Conditional Probabilities and Thermodynamics of Binary

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Conditional Probabilities and Thermodynamics of Binary Molten Alloys

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A simple statistical mechanical model based on pairwise interaction has been considered to obtain conditional probabilities for the occupation of neighbouring atoms in binary molten alloys. This has been extended to obtain simple analytical expressions for activity, free energy of mixing, concentration fluctuations in long wave limit and the chemical short range order parameter. Application is made to compute ordering energy and the concentration dependent thermodynamic properties for CuPb, NaK, LiMg and CdMg. The study reveals that self coordination among nearest neighbour atoms exist in CuPb and NaK whereas heterocoordination exist in LiMg and CdMg.

Key Words: Activity, concentration fluctuations, ordering energy.

1 INTRODUCTION

In recent years a great interest has been shown towards obtaining the microscopic properties of binary molten alloys from the knowledge of the bulk properties. Among others the recent work by Bhatia and Singh[1-2] on compound forming molten alloys paves the way in the desired direction. In the background knowledge of the bulk thermodynamic functions like activity and free energy of mixing, they have obtained very interesting information on chemical short range order (SRO) and concentration fluctuations in the long wave limit, $S_{cc}(0)$, in binary molten alloys. The necessity and the importance of SRO and $S_{cc}(0)$ in binary molten alloys have been greatly emphasized in the recent reviews by March *et al.*,[3] Chieux and Ruppersberg,[4] Steeb *et al.*[5] and Singh.[6] These quantities are of immense help to understand the

phase separation and the extent of local order in binary molten alloys. The phenomenon like metallic glass formation of which is achieved by quenching the molten state of binary alloys is also being understood[7-8] at the cost of SRO and $S_{cc}(0)$. The quantitative knowledge of the local order, which is measured through SRO, is also warranted[9-10] to explain the electronic transport in binary alloys. But the information on SRO, both theoretically and experimentally, is limited only to few systems.[6]

Thus in the present work we use a simple theory based on statistical mechanical model to compute the conditional probabilities in simple binary alloys. These are then used to compute the Warren–Cowley[11-12] short range order parameter as a function of composition. It has been shown that the conditional probabilities are intimately related to the activity through the ordering energy. The method has been extended to compute the free energy of mixing and $S_{cc}(0)$. Application is made to CuPb, NaK, LiMg and CdMg. These alloys have been preferred because each of them represents a class of characteristic equilibrium phase diagram. The study reveals that there is a preference for like atoms pairing as nearest neighbour in CuPb and NaK for all compositions. Heterocoordination however exists in LiMg and CdMg melts. In Section 2, the basic relations between the conditional probability and the partition function have been established. A connection of the conditional probabilities to the thermodynamic functions has been made in Section 3. Results for SRO and activity are presented in Section 4. Finally in Section 5, the results for free energy of mixing and $S_{cc}(0)$ are discussed.

2 CONDITIONAL PROBABILITY AND THE PARTITION FUNCTION

Consider a binary alloy consisting of A and B atoms in the proportions c and $(1 - c)$ respectively. The conditional probability (A/B), which denotes the probability of finding A atoms as a nearest neighbour of a given B atom, is related to Warren–Cowley[11-12] short range order parameter (α_1) for the first coordination shell as

$$(A/B) = c(1 - \alpha_1). \tag{1}$$

Similarly (B/A) is given by

$$(B/A) = (1 - c)(1 - \alpha_1). \tag{2}$$

Obviously,

$$c(B/A) = (1 - c)(A/B). \tag{3}$$

From a simple probabilistic approach the limiting values of α_1 can easily be shown to lie in the range,

$$-\frac{c}{(1 - c)} \leq \alpha_1 \leq 1 \qquad c \leq \tfrac{1}{2}$$

$$-\frac{(1 - c)}{c} \leq \alpha_1 \leq 1 \qquad c \geq \tfrac{1}{2} \tag{4}$$

For equiatomic composition ($c = 0.5$) one has $-1 \leq \alpha_1 \leq 1$. The minimum possible values of α_1 i.e. $\alpha_1^{min} = -1$, means complete ordering as A–B pairs of atoms as nearest neighbour, whereas $\alpha_1^{max} = 1$ suggests total segregation leading to the formation of A–A pairs or B–B pairs in the alloy.

In order to evaluate the conditional probability we first write the grand partition function for the binary alloy as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T)_e (\mu_A N_A + \mu_B N_B - E)/k_B T \tag{5}$$

Where N_A and N_B are the number of A and B atoms in the alloy with the configurational energy E. μ_i are the chemical potentials and $q_i(T)$ are partition functions associated with inner and translational degrees of freedom of atoms i ($i = A, B$).

