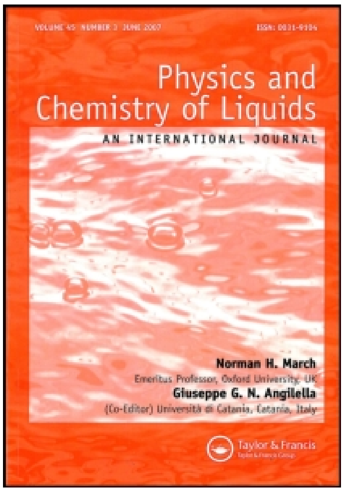

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Excess Entropy of Mixing of Equiatomic Binary Molten Alloys

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The Gibbs-Bogoliubov variational method has been considered to understand the alloying behavior of binary liquid alloys. The method has been used to study the entropy(S) of pure liquid metals (Cd, Mg, Zn, Al, In and Tl) and excess entropy of mixing, ΔS^{xs} of binary alloys (CdZn, MgZn, CdIn, CdTl, InZn and AlMg). The effect of electron-ion interaction on S and ΔS^{xs} has amply been discussed. The excess entropy of mixing have been found sensitive to the electron-ion potential. The computed values of S and ΔS^{xs} are in very good agreement with the experimental observation.

Key Words: Electron-ion interaction, hard spheres, packing fraction.

1 INTRODUCTION

Though enormous experimental data exist on entropy of pure liquid metals and alloys[1], the theoretical works lag behind. In recent years, hard sphere model has been widely used to remedy this lack. The most important physical quantity occuring here is the hard sphere diameter (σ) or the packing fraction (η). For pure metals this is usually obtained from the observed entropy and is utilized to compute the entropy of mixing of liquid alloys (see, for example, Yokoyama *et al.*[2]).

The Gibbs-Bogoliubov method[3,4] on the other hand, paves the way for the ab-initio calculation of the hard sphere diameter which is achieved by minimizing the free energy of the system. Many workers[5-10] have utilized Gibbs-Bogoliubov method to study the thermodynamic properties of liquid metals and alloys. It seems that electron-ion interaction plays an important role. The present work is an attempt in this direction to investigate its impact on the evaluation of the optimized values of hard-sphere diameters and hence on entropy and excess entropy of mixing of liquid alloys. Application is made to s,p bonded liquid metals like Cd, Mg, Zn, Al, In and Tl and equiatomic binary alloys such as CdZn, MgZn, CdIn, CdTl, InZn and AlMg. These alloys are either homovalent (valency difference between the constituent species is zero), or monovalent (valency difference is one) and we assume that the pseudopotential perturbation theory can be applied without committing appreciable error. The basic steps which connect the pseudopotential technique to the hard sphere results are outlined in Section 2. The results for the entropy of pure liquid metals are included in Section 3. The problem of excess entropy of mixing of binary molten alloys has been considered in Section 4, followed by few concluding remarks in Section 5.

2 FORMALISM

In the frame work of Gibbs-Bogoliubov method[2,3] the Helmholtz free energy, F, per ion at fixed temperature $T$and volume Ω can be expressed as

$$F = F_0 + F_1 \tag{1}$$

The first term amounts to the free energy for the reference system and the second denotes the small perturbation term averaged over the reference system. For hard sphere model as a reference system it is necessary to satisfy the condition,

$$\left(\frac{dF}{d\sigma}\right)_{\Omega,T} = 0 \tag{2}$$

σ is the diameter of hard sphere. In what follows we shall discuss the evaluation of F_0 and F_1.

