

## Thermodynamical Investigation of Liquid Alkali Metals with Gibbs–Bogoliubov Method

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In this article, the framework has been prepared to investigate the various thermodynamical properties namely; entropy  $S$ , internal energy  $E_{INT}$  and Helmholtz free energy  $F_H$  of some liquid alkali metals using the universal model potential given by Fiolhais *et al.* with Percus-Yevick hard sphere (PYHS) reference system. The screening influence of six different local field correction functions proposed by Hartree (H), Taylor (T), Ichimaru-Utsumi (IU), Farid *et al.* (F), Sarkar *et al.* (S) and Nagy (N) for the first time with universal model potential of Fiolhais *et al.* are reported. A very good agreement between the presently computed data and experimentally available data is found.

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

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### 1. INTRODUCTION

The complete thermodynamical study of alkali metal has its importance in heat transfer mechanism, metallurgy and material science. Many of the alkali metals have their melting points at or near to room temperature which makes necessary to investigate the properties of elements of this group in the liquid phase. The pseudopotential theory has proven its importance in the study of the liquid metals and alloys [1-19], but the liquid state of metal is very difficult to study with a very less adjustment in the parameter(s) of model potential because of its complex electron-ion interaction behavior in this state.

As a common observation, it is also found that the parameter fitting is required to achieve the agreement between the experimental data and the computed data in most of the cases. It shows a requirement of a kind of potential which can be useful to investigate as many as (ideally all) properties of matter in all physical states by setting minimum numbers of parameters. Hence, to remove this limitation of other potentials, in the present article, we thought it would be worthy to study of thermodynamical properties of some liquid alkali metals using the well-known universal model potential of Fiolhais *et al.* [16].

Six different types of local field correction functions viz. Hartree (H) [3-11], Taylor (T) [3-11], Ichimaru-Utsumi (IU) [3-11], Farid *et al.* (F) [3-11], Sarkar *et al.* (S) [3-11] and Nagy (N) [12] are used for the first time with the said potential to the best of our knowledge. The PYHS reference system as used in [3-11] is adopted in the present computation for generating the structure factor.

With the help of analysis of our results and that of a recent review article of Dubinin *et al.* [1], we established the fact that the PYHS method is sufficiently efficient for this study.

### 2. COMPUTATIONAL METHODOLOGY

The Gibbs-Bogoliubov (GB) approximation has been found an appropriate tool to study the thermodynamics of liquids metals [1-11]. According to it, the Helmholtz free energy  $F_H$  can be written as,

$$F_H = E_{INT} - TS. \quad (1)$$

$E_{INT}$  is the internal energy and can be further expressed as it consists three different contributions,

$$E_{INT} = E_{ion} + E_{ele} + E_{ele-ion}, \quad (2)$$

where  $E_{ion}$ ,  $E_{ele}$ ,  $E_{ele-ion}$  can be expressed as in the ref [1-11].

Further to obtain the electron-ion interaction, the involvement of the model potential is required. In the present work, we use well-known universal model potential proposed by Fiolhais *et al.* [16]. Initially, this local potential was given with two different types of parameters known as Universal and Individual parameters. In the both cases, the potential parameters are given for solid state by the authors [16]. The potential was constructed to apply a wide range of elements in solid state. Afterward, the potential was tested from its transferability point of view for liquids.

Apart from internal energy  $E_{INT}$ , the entropy  $S$  is also calculated by the following equation,

$$S = S_{gas} + S_{ele} + S_{PYHS}, \quad (3)$$

where  $S_{gas}$ ,  $S_{ele}$ , and  $S_{PYHS}$  are the various entropy contributions as expressed in [1-11]. Further, the excess entropy  $S_{exc}$  can be expressed as [1-11],

$$S_{exc} = S - S_{gas}. \quad (4)$$

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3. RESULTS AND DISCUSSION

The input parameters used in the present computation are narrated in Table 1. The computed values of the thermodynamic properties:  $E_{ion}$ ,  $E_{ele}$ ,  $E_{ele-ion}$ ,  $E_{INT}$ , and various contributions to the entropy ( $S$ ) and Helmholtz free energy are shown in Tables 2-6. From Table 2, it is observed that out of three parts of the internal energy  $E_{INT}$ , the  $E_{ele}$  and the  $E_{ion}$ , have negative values whereas the third part i.e.  $E_{ele-ion}$  gives the positive contribution.  $E_{ele-ion}$  and  $E_{ele}$  are potential dependent parts of the internal energy  $E_{INT}$ .

