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Temperature dependence of the Helmholtz free energy of liquid alkali metals

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Abstract

The Gibbs-Bogoliubov variational method has been considered to study the Helmholtz free energy of liquid alkali metals (Na, K, Rb and Cs) as a function of temperature, using Heine Abarenkov type model potential with Hubbard-Sham exchange and correlation function. The computed values are in very good agreement with experimental observations.

Keywords: Helmholtz free energy; Entropy; Specific heat; Boltzman constant; Perturbation energy; Madelung energy

1. Introduction

The variational prescription based on the Gibbs-Bogoliubov inequality [1] has provided a convenient computational tool for evaluating the free energy of liquid metals with the framework of a hard-sphere reference system and pseudopotential theory [2,3]. Recently, many workers [4-8] have utilized successfully the Gibbs Bagoliubov (GB) variational technique to study the thermodynamic properties of liquid metals and alloys. In most of the cases the earlier studies are confined near the melting temperature (Tm).

The present work is an attempt in this direction to investigate the thermal effect on the Helmholtz free energy of liquid metals for T > Tm, which is least understood. This will help us to examine the utility of hard-sphere reference system for election-ion interaction energy. We consider the Heine-Abarenkov (HA) form of model potential [9] in conjunction with the Hubbard- Sham [10-11] (HS) exchange and correlation function. For the present purpose we choose Na, K, Rb and Cs because the pseudopotential perturbation can be applied without committing any appreciable error [12].

2. Theory

The details of the variational method used for investigating the thermodynamic properties of liquid metals and alloys are available in the work of Umar et al [13] and Ashcroft and stroud [14]. In the framework of GB method the Helmholtz free energy, F, per ion at fixed temperature T and volume Ω can be expressed as

$$F = F_{hs} + F_{ps} \qquad (1)$$

Here F_{hs} is the Helmholtz free energy of the hard-sphere system, which can be expressed as

$$F_{hs} = (3/2)\ K_BT - TS \qquad (2)$$

where (3/2) K_BT is the mean kinetic energy and S, the entropy of the system can be written as

$$S = \mathrm{Sgas} + S\eta \qquad (3)$$

with $$\mathrm{Sgas} = (5/2)K_B + K_B \ln\{\Omega(mK_BT/2\pi\hbar 2)3/2\} \qquad (4)$$

$$S\eta = K_B \ln(1-\eta) + 3/2\ K_B\{1-(1-\eta)2\} \qquad (5)$$

Eq. (3) has further been improved by incorporating the low temperature specific heat contribution of electron gas. The resulting expression for the entropy becomes

$$S = \mathrm{Sgas} + S\eta + \mathrm{Selec} \qquad (6)$$

with $$S_{elec} = \pi^2 K_B^2 T / K_F^2 \qquad (7)$$

where K_B is the Boltzmann constant and K_F stand for the Fermi wave vector $(K_F^3 = 3\pi^2 nZ,$ n is the number density).

$$F_{ps} = \mathrm{Feg} + F_1 + F_2 + \mathrm{Fm} \qquad (8)$$

Where Feg is the free energy of the electron gas, F_1 and F_2 are, respectively, first and second order perturbation energies due to the electron-ion interaction. Fm is the Madelung contribution which takes into accounts for the ion-ion interaction. The expressions for these contributions for a metal have been worked out in detail by Harrison [2].

$$F_{eg} = nz[(3/10)K_F^2 - (3/4\pi)K_F - 0.0474 - 0.0155 \ln K_F] \qquad (9)$$

$$F_1 = \lim_{q\to 0} n\ z\{v(q) - 4\pi z/q^2\} \qquad (10)$$

$$F_2 = (1/16\pi^3)\int_0^\infty v^2(q) - s(q)[\{1/\in^*(q)\} - 1]q^4 dq \qquad (11)$$

$$F_m = (Z^2/\pi)\int_0^\infty \{s(q) - 1\}dq \qquad (12)$$

Where q is the phonon wave vector V(q) stands for unscreened from factor, which can be obtained using the HA potential,

$$V(q) = -(4\pi zn/q^2)\cos qr_m - (4\pi An/q^3)(\sin qr_m - qr_m \cos qr_m) \qquad (13)$$