2.1 Excess Entropy of Mixing of Liquid Alloys

Let the liquid alloy consist of C_1N hard spheres of diameter σ_1 of species '1' and C_2N hard spheres of diameter σ_2 of species 2 then under Percus-Yevick approximation one readily obtains

$$F_0 = \tfrac{3}{2}K_BT - TS_{\text{hs}} \tag{3}$$

S_{hs} is the entropy of the hard sphere mixture which consists of

$$S_{\text{hs}} = S_{\text{id}} + S_{\text{gas}} + S_\eta + S_\sigma \tag{4}$$

where S_{id} is the ideal entropy of mixing, S_{gas} is the ideal gas entropy, S_η is the contribution which depends solely on packing density and S_σ represents the entropy contribution due to mismatch of the hard sphere diameters σ_1 and σ_2. The working expressions for these quantities may be summarized as[7]

$$S_{\mathrm{id}} = -K_B \sum_{i=1}^{2} C_i \ln C_i \tag{5}$$

$$S_{\mathrm{gas}} = \tfrac{5}{2}K_B + K_B \ln\left\{\Omega\left(\frac{m_1^{C_1} m_2^{C_2} K_B T}{2\pi\hbar^2}\right)^{3/2}\right\} \tag{6}$$

$$S_\eta = K_B \ln\alpha + 1.5K_B(1-\alpha^2) \tag{7}$$

$$S_\sigma = K_B \pi C_1 C_2 (\sigma_1 - \sigma_2)^2 \alpha^2 \left\{\frac{\sigma_1 + \sigma_2}{2} - \pi\frac{(C_1\sigma_1^4 + C_2\sigma_2^4)}{24\Omega^2}\right\} \tag{8}$$

with $\alpha = (1-\eta)^{-1}$. The first two terms are structure independent terms and depend only on concentration C, atomic mass m and atomic volume Ω. The last two terms are obviously structure-dependent contributions due to presence of the packing fraction, $\eta[= \pi/6\Omega\,(C_1\sigma_1^3 + C_2\sigma_2^3)]$ and the hard sphere diameter, σ_i.

The entropy expressions for pure elements 'i' can be obtained using the above relations by setting either $C_1 = 0$ or $C_2 = 0$, in which case S_{id} and S_σ terms are identically zero leaving behind

$$S^i_{\mathrm{hs}} = S^i_{\mathrm{gas}} + S^i_\eta \tag{9}$$

with

$$S^i_{\mathrm{gas}} = \tfrac{5}{2}K_B + K_B \ln\left\{\Omega_i\left(\frac{m_i K_B T}{2\pi\hbar^2}\right)^{3/2}\right\} \tag{10}$$

$$S^i_\eta = K_B \ln(1-\eta_i) + \tfrac{3}{2}K_B(1-(1-\eta_i)^{-2}) \tag{11}$$

$\eta_i = \pi\sigma_i^3/\sigma\Omega_i$ is the packing fraction of the pure element i. It may be mentioned that the well known Carnahan–Starling[11] formula for the entropy of pure element can be obtained from Eq. (11) by expanding $\ln(1-\eta_i)$ and retaining only the terms up to η^2.

The excess entropy per atom in the alloy is defined as

$$\begin{aligned}\Delta S^{\mathrm{xs}} &= S_{\mathrm{hs}} - \sum_i C_i S^i_{\mathrm{hs}} - \sum_i C_i \ln C_i \\ &= K_B \ln(\Omega/\Omega_1^{C_1}\Omega_2^{C_2}) + S_\eta - \sum_i C_i S^i_\eta) + S_\sigma \end{aligned} \tag{12}$$

The first term on right hand side depends only on the atomic volume and is called gas term (ΔS_{gas}). The second bracketed term depends on the packing fraction η and is usually denoted as ΔS_η. The last term is, as usual, the mismatch term S_σ. Thus ΔS^{xs} is conveniently expressed as

$$\Delta S^{xs} = \Delta S_{gas} + \Delta S_\eta + S_\sigma \tag{13}$$

2.2 Pseudopotential Method for the Entropy

The pseudopotential method enters into the calculation of the Helmholtz free energy through the term F_1 and hence into the entropy calculation via Eq. (2). For a system of ions and electrons, F_1 is expressed as,

