Chapter 2

Analytical solutions for correlation functions of ordered phases

2.1 Introduction

The correlation functions (CFs) take different values for the same thermodynamic state of the system based on the basis used. However, the probability of occurrence of a specific atomic configuration on the selected cluster called cluster variable (CV) and the thermodynamic properties such as enthalpy, entropy, *etc.* remain invariant irrespective of the basis chosen. Sluiter and Kawazoe (2005) have shown that for a linear transformation of basis, the energy of the system remains invariant. Some of the bases used in literature are orthogonal basis, variable basis, mixed basis, tensorial basis (van de Walle, 2008), solvent basis, *etc.* Of these bases, orthogonal basis is widely used and variable basis is gaining greater attention in the recent times.

Sanchez *et al.* (1984) have provided general guidelines for selection of values in orthogonal basis for multi-component systems. In orthogonal basis, the CFs form an independent set of configurational variables. The variable basis is also introduced by Sanchez (2010). In this basis, the energy of formation of an alloy gets separated into two components: the energy of formation of random alloy as a function of composition and the ordering energy. The cluster expansion coefficients are composition dependent and the series converges faster in this basis. The mixed basis introduced by Laks *et al.* (1992) uses reciprocal method to obtain the CECs of the system. Due to the conditions used in this method, the pair interactions that are not necessary are set equal to '0'

and short ranged pairs are chosen in preference to long ranged ones. This method is able to predict the short range as well as the long range superlattices. Sarma *et al.* (2012) have used solvent basis for the disordered solid solution phases in which the CVs that are exclusively occupied by solute atoms become the CFs. Further, they expressed each CF as a product of random value of the corresponding CV and its departure from its random value. Such a transformation has resulted in factoring of the random values from the CVs and cancellation of terms corresponding to point CFs in the excess Gibbs energy expressions. These simplified equilibrium equations do not underflow even for compositions in the solvent rich ends.

In this Chapter, a new set of bases referred to as the sublattice solvent bases is introduced. Using these bases, the methodology followed to obtain the values of the CFs and their derivatives with respect to the point CF (u_0) and the long range order parameter (ξ) is discussed. Further, this methodology is demonstrated to obtain the limiting CFs and their derivatives in the sublattice solvent bases as well as in the orthogonal basis for the $B2$ and $L1_0$ phases at the corresponding stoichiometric compositions.

The details of the limiting values and derivatives of CFs in the orthogonal basis are provided in Appendix A for the BCC based ordered phases $B32$ and $D0_3$ using T approximation, FCC based ordered $L1_2$ phase using T and TO approximations, $L1_0$ and $L1_1$ phases using TO approximation, CPH based $B19$ and $D0_{19}$ phases using triangle-tetrahedron (TT) and TO approximations.

2.2 CE–CVM formulation for an ordered phase having two sublattices

Consider a crystalline system exhibiting long range chemical order having N atomic sites corresponding to two sublattices, say α and β. In a binary system, the α and β sublattice sites are occupied preferentially by, say atoms of components A and B respectively. The configuration of the system at the atomic level can be described using a site occupation operator (Inden, 2005) for each of the sites i on the sublattice

λ defined as

$$p^{\lambda}_{\mathrm{X},i} = \begin{cases} 1 & \text{if atom X (= A or B) is present onthe site } i \text{ of} \\ & \qquad \text{the sublattice } \lambda \left(= \alpha \text{ or } \beta\right) \\ 0 & \text{otherwise} \end{cases} \tag{2.1}$$

In the absence of vacancies, every site is occupied by one of the atoms of the chosen system. Hence, for the site i on the sublattice λ, it follows that

$$1 = p^{\lambda}_{\mathrm{A},i} + p^{\lambda}_{\mathrm{B},i} \tag{2.2}$$

Another operator, called site operator (σ^{λ}_{i}), is defined as

$$\sigma^{\lambda}_{i} = \tau^{\lambda}_{\mathrm{A}}\, p^{\lambda}_{\mathrm{A},i} + \tau^{\lambda}_{\mathrm{B}}\, p^{\lambda}_{\mathrm{B},i} \tag{2.3}$$

where $\tau^{\lambda}_{\mathrm{A}}$ and $\tau^{\lambda}_{\mathrm{B}}$ take different numerical values, which serve as labels for A and B atoms respectively. This set of values is known as the basis.

