

Thermodynamics of liquid alkali metals using pseudopotential Perturbation scheme

Jagendra Kamalsinh BARIA¹ and Ashvinkumar Ramaniklal JANI²

¹V. P. & R. P. T. P. Science College, Vallabh Vidyanagar, 388 120, Gujarat-INDIA

²Department of Physics, Sardar Patel University, Vallabh Vidyanagar,
388 120, Gujarat-INDIA

e-mail: jay_baria@yahoo.com

Received: 12.04.2010

Abstract

Recently proposed model potential of Baria and Jani is used with the exchange and correlation effect of Sarkar et al. to calculate internal energy (Enthalpy), Entropy and Helmholtz free energy of liquid Na, K, Rb and Cs at various temperatures with the variational approach. The parameter of the potential is determined with the standard zero pressure condition. The structure factor derived by Percus-Yevick solution for hard sphere fluids which is characterized by hard sphere diameter σ is used. A good agreement between theoretical investigations and experimental findings has confirmed the ability of the model potential to the liquid alkali metals.

Key Words: Pseudopotential, thermodynamics, Entropy, Enthalpy, Helmholtz free energy

PACS: 65.40.Gr, 71.15.Dx

1. Introduction

In recent years the variational technique has been extensively used to study the structural and thermodynamic properties of liquid metals. The major task in such studies concerns to choose an appropriate reference system for structure and pseudopotential for electron-ion interactions. Among the numerous existing methods, the use of hard-sphere (HS) system is largely justified because it provides analytical representation in terms of single parameter σ , the hard sphere diameter.

Umar et al. [1] presented the calculation of thermodynamic properties of Na, K, and Na-K alloys using pseudopotential theory and Gibbs-Bogoliubov (GB) variational method along with Percus-Yevick (PY) approximation. Kumaravadivel and Evans [2] performed a systematic study of the entropies and structure factors of fourteen liquid simple metals. Hafner [3] presented the “*ab initio*” calculation of the structure and the thermodynamic properties of simple liquid metals and alloys. He has used a system of HS as a reference system for describing the liquid structure. They determined effective hard-sphere diameters by a variational method based on GB inequality. They reported the results for Li, Na, K, Rb, Cs, Mg, Al and few alloys. Bratkovsky

et al. [4] investigated the accuracy of the various liquid theories for calculating the thermodynamics properties of liquid metals. The calculation are made for liquid Na, Rb, Mg and Al over a wide range of temperature and density using different theories including variational method and HS reference system. Kumaravadivel [5] discussed the ability of the model potentials to yield accurate thermodynamic properties of liquid metals.

Lai et al. [6] proposed an approach for treating a correction from the higher order perturbation terms to the usual low-order perturbation calculation for the one-valance electron states in a disordered metal. They presented the variational thermodynamics calculation in the framework of a HS reference system for the alkalis in the liquid phase and for the K-Rb, Na-K and Na-Cs liquid alloys. Ono and Yokoyama [7] calculated the Helmholtz free energy of liquid alkali metals using two kinds of one component plasma (OCP) structure factor as reference systems. They have evaluated various thermodynamic quantities with the variationally determined plasma parameter. Regnaut [8] computed the thermodynamic excess quantities of nine liquid metals which are calculated from the pseudopotential interatomic potential and the thermodynamic perturbation methods from the hard sphere fluid.

Li et al. [9] examined his early work and was improved so as to be applicable in principle to any disordered metal in liquid phase. Hansleitner and Hafner [10] presented the *ab initio* calculation of the structure and the thermodynamic properties of liquid transition metals. They have used the thermodynamic variational method for their work. Akinlade et al. [11] presented variational calculation of thermodynamic and structure for liquid Li and polyvalent liquid metals near the freezing point and for the other liquid alkali metals over a limited range of temperature above the freezing point. Bari et al. [12] discussed the effect of the soft component to the entropy of the system in the light of thermodynamic perturbation theory and obtained an expression as a function of the ingredients of the hard core reference system. They produced the structural and thermal properties reasonably well at and above melting point temperature.

