vallabh Vidyanagar-388 120, Gujarat, India

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We use recently proposed potential to calculate internal energy (enthalpy), entropy and Helmholtz free energy of liquid d- and f-shell metals with the variational approach. The parameter of the potential is determined with the standard zero pressure condition along with well established Taylor screening function for exchange and correlation effects to the liquid d- and f-shell metals. Here we clearly mention that the parameter of the potential is independent of any fitting procedure either with any experimental data or 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 previous 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 so 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 Derouiche[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 Derouiche[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[25,26] have proposed a model potential depending on an effective core radius but otherwise parameter free. They have reported a large number of physical properties of d- and f-shell metals successfully. In this Letter, we calculate the structure factor, radial distribution function, longitudinal and transverse phonon frequencies, elastic constants, bulk modulus, longitudinal and transverse velocities, Debye temperature, autocorrelation function, characteristic frequencies, Viscosity coefficient and surface tension of liquid Cu, Ag, Au, Ni, Pd, Pt, Rh and Ir at and above melting point temperatures.

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[27,28]

$$F = E - TS, \tag{1}$$

where E is the internal energy 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[27,28]

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

Here the first term $E_{\rm ion}$ is composed of kinetic energy $(3/2)k_BT$ of ions plus the contribution due to ion–ion interactions, usually known as Madelung contribution. Thus, we write,[27,28]

$$E_{\rm ion} = \left(\frac{3}{2}\right)k_BT + \left(\frac{Z^2}{\pi}\right)\int_0^\infty \{a(q) - 1\}{\rm d}q, \tag{3}$$

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Table 1. Enthalpy, entropy and Helmholtz free energy of liquid d- and f-shell metals at melting temperature.

Metal	Various contributions to the enthalpy (10^{-3} a.u.)			Total enthalpy (H) (10^{-3} a.u.)	Various contributions to the entropy			Total entropy	Helmholtz free energy
	$H_{\text{elect-ion}}$	H_{ion}	H_{elect}		S_{gas}/k_B	$-S/k_B$	S_{elect}/k_B	S/k_B	(F) (10^{-3} a.u.)
Cu	−59.223	−379.169	60.458	−377.933	14.256	−4.133	0.085	10.209	−14528.262
Ag	−74.590	−327.092	72.891	−328.792	15.386	−5.000	0.106	10.493	−13358.153
Au	−74.453	−328.284	81.392	−321.345	16.440	−4.133	0.118	12.425	−17681.906
Ni	−49.759	−887.275	125.128	−811.905	14.398	−3.262	0.077	11.213	−19882.652
Pd	−77.285	−841.067	166.101	−752.250	15.660	−4.333	0.099	11.425	−21172.984
Pt	−79.442	−834.769	169.309	−744.902	16.742	−4.333	0.111	12.520	−25704.522
Rh	−72.412	−835.669	157.270	−750.811	15.817	−3.942	0.114	11.989	−26810.249
Ir	−76.155	−776.987	161.044	−692.098	17.079	−3.942	0.141	13.270	−36120.375
La	−147.637	−1081.456	433.211	−795.882	16.389	−3.586	0.102	12.904	−16041.556
Yb	−141.314	−1145.821	434.972	−852.166	16.443	−3.586	0.084	12.941	−14534.442
Ce	−143.467	−1084.297	415.030	−812.734	16.194	−2.966	0.088	13.316	−15221.914
Th	−143.792	−1113.285	391.447	−865.630	17.766	−3.586	0.153	14.333	−29111.626

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_{elect} in Eq. (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[27,28]

$$E_{\text{elect}} = NZ\Big\{\Big(\frac{3}{10}\Big)k_F^2 - \Big(\frac{3}{4\pi}\Big)k_F - 0.0474 - 0.0155\ln k_F - \Big(\frac{1}{2}\Big)\Big(\frac{\pi k_B}{k_F}\Big)^2 T^2\Big\} \tag{4}$$

with k_F being the Fermi wavevector and N being the total number of atoms.

Within the framework of pseudopotential second-ordered perturbation theory, $E_{\text{elect-ion}}$ has been obtained by[27,28]

$$E_{\text{elect-ion}} = \lim_{q\to 0}\Big\{W_B(q) + \frac{8\pi Z}{q^2}\Big\}\Big(\frac{Z}{\Omega}\Big) + \frac{1}{16\pi^3}\int_0^\infty \{W_B(q)\}^2 a(q)\Big\{\frac{1}{\varepsilon(q)} - 1\Big\}q^4\,\mathrm{d}q, \tag{5}$$

where the first term on the right-hand side represents the first-order energy and the second is the band structure energy, $W_B(q)$ is bare ion pseudopotential[25,26] and $\varepsilon(q)$ is the modified Hartree dielectric function.

In this expression, $\varepsilon_H(q)$ is the Hartree dielectric function and $G(q)$ is the correction factor for the exchange and correlated motion of the conduction electrons. In the present study we consider the local field correction $G(q)$ due to Taylor.[29]

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 as[27,28]

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

with

$$S_{\text{gas}} = \Big(\frac{5}{2}\Big)k_B + k_B\ln\Big\{\Omega\Big(\frac{k_BT}{4\pi}\Big)^{1/2}\Big\}, \tag{7}$$

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

$$S_{\text{elec}} = \frac{\pi^2 k_B^2 T}{k_F^2}. \tag{9}$$

Table 2. Entropy liquid d- and f-shell metals at melting temperature.

Metal	Entropy		
	Experiment[30]	Others[30]	Others[1]
Cu	10.28	9.87	
Ag	10.96	10.84	
Au	12.00	12.04	
Ni	11.69	10.02	12.76
Pd	12.11	11.50	
Pt	12.93	12.46	
Rh	–		
Ir	–		
La	13.0	12.87	
Yb	–		
Ce	14.4	14.67	
Th	–		

We have calculated the various contributions to the internal energy, entropy and Helmholtz free energy of some d- and f-shell metals at melting temperature. In expressions (3) and (4), 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 the present calculation are shown in Table 1.

The present calculated values of internal energy, entropy and Helmholtz free energy are compared with the experimental results[30] as well as other theoretical data[9,10] in Table 2.

Thus it can be confirmed from Tables 1 and 2 that the presently calculated values of internal energy and entropy are in good agreement with the experimental data and are comparable to the other reported data.[9,10,30] This confirms the applicability

of our model potential in the investigation of thermodynamic properties of liquid d- and f-shell metals. Therefore, the present model potential is equally useful in the calculation of various properties of liquid metals without any modification.

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