$$F_1 = F_{eg} + F_f + F_s + F_M \tag{14}$$

where F_{eg} arises due to free electron gas, F_f and F_s are due to electron–ion interaction defined via first and second order pseudopotential perturbation theory respectively, and F_M takes into account for the ion–ion interaction. The interaction between conduction electrons has been buried in F_s. The expressions for these contributions for a metal have been worked out in detail by Harrison[12] which can easily be extended to binary alloy,

$$F_{eg} = \left[\frac{3}{10} K_F^2 - \frac{3}{4\pi} K_F - 0.0474 - 0.0155 \ln K_F - 0.5\left(\frac{K_B}{K_F}\right)^2 T^2\right]_{\bar{z}} \tag{15}$$

$$F_f = \lim_{q \to 0} \bar{z}n\left[\sum_i C_i V_i(q) + \frac{4\pi\bar{z}}{q^2}\right] \tag{16}$$

$$F_s = \frac{1}{16\pi^3} \int_0^\infty q^4 dq \sum_{i,j} V_i(q) V_j(q) (C_i C_j)^{1/2} S_{ij}(q) \left(\frac{1}{\varepsilon^*(q)} - 1\right) \tag{17}$$

$$F_M = \frac{1}{\pi} \sum_{i,j}^{1,2} Z_i Z_j (C_i C_j)^{1/2} \int_0^\infty (S_{ij}(q) - \partial_{ij}) dq \tag{18}$$

where, $K_F = (3\pi^2 \bar{z}n)^{1/3}$, $\bar{z}n = z_1 n_1 + z_2 n_2$ and $\bar{z} = C_1 z_1 + C_2 z_2$; z_1 and z_2 are valencies, n_1 and n_2 are number densities of the ion species and $n = n_1 + n_2$. $V(q)$ is the Fourier transform of the bare ion pseudopotential, $\varepsilon^*(q)$ is the modified Hartree dielectric screening function which takes into account of the conduction electrons interaction

$$\varepsilon^*(q) = 1 + \{\varepsilon(q) - 1\}\{1 - G(q)\} \tag{19}$$

$\varepsilon(q)$ is the Hartree dielectric function and $G(q)$ is the correction factor for the exchange and correlated motion of the conduction electrons.

Presently we consider $G(q)$ prescribed by Hubbard[13] and Sham[14].

$$G(q) = \tfrac{1}{2}q^2/\{q^2 + [2\pi K_F^2/(0.153 + \pi K_F)]\} \qquad (20)$$

The partial structure factors, S_{ij} appearing in Eqs (17) and (18) have been computed following the work of Ashcroft and Langreth[15]. This includes the detailed arrangement of ions in the system and requires the knowledge of the hard sphere diameter σ which have been determined in the variational thermodynamic sense ensuring minimum free energy for the system via Eq (2).

We now return to the electron-ion interaction measured through the bare ion pseudopotential matrix elements $V(q)$. In model potential theory, $V(q)$ explicitly depends on the form of the potential considered. The potential seen by conduction electron in the presence of ions is usually written[16] as consists of (i) the ion-core potential (for the region $r < r_m$, r_m is a chosen model radius) and (ii) and potential outside the core region r_m which is coulombic ($= -z/r$) in nature. In past, a great effort has been made to model the ion-core potential. Presently we consider three different forms of ion-core potentials which have been tested successfully for the electronic transport properties of liquid metals and alloys. In order to avoid numerical complexities, we consider l-independent form of the ion-core potential (for the region $r < r_m$),

$$\begin{aligned} V(r) &= 0 && \text{Ashcroft Pot.}^{17} \\ &= -A && \text{Heine-Abarenkov Pot.}^{18} \\ &= -(a - br^2) && \text{Harmonic Model Pot.}^{19} \end{aligned}$$

in atomic units ($e = \hbar = m = 1$). A, a and b are model parameters which are obtained quantum mechanically[19–21] by matching the wave functions at the chosen model radius $r = r_m$. The Fourier transform of $V(r)$ gives $V(q)$ to be used in Eqs (16) and (17) and this enables us to study the effect of the ion-core potential on entropy of liquid metals and alloys.