These equations can be expressed in matrix form as follows.

$$\begin{bmatrix} 1 \\ \sigma^{\lambda}_{i} \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ \tau^{\lambda}_{\mathrm{A}} & \tau^{\lambda}_{\mathrm{B}} \end{bmatrix} \begin{bmatrix} p^{\lambda}_{\mathrm{A},i} \\ p^{\lambda}_{\mathrm{B},i} \end{bmatrix} \tag{2.4}$$

The rows of the square matrix on the right hand side are orthogonal if

$$1 \cdot \tau^{\lambda}_{\mathrm{A}} + 1 \cdot \tau^{\lambda}_{\mathrm{B}} = 0 \quad \text{or} \quad \tau^{\lambda}_{\mathrm{B}} = -\tau^{\lambda}_{\mathrm{A}} \tag{2.5}$$

The columns of the above square matrix are orthogonal if

$$1 \cdot 1 + \tau^{\lambda}_{\mathrm{A}} \cdot \tau^{\lambda}_{\mathrm{B}} = 0 \quad \text{or} \quad \left(\tau^{\lambda}_{\mathrm{A}}\right)^{2} = 1 \tag{2.6}$$

Thus, the square matrix is orthogonal only if

$$\tau^{\lambda}_{\mathrm{A}} = \pm 1, \tau^{\lambda}_{\mathrm{B}} = \mp 1 \tag{2.7}$$

This leads to the commonly used orthogonal basis $\{\tau^{\lambda}_{\mathrm{A}}, \tau^{\lambda}_{\mathrm{B}}\} = \{\pm 1, \mp 1\}$. As shown by Sanchez *et al.* (1984), the orthogonal basis is complete. It follows that any other basis for which the basis matrix is non-singular is also complete. Any other choice of basis such as $\{\tau^{\lambda}_{\mathrm{A}}, \tau^{\lambda}_{\mathrm{B}}\} = \{0, 1\}$ or $\{1, 0\}$, is not orthogonal. For the case of disordered structures, these bases are referred to as solvent bases. For ordered phases such bases are defined specific to each sublattice, and are accordingly referred

to as sublattice–solvent bases by Gorrey *et al.* (2020). Zhang and Sluiter (2016) have discussed the completeness of a basis which is essentially equivalent to the solvent basis utilized here.

Using Eqs. (2.2) and (2.3), we get

$$p^{\lambda}_{\mathrm{A},i} = \frac{\tau^{\lambda}_{\mathrm{B}} - \sigma^{\lambda}_{i}}{\tau^{\lambda}_{\mathrm{B}} - \tau^{\lambda}_{\mathrm{A}}} \quad \text{and} \quad p^{\lambda}_{\mathrm{B},i} = \frac{-\tau^{\lambda}_{\mathrm{A}} + \sigma^{\lambda}_{i}}{\tau^{\lambda}_{\mathrm{B}} - \tau^{\lambda}_{\mathrm{A}}} \tag{2.8}$$

For the choice of $\tau^{\lambda}_{\mathrm{A}} = -1$ and $\tau^{\lambda}_{\mathrm{B}} = 1$ the site occupation operators become

$$p^{\lambda}_{\mathrm{A},i} = \frac{1 - \sigma^{\lambda}_{i}}{2} \quad \text{and} \quad p^{\lambda}_{\mathrm{B},i} = \frac{1 + \sigma^{\lambda}_{i}}{2} \tag{2.9}$$

