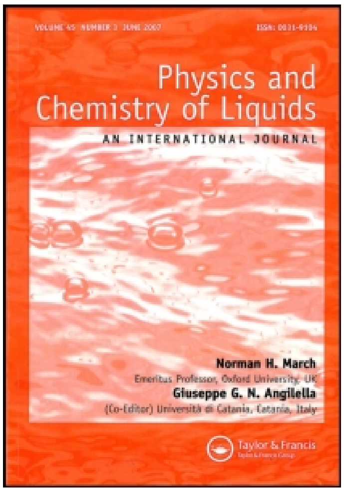

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Higher Order Conditional Probabilities And Short Range Order in Molten Alloys

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HIGHER ORDER CONDITIONAL PROBABILITIES AND SHORT RANGE ORDER IN MOLTEN ALLOYS

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A thermodynamic model based on cluster of four atoms is considered with a view to obtain conditional probabilities enumerating the higher order atomic correlations in the nearest neighbour shell of liquid binary alloys. This has helped to discuss as how the higher order atomic correlations in liquid alloys are related to pairwise distribution. The values of order energy, activity and the chemical short range order parameter computed for Bi-Cd, Li-Mg, Cd-Mg, Cd-Ga, Cu-Pb and K-Na are presented.

KEY WORDS: Atomic correlations, order energy, activity, chemical short range order.

1 INTRODUCTION

Though the diffraction experiments are very useful to yield structural informations of liquid alloys, often the analysis of the scattered intensity is a cumbersome[1] task which is difficult to achieve in practice due to involvement of three partial correlation functions. On the other hand, the thermodynamic model can readily be used to extract the microscopic chemical structure of such systems. Bhatia and Singh[2] proposed a simple scheme to connect the conditional probabilities enumerating the occupation of neighbouring sites by the atoms of the constituent elements in the compound forming liquid alloys to thermodynamic functions like activity or free energy of mixing. Later, Singh and Mishra[3] brought a simplified version to be applied to regular alloys.

By considering a model of cluster of two atoms (hereafter, we call it TACM i.e. two-atoms-cluster-model) which are interacting via pairwise interaction, it has become possible for them to obtain analytical expression for conditional probabilities (i/j, the probability of finding i atom as a nearest neighbour of a given j-atom) in terms of activity and the order energy. They have also used it to obtain excess free energy of mixing, concentration fluctuations and the chemical short range order parameter for Cu-Pb, K-Na, Cd-Mg and Li-Mg liquid alloys.

Hitherto, we extend the formulation of TACM to a cluster of four atoms (say, FACM i.e. four-atoms-cluster-model) with a view to obtain higher order conditional probabilities enumerating the atomic distributions in the nearest neighbour shell (for example, i/iji, the probability of finding i atoms on a given lattice site while other three neighbouring sites in the cluster are occupied by i, j and i-atoms). This should give us a more realistic value of the order energy (W) and the chemical short range order parameter (α), and thus a quantitative discussion is attempted for heterocoordination (i.e. preference for unlike atoms to pair as nearest neighbour) and self coordination (preference for like atoms to pair as nearest neighbours) in the molten alloys. Besides, the values of W are needed for other thermodynamic[4–5] and surface properties[6]. Similarly α is required to evaluate[7] the electrical resistivities of liquid alloys.

To be specific, the application is made to Bi-Cd, Li-Mg, Cd-Mg, Cd-Ga, Cu-Pb and K-Na liquid alloys which belong to both heterocoordinated and self coordinated groups of alloys. These alloys are carefully selected to represent the wide varieties of phase diagrams which are often found in many other binary alloys. The phase diagrams of these alloys are schematically represented in Figure 1. Section 2 deals with the salient features of the cluster-model of four atoms and the formulation of activity in terms of order energy. The higher order conditional probabilities enumerating the atomic distributions in the nearest neighbour shell of liquid binary alloys is discussed in Section 3. These are then used in Section 4 to obtain the values of chemical short range order parameter.

2 ACTIVITY AND THE ORDER ENERGY OF THE MOLTEN ALLOYS

Let the binary alloy contain in all N atoms of which N_A $(=NC_A)$ are A-atoms and N_B $(=NC_B)$ are B-atoms, then the grand partition function (Ξ) for the alloy can be written as

$$\Xi = \sum_{E} q_A^{N_A}(T) q_B^{N_B}(T) e^{\beta(\mu_A N_A + \mu_B N_B)} e^{-\beta E}; \qquad \beta = \frac{1}{K_B T} \tag{1}$$

where $q_i(T)$ are the partition functions of atoms i (A or B) associated with inner and vibrational degrees of freedom. μ_A and μ_B are the chemical potentials and E is the configurational energy. In order to solve Eq. (1), we resort to some simple assumptions:

(1) The interactions between the atoms are of short range and effective between nearest neighbours only.

(2) The atoms are located on the sites of a lattice and each site as Z nearest neighbours. The whole set of lattice sites is, further, divided into a small cluster of just a few lattice sites and the remainder. To facilitate we refer the cluster by suffix 1 (or domain 1) and the remainder by suffix 2 (or domain 2). Thus one writes

$$\begin{aligned} N_A &= N_{1A} + N_{2A} \\ N_B &= N_{1B} + N_{2B} \\ E &= E_1 + E_2 + E_{12} \end{aligned} \tag{2}$$