Now to define the configurational energy E explicitly, we follow the work of Cartier and Barriol[13] and Bhatia and Singh.[1] The atoms of two different species are supposed to be located on lattice sites—few nearest neighbour lattice sites are assumed to be located in domain 1 and the rest in domain 2. The atoms are so distributed that $N_A = N_{1A} + N_{2A}$, $N_B = N_{1B} + N_{2B}$ and $E = E_1 + E_2 + E_{12}$ where E_i ($i = 1, 2$) are the configurational energies of domain i. E_{12} takes into account of the interaction between atoms of domain 1 and 2. The simplified version like this enables us to write down the grand partition function as the product of the partition functions of the two domains (i.e. $\Xi = \Xi_1 \cdot \Xi_2$). The grand partition function for domain 1 becomes

$$\Xi_1 = \sum_{E_1} \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} e^{(-E_1 + \bar{E}_{12})/k_B T} \tag{6}$$

where

$$\zeta_A = q_A(T) e^{\mu_A/k_B T}, \; \zeta_B = q_B(T) e^{\mu_B/k_B T} \tag{7}$$

and a similar expression exists for Ξ_2. $\bar{E}_{12}/K_B T$ is the average energy of interaction through which atoms of domain 1 interact with the rest of the atoms of domain 2. Instead of making a rigorous approach, we resort to a simple approximation for $\bar{E}_{12}$ as in Fowler and Guggenheim[14] i.e.

$$e^{-\bar{E}_{12}/k_B T} \approx \phi_A^{Z_A} \phi_B^{Z_B} \tag{8}$$

where ϕ_A and ϕ_B are constants. Z_A are the number of lattice sites in domain 2 which are the nearest neighbours of A atoms located in the domain 1 and similarly Z_B. Thus Eq. (6) becomes

$$\Xi_1 = \sum_{E_1} \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} \phi_A^{Z_A} \phi_B^{Z_B} e^{-E_1/k_B T} \tag{9}$$

Ξ_1 for just one lattice site in domain 1 readily reduces to

$$\Xi_1^{(1)} = \zeta_A \phi_A^Z + \zeta_B \phi_B^Z \tag{10}$$

and for two lattice sites, one obtains

$$\Xi_1^{(2)} = \Xi_{AA} + \Xi_{BB} + 2\Xi_{AB} \tag{11}$$

where

$$\Xi_{AA} = \zeta_A^2 \phi_A^{2(Z-1)} e^{-\varepsilon_{AA}/k_B T} \tag{12}$$

$$\Xi_{BB} = \zeta_B^2 \phi_B^{2(Z-1)} e^{-\varepsilon_{BB}/k_B T} \tag{13}$$

$$\Xi_{AB} = \zeta_A \zeta_B (\phi_A \phi_B)^{Z-1} e^{-\varepsilon_{AB}/k_B T} \tag{14}$$

Where Z is the coordination number and ε_{ij} are the energies of $i - j$ bonds. By employing Eq. (11) we can immediately express the probability that the two neighbouring lattice sites are occupied by unlike atoms i.e.

$$(A, B) = (B, A) = \frac{\Xi_{AB}}{\Xi_1^{(2)}} \tag{15}$$

and similarly

$$(A, A) = \frac{\Xi_{AA}}{\Xi_1^{(2)}} \tag{16}$$

$$(B, B) = \frac{\Xi_{BB}}{\Xi_1^{(2)}} \tag{17}$$

It should also be noted that the probabilities (A, B), (A, A) and (B, B) are related to the conditional probabilities (A/B), (A/A) and (B/B) through the relations,

$$(A, B) = c(B/A); (B/A) = (1 - c)(A/B) \tag{18a}$$

$$(A, A) = c(A/A) \tag{18b}$$

$$(B, B) = (1 - c)(B/B) \tag{18c}$$

Also one has

$$A/B + B/B = 1 \tag{19a}$$

and

$$A/A + B/A = 1 \tag{19b}$$

Equations (15) to (19) yield

$$(A/B)^{-1} = 1 + \frac{\Xi_{BB}}{\Xi_{AB}} \tag{20}$$

$$(B/A)^{-1} = 1 + \frac{\Xi_{AA}}{\Xi_{AB}} \tag{21}$$

In the following section, we shall see that Ξ_{ij} can be expressed in terms of energies of the pairwise interaction of atoms A and B.