CE–CVM is formulated in terms of a basic cluster or set of clusters of atomic sites. A specific occupation of these sites by A or B atoms constitutes a cluster configuration. Each symmetry-wise distinct cluster in the disordered cluster is identified with a serial number i. On ordering, there is a loss of symmetry and as a result each cluster of type i may give rise to several symmetry-wise distinct clusters designated as $i.j$. The probability of occurrence of a specific configuration of atoms on a cluster in the structure can be expressed as the average of the product of the appropriate site occupation operators in the structure (Inden, 2005). This averaged product is referred to as cluster variable (CV), denoted by $y^{i.j}_{\mathrm{X}}$ for configuration X of cluster type $i.j$. The point CVs are identical to the mole fractions on that sublattice as shown below. Using Eq. (2.9), the mole fractions can be expressed as

$$\begin{aligned}
x^{\alpha}_{\mathrm{A}} &= \langle p^{\alpha}_{\mathrm{A},i} \rangle = \langle (1 - \sigma^{\alpha}_{i})/2 \rangle = (1 - u_{0.1})/2 \\
x^{\alpha}_{\mathrm{B}} &= \langle p^{\alpha}_{\mathrm{B},i} \rangle = \langle (1 + \sigma^{\alpha}_{i})/2 \rangle = (1 + u_{0.1})/2 \\
x^{\beta}_{\mathrm{A}} &= \langle p^{\beta}_{\mathrm{A},i} \rangle = \langle (1 - \sigma^{\beta}_{i})/2 \rangle = (1 - u_{0.2})/2 \\
x^{\beta}_{\mathrm{B}} &= \langle p^{\beta}_{\mathrm{B},i} \rangle = \langle (1 + \sigma^{\beta}_{i})/2 \rangle = (1 + u_{0.2})/2
\end{aligned} \tag{2.10}$$

where we have introduced the point CFs, $\langle \sigma^{\alpha}_{i} \rangle = u_{0.1}$ and $\langle \sigma^{\beta}_{i} \rangle = u_{0.2}$. Accordingly, the point CFs can be expressed as

$$\begin{aligned}
u_{0.1} &= 1 - 2x^{\alpha}_{\mathrm{A}} = 2x^{\alpha}_{\mathrm{B}} - 1 \\
u_{0.2} &= 1 - 2x^{\beta}_{\mathrm{A}} = 2x^{\beta}_{\mathrm{B}} - 1
\end{aligned} \tag{2.11}$$

In a similar manner, CVs corresponding to larger clusters can be expressed as linear functions of the CFs ($u_{i.j}$), which are defined as the averages of the products of site

operators corresponding to symmetry-wise distinct clusters of the type $i.j$ (Inden, 2005).

The point CFs corresponding to the two sublattices of the ordered phase are related to point CF of its disordered counterpart (u_0) through

$$u_0 = \frac{m_{0.1}u_{0.1} + m_{0.2}u_{0.2}}{m_0} = m_{0.1}u_{0.1} + m_{0.2}u_{0.2} \tag{2.12}$$

The multiplicities of the ordered clusters are denoted as $m_{i.j}$ and are equal to the number of such clusters present in the structure per atomic site. Here, $m_{0.1}$ and $m_{0.2}$ are the multiplicities of the point clusters on α and β sublattice sites, which are also equal to the respective site fractions with m_0 being unity.

The Bragg-Williams long range order parameter ξ can be defined as

$$\xi = x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha} = \left(u_{0.2} - u_{0.1}\right)/2 \tag{2.13}$$

Using cluster expansion (Inden, 2005; Sanchez *et al.*, 1984), the configurational energy of the system is expressed as a trilinear sum of the products of all the $u_{i.j}$, their respective energy coefficients e_i and the $m_{i.j}$, *i.e.*,

$$U = \sum_{i.j} e_i m_{i.j} u_{i.j} \tag{2.14}$$

The e_i in the above summation are taken to be identical for the disordered as well as the ordered structures. The configurational energy of mixing is written as

$$U^{mix} = U - \left(1 - x_{\mathrm{B}}\right) U_{\mathrm{A}} - x_{\mathrm{B}} U_{\mathrm{B}} \tag{2.15}$$

where U_{A} and U_{B} are the energies of pure A and pure B.