Table 1 – The input parameters and constants

Metal	Valance	Atomic volume (a.u.)	Packing fraction ( $\eta$ )	$\alpha$ [16]	$R$ [16]
Li	1	142.47	0.46	3.549	0.361
Na	1	277.93	0.46	3.075	0.528
K	1	535.33	0.46	2.807	0.745
Rb	1	656.17	0.43	2.748	0.824
Cs	1	830.57	0.43	2.692	0.920

From the data given in Table 3 the influence of the various correction functions with respect to static Hartree dielectric function ( $H$ ) on  $E_{ele-ion}$  of Li, Na, Rb and Cs is found maximum upto 2.10%, 2.38%, 2.60% and

Table 3 –  $E_{ele-ion}$  comparison with other theoretical results

Metal	$E_{ele-ion}$ (in $10^{-3}$ au)						Others [3, 14]
	Present						
	H	T	IU	F	S	N	
Li	139.81	141.65	141.99	142.01	141.01	142.75	17.81, 32.07, 73.47, 87.12, 87.22, 102.40
Na	119.45	120.87	121.13	121.15	120.39	122.29	43.48, 65.07, 103.51, 117.87, 118.17, 139.48
K	109.60	110.60	110.75	110.77	111.23	111.99	39.24, 56.67, 89.32, 103.03, 103.19, 126.03
Rb	108.47	109.67	109.80	109.84	109.20	111.30	25.34, 35.52, 69.98, 85.05, 85.09, 108.24
Cs	98.59	99.69	99.81	99.85	99.26	101.38	18.11, 18.42, 53.01, 68.73, 68.94, 91.50

Table 4 – Calculated results for  $E_{INT}$

Metal	$-E_{INT}$ (in $10^{-3}$ a.u.)							Expt. [1]
	Present						Others [3, 14]	
	H	T	IU	F	S	N		
Li	264.26	262.42	262.07	262.05	263.05	261.31	236.63 251.80, 251.55, 265.55, 306.94, 388.97	254.00
Na	224.49	223.07	222.81	222.79	223.56	221.64	157.69, 178.99, 179.30, 193.59, 232.08, 302.02	226.00
K	180.51	178.51	178.37	179.35	179.88	177.11	126.11, 148.95, 149.11, 162.82, 195.61, 259.54	193.00
Rb	164.65	163.45	163.31	163.28	163.91	161.81	31.39, 154.54, 154.58, 169.66, 204.11, 248.17	179.00
Cs	154.31	153.22	153.10	153.06	153.65	151.52	134.54, 157.10, 157.31, 173.03 207.62, 239.17	169.00

The presently calculated entropy contribution is compared with the experimental data cited in [1] in Table 5. The deviation from for Li, Na, K, Rb and Cs is found 17.94%, 8.34%, 8.86%, 1.50% and 5.37%, respectively. The excess entropy  $S_{exc}$  is found for Li, Na, K, Rb and Cs 4.1%, 4.08%, 4.12%, 3.49% and 3.47%, respectively. It is also very near and experimental values those compiled in Ref [1]. The hard sphere reference system estimates the more promising value of excess entropy  $S_{exc}$  than the other system. Present results also follow the same fashion for this estimation for PYHS [3-11] reference system instead just as HS reference system. As compared to the  $S_{exc}$  by OCP reference system given in the article of Dubinin et al. [1], the  $S_{exc}$  calculated in the HS reference system is found higher.

2.83% due to N-function, respectively, while 2.18% due to T in case of K. Also, it is found minimum 0.86% due to S, 0.79% due to S, 0.91% due to T, 0.67% due to S and 0.68% due to S for Li, Na, K, Rb and Cs metals, respectively. From Table 4, the influence of the various local field correction functions with respect to static Hartree dielectric function ( $H$ ) on  $E_{INT}$  of Li, Na, K, Rb and Cs are found minimum upto 0.46%, 0.41%, 0.35%, 0.45% and 0.43% due to S-function, respectively. It is found maximum in percentage upto 1.12%, 1.27%, 1.88%, 1.72% and 1.80% due to N-function respectively.

Table 2 – Values of  $E_{ion}$  and  $E_{ele}$

Metal	$-E_{ion}$ (in $10^{-3}$ au)		$-E_{ele}$ (in $10^{-3}$ au)	
	Present	Others [2, 14]	Present	Others [3, 14]
Li	328.51	325.75, 262.37, 262.38, 262.39	75.51	76.03, 76.63
Na	262.23	266.08, 215.45, 215.46	81.71	81.60, 81.71
K	210.07	218.14, 172.07	80.04	80.64, 80.07
Rb	194.18	194.64, 161.03	78.94	78.87, 78.61
Cs	176.40	181.02, 149.38	76.50	77.08, 76.66

Apart from OCP, our results also show the same type of trend in the case of CHS method [2]. In other words, it is clear that (as HS system) the PYHS approximation also estimates higher values of Excess entropy  $S_{exc}$  than provided by OCP.

As shown in Table 6, the influence of the various correction functions with respect to static Hartree dielectric function ( $H$ ) on  $F_H$  of Li, Na, K, Rb and Cs are found the minimum in percentage 0.45%, 0.40%, 0.33%, 0.42% and 0.40% due to S-function, respectively.

The influence of the various correction functions with respect to static Hartree dielectric function ( $H$ ) on  $F_H$  of Li, Na, K, Rb and Cs are found the maximum in percentage 1.12%, 1.27%, 1.88%, 1.72% and 1.80% due to N-function, respectively.