3 CONNECTION OF CONDITIONAL PROBABILITIES TO THE THERMODYNAMIC FUNCTIONS

We first note the standard thermodynamic relations for the chemical potentials μ_A and μ_B of the two component elements A and B in the binary mixture,

$$\mu_A - \mu_A^0 = k_B T \ln a_A \tag{22a}$$

$$\mu_B - \mu_B^0 = k_B T \ln a_B, \tag{22b}$$

where a_A and a_B are activities of components A and B in the alloy, μ_A^0 and μ_B^0 are chemical potentials of pure species A and B. By making use of the partition function and Eq. (22) we readily obtain

$$\mu_A^0 = -k_B T \ln q_A(T) + \tfrac{1}{2} Z \varepsilon_{AA} \tag{23a}$$

$$\mu_B^0 = -k_B T \ln q_B(T) + \tfrac{1}{2} Z \varepsilon_{BB} \tag{23b}$$

Equations (22), (23) and (7) further yield

$$a = \frac{a_B}{a_A} = \frac{\xi_B}{\xi_A} \exp\left\{\frac{Z}{k_B T}(\varepsilon_{AA} - \varepsilon_{BB})\right\} \tag{24}$$

In order to eliminate ξ_B/ξ_A from Eq. (24) we recall expression (9) for Ξ_1. Average values of A and B atoms in the inner domain can be expressed as

$$\bar{N}_{1A} = k_B T \frac{\partial \ln \Xi_1}{\partial \mu_A} = \xi_A \frac{\partial \ln \Xi_1}{\partial \xi_A} \tag{25a}$$

$$\bar{N}_{1B} = k_B T \frac{\partial \ln \Xi_1}{\partial \mu_B} = \xi_B \frac{\partial \ln \Xi_1}{\partial \xi_B} \tag{25b}$$

Therefore

$$\frac{\bar{N}_{1B}}{\bar{N}_{1A}} = \frac{1-c}{c} = \left(\frac{\xi_B}{\xi_A}\right)\left(\frac{\partial \ln \Xi_1}{\partial \xi_B}\right)\left(\frac{\partial \ln \Xi_1}{\partial \xi_A}\right)^{-1}. \tag{26}$$

On substituting Eqs (10) and (11) to Eq. (26), we obtain

$$\frac{\xi_B}{\xi_A}\left(\frac{\phi_B}{\phi_A}\right)^Z = \frac{1-c}{c}, \tag{27}$$

$$\frac{\Xi_{BB} + \Xi_{AB}}{\Xi_{AA} + \Xi_{AB}} = \frac{1-c}{c}. \tag{28}$$

By setting

$$\sigma = \left(\frac{\phi_B}{\phi_A}\right)\exp\left\{\frac{\varepsilon_{BB} - \varepsilon_{AA}}{2k_B T}\right\}, \tag{29}$$

Equations (27) and (28) provide

$$\sigma^2 + \left(\frac{1-2c}{\eta c}\right)\sigma - \frac{1-c}{c} = 0 \tag{30}$$

$$\eta = \exp\left\{\frac{2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}}{2k_B T}\right\} = \exp\left(\frac{\omega}{zk_B T}\right) \tag{31}$$

where $\omega = z\{\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2\}$ is usually called the interchange energy or ordering energy for the alloy. The valid solution of the quadratic expression (30) gives the working expression for σ i.e.

$$\sigma = \frac{\beta - 1 + 2c}{2\eta c} \tag{32}$$

where

$$\beta^2 = 1 + 4c(1 - c)(\eta^2 - 1) \tag{33}$$

σ can easily be calculated from Eq. (32) with the knowledge of the ordering energy ω. Now by eliminating ξ_B/ξ_A from (24) with the help of Eqs (27) and (29), we obtain an expression for the activity ratio $a(= a_B/a_A)$ i.e.

$$a = \left(\frac{1-c}{c}\right)\sigma^{-z} \tag{34}$$

Equation (34) can easily be used to obtain an analytic expression for the excess free energy of mixing, $G_M^{xs}(G_M^{xs} = G_M - Nk_BT\sum_i c_i \ln c_i)$ by using the standard thermodynamic relation[1]

$$\frac{d}{dc}\left(\frac{G_M^{xs}}{Nk_BT}\right) = \ln\frac{1-c}{ca} \tag{35}$$

Equations (34) and (35) lead to

$$\frac{G_M^{xs}}{Nk_BT} = \int_0^c \ln \sigma^z dc. \tag{36}$$

With σ as in Eq. (32), the above equation is readily integrable (η has been considered independent of c) and one obtains just the same expression for G_M^{xs} as given by Guggenheim.[15] For convenience we record it as

$$\frac{G_M^{xs}}{Nk_BT} = c \ln\left[\frac{\beta - 1 + 2c}{c(1 + \beta)}\right]^{Z/2} + (1 - c) \ln\left[\frac{\beta + 1 - 2c}{(1 - c)(1 + \beta)}\right]^{Z/2} \tag{37}$$

The long wave length limit ($q \to 0$) of the concentration fluctuation structure factor, $S_{cc}(0)$ is given by[16]

$$S_{cc}(0) = Nk_BT\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}^{-1} \tag{38}$$

Equations (37) and (38) yield

$$S_{cc}(0) = \frac{S_{cc}^{id}(0)}{1 + \dfrac{Z}{2\beta}(1 - \beta)} \tag{39}$$

$S_{cc}^{id}(0) = c(1 - c)$ is the concentration fluctuation of the ideal solution.