The CVM configurational entropy of mixing is written in terms of the Boltzmann entropy summations of the subclusters ($S_{i.j}$) using the K-B overlap correction coefficients ($\gamma_{i.j}$) such that each symmetry-wise distinct cluster is counted only once (Inden, 2005; Kikuchi, 1951), as in the following.

$$S^{mix} = \sum_{i.j} m_{i.j} \gamma_{i.j} S_{i.j} \tag{2.16}$$

Here the $S_{i.j}$ can be written in terms of Boltzmann entropy summation of all the CVs pertaining to that cluster. As an example, for the first neighbour pair $\alpha\beta$ cluster,

$$S_{i.j} = -\mathrm{R}\left(y_{\mathrm{AA}}^{i.j} \ln y_{\mathrm{AA}}^{i.j} + y_{\mathrm{AB}}^{i.j} \ln y_{\mathrm{AB}}^{i.j} + y_{\mathrm{BA}}^{i.j} \ln y_{\mathrm{BA}}^{i.j} + y_{\mathrm{BB}}^{i.j} \ln y_{\mathrm{BB}}^{i.j}\right) \tag{2.17}$$

The configurational Helmholtz energy of mixing is thus written as

$$A^{mix} = U^{mix} - TS^{mix} \tag{2.18}$$

For a given set of CECs, the equilibrium values of CFs corresponding to a thermodynamic state defined by x_{B} and T, are given by

$$\left(\frac{\partial A^{mix}}{\partial \xi}\right)_{u_{i.j}} = 0 \qquad \text{and} \qquad \left(\frac{\partial A^{mix}}{\partial u_{i.j}}\right)_{u_{k.l,k.l\neq i.j},\xi} = 0 \tag{2.19}$$

It is convenient to introduce a set of dimensionless parameters η_i as in the following,

$$\eta_i = \exp\left(\frac{-2^{r_i}\, e_i}{\mathrm{R}T}\right) \tag{2.20}$$

in which, r_i is the number of sites in the ith cluster. The limiting values of the CFs in the limit of perfect ordering and other results are discussed in terms of these dimensionless parameters. For the ordering system, for which $e_i > 0$, the value of η_i varies smoothly from 0 to 1 as T varies from 0 to ∞. However for the phase separating system, $e_i < 0$, and accordingly η_i varies from 1 to ∞ as T varies from 0 to ∞. This is depicted in Figure 4.1.

2.3 Correlation functions in sublattice solvent bases

Sarma *et al.* (2012) have considered non-orthogonal basis with $\tau_{\mathrm{A}} = 0$ and $\tau_{\mathrm{B}} = 1$ for obtaining the values of the CFs and their derivatives with respect to composition in the limit of infinite dilution of B atoms in solvent of A atoms for disordered structures. For this choice, the CVs for configurations in which all the sites are occupied by the solute atoms, *i.e.*, B atoms, become identical to the CFs in the new basis. This choice of basis is referred to as A-solvent basis.

In the present Chapter, a separate solvent basis is chosen for each sublattice with $\tau_{\mathrm{A}}^{\alpha} = 0$ and $\tau_{\mathrm{B}}^{\alpha} = 1$ for the α sublattice and $\tau_{\mathrm{A}}^{\beta} = 1$ and $\tau_{\mathrm{B}}^{\beta} = 0$ for the β sublattice, as the α sublattice is preferentially occupied by A atoms and β sublattice by B atoms. For this choice, the CVs for configurations in which all α sublattice sites are occupied by B atoms and all β sublattice sites occupied by A atoms become identical to the corresponding CF. These bases are referred to as the sublattice-solvent bases. Each of the CVs for which the cluster configurations exclusively contain wrong occupancies