Here A is the well depth and rm is the model radius. These are obtained quantum mechanically by matching the wave function at $r = r_m \cdot \in^*(q)$ in Eq. (11) is the modified Hartree dielectric screening function which takes into account of the conducting electron interaction,

$$\in^*(q) = 1 + \{\epsilon(q) - 1\}\{1 - G(q)\} \tag{14}$$

$\in(q)$ is the Hartree dielectric function and G(q) is the correction factor for the exchange and correlated motion of the conducting electron. Presently we consider G(q) prescribed by Hubbard and Sham

$$G(q) = \frac{1}{2} q^2 / [q^2 + \{2\pi k_F^3 / (0.153 + \pi k_F)\}] \tag{15}$$

The structure factor, s(q), for liquid metals appearing in Eq. (11) and (12) can be calculated from the Parcus-Yevick approximation for hard–sphere potential, which is characterized by the hard-sphere diameter(σ),or equivalently, by the packing fraction $\eta (= \pi \sigma_M^3 / 6)$

3. Results and Discussion

The general expression for the Helmholtz free energy of pure liquid metals can be written as

$$F = F_{eg} + F_1 + F_2 + F_M + (3/2)K_B T - TS \tag{16}$$

The different terms occurring in Eq. (16) are already defined in Section 2. It is well known that hard-sphere potential serves as an effective reference system for liquid metals. The best hard sphere reference system is obtained by selecting those diameters which minimize the Helmholtz free energy, F, at the same temperature T and volume **Ω** through

$$\left(\frac{\partial F}{\partial \sigma}\right)_{\Omega,T} = 0 \tag{17}$$

The optimum values of the parameters used in the calculation of the Helmholtz free energy of liquid alkali metals as a function of temperature are compiled in Table 1. The volume of the liquid metals at different temperatures required in the calculation is determined from the relation provided in the work of Huijben [17]. The experimental values of the entropies at appropriate temperature are obtained from tables found in Hultgren et al [18-21].

Using Table 1, we can calculate easily the various terms of Eq. (16). The computed values of Feg, F_1, F_2, Fm and Fhs are listed in Table 2. A perusal of Table 2 show that the major contribution to the theoretical determined Helmholtz free energies comes from the Madelung terms Fm, the other terms contribute a relatively small amount and in order of magnitude falls as F_1, Feg, F_{hs} and F_2. Table 2 shows that the magnitude of F_1 and Fm decreases with the rise of temperature where as the magnitude of Feg, F_2, F_{hs} increases. The computed values of F for liquid alkali metals are displayed in Fig.1 as a function of temperature along with the experimental observation of Hultgren et al [18]. The best agreement is obtained for Cs followed by Rb, K and Na. It may be noted that the Helmholtz free energy of liquid alkali metals depend sensitively on temperature above the melting point. The rise of temperature experiences a decrease in the Helmholtz free energy. Our results reveal that the decrease of magnitude of the Helmholtz free energy due to first order energy and Madelung energy is compensated due to increasing values of F_2, Feg and F_{hs} as a result F only depends considerably on temperature above the melting point.

