

## Thermodynamics of $d$ and $f$ – shell liquid metals – a variational approach

J K Baria, H J Trivedi, P N Gajjar and A R Jani\*

Department of Physics, Sardar Patel University,  
Vallabh Vidyanagar-388 120, India

E-mail : jay\_baria@yahoo.com

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**Abstract** . . . Recently proposed potential is used to calculate internal energy (enthalpy), entropy and Helmholtz free energy of  $d$  and  $f$  – shell liquid 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 effect. 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.

**Keywords** . . . Pseudopotential, thermodynamics, entropy

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### 1. Introduction

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 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 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, entirely depends on the validity of a given interatomic potential and the model used.

Recently, we have proposed [25, 26] a model potential depending on an effective core radius but otherwise parameter free. We have reported large number of physical properties of transition metals successfully. In the present paper, we have calculated 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.

### 2. The temperature dependence of thermodynamic properties

For the investigation of thermodynamic properties of liquid metals, the Helmholtz free energy  $F$  lies at the heart of the

\*Corresponding Author

pseudopotential perturbation scheme. The standard thermodynamic relation for the free energy is [27,28],

$$F = E - TS, \quad (1)$$

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]

$$E = E_{ion} + E_{elec} + E_{elec-ion}. \quad (2)$$

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 [27, 28]

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

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 ( $\sigma$ ) or, equivalently, by the packing fraction  $\eta = (\pi\sigma^3/6\Omega)$ .

The term  $E_{elec}$  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]

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

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

In the framework of pseudopotential, second order perturbation theory  $E_{elec-ion}$  has been obtained by [27, 28]

$$E_{elec-ion} = \lim_{q \rightarrow 0} \left\{ W_B(q) + \frac{8\pi Z}{q^2} \right\} \left\{ \frac{Z}{\Omega} \int_{\infty}^{\infty} \{W_B(q)\}^2 a(q) \frac{1}{\epsilon(q)} - 1 \right\} q^4 dq,$$

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 [25,26] and  $\epsilon(q)$  is the modified Hartree dielectric function.

In this expression,  $\epsilon_H(q)$  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 ( $\sigma$ ) or packing fraction  $\eta$ , one can evaluate the entropy  $S$  as [27, 28]

$$S = S_{gas} + S_{\eta} + S_{elec}, \quad (5)$$

$$\text{with } S_{gas} = \left(\frac{5}{2}\right)k_B + k_B \ln \left\{ \Omega \left(\frac{k_B T}{4\pi}\right)^2 \right\}, \quad (6)$$

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

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

Metal	Various contributions to the enthalpy $\times 10^{-1}$ (au)			Total enthalpy (H) $\times 10^{-1}$ (au)	Various contributions to the entropy			Total entropy $S/k_B$	Helmholtz free energy (F) $\times 10$ (au)
	$H_{\infty}$	H	$H_{\infty}$		$S_{gas}/k_B$	$-S_{\eta}/k_B$	$S_{elec}/k_B$		
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	5.386	-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

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

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 (3), 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 calculations are shown in Table 1.

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

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

Metal	Entropy		
	Expt [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	13.00	12.87	
Yb	–		
Ce	14.4	14.67	
Th	–		

Thus, it is 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 in the literature [9, 10, 30]. This confirms the applicability of our model potential in the investigation of thermodynamic properties of liquid *d* and *f*-shell metals.

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#### References

- [1] C Hausleitner and J Hafner *J Phys* **F18** 1025 (1988)
- [2] R N Joarder and R V Gopal Rao *Phys Stat Sol (b)* **109** 137 (1982)
- [3] C Regnault *Z Phys* **B76** 179 (1989)
- [4] S Natio, T Arai, I Yokoyama and Y Waseda *High Temp Mater Proc (GB)* **8** 125 (1989)
- [5] O Akmlade, A M Umar and L A Hussain *Pramana J Phys* **47** 771 (1996)
- [6] I Yokoyama and T Arai *Mater Trans JIM* **37** 527 (1996)
- [7] H Sasajima, T Arai and I Yokoyama *Mater Trans JIM* **39** 551 (1998)
- [8] I Yokoyama, I Ohkoshi and T Satoh *J Phys* **F13** 729 (1983)
- [9] J L Bretonnet, G M Bhuiyan and M Silbert *J Phys Condens Matter* **4** 5359 (1992)
- [10] N Jakse, J F Wax, J L Bretonnet and A Pasturel *J Non Cryst Solids* **205** 434 (1996)
- [11] J L Bretonnet and A Derouiche *Phys Rev* **B34** 8924 (1991)
- [12] G M Bhuiyan, M Silbert and M J Stott *Phys Rev* **B53** 636 (1996)
- [13] A Bari, T Das and R N Joarder *J Non-Cryst Sol* **136** 173 (1991)
- [14] R Hultgren *Selected Values of Thermodynamic Properties of Elements* (Am Soc for Metals, Ohio) (1973)
- [15] Y Waseda *The Structure of Non Crystalline Materials* (New York McGraw-Hill) (1980)
- [16] N W Aschcroft and D Stroud *Solid State Physics* (New York Academic) (1978)
- [17] M Simop *Liquid Metals* (London Academic) (1977)
- [18] J Hafner *Amorphous Solids and Liquid States* (New York Plenum) (1985)
- [19] C Hausleitner, G Kahl and J Hafner *J Phys Condens Matter* **3** 1589 (1991)
- [20] J M Wills and W A Harrison *Phys Rev* **B28** 4363 (1983)
- [21] V Russier, C Regnaut and J P Badiali *Z Phys Chem* **156** 489 (1988)
- [22] K C Jain, N Gupta and N S Saxena *Phys State Sol (b)* **160** 433 (1990)
- [23] Arun Pratap, Meeta Rani, K C Jain and N C Saxena *Indian J Pure Appl Phys* **28** 657 (1990)
- [24] Meeta Rani, Arun Pratap and N S Saxena *Indian J Pure Appl Phys* **27** 269 (1989)
- [25] J K Baria and A R Jani *Physica* **B328** 317 (2003)
- [26] J K Baria and A R Jani *Pramana-J Phys* **60** 1 (2003)
- [27] J Hafner *Phys Rev* **A16** 351 (1977)
- [28] S Singh and R N Singh *Phys Chem Liq* **24** 203 (1994)
- [29] R Taylor *J Phys* **F8** 1699 (1978)
- [30] M M G Alemany, M Calleja, C Rey, L J Gallego, J Casa and L E Gonzalez *J Non Cryst Sol* **250** 53 (1999)