Lie et al. [13] reexamined the thermodynamic properties of liquid alkali metals with GB inequality and the fluid of CHS in the mean spherical approximation as reference system. Their perturbative variational calculation of the Helmholtz free energy was based on *ab initio* and non-local pseudopotential. Singh and Singh [14] used the pseudopotential method to study the enthalpy and compressibility of alkali metals as function of temperature. The diameters of the HS reference system were determined by minimizing the Helmholtz free energy to ensure thermodynamic stability. They also explained the weak dependency of enthalpy on temperature. Badirkhan et al. [15] calculated the Helmholtz free energies of the liquid alkali metals at various temperatures and those of several polyvalent metals near freezing. They used the variational approach based on the GB inequality with the CHS reference fluid with *ab initio* non-local pseudopotential for the electron interaction. Akinlade [16] used the GB inequality to compute the thermodynamic and structural properties of alkali metals and Mg, Cd, Al, In, Tl, Pb using the soft sphere reference fluid. Akinlade [16] found that the SS reference fluid gives better results than the CHS. Thus, indicating that the SS is a preferred system. Singh and Sommer [17] evaluated the specific heat in the under cooled region ($T < T_m$, where T_m is the melting point temperature) of liquid metals Na, K, Rb and Cs. They used a simple scheme based on pseudopotential and HS results for the above study. They have also computed the diffusion coefficients which show T^2 dependence at temperatures lower than melting point temperature T_m .

Singh and Singh [18] discuss the effect of the core-ion potential on the thermodynamic properties of liquid alkali metals and alloys. A pseudopotential perturbation scheme based on GB variational technique is considered to investigate the structure and volume dependent contribution to the internal energies of liquid alkali metals. They analyzed the effect of core-ion potentials on Helmholtz free energy, enthalpy, and entropy

of liquid alkali metals. Singh and Jaju [19] investigated the specific heat of liquid Rb in the under cooled region ($T < T_m$) using a first principle theoretical scheme which is based on pseudopotential perturbation theory, the thermodynamics of HS systems and the variational method based on GB inequality.

The GB variational approach is widely used to investigate the thermodynamic properties of liquid alkali metals using pseudopotential theory [1–19]. In such type of studies, one requires appropriate reference system for structure and the pseudopotential for electron-ion interactions. People have used HS [6, 9, 14, 17, 18] or OCP [7] or optimized random phase approximation [8] or CHS [11, 13] or SS [10, 16] as a reference system. For the electron-ion interactions they have employed either Ashcroft empty core model [20] or Heine-Abarenkov model [21] or Harmonic model potential [22] or Generalized nonlocal model potential [16] or energy independent nonlocal model potential [6, 9]. All such studies reveal that the accuracy of the results depends on the application of model potential. The different forms of the model potential have generated different values of the thermodynamic properties.

Hence, we thought it worthwhile to investigate thermodynamic properties of liquid alkali metals using recently proposed successful model potential of Baria and Jani [23–25]. In the present work we choose the HS reference system which provides analytical representation in term of single parameter, σ , the hard sphere diameter [26, 27] and instead of working with historical model potentials like AS model and HA model, we have used our own single parametric model to describe electron-ion interaction [23–25]. We have used the potential parameter determined from standard zero pressure condition along with Sarkar et al. [28] screening function. We strongly emphasize that the present investigations are free from any fitting procedure with the observed physical quantities.

2. Theory

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 [3, 18]

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

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 [3, 18]

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

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 the Madelung contribution.

Thus, we write [3, 18]

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

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 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 [3, 18]

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

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

In the framework of pseudopotential second ordered perturbation theory $E_{elec-ion}$ has been obtained by [3, 18],

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

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 and $\varepsilon_H(q)$ is the modified Hartree dielectric function and $G(q)$ is the exchange and correlation function due to Sarkar et al. [28].

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 [3, 18].

$$S = S_{gas} + S_\eta + S_{elec}, \quad (6)$$

where

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

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

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

3. Results and discussion

We have calculated the various contributions to the internal energy, entropy and Helmholtz free energy of Na, K, Rb and Cs at various temperatures including 373 K. 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 calculations are shown in Table 1.

Table 1. Input parameters used in the computation.

Metal	T (K)	Z	r_c (a.u.)	Ω (a.u.)	k_F (a.u.)	σ (a.u.)
Na	373	1	2.1442	277.932	0.4740	6.2046
K	373	1	3.0707	535.332	0.3810	7.7199
Rb	373	1	2.8092	656.168	0.3560	8.2618
Cs	373	1	3.0682	830.565	0.3291	8.9370

The presently calculated values of internal energy, entropy and Helmholtz free energy are compared with experimental [30] as well as others theoretical data [18] in Tables 2 to 4. Singh and Singh [18] have reported internal energy and entropy using AS model, HA model and HMP. Singh and Singh [18] have calculated the thermodynamic properties of alkali metals at 373K and noticed that the Helmholtz free energy due to AS model deviates from the experimental data by 1.55% to 4.07%. The outcome due to HA model gives 0.24% to 2.47% deviation from the experimental findings. In the case of HMP this deviation is 6.62% to 14.65%. They have employed HS reference system for structure contribution. In comparison to AS and HA model the results due to HMP are poor. Thus it gets confirmed from Tables 2 and 3 that the presently calculated values of internal

Table 2. Various contributions to the internal energy.