3 APPLICATION TO PURE LIQUID METALS

3.1 Optimized Hard Sphere Parameters

The main thrust here is to compute hard sphere parameter (σ or η) from the first principle for divalent (Cd, Mg and Zn) and trivalent (Al, In and Tl) liquid metals. This has been achieved by minimizing the Helmholtz free energy of the system with respect to σ, for different ion-core potentials. The only model parameter r_m needed in the Ashcroft potential[17] has been taken from Cohen and Heine[16] where it has been fixed to reproduce the observed electrical resistivity. The well depth A for $l = 0$ required in the Heine-Abarenkov (HA) potential has been taken from the work by Ese and Reissland[20]. The model parameters a and b occuring in the harmonic model potential (HMP) have been opted from the work by Sahay and Srivastava[21]. It may be mentioned that the parameters occuring in HA and HMP potentials have not been fixed with reference to any observed properties rather have been evaluated independently by matching the wave functions. The densities appropriate to pure liquid metals at relevant temperatures have been calculated from Smithels metal book[22].

The computed values of the hard sphere diameter σ and the packing fraction η are tabulated in Table 1. The different forms of the ion-core potentials affect σ only slightly with a minimum of about 2% in Tl to a maximum of about 6% in Al. Though for pure liquid metals this is a very small number but we shall see later that it becomes very important in the calculation of the excess entropy of mixing when we make alloy out of these metals.

Table 1 Optimized values of hard sphere parameters of pure liquid metals.

Metals	Temp. (K)	Atomic volume (Ω)	Model potential	Hard sphere parameters	
				Diameter (σ)	Packing fraction (η)
Cd	800	168.97	HMP	5.3292	0.4690
			HA	5.2179	0.4402
			ASCH	5.1678	0.4276
Mg	923	179.60	HMP	5.3192	0.4388
			HA	5.4916	0.4828
			ASCH	5.4348	0.4680
Zn	800	119.19	HMP	4.7358	0.4666
			HA	4.7702	0.4768
			ASCH	4.9542	0.5342
Al	1000	128.00	HMP	5.1463	0.5575
			HA	5.0870	0.5385
			ASCH	4.8392	0.4636
In	700	193.61	HMP	5.7367	0.5106
			HA	5.5870	0.4717
			ASCH	5.5374	0.4592
Tl	750	215.98	HMP	5.4854	0.4007
			HA	5.4754	0.3986
			ASCH	5.3864	0.3794

3.2 Entropy of Pure Liquid Metals

The entropy of pure liquid metals have been computed through Eq. (9). The atomic volume Ω and the packing fraction, η, required in the calculation are taken from Table 1. The values of entropy computed with different forms of electron-ion potentials are tabulated in Table 2. S_{gas} depends only upon the density and are thus independent of the potential. The potential affects the entropy through $S\eta$. The magnitude of S_{gas} is larger than $S\eta$. The former increases the absolute value of the entropy whereas the latter tends to decrease the total entropy of the system.

The computed values of entropy of pure liquid metals are in good agreement with the experimental values[1]. For Al and In close agreement has been obtained with Ashcroft potential whereas for Cd, Tl, Zn and Mg, the HMP results are in better agreement with the experimental observation. The effect of electron-ion interaction is more visible in Al than other liquid metals considered here.

Table 2 Entropy of pure liquid metals.