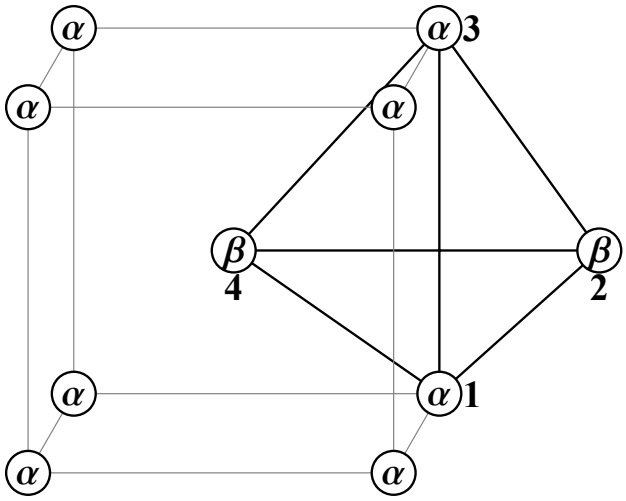

Figure 2.1: The irregular tetrahedron basic cluster [1-2-3-4] in the $B2$ phase along with the sublattice sites designated α and β.

(which are identical to the corresponding CFs) in the sublattice solvent bases can be expressed as product of its random value and a new variable ($v_{i.j}$) denoting its departure from the random value.

$$y^{i.j}_{\mathrm{B}p\mathrm{A}q} = \left(x^{\alpha}_{\mathrm{B}}\right)^{p} \left(x^{\beta}_{\mathrm{A}}\right)^{q} v_{i.j} \tag{2.21}$$

where p and q are the number of α and β sites respectively in the $i.j$th cluster. This transformation of CFs leads to a considerable simplification of the equilibrium equations analogous to those given in Eq. (2.19). These new variables $v_{i.j}$ can be referred to as transformed CFs which take the value of unity corresponding to random occupation of the sites in each of the sublattices. The CFs in the orthogonal basis can be expressed in terms of those in the sublattice solvent bases by using equations such as Eq. (2.11). The values of the CFs and their derivatives with respect to u_0 and ξ at the stoichiometric composition in the limit of perfect ordering are calculated using these bases. Subsequently, these values are used to calculate the CFs and their derivatives in the orthogonal basis. The procedure is demonstrated using T approximation for $B2$ and $L1_0$ phases respectively in the next two Sections.

2.4 Analytical solutions for the CFs of $B2$ phase

The irregular tetrahedron cluster in $B2$ phase is shown in Figure 2.1. The details of the distinct clusters in the $B2$ ordered phase, their designations, $m_{i.j}$ and $\gamma_{i.j}$ (Inden, 2005) are given in Table 2.1.

Table 2.1: Details of the clusters, their designations ($i.j$), multiplicities ($m_{i.j}$), number of sub-clusters $k.l$ present in each cluster $i.j$ ($n_{i.j}^{k.l}$) and K-B coefficients ($\gamma_{i.j}$) for the $B2$ structure using T approximation.

Clusters	Ordered $B2$ cluster	$i.j$	$m_{i.j}$	$n_{i.j}^{4.1}$	$n_{i.j}^{3.2}$	$n_{i.j}^{3.1}$	$n_{i.j}^{2.2}$	$n_{i.j}^{2.1}$	$n_{i.j}^{1.1}$	$n_{i.j}^{0.2}$	$n_{i.j}^{0.1}$	$\gamma_{i.j}$
Irregular tetrahedron	$\alpha\alpha\beta\beta$ (1,3,2,4)	4.1	6	1	2	2	1	1	4	2	2	1
Isosceles triangle	$\alpha\beta\beta$ (1,2,4)	3.2	6	0	1	0	1	0	2	2	1	-1
	$\alpha\alpha\beta$ (1,3,2)	3.1	6	0	0	1	0	1	2	1	2	
II-n pair	$\beta\beta$ (2,4)	2.2	3/2	0	0	0	1	0	0	2	0	1
	$\alpha\alpha$ (1,3)	2.1	3/2	0	0	0	0	1	0	0	2	
I-n pair	$\alpha\beta$ (1,2)	1.1	4	0	0	0	0	0	1	1	1	1
Point	β (2)	0.2	1/2	0	0	0	0	0	0	1	0	-1
	α (1)	0.1	1/2	0	0	0	0	0	0	0	1	