Metal	$E_{elec} \times 10^{-3}$ (au)		$E_{ion} \times 10^{-3}$ (au)		$E_{elec-ion} \times 10^{-3}$ (au)		Internal energy (E) $\times 10^{-3}$ (au)		Expt. [30]
	Present	Others [29]	Present	Others [29]	Present	Others [29]	Present	Others [29]	
Na	-81.70	-81.61	-195.09	-212.9	54.35	76.50	-222.44	-217.31	-226.0
		-81.61		-211.92		72.57		-220.96	
		-81.61		-210.16		50.00		-241.77	
K	-80.04	-79.89	-150.43	-169.03	39.68	66.49	-190.79	-182.43	-190.0
		-79.89		-168.39		58.47		-189.81	
		-79.89		-166.41		38.29		-208.01	
Rb	-78.57	-78.41	-152.44	-156.77	49.97	58.54	-181.04	-176.64	-180.0
		-78.41		-156.49		53.37		-181.53	
		-78.41		-151.45		26.98		-202.88	
Cs	-76.50	-76.31	-139.14	-143.53	44.10	56.33	-171.54	-163.51	-170.0
		-76.31		-144.19		50.84		-169.66	
		-76.31		-134.38		14.97		-195.72	

Table 3. Various contributions to the entropy.

Metal	Entropy								
	S_{gas} / k_B		$-S_{\eta} / k_B$		S_{elec} / k_B		S / k_B		Expt. [31]
	Present	Others [18]	Present	Others [18]	Present	Others [18]	Present	Others [18]	
Na	11.222	11.2238	3.9391	4.2284	0.0519	0.0518	7.3352	7.047	7.79
		11.2238		4.1400		0.0518		7.136	
		11.2238		3.6523		0.0518		7.623	
K	12.6742	12.6756	3.9417	3.7968	0.0803	0.0803	8.8128	8.959	9.45
		12.6756		3.6037		0.0803		9.152	
		12.6756		3.1211		0.0803		9.635	
Rb	14.0434	14.0522	3.9409	3.4692	0.0920	0.0919	10.1944	10.67	10.35
		14.0522		3.3929		0.0919		10.75	
		14.0522		2.4472		0.0919		11.69	
Cs	14.9488	14.9501	3.1407	3.1283	0.1076	0.1076	11.9157	11.92	12.12
		14.9501		3.2983		0.1076		11.75	
		14.9501		1.8473		0.1076		13.21	

energy, entropy, and Helmholtz free energy are in excellent agreement with experimental data as well as much better other theoretically reported data [18, 29]. This confirms the applicability of our model potential in the investigation of thermodynamic properties of liquid alkali metals.

We have also investigated the temperature dependence of enthalpy, entropy, and Helmholtz free energy of Na, K, Rb and Cs based on same technique. The input parameters used are shown in the Table 5 and

Table 4. Contribution to the Helmholtz free energy.

Metal	Helmholtz free energy $F \times 10^{-3}$ (au)		
	Present	Others [18]	Expt. [31]
Na	-233.861	-225.6262	-235.2061
		-229.3932	
		-250.7787	
K	-199.964	-193.0176	-201.1167
		-200.6257	
		-219.3965	
Rb	-191.266	-189.2497	-192.2315
		-194.2342	
		-216.6951	
Cs	-184.682	-177.5969	-184.3233
		-183.5460	
		-211.3314	

Table 5. The input parameters and constants used in present calculations.