Table 1: Input Parameters in the Calculation of the Helmholtz free energy of Na, K, Rb and Cs at different temperatures

Liquid Metals	T(°K)	Ω(a.u)	σ(a.u)	S/KB
Na	371.0	278.187	6.2579	7.1043
	473.0	285.722	6.1659	8.0953
	573.0	293.427	6.0922	8.8416
	673.0	301.495	6.0293	9.4533
	773.0	310.077	5.9741	9.9751
K	336.6	530.504	7.6633	8.7493
	423.0	543.360	7.5449	9.6486
	523.0	559.190	7.4313	10.4569
	623.0	576.037	7.3349	11.1095
	723.0	593.824	7.2502	11.6587
Rb	312.6	667.200	7.2179	10.1972
	373.0	681.292	8.1174	10.9056
	473.0	705.516	7.9788	11.8184
	573.0	731.796	7.8625	12.5406
	673.0	759.994	7.7624	13.1400
Cs	301.8	804.117	8.7922	10.8790
	373.0	824.402	3.6678	11.7315
	473.0	852.587	8.5192	12.6487
	573.0	884.556	8.3973	13.3825
	673.0	919.709	8.2915	13.9931

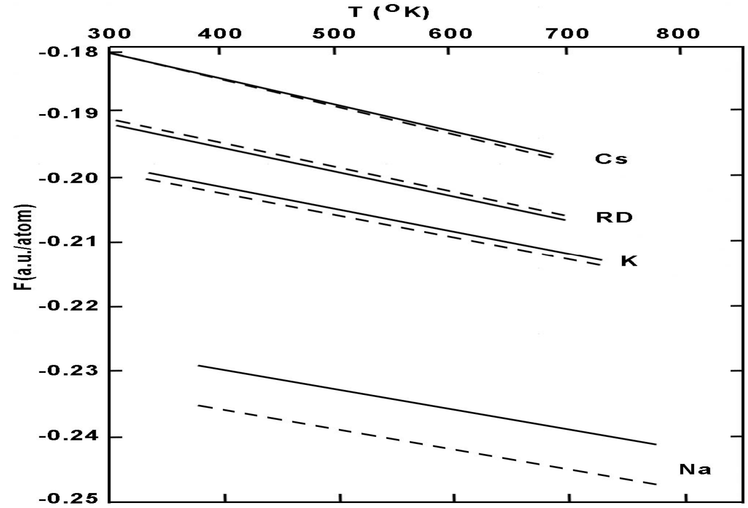

Fig. 1 : Helmholtz free energy of Na, K, Rb and Cs as a function of temperature. Full and broken curve refer to theoretical and experimental values respectively

Table 2: **Contribution to Helmholtz free energy of liquid alkali metals as function of temperature**

Liquid Metals	T(°K)	-Feg	F_1	$-F_2$	-Fm	$-F_{hs}$
Na	371.0	0.08162	0.07734	0.00479	0.21371	0.00656
	473.0	0.08168	0.07530	0.00619	0.20968	0.00988
	573.0	0.08175	0.07332	0.00761	0.20575	0.01333
	673.0	0.08180	0.07136	0.00910	0.20181	0.01695
	773.0	0.08185	0.06938	0.01066	0.19781	0.02075
K	336.6	0.07995	0.06419	0.00465	0.17144	0.00773
	423.0	0.07982	0.06267	-0.00587	0.16825	0.01092
	523.0	0.07966	0.06089	0.00737	0.16454	0.01434
	623.0	0.07949	0.05912	0.00894	0.16079	0.01896
	723.0	0.07933	0.05734	0.01057	0.15702	0.02326
Rb	312.6	0.07826	0.05782	0.00476	0.15837	0.00859
	373.0	0.07841	0.05779	0.00543	0.15827	0.01111
	473.0	0.07784	0.05467	0.00747	0.15172	0.01546
	573.0	0.07757	0.05272	0.00929	0.14753	0.02004
	673.0	0.07720	0.05076	0.01122	0.14327	0.02481
Ca	301.8	0.07660	0.05795	0.00419	0.14917	0.00896
	373.0	0.07638	0.05653	0.00521	0.14641	0.01209
	473.0	0.07610	0.05466	0.00672	0.14265	0.01670
	573.0	0.07578	0.05265	0.00835	0.13868	0.02157
	673.0	0.07545	0.05067	0.01009	0.13466	0.02663

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