The point CFs corresponding to the two sublattices in the $B2$ phase are related to point CF (u_0) of the disordered $A2$ phase through

$$u_0 = \left(u_{0.1} + u_{0.2}\right)/2 \tag{2.22}$$

Recall the definion of ξ given in Eq. (2.13) as

$$\xi = x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha} = \left(u_{0.2} - u_{0.1}\right)/2$$

For the limiting case of perfect order in stoichiometric $B2$ phase, $u_{0.1} = \mp 1$ and $u_{0.2} = \pm 1$, corresponding to $u_0 = 0$ and $\xi = \pm 1$.

The configurational energy, entropy and Helmholtz energy of mixing can be obtained by substituting from Table 2.1 for $m_{i.j}$ and $\gamma_{i.j}$ in Eqs. (2.15), (2.16) and

(2.18) respectively. The CFs in the orthogonal basis can be expressed in terms of those in the sublattice solvent bases after transformation as given in Eq. (2.21), by using equations such as Eq. (2.11). Thus, we obtain

$$
\begin{aligned}
u_{1.1} &= -1 + 2x_{\mathrm{B}}^{\alpha} + 2x_{\mathrm{A}}^{\beta} - 4x_{\mathrm{A}}^{\beta}x_{\mathrm{B}}^{\alpha}v_{1.1} \\
u_{2.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{2.1} \\
u_{2.2} &= 1 - 4x_{\mathrm{A}}^{\beta} + 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{2.2} \\
u_{3.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} - 2x_{\mathrm{A}}^{\beta} + 8x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta}v_{1.1} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{2.1} - 8\left(x_{\mathrm{B}}^{\alpha}\right)^2 x_{\mathrm{A}}^{\beta}v_{3.1} \\
u_{3.2} &= -1 + 2x_{\mathrm{B}}^{\alpha} + 4x_{\mathrm{A}}^{\beta} - 8x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta}v_{1.1} - 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{2.2} + 8x_{\mathrm{B}}^{\alpha}\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{3.2} \\
u_{4.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} - 4x_{\mathrm{A}}^{\beta} + 16x_{\mathrm{A}}^{\beta}x_{\mathrm{B}}^{\alpha}v_{1.1} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{2.1} + 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{2.2} \\
&\quad - 16\left(x_{\mathrm{B}}^{\alpha}\right)^2 x_{\mathrm{A}}^{\beta}v_{3.1} - 16x_{\mathrm{B}}^{\alpha}\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{3.2} + 16\left(x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta}\right)^2 v_{4.1}
\end{aligned}
\tag{2.23}
$$

Using these relations, one can write the configurational energy of mixing as well as the configurational entropy of mixing in terms of $v_{i.j}$. A dimensionless ratio $K = x_{\mathrm{A}}^{\beta}/x_{\mathrm{B}}^{\alpha}$ is introduced such that K remains finite and non-vanishing, even in the limit $x_{\mathrm{B}}^{\alpha} \to 0$ and $x_{\mathrm{A}}^{\beta} \to 0$ and is used to eliminate x_{A}^{β} from the Helmholtz energy function. The configuration space of (u_0, ξ) and $(u_{0.1}, u_{0.2})$ is given in Figure 2.2 showing the locus of points corresponding to a particular value of K. The equilibrium equations in terms of the new variables $v_{i.j}$ become

$$
\left(\frac{\partial A^{mix}}{\partial \xi}\right)_{v_{i.j}} = 0 \qquad \text{and} \qquad \left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l,k.l\neq i.j},\xi} = 0 \tag{2.24}
$$