Metal	r_c (au)	T (K)	Ω (au)	σ (au)	k_F (au)
Na	2.1442	371	277.9679	6.0639	0.4740
		473	285.7080	6.1196	0.4697
		573	294.1938	6.1796	0.4652
		673	303.1990	6.2420	0.4605
		773	312.7729	6.3071	0.4557
K	3.0707	336.4	529.6614	7.5177	0.3824
		423	543.3267	7.5177	0.3791
		523	559.2823	7.6553	0.3755
		623	576.5828	7.7334	0.3717
		723	594.9878	7.8148	0.3678
Rb	2.8092	312.6	643.4080	8.0213	0.3584
		373	655.7914	8.0725	0.3500
		473	677.1733	8.1593	0.3523
		573	699.9966	8.2499	0.3484
		673	724.4121	8.3447	0.3445
Cs	3.0682	301.6	812.3274	8.6695	0.3316
		373	830.0812	8.7322	0.3292
		473	856.3405	8.8233	0.3258
		573	884.3156	8.9184	0.3223
		673	914.1801	9.0176	0.3188

corresponding output results are shown in the Table 6. It is seen from these tables that the entropy increases with increase in the temperature because of increase in hard sphere diameter. It is clear from Table 6 that our presently investigated findings are excellent in agreement with the experimental findings as well as other such theoretical findings [18, 29–31]. Here we clearly mention that we have not fitted parameter of the potential with any of the experimental data to reproduce the physical properties unlike Singh and Singh [18].

Table 6. Enthalpy, Entropy, and Helmholtz free energy of liquid alkali metals.

Metal	T (K)	Various contributions to the enthalpy $\times 10^{-3}$ (au)			Total enthalpy $(E) \times 10^{-3}$ (au)	Various contributions to the entropy			Total entropy S / k_B	Helmholtz free energy $(F) \times 10^{-3}$ (au)
		E_{elec}	E_{ion}	$E_{elec-ion}$		S_{gas} / k_B	$-S\eta / k_B$	S_{elec} / k_B		
Na	371.00	-81.7058	-208.1610	63.0281	-226.8390	11.2221	-3.4209	0.0516	7.8528	-236.0700
	473.00	-81.8351	-205.2640	61.2965	-225.8020	11.2496	-3.4209	0.0670	7.8957	-237.6350
	573.00	-81.9739	-202.2770	59.5031	-224.7480	11.2789	-3.4209	0.0828	7.9408	-239.1640
	673.00	-82.1217	-199.2500	57.7099	-223.6610	11.3090	-3.4209	0.0992	7.9873	-240.6930
	773.00	-82.2794	-196.1790	55.9169	-222.5420	11.3401	-3.4209	0.1164	8.0356	-242.2220
K	336.40	-80.0738	-167.5530	45.1998	-202.4270	12.6636	-3.4209	0.0720	9.3146	-199.3550
	423.00	-80.0061	-165.3210	43.5081	-201.8190	12.6884	-3.4209	0.0920	9.3595	-201.3630
	523.00	-79.9452	-162.7110	42.5499	-200.1060	12.7180	-3.4209	0.1160	9.4130	-203.7040
	623.00	-79.9046	-160.0670	40.5920	-198.3790	12.7484	-3.4209	0.1410	9.4685	-206.0690
	723.00	-79.8856	-157.3870	39.6342	-197.6390	12.7799	-3.4209	0.1671	9.5260	-208.4600
Rb	312.60	-78.6695	-157.0580	46.7194	-189.0080	14.0311	-3.4209	0.0761	10.6863	-199.5920
	373.00	-78.5822	-155.4700	45.8245	-188.2280	14.0501	-3.4209	0.0920	10.7212	-200.8980
	473.00	-78.4567	-152.8290	44.3565	-186.9290	14.0822	-3.4209	0.1192	10.7805	-203.0850
	573.00	-78.3536	-150.1500	42.8887	-185.6150	14.1154	-3.4209	0.1476	10.8420	-205.2980
	673.00	-78.2745	-147.4320	41.4212	-184.2850	14.1497	-3.4209	0.1774	10.9061	-207.5400
Cs	301.60	-76.6273	-145.1980	44.1622	-177.6630	14.9264	-3.4209	0.0858	11.5913	-188.7390
	373.00	-76.5095	-143.4560	43.2043	-176.7610	14.9480	-3.4209	0.1076	11.6347	-190.5110
	473.00	-76.3681	-140.9880	41.8605	-175.4950	14.9792	-3.4209	0.1394	11.6976	-193.0260
	573.00	-76.2565	-138.4870	40.5170	-174.2270	15.0113	-3.4209	0.1725	11.7629	-195.5820
	673.00	-76.1770	-135.9530	39.1736	-172.9560	15.0445	-3.4209	0.2071	11.8307	-198.1830

Finally we conclude that, the present investigations are free from any artificial fitting procedure to predict correct experimental data. Hence, the reported data are more meaningful and will provide a better source for further comparison with other such theoretical and experimental findings. This confirms the applicability of our model potential for predicting the thermodynamic properties of liquid metals.