The denominator of the equation (39), which depends upon the ordering energy ω, brings the deviation from the ideal behaviour. As $\omega \to 0$ [i.e. $\varepsilon_{AB} = (\varepsilon_{AA} + \varepsilon_{BB})/2$], $\beta \to 1$ and $S_{cc}(0) \to S_{cc}^{id}(0)$. The reciprocal of $S_{cc}(0)$ is also known as Darken[17] stability function. $S_{cc}(0)$ has been proved very useful to understand the microscopic behaviour[4,18-19] of liquid alloys.

Lastly we furnish the expression for the short range order parameter. By substituting Eqs (27) and (29) into Eqs (20) and (21), the conditional probabilities emerge as,

$$(A/B) = \cfrac{1}{1 + \cfrac{1-c}{c}\,\sigma^{-1}\exp\left(\cfrac{\omega}{Zk_BT}\right)} \qquad (40)$$

$$(B/A) = \cfrac{1}{1 + \cfrac{c}{1-c}\,\sigma\exp\left(\cfrac{\omega}{Zk_BT}\right)} \qquad (41)$$

With the knowledge of the ordering energy (ω), (A/B) and (B/A) can easily be determined from Eqs (40) and (41). By virtue of Eqs (1) and (2) the above equations can also be expressed in terms of SRO (α_1) i.e.

$$\left(1 + \frac{\alpha_1}{c(1-c)(1-\alpha_1)^2}\right) = \exp\left(\frac{2\omega}{Zk_BT}\right) \qquad (42)$$

This is the desired relation between the short range order parameter and the ordering energy for the first shell. Though this relation is generalisable for higher shells, but for liquid alloys it suffices the purpose. Liquid alloys are known for its short range order. The structure factor measurements[20] testifies it which exhibit only a well pronounced principal peak. Even the magnitude of the second nearest peak is very much reduced than the first peak.

It is interesting to note that a relation similar to Eq. (42) can also be obtained[21] by following an entirely different approach of the pseudopotential method in second order perturbation theory. The Cowley[12] and Clapp and Moss[22] expressions for the short range order for the first shell also reduce to the equation of the form (42).

The success of the Eq. (42) for the determination of SRO as a function of composition depends upon the true knowledge of the ordering energy ω. The latter can be determined from the first principle by using pairwise interaction of the pseudopotential method[23-24] but very little work has been done in this direction. Contrary to this ω can also be

Table 1 Ordering energy (ω), excess free energy of mixing (G^{xs}), concentration fluctuations, $S_{cc}(0)$, and short range order parameter (α_1) at $T = T_c$ for simple lattice structure.

Lattice structure	$\dfrac{\omega}{K_B T_c}$	$\left(\dfrac{G^{xs}}{NK_B T}\right)_{T=T_c}$	$[S_{cc}(0)]_{T=T_c}$	$(\alpha_1)_{T=T_c}$
Simple Cubic ($Z = 6$)	2.432	0.5469	9.3×10^5	0.19
bcc ($Z = 8$)	2.301	0.5341	3.3×10^4	0.14
fcc ($Z = 12$)	2.187	0.5220	∞	0.09

determined very easily from the observed activity data or from the free energy of mixing. For example, Eq. (37) for $C = \frac{1}{2}$ reduces to

$$\frac{G_M^{xs}}{Nk_B T} = \ln 2^{z/2} \left\{ 1 + \exp\left(-\frac{\omega}{Zk_B T} \right) \right\}^{-Z/2} \qquad (43)$$

Thus Eq. (43) determines the ordering energy ω. Before we enter into the application to real systems, it is of interest to shed some light on the role of ordering energy on phase separation. For alloys where size difference is prominent, it has recently been pointed out[25] that both the ordering energy and the size effect jointly control the phase separation. But for binary alloys whose constituent elemental atoms are approximately of the same size, the condition of critical mixing for equiatomic composition is given[15] by

$$\frac{\omega}{k_B T_c} = Z \ln \frac{Z}{Z - 2} \qquad (44)$$

T_c is the temperature of critical mixing above which the alloy remains in one phase and below the critical temperature it separates into two phases. The values obtained for ordering energy, excess free energy of mixing, concentration fluctuations and the short range order parameter at $T = T_c$ for simple lattice structures are tabulated in Table 1. It is obvious that concentration fluctuation becomes exorbitantly high at $T = T_c$.