Metals	Temp. (K)	Model potential	S_{gas}	S_η	S/K_B	
			K_B	K_B	(Theory)	(Expt.)
Cd	800	HMP	14.2509	−4.3129	9.9380	10.2
		HA	14.2509	−3.7641	10.4868	
		ASCH	14.2509	−3.5469	10.7040	
Mg	923	HMP	12.2294	−3.7382	8.4912	8.88
		HA	12.2294	−4.6057	7.6237	
		ASCH	12.2294	−4.2920	7.9374	
Zn	800	HMP	13.0891	−4.2641	8.8250	9.06
		HA	13.0981	−4.4765	8.6126	
		ASCH	13.0891	−5.9021	7.1870	
Al	1000	HMP	12.1675	−6.6231	5.5440	
		HA	12.1675	−6.0284	6.1391	
		ASCH	12.1675	−4.2033	7.9642	8.85
In	700	HMP	14.2186	−5.2623	8.9563	
		HA	14.2186	−4.3682	9.8504	
		ASCH	14.2186	−4.1180	10.1006	10.82
Tl	750	HMP	15.2949	−3.1221	12.1728	11.47
		HA	15.2949	−3.0899	12.2050	
		ASCH	15.2949	−2.8194	12.4755	

4 EXCESS ENTROPY OF MIXING OF BINARY LIQUID ALLOYS

4.1 σ and η for Binary Liquid Alloys

The values of hard sphere diameters for CdZn, MgZn, CdIn, CdTl, InZn and AlMg equiatomic molten alloys have been obtained by undergoing repeated optimization of the Helmholtz free energy through Eqs (1) and (2). The computed values for different forms of electron-ion interaction are listed in Table 3. The densities appropriate to equiatomic composition have been obtained by considering the values of excess volume of mixing[23,24]. The percentage excess volumes [$\Delta\Omega/\Omega_0 = (\Omega_{\text{alloy}} - \Omega_0)/\Omega_0$; $\Omega_0 = C_1\Omega_1^0 + C_2\Omega_2^0$; Ω_1^0 and Ω_2^0 are the specific volumes for the pure liquids] are also collected in Table 3. We have observed that $\Delta\Omega/\Omega_0\,\%$ occurs as very important input data. Even a small change in this value affects the excess entropy of mixing considerably.

An inspection of Tables 1 and 3 reveals that the sizes of the hard sphere of the constituent element change on alloying. In each case the constituent components have tendencies to equalise ($\sigma_A/\sigma_B \simeq 1.0$) the size of the hard spheres in the mixture. In general, hard spheres representing the heavier elements contracts and that of lighter elements

Table 3 Optimized hard sphere parameters for equiatomic liquid alloys.

Alloy A,B	Temp. (K)	$\frac{\Delta\Omega}{\Omega_0}\,\%$	Model potential	Diameters (σ_A)	(σ_B)	Pack. frac. (η_{AB})	Change in packing fraction on alloying ($\Delta\eta$)
Cd,Zn	800	0.53	HMP	5.271	4.822	0.4673	−0.00027
			HA	5.127	4.896	0.4557	−0.00598
			ASCH	5.057	5.131	0.4779	−0.01220
Mg,Zn	923	−8.81	HMP	5.154	4.737	0.4598	0.01547
			HA	5.348	4.731	0.4894	0.02124
			ASCH	5.227	5.017	0.5087	0.01328
Cd,In	623	2.94	HMP	5.284	5.604	0.5420	0.00071
			HA	5.189	5.494	0.5121	−0.00439
			ASCH	5.155	5.493	0.5072	−0.00026
Cd,Tl	750	0.93	HMP	5.623	5.393	0.4528	+0.00686
			HA	5.357	5.413	0.4228	−0.00604
			ASCH	5.255	5.374	0.4064	−0.00682
In,Zn	700	0.516	HMP	5.649	4.888	0.4982	+ 0.00468
			HA	5.489	4.955	0.4814	−0.00387
			ASCH	5.461	5.178	0.5059	−0.01214
Al,Mg	1000	−2.77	HMP	5.408	4.997	0.5058	−0.00105
			HA	5.212	5.267	0.5143	−0.00019
			ASCH	4.976	5.193	0.4707	0.00456