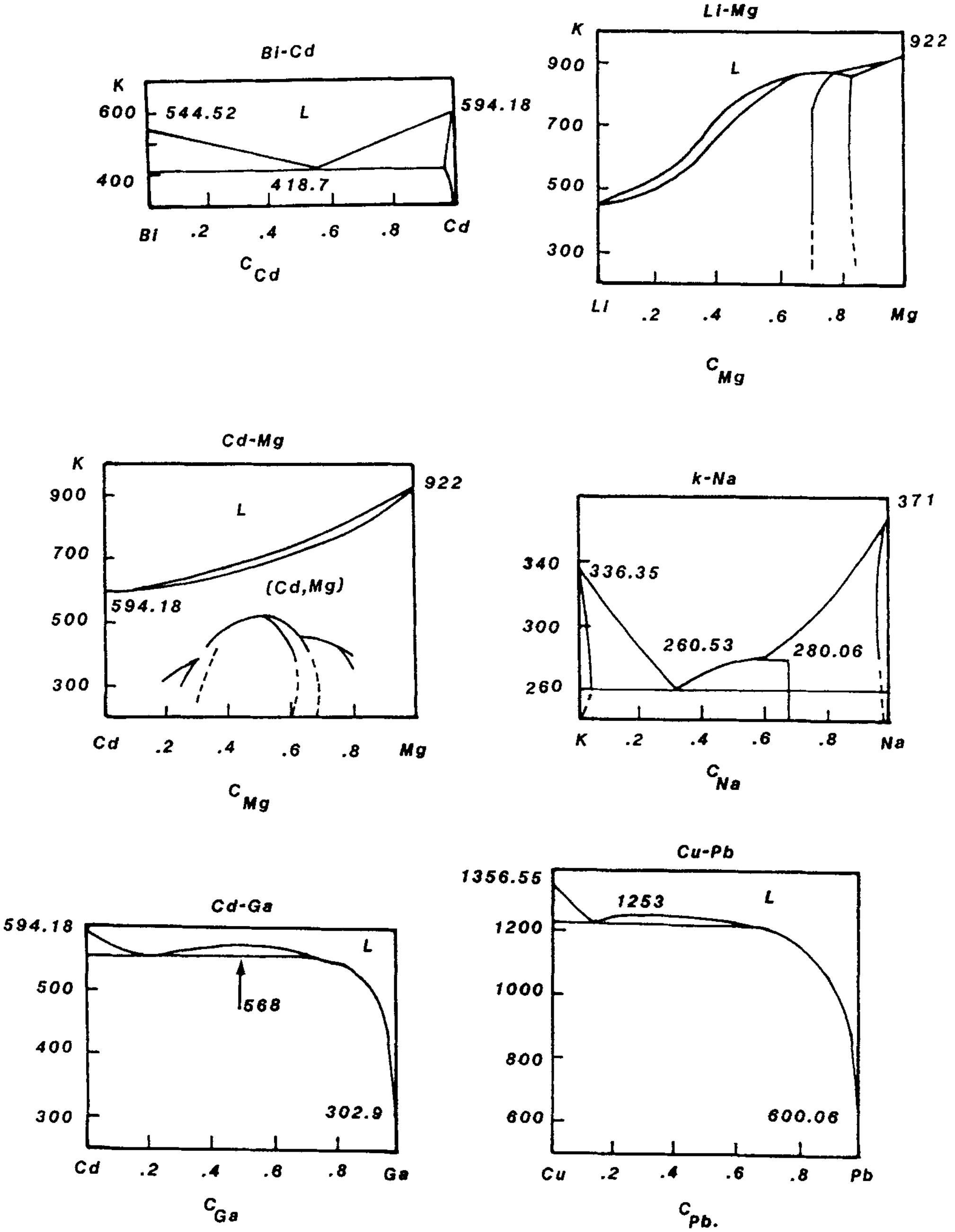

Figure 1 Phase diagram of alloys; (a) Bi-Cd (b) Li-Mg (c) Cd-Mg (d) K-Na (e) Cd-Ga and (f) Cu-Pb. [Source: Hutgren *et al.*[9]].

where E_i ($i = 1, 2$) are the configurational energies of domain i and E_{12} takes into account of the interaction between atoms of cluster and the remainder. 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. $\Xi = \Xi_1 \times \Xi_2$). Ξ_1, the grand partition function for the cluster becomes[2,8]

$$\Xi_1 = \sum_{E_1} \xi_A^{N_{1A}} \xi_B^{N_{1B}} \phi_A^{Z_A} \phi_B^{Z_B} e^{-\beta E_1} \tag{3}$$

with

$$\xi_A = q_A(T) e^{\beta\mu_A}; \qquad \xi_B = q_B(T) e^{\beta\mu_B} \tag{4}$$

ϕ_A and ϕ_B are constants to be eliminated from the final result. 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. From the definition of Ξ_1, the average values of A and B atoms in the cluster are given by

$$\bar{N}_{1A} = \frac{\partial \ln \Xi_1}{\beta \partial \mu_A}; \ \bar{N}_{1B} = \frac{\partial \ln \Xi_1}{\beta \partial \mu_B} \tag{5}$$

or,

$$\frac{C_B}{C_A} = \frac{\bar{N}_{1B}}{\bar{N}_{1A}} = \left(\frac{\xi_B}{\xi_A}\right)\left(\frac{\partial \ln \Xi_1}{\partial \xi_B}\right)\left(\frac{\partial \ln \Xi_1}{\partial \xi_A}\right)^{-1} \tag{6}$$

Equation (6) can be utilised to eliminate ϕ_A and ϕ_B after using, two different sizes of the cluster. For example, for a cluster consisting of just one lattice site, there are no A-A, A-B or B-B bonds in the cluster and hence $E_1 = 0$. The single site can be occupied by either an A atom or a B atom, and $Z_A = Z_B = Z$, Eq. (3) becomes

$$\Xi_1^{(1)} = \xi_A \phi_A^Z + \xi_B \phi_B^Z \tag{7}$$

The superscript (1) indicates that the expression for Ξ_1 stands for the cluster of one atom. Next we consider a cluster of four lattice-sites in the inner domain (i.e. domain 1), the possible arrangements of atoms on sites can be obtained statistically and are depicted in Table 1. Equation (3) thus becomes

$$\begin{aligned} \Xi_1^{(4)} = {} & \xi_A^4 \phi_A^{4(Z-3)} P_{AA}^6 - 4\xi_A^3 \xi_B \phi_A^{3(Z-3)} \phi_B^{(Z-3)} P_{AA}^3 P_{AB}^3 \\ & + 6\xi_A^2 \xi_B^2 \phi_A^{2(Z-3)} \phi_B^{2(Z-3)} P_{AA} P_{BB} P_{AB}^4 \\ & + 4\xi_A \xi_B^3 \phi_A^{(Z-3)} \phi_B^{3(Z-3)} P_{BB}^3 P_{AB}^3 + \xi_B^4 \phi_B^{4(Z-3)} P_{BB}^6 \end{aligned} \tag{8}$$