4 NUMERICAL VALUES OF THE SHORT RANGE ORDER AND ACTIVITY

The various expressions developed in the previous section are utilized here to compute the concentration dependence of the conditional

Table 2 Coordination number (Z) and the ordering energy (ω).

Alloys	$T(°K)$	Z	ω (eV)
CuPb	1473	12	0.2264
KNa	384	12	0.0328
CdMg	923	12	−0.1871
LiMg	887	10	−0.0764

probabilities $(A/B$ or $B/A)$, activity $(a = a_B/a_A)$ and the short range order (α_1) for CuPb, NaK, CdMg and LiMg liquid alloys. The co-ordination number (Z) and the ordering energy (ω) used for different systems are tabulated in Table 2. At the out-set it should be emphasized that ω and Z are considered here independent of concentration. Though Z for liquid alloys can be determined from the number–number structure factor, $S_{NN}(q)$, introduced by Bhatia and Thornton,[16] but very little progress has been made in this direction. Usually, in liquid alloys, Z varies[1] from 8 to 12. For want of better knowledge we take $Z = 12$ for CuPb, NaK, CdMg and $Z = 10$ for LiMg. During our investigation we have found that any other choice of Z modifies our results only slightly.

CuPb Liquid Alloys

The conditional probabilities, activity ratio and the short range order parameter for CuPb liquid alloys are tabulated in Table 3. The computed values of the activity ratio are in very good agreement with the

Table 3 Conditional probability $(A/B, B/A)$, activity ratio (a_B/a_A), and short range order parameter (α_1) for CuPb alloys at $T = 1473°K$. $(A \equiv Cu, B \equiv Pb)$.

c_A	(A/B)	(B/A)	Activity ratio $a = (a_B/a_A)$		S.R.O. α_1
			Theory	Expt.[26]	
0.1	0.8735	0.0971	2.246	2.187	0.029
0.2	0.7600	0.1900	1.443	1.352	0.05
0.3	0.6554	0.2809	1.193	1.218	0.064
0.4	0.5570	0.3713	1.076	1.150	0.072
0.5	0.4629	0.4629	1.000	0.962	0.074
0.6	0.3713	0.5570	0.930	0.988	0.072
0.7	0.2809	0.6554	0.838	0.864	0.064
0.8	0.1899	0.7600	0.693	0.680	0.05
0.9	0.0971	0.8735	0.445	0.405	0.029

experimental observation[26] at all concentrations. The short range order parameter (α_1) is positive throughout. This indicates segregation of preference for like atoms pairing as nearest neighbour in the alloy. CuPb liquid alloys belongs to monotectic system which is well known for the existence of miscibility gap in the liquid state. The computed values of α_1 supports the above fact. We shall see later that the computed values of $S_{cc}(0)$ strongly indicates the existence of miscibility gap in the liquid state.

NaK Liquid Alloys:

The results for NaK liquid alloys are tabulated in Table 4. The present values of the activity ratio agree well with the observed values.[26] The values of α_1 for NaK liquid alloys are also positive at every composition, which indicates the tendency of like atoms pairing in the first coordination shell but not as strong as in CuPb system. It may be noted

Table 4 Conditional probability $(A/B, B/A)$, activity ratio (a_B/a_A) and short range order parameter (α_1) for KNa alloys at $T = 384°K$. $(A \equiv k, B \equiv Na)$.

c_A	(A/B)	(B/A)	Activity ratio $a = (a_B/a_A)$		S.R.O. α_1
			Theory	Expt.[26]	
0.1	0.098	0.886	4.117	4.299	0.016
0.2	0.195	0.778	2.241	2.251	0.027
0.3	0.290	0.675	1.590	1.560	0.035
0.4	0.384	0.576	1.239	1.198	0.040
0.5	0.479	0.479	1.000	0.965	0.041
0.6	0.576	0.384	0.807	0.783	0.040
0.7	0.675	0.289	0.630	0.619	0.035
0.8	0.778	0.195	0.446	0.447	0.027
0.9	0.886	0.098	0.243	0.248	0.016

that the values of α_1 in CuPb liquid alloys are almost double than the NaK liquid alloys. The equilibrium phase diagram of NaK is in contrast to CuPb system. The former is a deep eutectic whereas the latter belongs to a monotectic system. In the following section, we shall see that $S_{cc}(0)$ for NaK is much smaller than the CuPb, but in either case it is greater than the ideal values.