Table 5 – Entropy ( $S$ ) calculation

Metal	Entropy contributions								
	$S_{gas} / k_B$		$S_{ele} / k_B$		$S_{PHYS} / k_B$		$S / k_B$		
	Present	Others [3, 14]	Present	Others [3, 14]	Present	Others [3, 14]	Present	Others [3, 14]	Expt. [1]
Li	10.87	8.7848 8.8200	0.0351	0.0411 0.0431	-4.1331	-4.1331	6.77	5.080,4.692	5.74
Na	11.2214	11.2220 11.2238	0.0519	0.0519 0.0518	-4.1331	-4.2284 -4.1400 -3.6523	7.1402	7.331,7.047 7.136,7.326	7.79
K	12.67	12.6742 12.6756	0.0803	0.0803 0.0803	-4.1331	-3.7968 -3.6037 -3.1211	8.6123	8.812,8.959 9.152,9.635	9.45
Rb	14.00	14.0507 14.0522	0.0892	0.0920 0.0919	-3.5866	-3.4692 -3.3929 -2.4472	10.5062	10.200,10.670 10.750,10.690	10.35
Cs	14.9486	14.9486 14.9501	0.1077	0.1076 0.1076	-3.587	-3.1283 -3.2983 -1.8473	11.4697	11.114,11.920 11.750,13.210	12.12

Table 6 – Results for Helmholtz free energy ( $F_H$ )

Metal	$-F_H 10^{-3}$ (a.u.)							
	Present						Expt. [1]	Others [3, 14, 15]
	H	T	IU	F	S	N		
Li	269.76	267.92	267.58	267.55	268.55	266.81	265	244.09, 259.26, 259.36, 273.10, 314.40
Na	232.90	231.48	231.21	231.20	231.97	230.05	236	238.90,225.62, 229.39, 250.77
K	190.70	189.71	188.56	188.54	190.07	188.30	202	200.61, 193.01,200.62,219.39
Rb	177.07	175.87	175.73	175.69	176.33	174.23	190	190.91, 189.24, 194.23, 216.69
Cs	167.87	166.78	166.65	166.61	167.20	165.08	182	179.23, 177.59, 183.54, 211.33

The above analysis shows that for all elements under study, the influence of corrections functions with respect to static Hartree dielectrics function ( $H$ ) on  $E_{ele-ion}$ , on  $E_{INT}$  and on  $F_H$  is the minimum for  $S$ - and maximum for  $N$ -function (except in the single case of  $E_{ele-ion}$  for K).

The comparison with the experimental data and present calculation can decide the efficiency of the method used here. The deviation from the experimentally available data cited in ref [1] with our calculation of  $E_{INT}$  for Li, Na, K, Rb and Cs (in percentage) is 2.88-4.04%, 0.67-1.92%, 6.47-8.23%, 8.02-9.60% and 8.69-10.34% respectively. Some ab-initio based results are cited by Dubinin et al. [1]. In which, they observed that the deviations from the experimental values for internal energy  $E_{INT}$  for Li, Na, K, Rb and Cs metals are 4.37 %, 3.12%, 4.18%, 4.40% and 1.33% respectively. It means that for Li and Na, our results are much better than that those from ab-initio calculation. While for other elements like K, Rb and Cs with higher volumes that ab-initio calculation provides less deviation than the present results. It also shows that the change in trend, the deviation of our results from experimental values of the internal energy  $E_{INT}$  in case of Li is comparatively less and in case of other than Li is found more, whereas for results of Vora [3] and for results cited in article [1] the situation is inverse. This trend in results favors the results of Thakor et al. [14, 15].

The deviation from experimental data [1] in case of Helmholtz free energy  $E_{INT}$  for Li, Na, K, Rb and Cs is 0.68-1.80%, 1.31-2.52%, 5.59-6.78%, 6.80-8.30% and 7.76-9.30% respectively. This shows that the very good

agreement between the present calculation and the experimental data.

The potential used in the current article shows more influence of the correction functions than the potential used by Vora [3] and less influence of the correction functions than the potential used by Thakor et al. [14]. This means that the presently used potential is optimum sensitive to the local field correction functions and preferable to study the thermodynamical properties of the liquid alkali metals.

The established agreement between the experimental data and the presently calculated properties itself proves the worthiness of the application of the potential for a group of elements under study. Results show that the said potential is suitable and applicable to the liquid phase of the alkali elements also.

#### 4. CONCLUSIONS

In the current investigation, five liquid alkali metals studied from the thermodynamical point of view. The internal energy  $E_{INT}$ , entropy  $S$  and Helmholtz free energy  $F_H$  are obtained using pseudopotential theory. Overall very good agreement between our prediction and experimental values of various properties are found. In the case of thermodynamical properties, we prove the transferability of the potential given by Fiolhais et al. [16]. The present study itself provides the excellent database for research, working with the liquid alkali metals. The seven different types of the local field correction functions are used for the first time with this potential. It is found sensi-

tive to the selection of the proper local field correction functions on the aforementioned study.

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