Table 1 Possible arrangements of atoms in the cluster of four lattice sites:

N_{1A}	N_{1B}	Z_A	Z_B	E_1
4	0	$4(Z-3)$	0	$6\varepsilon_{AA}$
3	1	$3(Z-3)$	$(Z-3)$	$3\varepsilon_{AA}+3\varepsilon_{AB}$
2	2	$2(Z-3)$	$2(Z-3)$	$\varepsilon_{AA}+\varepsilon_{BB}+4\varepsilon_{AB}$
1	3	$(Z-3)$	$3(Z-3)$	$3\varepsilon_{BB}+3\varepsilon_{AB}$
0	4	0	$4(Z-3)$	$6\varepsilon_{BB}$

ε_{ij} is the energy of i–j bond.

with

$$P_{ij} = e^{-\beta\varepsilon_{ij}}, \qquad ij = A, B. \tag{9}$$

where ε_{ij} are the energies of i–j bonds and Z is the coordination number. On substituting Eqs. (7) and (8) to Eq. (6), we obtain

$$\frac{C_B}{C_A} = \xi\phi^Z \tag{10}$$

$$\frac{C_B}{C_A} = \frac{\xi A_1 + 3\xi^3 A_2 + 3\xi^2 A_3 + \xi A_4}{\xi^3 A_2 + 3\xi^2 A_3 + 3\xi A_4 + 1} \tag{11}$$

where

$$\xi = \xi_B/\xi_A; \qquad \phi = \phi_B/\phi_A \tag{12}$$

$$A_1 = \phi^{4(Z-3)}\left(\frac{P_{BB}}{P_{AA}}\right)^6 \tag{13}$$

$$A_2 = \phi^{3(Z-3)}\,\frac{P_{AB}^3 P_{BB}^3}{P_{AA}^6} \tag{14}$$

$$A_3 = \phi^2(Z-3)\,\frac{P_{AB}^4 P_{BB}}{P_{AA}^5} \tag{15}$$

$$A_4 = \phi^{(Z-3)}\cdot\frac{P_{AB}^3}{P_{AA}^3} \tag{16}$$

Equations (10) and (11) have been solved to obtain

$$\sigma^{12} - B_1\sigma^9 - B_2\sigma^6 - B_3\sigma^3 - B_4 = 0 \tag{17}$$

where

$$\sigma = \phi(P_{AA}/P_{BB})^{1/2} \tag{18}$$

$$B_1 = (1 - 3x)\eta^{-3} \tag{19}$$

$$B_2 = 3x(1 - x)\eta^{-4} \tag{20}$$

$$B_3 = 3x^2(1 - x/3) \cdot \eta^{-3} \tag{21}$$

$$B_4 = x^3 \tag{22}$$

$$x = C_B/C_A \text{ and } \eta = \exp \beta\left\{\frac{2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}}{2}\right\}$$

$$= \exp(\beta W/Z) \tag{23}$$

where $W = Z\{\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2)\}$ is usually called the interchange or order energy for the alloy. ε_{ij} are the bond energies for ij nearest neighbour bonds. By its logical implications, W may depend on temperature and pressure, but is independent of concentration.

Unlike two atoms cluster model where on obtains[3] an analytic expression for σ, we have a polynomial-like expression (Eq. 17) for σ. It can be solved numerically to obtain the value of σ. The only unknown quantity in the expression (17) is the order energy W, to be determined later. We shall see shortly that σ is the quantity of central importance because it enters directly into the expression of activity.

In order to connect σ to activity, we first recall the thermodynamic relations for the chemical potentials μ_A and μ_B of the two component element A and B in the binary mixture.

$$\mu_A = \mu_0^A + \beta \ln a_A \tag{24a}$$

$$\mu_B = \mu_0^B + \beta \ln a_B \tag{24b}$$

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. (24) we obtain

$$\mu_A^0 = -\beta \ln q_A(T) + \tfrac{1}{2}Z\varepsilon_{AA} \tag{25a}$$

$$\mu_B^0 = -\beta \ln q_B(T) + \tfrac{1}{2}Z\varepsilon_{BB} \tag{25b}$$

Equations (24), (25) and (4) yield

$$a = \frac{a_B}{a_A} = \frac{\xi_B}{\xi_A}\left(\frac{P_{BB}}{P_{AA}}\right)^{Z/2} \tag{26}$$

By substituting Eqs. (26) and (18) into (11), we obtain an expression which connects activity, a, to σ i.e.

$$C_A f_1(a, \sigma) = C_B f_2(a, \sigma) \tag{27}$$

with

$$f_1(a, \sigma) = a^4\sigma^{4(Z-3)} + 3a^3\sigma^{3(Z-3)}\eta^{-3} + 3a^2\sigma^{2(Z-3)}\eta^{-4} + a\sigma^{(Z-3)}\eta^{-3} \tag{28}$$

$$f_2(a, \sigma) = a^3\sigma^{3(Z-3)}\eta^{-3} + 3a^2\sigma^{2(Z-3)}\eta^{-4} + 3a\sigma^{(Z-3)}\eta^{-3} + 1 \tag{29}$$

