

Thermodynamical Investigation of Liquid Alkali Metals with Gibbs-Bogoliubov Method

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(Received 10 October 2017; revised manuscript received 12 February 2018; published online 24 February 2018)

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 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.

DOI: [10.21272/jnep.10\(1\).01002](https://doi.org/10.21272/jnep.10(1).01002)

PACS numbers: 61.25.Mv, 65.40.Gr, 71.15.Dx

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 [1-3], 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. [4].

Six different types of local field correction functions viz. Hartree (H) [3], Taylor (T) [3], Ichimaru-Utsumi (IU) [3], Farid et al. (F), Sarkar et al. (S) [3] and Nagy (N) [5] are used for the first time with the said potential to the best of our knowledge. The PYHS [6] reference system is adopted in the present computation for 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 is sufficiently efficient for the present study.

2. COMPUTATIONAL METHODOLOGY

The Gibbs-Bogoliubov (GB) approximation has been found an appropriate tool to study the thermodynamics

of liquids metals [1-3]. 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} and $E_{ele-ion}$ can be expressed as in the ref [2].

Further to obtain the electron-ion interaction, the involvement of the model potential is required. In the present work, we have used well-known universal model potential proposed by Fiolhais et al. [4].

Initially, this local potential was given with two different types of parameters known as universal and individual parameters. In the both cases, the parameters are given for solid state by Fiolhais et al. [4]. 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 [2, 3]. Further, the excess entropy S_{exc} can be expressed as [1],

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

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_{ele} , E_{ion} , $E_{ele-ion}$, E_{INT} ,

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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. Whereas $E_{ele-ion}$ and E_{ele} are the potential dependent parts of the internal energy E_{INT} .

Table 1 – The input parameters and constants

| Metal | Valance | Atomic volume (a.u.) | Packing fraction (η) | α [4] | R [4] |
|-------|---------|----------------------|-----------------------------|--------------|---------|
| 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, K, Rb and Cs is found maximum 2.10 %, 2.38 %, 2.60 %, 2.18 and 2.83 % due to N-function, respectively. While, it is found minimum 0.86 % due to S for Li, 0.79 % due to S

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

| Metal | $E_{ele-ion} \cdot (10^{-3} \text{ a.u.})$ | | | | | | Others [3, 7] |
|-------|--|--------|--------|--------|--------|--------|--|
| | 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 | $E_{INT} \cdot 10^{-3} \text{ (a.u.)}$ | | | | | | | Expt. [1] |
|-------|--|--------|--------|--------|--------|--------|--|-----------|
| | Present | | | | | | Others [3, 7] | |
| | 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 [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 nearer to the calculated results of Iwatsumi et al. [1] and experimental values those compiled in Ref [1]. The hard sphere reference system estimates the more value of excess entropy S_{exc} than the CHS system. Present results also follow the same fashion for this estimation for PYHS [3] reference system instead just as HS reference system. As compared to the S_{exc} in the OCP reference system given in the article of Dubinin et al. [1], the S_{exc} calculated in the HS reference system is higher. Apart from OCP, our results also show the same type of trend in the case of CHS. In other words, it is clear that (as HS system)

for Na, 0.91 % due to T for K, 0.67 % due to S for Rb and 0.68 % due to S for Cs, respectively.

From Table 4, the influence of the various correction functions with respect to static H -function on E_{INT} of Li, Na, K, Rb and Cs are established minimum of the order of 0.46 %, 0.41 %, 0.35 %, 0.45 % and 0.43 % due to S-function. It is found maximum in percentage in order of 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 | $-E_{ion} \cdot 10^{-3} \text{ (a.u.)}$ | | $-E_{ele} \cdot 10^{-3} \text{ (a.u.)}$ | |
|-------|---|--------------------------------|---|---------------|
| | Present | Others [3, 7] | Present | Others [3, 7] |
| 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 |

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.

While the influence of the various correction functions on F_H of Li, Na, K, Rb and Cs are found the maximum in percentage order are 1.12 %, 1.27 %, 1.88 %, 1.72 % and 1.80 % due to N-function, respectively.

The above analysis shows that for all the elements considered under study, the influence of various local field 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-function and maximum for

Table 5 – Entropy (S) calculation

| Metal | Entropy contributions | | | | | | | | |
|-------|-----------------------|--------------------|--------------|------------------|----------------|----------------------------------|---------|--------------------------------|----------|
| | S_{gas}/k_B | | S_{el}/k_B | | S_{PVHS}/k_B | | S/k_B | | |
| | Present | Others [3, 7] | Present | Others [3, 7] | Present | Others [3, 7] | Present | Others [3, 7] | 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 | $-F_H \cdot 10^{-3}$ (a.u.) | | | | | | | |
|-------|-----------------------------|--------|--------|--------|--------|--------|--------------|--|
| | Present | | | | | | Expt. [1] | Others [3, 6, 7] |
| | 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 |

N-function in comparison with other functions.

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 [1] with our calculation of E_{INT} for Li, Na, K, Rb and Cs is (in percentage) 2.88-4.04 %, 0.67-1.92 %, 6.47-8.23 %, 8.02-9.60 % and 8.69-10.34 %, respectively. Hafner has done the ab initio calculation for alkali elements and reported the comparison with the experimental data. In his article, the deviation from the experimental values [1] for internal energy E_{INT} for Li, Na, K, Rb and Cs elements is shown of the order of 4.37 %, 3.12 %, 4.18 %, 4.40 % and 1.33 %, respectively. This means that for Li and Na, our results are better than the ab initio calculation. While for elements (K, Rb, Cs) with higher volumes the ab initio calculation by Hafner provides less deviation than our results. It also shows the change in trend that for calculations of internal energy E_{INT} for Li done by Vora [3] and by Hafner [1] which deviates more than that of the other elements, Whereas as in our calculation, there is lesser deviation found for the internal energy E_{INT} of Li. This trend in results favors the results of Thakor et al. [6, 7].

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 occurs 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. [6]. 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. The present 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 [1] of various properties are found. In the case of thermodynamical properties, we prove the transferability of the potential given by Fiolhais et al. the study itself provides the excellent database for research working with liquid alkali metals. The seven different correction functions are used for the first time with this potential. It is found sensitive to the local field correction functions.

ACKNOWLEDGEMENTS

Computer facility developed under DST-FIST programme from Department of Science and Technology, Government of India, New Delhi, India and financial assistance under DRS-SAP-I from University Grants Commission, New Delhi, India is highly acknowledged by the author (AMV).

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