CdMg Liquid Alloys:

Table 5 enlists the computed values of the conditional probabilities, activity ratio and the short range order parameter. The theoretical and

Table 5 Conditional probability $(A/B, B/A)$, activity ratio (a_B/a_A) and short range order parameter (α_1) for CdMg alloys at $T = 923°K$. ($A \equiv Cd$, $B \equiv Mg$).

c_A	(A/B)	(B/A)	Activity ratio $a = (a_B/a_A)$		S.R.O. α_1
			Theory	Expt.[26]	
0.1	0.9279	0.1031	62.971	59.133	−0.031
0.2	0.8465	0.2116	17.928	18.575	−0.058
0.3	0.7556	0.3238	6.481	6.621	−0.079
0.4	0.6558	0.4372	2.517	2.452	−0.093
0.5	0.5489	0.5489	1.000	1.068	−0.098
0.6	0.4372	0.6558	0.397	0.367	−0.093
0.7	0.3238	0.7556	0.154	0.147	−0.079
0.8	0.2116	0.8465	0.056	0.057	−0.058
0.9	0.1031	0.9279	0.016	0.018	−0.031

observed values[26] of the activity ratio are in reasonable agreements. Some minor discrepancies exist for smaller contents of Cd in the alloy. With increasing concentration of Cd, the agreement improves significantly. CdMg liquid alloys behave differently than CuPb and NaK. The activity ratio in CdMg is much larger than CuPb or NaK. Unlike the latter systems, the short range order parameter in CdMg is negative at all concentrations. This indicates a preference for heterocoordination in the liquid phase. At this stage we may recall that the phase diagram of CdMg liquid alloys consists of a simple monotonous line, rising from Cd to Mg end. Boos and Steeb[27] have measured $\alpha_1 = -0.13$ for $Cd_{25}Mg_{75}$ liquid alloys at $823°K$ for $Z = 7$. If we repeat our calculation for the same Z and T then we obtain $\alpha_1 = -0.11$ which is in good agreement with the experimental observation. The heterocoordination in CdMg liquid alloys is supported by $S_{cc}(0)$ values which are to be presented in the following section.

LiMg Liquid Alloys:

In recent years great interest has been shown in LiMg liquid alloys. The up to date experimental information on various physical and thermo-dynamical properties are well summarized in the work by Ruppersberg et al.[28] and Marel and Lugt.[29] The theoretical understanding of the alloying behaviour of LiMg melt has recently been discussed by Singh et al.[30] The basic thrust has been to examine the deviation from the ideal solution behaviour. Though the present work can not be considered as a rigorous first principle theoretical approach, none the less it

Table 6 Conditional probability $(A/B, B/A)$, activity ratio (a_B/a_A) and short range order parameter (α_1) for LiMg alloys at $T = 887°K$. $(A \equiv Li, B \equiv Mg)$.

c_A	(A/B)	(B/A)	Activity ratio $a = (a_B/a_A)$		S.R.O. α_1
			Theory	Expt.[31]	
0.101	0.9143	0.1027	20.0481	24.021	−0.0170
0.238	0.7889	0.2464	5.5138	6.164	−0.0353
0.357	0.6722	0.3732	2.4299	2.874	−0.0455
0.466	0.5605	0.4892	1.2306	1.464	−0.0497
0.541	0.4818	0.5678	0.7781	0.841	−0.0496
0.594	0.4255	0.6225	0.5612	0.608	−0.0480
0.646	0.3700	0.6753	0.4038	0.437	−0.0453
0.67	0.3444	0.6993	0.3452	0.368	−0.0437
0.702	0.3103	0.7309	0.2786	0.288	−0.0411

shed some light on the local behaviour of the alloying elements. The computed values of the conditional probabilities, activity ratio and the short range order parameter for LiMg liquid alloys are given in Table 6. The choice of the concentrations in Table 6 is irregular because it helps to compare our results directly to the observed activity.[31] Towards the Mg rich end the agreement between the theory and the experiment is very good but some discrepancies exist towards the Li-rich end. The activity ratio in LiMg is greater than CuPb and NaK, but less than CdMg liquid alloys. The short range order parameter is always negative and thereby indicates heterocoordination in the liquid phase. Our computed values of $\alpha_1 = -0.05$ for $Li_{0.7}Mg_{0.3}$ liquid alloys ($T = 887°K$) is in good agreement with $\alpha_1 = -0.035$ (875°K) obtained from the Neutron diffraction experiments.[28]