Equation (27) has been used to determine activity for Bi-Cd, Li-Mg, Cd-Mg, Cd-Ga, Cu-Pb and K-Na liquid alloys for different concentrations. The basic ingredient which acts as an input is the order energy, W. As a starting point, we determine W from the expression of the excess free energy of mixing for equiatomic ($C_A = C_B = \frac{1}{2}$) liquid alloys resulting from two atoms cluster model[3] i.e.

$$\exp\left(-\frac{\beta W}{Z}\right) = 1 + \exp\left(\frac{2G_M^{xs}}{ZRT}\right) \tag{30}$$

where G_M^{xs} is the excess free energy of mixing of liquid alloys at equiatomic composition. By taking experimental values[9–10] of G_M^{xs}, W is first determined from Eq. (30). This was, in turn, used in expression (17) to obtain σ and finally the activity was determined from Eq. (27). The process was repeated to optimise the values of W in order to get a good representation of activity at all concentrations. Usually, in liquid alloys, Z varies from 8 to 12 but in actual calculation it was fixed here to 10 which is a reasonable choice for simple liquid alloys[1]. Besides it was observed[2–3] earlier that the variation of Z in the range 8 to 12 makes little impact on the actual calculation.

The optimised values of W for Bi-Cd, Li-Mg, Cd-Mg, Cd-Ga, Cu-Pb and K-Na are given in Table 2. These are compared to those obtained from two-atoms cluster model[3]. In order to keep consistency the two atoms cluster work of Singh and Mishra[3] was repeated for $Z = 10$ and was also extended to compute W for Bi-Cd and Cd-Ga. That is how W for TACM in Table 2 slightly differs from the values quoted by Singh and Mishra[3].

The results of Table 2 suggest that W does not change drastically in going from 2-atoms (TACM) to 4-atoms cluster model (FACM). In some cases the effect is substantial but depends upon the system. The deviation is maximum for Li-Mg and minimum for K-Na. W with FACM in case of Li-Mg is about 18% lower to TACM and 15% lower in case of Bi-Cd. In other systems, the deviations are negligibly small which range from 2 to 5%. The sign and magnitude of W implies that Bi-Cd, Li-Mg

Table 2 Order energy W in e.v. in binary liquid alloys

Alloys	*Temp. (°K)*	*Z*	*W (ev)*	
			(FACM)	*TACM*
Bi-Cd	773	10	−0.0175	−0.0148
Li-Mg	887	10	−0.0932	−0.0764
Cd-Mg	923	10	−0.1807	−0.1864
K-Na	384	10	+0.0335	+0.0330
Cd-Ga	700	10	+0.1190	+0.1132
Cu-Pb	1473	10	+0.2130	+0.2289

FACM = Four atoms cluster model;
TACM = Two atoms cluster model.

Table 3 Activity ratio, a, $(=a_B/a_A)$ for Cd-Bi, Li-Mg and Cd-Mg liquid alloys ($A \equiv$ Cd, Li and Cd)

Cd-Bi (773 K)			*Li-Mg (887 K)*			*Cd-Mg (923 K)*		
C_{cd}	a_{th}	a_{exp}	C_{Li}	a_{th}	a_{exp}	C_{cd}	a_{th}	a_{exp}
0.1	11.116	11.134	0.101	24.031	24.021	0.1	59.166	59.133
0.2	4.689	5.012	0.238	6.228	6.164	0.2	17.046	18.575
0.3	2.594	2.727	0.357	2.599	2.874	0.3	6.236	6.621
0.4	1.581	1.532	0.466	1.250	1.464	0.4	2.463	2.452
0.5	1.000	0.923	0.541	0.763	0.841	0.5	1.000	1.068
0.6	0.632	0.577	0.594	0.536	0.608	0.6	0.405	0.367
0.7	0.385	0.368	0.646	0.376	0.437	0.7	0.160	0.147
0.8	0.213	0.220	0.670	0.318	0.368	0.8	0.058	0.057
0.9	0.089	0.103	0.702	0.253	0.288	0.9	0.016	0.018

Table 4 Activity ratio a $(=a_B/a_A)$ for K-Na, Cd-Ga and Cu-Pb liquid alloys ($A \equiv$ K, Cd, Cu)

K-Na (384 K)			*Cd-Ga (700 K)*			*Cu-Pb (1473 K)*		
C_K	a_{th}	a_{exp}	C_{cd}	a_{th}	a_{exp}	C_{Cu}	a_{th}	a_{exp}
0.1	4.066	4.027	0.1	1.980	1.974	0.1	2.460	2.468
0.2	2.224	2.238	0.2	1.330	1.358	0.2	1.552	1.470
0.3	1.585	1.615	0.3	1.140	1.164	0.3	1.256	1.158
0.4	1.237	1.277	0.4	1.053	1.073	0.4	1.104	1.012
0.5	1.000	1.037	0.5	1.000	1.024	0.5	1.000	0.932
0.6	0.807	0.835	0.6	0.948	0.950	0.6	0.905	0.870
0.7	0.630	0.641	0.7	0.876	0.846	0.7	0.795	0.821
0.8	0.449	0.444	0.8	0.749	0.681	0.8	0.644	0.739
0.9	0.245	0.233	0.9	0.504	0.473	0.9	0.406	0.457

and Cd-Mg are heterocoordinated systems in ascending order. K-Na, Cd-Ga and Cu-Pb are self-coordinated systems, again, in ascending order.

W is now used in Eq. (17) to calculate σ and finally the activity ratio, a, from Eq. (27). The computed values of "a" for Cd-Bi, Li-Mg and Cd-Mg are given in Table 3. The results for K-Na, Cd-Ga and Cu-Pb are tabulated in Table 4. The theoretical results are compared with the experimental values. From Tables 3 and 4, it is apparent that the theoretical and the experimental values are in good agreement. We may recall that the activity is one of those thermodynamic functions which can be measured directly from the experiment. Therefore, it can be used with greater confidence to check the validity of the theoretically derived expressions and hence, the values of the order energies for liquid binary alloys.