expand on alloying. This can qualitatively be understood by considering the redistribution of the electronic charges at the Fermi surface on alloying. The Fermi wave vector of Cd ($K_F^{\mathrm{Cd}} = 0.705$) is smaller than Zn($K_F^{\mathrm{Zn}} = 0.792$ a.u.). When Cd and Zn are mixed together then the flow of electrons takes place from Cd to Zn as the latter has lower Fermi energy. This leads to the expansion of Zn atoms and the contraction of Cd atoms. Similar is the case with other alloys. The contraction and expansion of the $\hbar$ hard spheres in the alloy have also been discussed by Singh and Choudhary[25] on the basis of electronegativity factor.

We have also computed $\Delta\eta(= \eta_{\mathrm{alloy}} - (\eta_A^0\Omega_B^0 + \eta_B^0\Omega_A^0)/(\Omega_A^0 + \Omega_B^0)$ where η_i^0 and Ω_i^0 are packing fraction and atomic volumes of pure metals. The values of $\Delta\eta$ which is a measure of increase in the packing fraction on alloying are listed in Table 3. It appears that the values of $\Delta\eta$ depends on the electron–ion interaction. $\Delta\eta$ for CdZn is negative and it is positive in MgZn with all the three forms of potentials considered here. We observe that $\Delta\eta$ gets influenced both by excess volume of mixing and electron–ion interaction. The effect of the core region potential on the values of η is limited to 5% in InZn to a maximum of 11% in CdTl. We shall see, in the following section, that even a small variation in the value of η like this plays a dominant role in computing the excess entropy of mixing for the alloy.

4.2 Excess Entropy of Mixing of Liquid Alloys

Having determined the optimum values of the packing fraction (η) for pure metals and alloys, it is now straight-forward (see Eqs (12), (13) to compute the various contributions to the excess entropy of mixing. The various contributions ΔS_{gas}, $\Delta S\eta$ and $S\sigma$ are tabulated in Table 4. We observe that $|\Delta S\eta| > |\Delta S_{\mathrm{gas}}| > S\sigma$. The contribution $S\sigma$, which arises due to difference in the sizes of the effective hard spheres of the constituent elements is found to be small and gives a correction to third or fourth decimal place. In Section 3.2 it was observed that the entropy of pure liquid metals is dominated mainly by gas term (S_{gas}) but in case of alloy the packing fraction term ($\Delta S\eta$) plays a dominant role.

The core-region pseudopotential affects the excess entropy of mixing through $\Delta S\eta$ and $S\sigma$. As $S\sigma$ is very small the major contribution comes from the former. The effect of the potential is distinctively visible on the values of $\Delta S\eta$. Though the packing fraction η is only affected to a maximum of 11% by the potential, $\Delta S\eta$ even changes its sign as in AlMg, CdTl and InZn.

The computed values of the excess entropy of mixing have been compared in Table 4 with the experimental values[1] and the theoretical

Table 4 Excess entropy of mixing of equiatomic alloys.