Further simplification of equilibrium equations such as those in Eq. (2.24) occurs due to factorization and subsequent cancellation of terms such as $K^q\left(x_{\mathrm{B}}^{\alpha}\right)^{p+q}$. This facilitates evaluation of CFs in the limit of perfect ordering at stoichiometric composition. In the case of ordered structures, usually ξ is treated as an independent variable in addition to u_0 for computing the variation of other microscopic variables, $v_{i.j}$ by solving the equilibrium equations for chosen values of u_0 and ξ.

At the stoichiometric composition for the state of perfect order, u_0=0 and ξ=1, *i.e.*, x_{B}^{α}=0 and x_{A}^{β}=0, the equilibrium equations become independent of K which can be solved directly for $v_{i.j}$. The values of the transformed CFs in this limit are denoted by $v_{i.j}^0$ and are given by

$$
v_{1.1}^0 = \frac{\eta_4^{3/2}}{\eta_1}; \qquad v_{2.1}^0 = \eta_1\eta_3^2\eta_4; \qquad v_{2.2}^0 = \frac{\eta_2\eta_4}{\eta_3^2}
$$

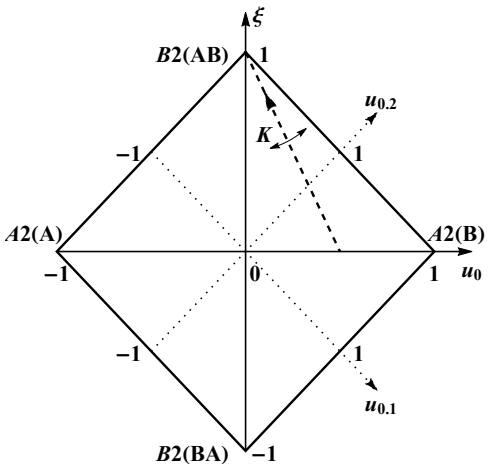

Figure 2.2: The configuration space of (u_0, ξ) and $(u_{0.1}, u_{0.2})$ for $B2$ phase. The ground states of the system correspond to the vertices of the configuration square. The dashed arrow represents a particular value of $K = x_{\mathrm{A}}^{\beta}/x_{\mathrm{A}}^{\beta}$. Variation of K corresponds to rotation of the dashed arrow.

$$v_{3.1}^0 = \frac{\eta_2\eta_3\eta_4^3}{\eta_2^2} \qquad v_{3.2}^0 = \frac{\eta_2\eta_4^3}{\eta_1^2\eta_3}; \qquad v_{4.1}^0 = \frac{\eta_2^2\eta_4^5}{\eta_1^4} \tag{2.25}$$

The first order variation of $v_{i.j}$ with respect to u_0 in the limit of perfect ordering at stoichiometric composition can be found by considering the equilibrium equations (for all values of $i.j$), corresponding to infinitesimally small changes in u_0, as follows.

$$\left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l}, k.l\neq i.j, \xi}\Bigg|_{u_0+\delta u_0} = 0 \tag{2.26}$$

By considering Taylor series expansion around u_0, Eq. (2.26) becomes

$$\left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l}, k.l\neq i.j, \xi} + \frac{d}{du_0}\left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l}, k.l\neq i.j, \xi} \delta u_0 = 0 \tag{2.27}$$

The first term in Eq. (2.27) vanishes at equilibrium. Note that the second term involves a total derivative with respect to u_0, the explicit and implicit variations of which can be expressed as

$$\begin{aligned}&\left(\frac{\partial}{\partial u_0}\left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l}, k.l\neq i.j, \xi, u_0}\right)_{v_{i.j}, \xi} \\ &\quad + \sum_{m.n}\left(\frac{\partial}{\partial v_{m.n}}\left(\frac{\partial A^{mix}}{\partial v_{i.j}}\right)_{v_{k.l}, k.l\neq i.j, \xi, u_0}\right)_{v_{i.j}, i.j\neq m.n, \xi, u_0} \frac{dv_{m.n}}{du_0} = 0\end{aligned} \tag{2.28}$$