3 HIGHER ORDER CONDITIONAL PROBABILITIES FOR ATOMIC DISTRIBUTIONS

Even in the framework of quasilattice model of liquid binary alloys, the probability of finding an atom A or atom B on any given lattice site is not equal to the average distribution of both kinds but depends on the nature of the atom already present on the neighbouring site. Likewise the probabilities of occupation for two lattice sites cluster[3], we define here the probabilities of occupation when there are four atoms in the cluster. Let (A, A, A, A) represents the probability that all the four lattice sites of the cluster are occupied by atoms A and similarly others. From the definition of grand partition functions (see Table 1 and Eq. 8), one writes:

$$(A, A, A, A) = \frac{\xi_A^4 \phi_A^{4(Z-3)} P_{AA}^6}{\Xi_1^{(4)}} \tag{31}$$

$$(A, A, A, B) = \frac{4\xi_A^3 \xi_B \phi_A^{3(Z-3)} \phi_B^{(Z-3)} P_{AA}^3 P_{AB}^3}{\Xi_1^{(4)}} \tag{32}$$

$$(A, A, B, B) = \frac{6\xi_A^2 \xi_B^2 \phi_A^{2(Z-3)} \phi_B^{2(Z-3)} P_{AA} P_{BB} P_{AB}^4}{\Xi_1^{(4)}} \tag{33}$$

$$(A, B, B, B) = \frac{4\xi_A \xi_B^3 \phi_A^{(Z-3)} \phi_B^{3(Z-3)} P_{AB}^3 P_{BB}^3}{\Xi_1^{(4)}} \tag{34}$$

$$(B, B, B, B) = \frac{\xi_B^4 \phi_B^{4(Z-3)} P_{BB}^6}{\Xi_1^{(4)}} \tag{35}$$

The above probabilities, (i, j, k, l), can readily be reduced to higher order conditional probabilities i.e. i/iji (the probability of finding i atom on a given lattice site while other three sites in the cluster are occupied by i,j and i atoms), and similarly others, i.e.

$$(A,\ A,\ A,\ A) = C_A(A/A)(A/AA)(A/AAA) \tag{36}$$

$$\begin{aligned}(AAAB/4) &= C_A(A/A)(A/AA)(B/AAA) = C_A(A/A)(B/AA)(A/AAB)\\ &= C_A(B/A)(A/AB)(A/AAB) = C_B(A/B)(A/AB)(A/AAB)\end{aligned} \tag{37}$$

$$\begin{aligned}(AABB/6) &= C_A(A/A)(B/AA)(B/AAB) = C_A(B/A)(A/AB)(B/AAB)\\ &= C_A(B/A)(B/AB)(A/ABB) = C_B(A/B)(A/AB)(B/AAB)\\ &= C_B(A/B)(B/AB)(A/ABB) = C_B(B/B)(A/BB)(A/ABB)\end{aligned} \tag{38}$$

$$\begin{aligned}(ABBB/4) &= C_A(B/A)(B/AB)(B/ABB) = C_B(A/B)(B/AB)(B/ABB)\\ &= C_B(B/B)(A/BB)(B/ABB) = C_B(B/A)(B/BB)(A/BBB)\end{aligned} \tag{39}$$

$$(B,\ B,\ B,\ B) = C_B(B/B)(B/BB)(B/BBB) \tag{40}$$

where (i/j), (i/ij) and (i/iji) denote respectively the probabilities of finding i atom on a lattice site when nearest neighbour sites are occupied by one atom (i.e. j-atom), two atoms (i.e. i,j-atoms) and three atoms (i.e. iji-atoms).

By solving Eqs. (31) to (40), we obtain the ratio of the conditional probabilities,

$$\frac{(B/AAA)}{(A/AAA)} = a\sigma^{(Z-3)}\eta^{-3} \tag{41}$$

$$\frac{(B/AAB)}{(A/AAB)} = a\sigma^{(Z-3)}\eta^{-1} \tag{42}$$

$$\frac{(B/ABB)}{(A/ABB)} = a\sigma^{(Z-3)}\eta \tag{43}$$

$$\frac{(B/BBB)}{(A/BBB)} = a\sigma^{(Z-3)}\eta^{3} \tag{44}$$

Now, we recall some simple rules of probabilities i.e.

$$(A/AAA) + (B/AAA) = 1 \tag{45}$$

$$(A/AAB) + (B/AAB) = 1 \tag{46}$$

$$(A/ABB) + (B/ABB) = 1 \tag{47}$$

$$(A/BBB) + (B/BBB) = 1 \tag{48}$$

Therefore, Eqs. (41) to (48) readily yield

$$(A/AAA) = \frac{1}{1 + a\sigma^{(Z-3)}e^{-3\beta W/Z)}} \tag{49}$$

$$(A/AAB) = \frac{1}{1 + a\sigma^{(Z-3)}e^{(-\beta W/Z)}} \tag{50}$$

$$(A/ABB) = \frac{1}{1 + a\sigma^{(Z-3)}e^{(\beta W/z)}} \tag{51}$$

$$(A/BBB) = \frac{1}{1 + a\sigma^{(Z-3)}e^{(3\beta W/Z)}} \tag{52}$$

Similar expressions for (B/AAA), (B/AAB), (B/ABB) and (B/BBB) can also be obtained. The most important input here is the order energy W of the alloy because σ and a are obtainable from it via Eqs. (17) and (27) respectively.

The values of W as determined in previous sections are used in Eqs. (49) to (52) to obtain the conditional probabilities for atomic distributions in the nearest neighbour shell of Bi-Cd, Li-Mg, Cd-Mg, K-Na, Cd-Ga and Cu-Pb liquid alloys. The results are tabulated in Tables 5 to 10. Further, the higher order conditional probabilities, (i/iji), are reduced to lower order is $(i/ij$, the probability of finding i atom on a given site when two other nearest sites are occupied by i and j atoms) or $(i/j$, the probability of finding i atoms as a nearest neighbour of a given j atom) with the help of standard probabilities relations (see Appendix A). These are also tabulated in Tables 5 to 10.