## 5 EXCESS FREE ENERGY OF MIXING AND CONCENTRATION FLUCTUATIONS

With the knowledge of the ordering energy (ω) given in Table 2, Eqs (37) and (39) are used to compute the excess free energy of mixing (G^{xs}) and the concentration–concentration structure factors, $S_{cc}(0)$, in the long wavelength limit. The G^{xs} for CuPb, NaK, CdMg and LiMg liquid alloys are plotted in Figure 1. The computed values are in very good agreement with the experimental observation.[26] G^{xs} for LiMg could not be compared as no experimental data exists at $T = 887°K$. The excess
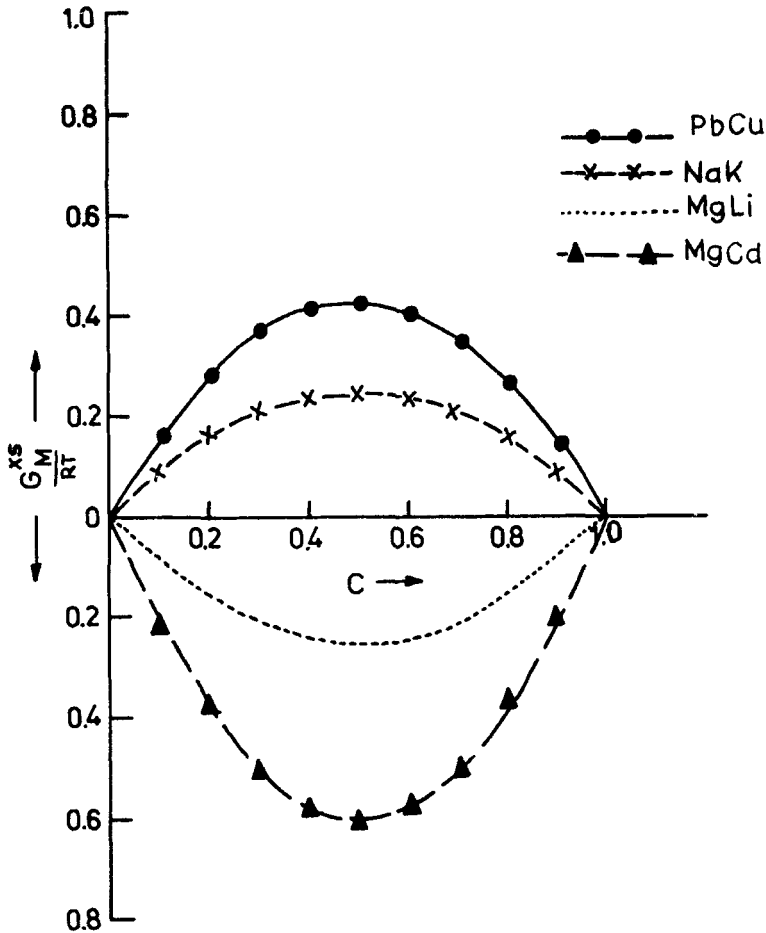
Figure 1   Excess free energy of mixing (G_M^{xs}/RT) as a function of concentration (C): _____ theory, ● ● ● expt,[26] $C \equiv C_{Cu}$ (PbCu at 1473°K); ---- theory, × × × expt,[26] $C \equiv C_K$ (NaK at 384°K); ⋯⋯ theory, $C \equiv C_{Li}$ (MgLi at 887°K); and — — — theory, ▲ ▲ ▲ expt,[26] $C \equiv C_{Cd}$ (MgCd at 923°K).

free energy of mixing for CuPb and NaK are positive whereas for LiMg and CdMg it is negative. If we recall the values of α_1 for these systems then we find that the positive values of G^{xs} lead to like atoms pairing in the alloys and the negative values correspond to heterocoordination.