Alloys		Temp. (K)	Model potential	$\frac{\Delta S_{gas}}{K_B}$	$\frac{\Delta S_\eta}{K_B}$	$\frac{S_\sigma}{K_B}$	$\frac{\Delta S^{xs}}{K_B}$ (Theory) (Ours)	$\frac{\Delta S^{xs}}{K_B}$ (Theory) (Yokoyama *et al.*)	Expt (Hultgren *et al.*)
Cd	Zn	800	HMP	+0.020	0.009	0.00263	0.032	—	0.015
			HA	+0.020	0.071	0.00064	0.092	—	—
			ASCH	+0.020	0.225	0.00007	0.245	—	—
Mg	Zn	923	HMP	−0.065	−0.306	0.0022	−0.369	—	—
			HA	−0.065	−0.401	0.0059	−0.461	—	—
			ASCH	−0.065	−0.393	0.0008	−0.458	−0.301	—
Cd	In	623	HMP	0.033	0.026	0.0022	0.061	—	0.066
			HA	0.033	0.135	0.0015	0.170	—	—
			ASCH	0.033	0.009	0.0019	0.044	0.08	—
Cd	Tl	750	HMP	0.0173	−0.194	0.00051	−0.176	—	—
			HA	0.0173	0.034	0.00002	0.052	—	—
			ASCH	0.0173	0.045	0.0001	0.062	0.082	0.122
In	Zn	700	HMP	0.0365	−0.019	0.0089	0.026	—	—
			HA	0.0365	0.032	0.0039	0.073	—	—
			ASCH	0.0365	0.155	0.0013	0.190	0.122	0.144
Al	Mg	1000	HMP	−0.0159	+0.036	0.0029	0.023	—	—
			HA	−0.0159	−0.047	0.00005	−0.064	—	—
			ASCH	−0.0159	−0.083	0.00062	−0.098	−0.079	−0.099

values of Yokoyama *et al.*[2]. Though ΔS^{xs} is a very small number but the agreement between the theory and the experiment is quite satisfactory. From the point of view of the entropy of mixing ($\Delta S_M/K_B = \Delta S^{xs}/K_B + \sum_i C_i \ln C_i$) the agreement is almost exact. The different form of the potential in the core region of the atom affects ΔS^{xs} considerably but the same potential could not provide consistently good result for all systems considered here. The Ashcroft potential exhibits good result of ΔS^{xs} for AlMg, CdTl and InZn. However for CdIn and CdZn, HMP seems suitable.

It is worth mentioning that the excess entropy of mixing (ΔS^{xs}) computed with HMP and HA potentials differ considerably though the nature of the two potentials in the core region is not very much different. Even the sign of ΔS^{xs} in CdTl and AlMg is opposite. This may be due to the small error involved in the evaluation of model potential parameters. The latter have been evaluated at the Fermi level corresponding to the pure elements. In true sense, however, these parameters should be evaluated at E_F corresponding to alloy. The extrapolation of parameters at E_F from the term values is also not unique. Since the magnitude of ΔS^{xs} is so small that even a minor error affects $\Delta S\eta$ significantly and in turn ΔS^{xs}.

It should be noted that the excess entropy of mixing for MgZn equiatomic alloy is a large negative quantity which is not usually found in simple binary alloys. As both ΔS_{gas} and $\Delta S\eta$ are negative for this system, they add together to give a large negative value for ΔS^{xs}. We could not compare our result to the experimental values as no such measurements exists. Nonetheless the interest in the MgZn liquid alloy system is increasing because it readily forms a metallic glass on quenching.

Yokoyama *et al.*[2] have made an extensive study of the ΔS^{xs} based on Gibbs-Bogoliubov method. They have also noticed the importance of electron-ion interaction for the evaluation of ΔS^{xs}. In order to compute ΔS^{xs} they first fitted the core radius of the Ashcroft potential to the observed entropy of pure liquid metals, which in turn were used to compute the excess entropy of mixing of the alloy. Unlike their work we avoid the fitting of potentials to the entropy rather HA and HMP parameters have been determined quantum mechanically by matching the wave functions. It may be mentioned that these forms of the potentials also provide reasonable picture for the transport properties of liquid metals and alloys[26–31]. Thus it seems possible to obtain a consistent picture of electrical and thermodynamic properties of liquid metals and alloys with the same pseudopotential matrix elements. It is likely that the results of ΔS^{xs} may further be improved if one considers the l-dependence of the potential parameters and be made energy dependent.

5 CONCLUSION

The Gibbs-Bogoliubov variational technique which establishes a link between the hard sphere results and the pseudopotential method is a useful tool to understand the alloying behaviour of binary liquid alloys. The ion-core potential affects the excess entropy of mixing significantly. There is evidence for a large negative excess entropy of mixing for the MgZn equiatomic liquid alloy system.

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