Acknowledgement

One of the authors (JKB) is thankful to the University Grants Commission (UGC-WRO, Pune) for providing financial support under minor research project grant (F. No.: 47-719/08).

References

- [1] I. H. Umar, A. Mayar, M. Watabe and W. H. Young, *J. Phys. F: Met. Phys.*, **4**, (1974), 1691.
- [2] R. Kumaravadivel and R. Evans, *J. Phys. C: Solid State Phys.*, **9**, (1976), 3877.
- [3] J. Hafner, *Phys. Rev.*, **A16**, (1977), 351.
- [4] A. M. Bretovsky, V. G. Vaks and A. V. Trefilov, *J. Phys. F: Met. Phys.*, **13**, (1983), 2517.
- [5] R. Kuamravadivel, *J. Phys. F: Met. Phys.*, **13**, (1983), 1607.
- [6] S. K. Lai, M. Matsuura and S. Wang, *J. Phys. F: Met. Phys.*, **13**, (1983), 2033.
- [7] S. Ono and I. Yokoyama, *J. Phys. F: Met. Phys.*, **14**, (1984), 2909.
- [8] C. Regnaut, *J. Phys. F: Met. Phys.*, **16**, (1986), 295.
- [9] D. H. Li, X. R. Li and S. Wang, *J. Phys. F: Met. Phys.*, **16**, (1986), 309.
- [10] C. Hausleitner and J. Hafner, *J. Phys. F: Met. Phys.*, **18**, (1988), 1025.
- [11] O. Akinlade, S. K. Lai and M. P. Tosi, *Physica B*, **167**, (1990), 61.
- [12] A. Bari, T. Nammalvar and R. N. Joarder, *Phys. Chem. Liq.*, **21**, (1990), 9.
- [13] S. K. Lie, O. Akinlade and M. P. Tosi, *Phys. Rev.*, **A41**, (1990), 5482.
- [14] R. N. Singh and V. N. Singh, *Phys. Chem. Liq.*, **22**, (1991), 235.
- [15] Z. Badirkhan, O. Akinlade, G. Pastore and M. P. Tosi, *J. Phys.: Condens Matter*, **4**, (1992), 6173.
- [16] O. Akinlade, *Phys. Stat. Sol. (b)*, **169**, (1992), 23.
- [17] R. N. Singh and F. Sommer, *Phys. Chem. Liq.*, **28**, (1994), 129.
- [18] S. Singh and R. N. Singh, *Phys. Chem. Liq.*, **24**, (1994), 203.
- [19] R. N. Singh and R. P. Jaju, *Phys. Chem. Liq.*, **36**, (1998), 67.
- [20] N. W. Ashcroft, *Phys. Lett.* **23**, 48 (1966), *J. Phys. C*, **1**, (1968), 232.
- [21] V. Heine and I. Abarenkov, *Phil. Mag.*, **9**, (1964), 451.
- [22] R. N. Singh, and P. L. Srivastava, *Phys. Stat. Sol. (b)*, **89**, (1978), k13.
- [23] J. K. Baria, and A. R. Jani, *Physica B*, **328**, (2003), 317.
- [24] J. K. Baria, and A. R. Jani, *Pramana J. Phys.*, **60**, (2003), 1235.
- [25] J. K. Baria, *Physica B*, **371**, (2006), 280.
- [26] N. W. Ashcroft, and D. C. Langreth, *Phys. Rev.*, **156**, (1967), 685.
- [27] N. W. Ashcroft, and D. C. Langreth, *Phys. Rev.*, **159**, (1967), 500.
- [28] A. Sarkar, D. Sen, S. Haldar, and D. Roy, *Modern Physics Letters*, **12**, (1998), 639.
- [29] M. J. Hujiben and W. Van der lugt, *Acta crystaogr. Sect.*, **A35**, (1979), 431.
- [30] M. Ross, H. E. Dewitt and W. B. Hubbard, *Phys. Rev.*, **A24**, (1981), 1016.
- [31] R. Hultgren, P. D. Desai, D. T. Howking, M. Gleiser, K. K. Kelly and D. Wagman, Selected Values of the Thermodynamic Properties of the Element and Alloys, (Ohio, Am Soc Metals, Metal Park. 1973).