It is interesting to observe that how the higher order conditional probability (i/iji), which is in a way the manifestation of the higher order atomic correlations in liquid binary alloys, is related to lower order functions like (i/ij) and (i/j). For example, $(A/BBB) = 0.6641$ at $C = \frac{1}{2}$ for Cd-Mg ($A \equiv$ Cd) alloys reduces to $(A/BB) = 0.5996$ and finally to $(A/B) = 0.5453$. Similar trend is also observed for Li-Mg and Cd-Bi.

Table 5 Conditional probabilities for atomic distributions in the nearest neighbour shell of Bi-Cd liquid alloys

C_{Cd}	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.1	0.0879	0.0922	0.0967	0.1014	0.0918	0.0962	0.1009	0.1004
0.2	0.1805	0.1884	0.1965	0.2050	0.1869	0.1950	0.2033	0.2016
0.3	0.2772	0.2879	0.2988	0.3099	0.2848	0.2956	0.3065	0.3032
0.4	0.3774	0.3899	0.4024	0.4151	0.3851	0.3974	0.4099	0.4049
0.5	0.4802	0.4934	0.5065	0.5197	0.4870	0.4999	0.5129	0.5063
0.6	0.5848	0.5975	0.6100	0.6225	0.5900	0.6025	0.6148	0.6073
0.7	0.6900	0.7011	0.7120	0.7227	0.6934	0.7044	0.7151	0.7075
0.8	0.7949	0.8034	0.8115	0.8194	0.7966	0.8049	0.8130	0.8065
0.9	0.8985	0.9032	0.9077	0.9120	0.8990	0.9037	0.9081	0.9041

Table 6 Conditional probabilities for atomic distributions in the nearest neighbour shell of Li-Mg liquid alloys

C_{Li}	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.101	0.0546	0.0687	0.0861	0.1073	0.0677	0.0846	0.1051	0.1030
0.238	0.1506	0.1846	0.2241	0.2694	0.1785	0.2156	0.2577	0.2473
0.357	0.2564	0.3056	0.3597	0.4176	0.2913	0.3412	0.3947	0.3747
0.466	0.3708	0.4293	0.4898	0.5506	0.4056	0.4619	0.5191	0.4910
0.541	0.4576	0.5185	0.5788	0.6369	0.4887	0.5459	0.6019	0.5700
0.594	0.5217	0.5820	0.6399	0.6940	0.5489	0.6048	0.6583	0.6249
0.646	0.5860	0.6437	0.6975	0.7464	0.6086	0.6619	0.7116	0.6779
0.670	0.6160	0.6718	0.7232	0.7693	0.6363	0.6879	0.7354	0.7020
0.702	0.6560	0.7088	0.7564	0.7985	0.6732	0.7220	0.7663	0.7338

Table 7 Conditional probabilities for atomic distributions in the nearest neighbour shell of Cd-Mg liquid alloys

C_{Cd}	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.1	0.0309	0.0479	0.0734	0.1110	0.0471	0.0716	0.1070	0.1033
0.2	0.0756	0.1142	0.1688	0.2424	0.1099	0.1600	0.2258	0.2118
0.3	0.1389	0.2027	0.2859	0.3868	0.1905	0.2639	0.3514	0.3231
0.4	0.2251	0.3139	0.4189	0.5318	0.2883	0.3791	0.4778	0.4349
0.5	0.3358	0.4434	0.5565	0.6641	0.4003	0.4999	0.5996	0.5453
0.6	0.4681	0.5810	0.6860	0.7748	0.5221	0.6208	0.7116	0.6524
0.7	0.6131	0.7140	0.7972	0.8610	0.6485	0.7360	0.8094	0.7540
0.8	0.7575	0.8311	0.8857	0.9243	0.7741	0.8399	0.8900	0.8475
0.9	0.8889	0.9265	0.9520	0.9690	0.8930	0.9283	0.9528	0.9300

Table 8 Conditional probabilities for atomic distributions in the nearest neighbour shell of Na-K liquid alloys

C_K	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.1	0.1604	0.1349	0.1130	0.0942	0.1385	0.1155	0.0960	0.0979
0.2	0.2877	0.2480	0.2122	0.1803	0.2582	0.2201	0.1862	0.1927
0.3	0.3947	0.3475	0.3031	0.2620	0.3647	0.3171	0.2733	0.2858
0.4	0.4890	0.4386	0.3895	0.3426	0.4619	0.4096	0.3594	0.3784
0.5	0.5753	0.5252	0.4747	0.4246	0.5529	0.4999	0.4470	0.4720
0.6	0.6573	0.6104	0.5613	0.5110	0.6405	0.5903	0.5380	0.5677
0.7	0.7379	0.6968	0.6524	0.6052	0.7266	0.6828	0.6352	0.6669
0.8	0.8196	0.7877	0.7519	0.7122	0.8137	0.7798	0.7417	0.7711
0.9	0.9057	0.8869	0.8650	0.8395	0.9039	0.8844	0.8615	0.8817

Table 9 Conditional probabilities for atomic distributions in the nearest neighbour shell of Cu-Pb liquid alloys

C_{Cu}	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.1	0.2134	0.1624	0.1217	0.0900	0.1711	0.1269	0.0930	0.0963
0.2	0.3546	0.2820	0.2192	0.1671	0.3040	0.2339	0.1763	0.1871
0.3	0.4605	0.3790	0.3037	0.2377	0.4126	0.3284	0.2545	0.2748
0.4	0.5473	0.4636	0.3818	0.3063	0.5059	0.4158	0.3313	0.3619
0.5	0.6233	0.5418	0.4581	0.3766	0.5899	0.5000	0.4100	0.4506
0.6	0.6939	0.6181	0.5363	0.4526	0.6686	0.5841	0.4940	0.5429
0.7	0.7622	0.6962	0.6209	0.5394	0.7454	0.6715	0.5873	0.6413
0.8	0.8328	0.7807	0.7179	0.6453	0.8236	0.7660	0.6959	0.7484
0.9	0.9098	0.8782	0.8375	0.7865	0.9069	0.8730	0.8288	0.8672

On the other hand, $(A/BBB) = 0.3561$ at $C = \frac{1}{2}$ for Cd-Ga ($A \equiv$ Cd) increases to $(A/BB) = 0.3934$ and to $(A/B) = 0.4403$. The results for Cu-Pb (A = Cu) and K-Na ($A \equiv K$) also indicate that (A/B) is greater than (A/BBB).