The computed values of $S_{cc}(0)$ are plotted in Figure 2. What is interesting here is to observe the deviation in $S_{cc}(0)$ from the ideal solution values $S_{cc}^{id}(0) = c(1 - c)$. For CuPb and NaK, $S_{cc}(0)$ are greater than the ideal values $S_{cc}^{id}(0)$. On the other hand $S_{cc}(0)$ for LiMg and
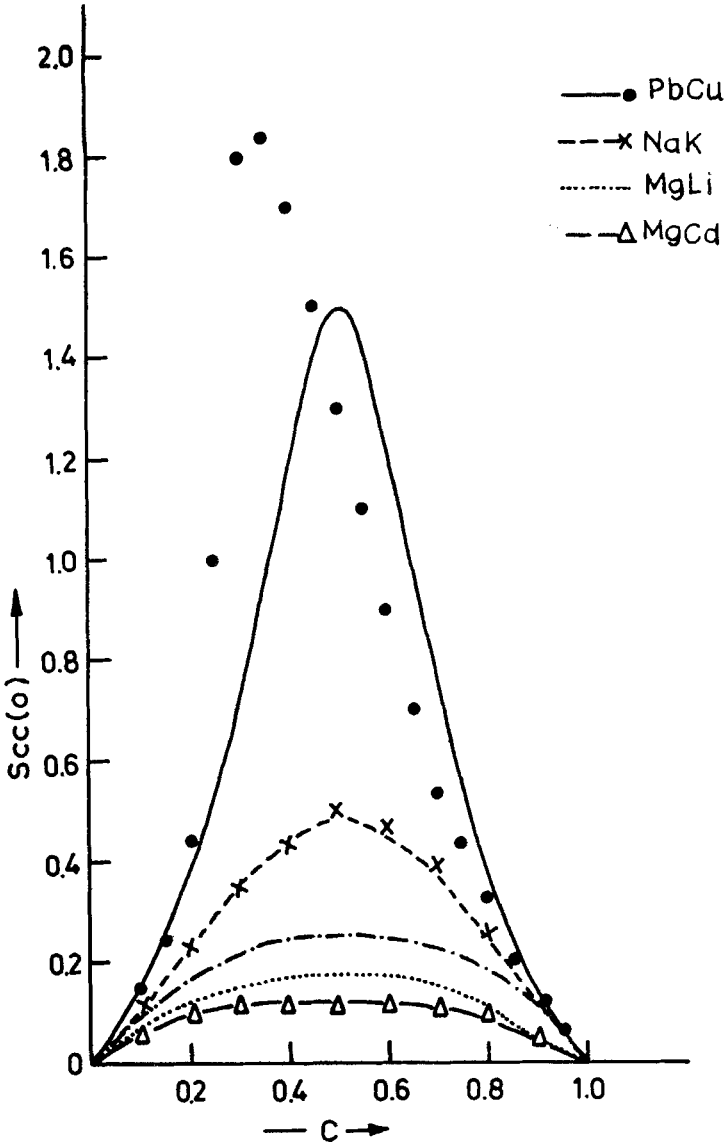
Figure 2 Concentration fluctuations $[S_{cc}(0)]$ as a function of concentration (C): _____ theory, ● ● ● expt, $C \equiv C_{Cu}$ (PbCu at 1473°K); ----theory, × × × expt, $C \equiv C_K$ (NaK at 384°K); ······ theory, $C \equiv C_{Li}$ (MgLi at 887°K); — — — theory, △ △ △ expt, $C \equiv C_{Cd}$ (MgCd at 923°K); — · — · — refers to $S_{cc}^{id}(0)$; Experimental $S_{cc}(0)$ refers to the values obtained directly from measured activity (see text).

CdMg are less than $S_{cc}^{id}(0)$. The positive deviation from the ideal values indicates preference for like atoms pairing as nearest neighbour whereas the negative deviation corresponds to unlike atoms pairing.

It is also interesting to compare the computed values of $S_{cc}(0)$ to that obtained directly from the observed activity data

$$S_{cc}(0) = \frac{(1-c)a_A}{(\partial a_A/\partial c)_{T,P,N}} = \frac{ca_B}{(\partial a_B/\partial(1-c)_{T,P,N}} \tag{45}$$

We observe that $S_{cc}(0)$ of CdMg and NaK computed both from Eqs (39) and (45) are in very good agreement to each other. Both are symmetric about equiatomic composition. But in case of CuPb, the directly obtained $S_{cc}(0)$ from the activity data (via Eq. (45)) differ considerably to that obtained from equation (39). The earlier values exhibit asymmetry about $c = \frac{1}{2}$. The asymmetry corresponds to $c_{cu} = 0.35$. The observed asymmetry might be due to the size effect (Pb atoms are about 2.7 times larger than Cu atoms). Recently[25,32-33] it has been shown that $S_{cc}(0)$ is very sensitive to the size effect and the latter might create asymmetry. Other thermodynamic functions like a and G^{xs} are not so sensitive to the size effect as $S_{cc}(0)$. This is why agreement for a and G^{xs} are almost exact in CuPb but noticeable disagreement exists for $S_{cc}(0)$. The role of size effect on $S_{cc}(0)$ of CuPb liquid alloys shall be considered later.

For LiMg, $S_{cc}(0)$ could not be obtained from equation (45) because observed activity[30] data exist only for $C_{Li} \geq 0.3$ and are available at irregular concentrations. Recently Singh et al.[30] have fitted the observed activity of LiMg to a seventh order polynomial and then evaluated $S_{cc}(0)$. They found that $S_{cc}(0) > S_{cc}^{id}(0)$ for $c_{Li} = 0.1$ to 0.32 and $S_{cc}(0) < S_{cc}^{id}(0)$ for $C_{Li} \geq 0.32$. However our values of $S_{cc}(0)$ computed from Eq. (39) for $Li_{0.7}Mg_{0.3}$ amount to 0.1464 as compared to 0.142 obtained by neutron diffraction experiments.[28]

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