4 CHEMICAL SHORT RANGE ORDER PARAMETER

The pairwise conditional probability (A/B) is directly related to the Warren–Cowley[11–12] short range order parameter (α_1) for the first coordination shell,

$$(A/B) = C_A(1 - \alpha_1) \tag{53}$$

Bhatia and Singh[1] showed that the boundaries values of α_1 lie in the range

$$\begin{aligned} -\frac{C_A}{C_B} \leq \alpha_1 \leq 1, &\qquad C_A \leq \frac{1}{2} \\ -\frac{C_B}{C_A} \leq \alpha_1 \leq 1, &\qquad C_A \geq \frac{1}{2}. \end{aligned} \tag{54}$$

Table 10 Conditional probabilities for atomic distributions in the nearest neighbour shell of Cd-Ga liquid alloys

C_{Cd}	(A/AAA)	(A/AAB)	(A/ABB)	(A/BBB)	(A/AA)	(A/AB)	(A/BB)	(A/B)
0.1	0.2403	0.1757	0.1256	0.0882	0.1878	0.1322	0.0916	0.0955
0.2	0.3858	0.2974	0.2219	0.1612	0.3263	0.2401	0.1717	0.1843
0.3	0.4898	0.3928	0.3036	0.2271	0.4350	0.3333	0.2459	0.2695
0.4	0.5726	0.4744	0.3782	0.2907	0.5261	0.4185	0.3186	0.3540
0.5	0.6438	0.5491	0.4508	0.3561	0.6065	0.5000	0.3934	0.4403
0.6	0.7092	0.6217	0.5255	0.4273	0.6813	0.5814	0.4739	0.5310
0.7	0.7728	0.6963	0.6071	0.5101	0.7540	0.6666	0.5649	0.6288
0.8	0.8387	0.7780	0.7025	0.6141	0.8283	0.7598	0.6736	0.7372
0.9	0.9117	0.8743	0.8242	0.7597	0.9083	0.8677	0.8121	0.8599

For equiatomic concentration, $C_A = \frac{1}{2}$, α_1 attains its lower and upper limit values, i.e.

$$-1 \leq \alpha_1 \leq 1 \tag{55}$$

The lower limit i.e. $\alpha_1^{\min} = -1$, means total order as A–B pairs of atoms as nearest neighbour, whereas $\alpha_1^{\max} = 1$ suggests segregation leading to the formation of A-rich phase and B-rich phase in the binary alloy.

The values of (A/B) as appeared in Tables 5 to 10 are used in Eq. (53) to compute α_1 for Bi-Cd, Li-Mg, Cd-Mg, K-Na, Cd-Ga and Cu-Pb as a function of concentration. These are given in Tables 11 to 12, and are compared with those obtained from two-atoms cluster model[3] (TACM). The later values are obtained by using an analytical expression (42) by Singh and Mishra[3]

$$\frac{\alpha_1}{(1-\alpha_1)^2} = C_A C_B(\exp(2W/ZK_BT) - 1), \tag{56}$$

W for TACM and Z are given in Table 2.

α_1 for Bi-Cd, Li-Mg and Cd-Mg are negative at all concentrations which imply heterocoordination in the liquid phase i.e. unlike atoms are preferred as nearest neighbour in the first coordination shell. There is little difference in the values of α_1 computed with four atoms cluster model (FACM) and two atoms cluster model (TACM). Among the systems considered Cd-Mg is most heterocoordinated liquid alloys followed by Li-Mg and Cd-Bi. It is interesting to correlate the short range order in liquid alloys with the measurable thermodynamic functions like activity and the liquidus lines. For example, the activity ration, a $(=a_B/a_A)$ for $C_A < C_B$, follows the same sequence being maximum for Cd-Mg followed by Li-Mg and Cd-Bi. We also recall (see Figure 1) that the liquidus line of Cd-Mg is a simple monotonous line, rising from Cd to Mg end and similarly for Li-Mg with a slight bump towards

Table 11 Chemical Short Range Order Parameter (α_1) for Cd-Mg, Li-Mg and Cd-Bi liquid alloys for the first coordination shell

C_{Cd}	α_1 (Cd-Mg) 923 K		C_{Li}	α_1 (Li-Mg) 887 K		C_{Cd}	α_1 (Bi-Cd) 773 K	
	FACM	TACM		FACM	TACM		FACM	TACM
0.1	−0.0334	−0.0361	0.101	−0.0198	−0.0170	0.1	−0.0046	−0.0039
0.2	−0.0594	−0.0683	0.238	−0.0393	−0.0352	0.2	−0.0081	−0.0070
0.3	−0.0772	−0.0941	0.357	−0.0496	−0.0455	0.3	−0.0107	−0.0093
0.4	−0.0873	−0.1108	0.466	−0.0537	−0.0497	0.4	−0.0122	−0.0106
0.5	−0.0906	−0.1167	0.541	−0.0536	−0.0496	0.5	−0.0127	−0.0111
0.6	−0.0873	−0.1108	0.594	−0.0521	−0.0480	0.6	−0.0122	−0.0106
0.7	−0.0772	−0.0941	0.646	−0.0494	−0.0453	0.7	−0.0107	−0.0093
0.8	−0.0594	−0.0683	0.670	−0.0478	−0.0437	0.8	−0.0081	−0.0070
0.9	−0.0334	−0.0361	0.702	−0.0453	−0.0411	0.9	−0.0046	−0.0039

FACM = Four atoms cluster model; TACM = Two atoms cluster model.

Table 12 Chemical Short Range Order Parameter (α_1) for Cd-Ga, Cu-Pb and Na-K liquid alloys for the first coordination shell

C_{Cd}	α_1 *(Cd-Mg) 700 K*		C_{Cu}	α_1 *(Cu-Pb) 1473 K*		C_K	α_1 *(Na-K) 384 K*	
	FACM	*TACM*		*FACM*	*TACM*		*FACM*	*TACM*
0.1	0.0444	0.0379	0.1	0.0364	0.0363	0.1	0.0202	0.0191
0.2	0.0784	0.0638	0.2	0.0644	0.0612	0.2	0.0360	0.0330
0.3	0.1016	0.0808	0.3	0.0838	0.0776	0.3	0.0471	0.0440
0.4	0.1149	0.0904	0.4	0.0950	0.0869	0.4	0.0537	0.0500
0.5	0.1193	0.0935	0.5	0.0987	0.0899	0.5	0.0559	0.0520
0.6	0.1149	0.0904	0.6	0.0950	0.0869	0.6	0.0537	0.0500
0.7	0.1016	0.0808	0.7	0.0838	0.0776	0.7	0.0471	0.0437
0.8	0.0784	0.0638	0.8	0.0644	0.0612	0.8	0.0360	0.0330
0.9	0.0444	0.0379	0.9	0.0364	0.0363	0.9	0.0203	0.0191

FACM = Four atoms cluster model; TACM = Two atoms cluster model.

Mg end. Cd-Bi has a shallow eutectic, and thereby indicate only small value for α_1 i.e. closest to ideal behaviour. The limiting value for the total heterocoordination is -1 and for ideal behaviour it is zero. Boos and Steeb[13] 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 $\alpha_1 \approx -0.11$, which is in good agreement with the experimental observation. There is another data from the neutron diffraction experiments[14] for Li_{70} M_{30} which is, $\alpha_1 = -0.035$, in good agreement with our computed values of $\alpha_1 = -0.045$.

The chemical short range order parameters for Cd-Ga, Cu-Pb and K-Na are positive at all concentrations which suggest that these are self coordinated systems i.e. like atoms tend to pair as nearest neighbour. Cd-Ga exhibits maximum self coordination followed by Cu-Pb and K-Na. Likewise earlier, the activity ratio, *a*, for self coordinated systems is also found to be intimately related to the nature of atomic order in liquid alloys. The activity ratio is minimum in Cd-Ga for maximum self coordination and then it follows the sequence of Cu-Pb and K-Na. Cd-Ga and Cu-Pb alloys possess monotectic liquidus lines and there is a possibility of the existence of miscibility gap in the liquid phase. Recently Singh and Sommer[15] have proposed a simple model to explain the behaviour of demixing liquid alloys where the existence of polyatomic self associates (cluster of like atoms) has been considered. It will be of interest to use such concepts to investigate the nature of self associates in these systems.

It is, generally, believed that the size factor, which is the ratio of the atomic volumes of the constituent atoms, is responsible for dictating the demixing characteristic of liquid alloys. In these systems the size factor is maximum in Cu-Pb (2.5) followed by K-Na (1.9) and Cd-Ga (1.2). But the values of α_1 are not inconsistent with the size factors. Though the size factor is minimum in Cd-Ga, but α_1 is large in comparison to Cu-Pb and K-Na. This suggests that the energetics of atomic distributions in liquid alloys, which enter into our formalism through the order energy, is not solely controlled by the size factor.

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APPENDIX A

The laws of probabilities allow us to express the conditional probabilities, as

$$(A/AA) = (A/AA)(A/AAA) + (B/AA)(A/AAB) \tag{A.1}$$

Also we have

$$(A/AA) + (B/AA) = 1 \tag{A.2}$$

The above two relations yield

$$(A/AAB) = (A/AA)\,[1 - (A/AAA) + (A/AAB)] \tag{A.3}$$

By using Eq. (45) in Eq. (A.3), we have

$$(A/AA) = \frac{(A/AAB)}{(B/AAA)+(A/AAB)}. \tag{A.4}$$

Likewise Eq. (A.1), we again write

$$(A/AB) = (A/AB)\,(A/AAB) + (B/AB)\,(A/ABB) \tag{A.5}$$

and also,

$$(A/AB) + (B/AB) = 1 \tag{A.6}$$

Therefore,

$$(A/ABB) = (A/AB)\,[1 - (A/AAB) + (A/ABB)] \tag{A.7}$$

This in conjunction with Eq. (46) provides

$$(A/AB) = \frac{(A/ABB)}{(B/AAB) + (A/ABB)} \tag{A.8}$$

Similar to Eqs. (A.1) and (A.5), one now writes

$$(A/BB) = (A/BB)\,(A/BBA) + (B/BB)\,(A/BBB) \tag{A.9}$$

and,

$$(A/BB) + (B/BB) = 1 \tag{A.10}$$

The above two equations give

$$(A/BBB) = (A/BB)\,[1 - (A/BBA) + (A/BBB)] \tag{A.11}$$

By substituting Eq. (47) in Eq. (A.11), we get

$$(A/BB) = \frac{(A/BBB)}{(B/ABB) + (A/BBB)}. \tag{A.12}$$

Finally we write

$$(A/B) = (A/B)\,(A/BA) + (B/B)\,(A/BB) \tag{A.13}$$

and,

$$(A/B) + (B/B) = 1 \tag{A.14}$$

Equations (A.13), (A.14) and (A.6) yield

$$(A/B) = \frac{(A/BB)}{(B/AB) + (A/BB)} \tag{A.15}$$