Using standard abbreviated notation for partial derivatives, this equations can be expressed as follows.

$$A_{(i.j)0}^{mix} + A_{(i.j)(m.n)0}^{mix} v_{(m.n)0} = 0 \tag{2.29}$$

Here the subscripts $i.j$ and 0 stand for partial derivative with respect to $v_{i.j}$ and u_0 respectively. The derivatives of the energy expression with respect to the CFs can be evaluated directly at $u_0 = 0$ and $\xi = 1$ using the equilibrium CFs, given in Eq. (2.25) and the limiting derivatives of the transformed CFs with respect to u_0, represented as $v^0_{(i.j)0}$ are obtained as given below.

$$
\begin{aligned}
v^0_{(1.1)0} &= -\frac{3}{2}v^0_{1.1}\left(v^0_{2.1} - v^0_{2.2}\right) + \frac{3}{2}\left(v^0_{3.1} - v^0_{3.2}\right) \\
v^0_{(2.1)0} &= v^0_{2.1}\left(-1 + 4v^0_{1.1} - v^0_{2.1}\right) - 2v^0_{3.1} \\
v^0_{(2.2)0} &= v^0_{2.2}\left(1 - 4v^0_{1.1} + v^0_{2.2}\right) + 2v^0_{3.2} \\
v^0_{(3.1)0} &= v^0_{3.1}\left(-\frac{1}{2} + 2v^0_{1.1} - 3v^0_{2.1} + 2v^0_{2.2} + \frac{2v^0_{3.1} - v^0_{3.2}}{v^0_{1.1}} - \frac{v^0_{3.1}}{2v^0_{2.1}}\right) - v^0_{4.1} \\
v^0_{(3.2)0} &= v^0_{3.2}\left(\frac{1}{2} - 2v^0_{1.1} - 2v^0_{2.1} + 3v^0_{2.2} + \frac{v^0_{3.1} - 2v^0_{3.2}}{v^0_{1.1}} + \frac{v^0_{3.2}}{2v^0_{2.2}}\right) + v^0_{4.1} \\
v^0_{(4.1)0} &= v^0_{4.1}\left(-4v^0_{2.1} + 4v^0_{2.2} + 2\frac{v^0_{3.1} - v^0_{3.2}}{v^0_{1.1}} - \frac{v^0_{4.1}}{v^0_{3.1}} + \frac{v^0_{4.1}}{v^0_{3.2}}\right)
\end{aligned}
\tag{2.30}
$$

By considering Taylor series expansion of equilibrium equations given in Eq. (2.24) with respect to ξ, the derivatives of the CFs with respect to ξ can be calculated using the equation

$$
A^{mix}_{(i.j)\xi} + A^{mix}_{(i.j)(m.n)}v_{(m.n)\xi} = 0 \tag{2.31}
$$

The limiting derivatives of the transformed CFs with respect to ξ at $u_0 = 0$ and $\xi = 1$, $v^0_{(i.j)\xi}$, are given by

$$
\begin{aligned}
v^0_{(1.1)\xi} &= \frac{1}{2}v^0_{1.1}\left(-8 + 8v^0_{1.1} + 3v^0_{2.1} + 3v^0_{2.2}\right) - \frac{3}{2}\left(v^0_{3.1} + v^0_{3.2}\right) \\
v^0_{(2.1)\xi} &= v^0_{2.1}\left(-3 + 4v^0_{1.1} + v^0_{2.1}\right) - 2v^0_{3.1} \\
v^0_{(2.2)\xi} &= v^0_{2.2}\left(-3 + 4v^0_{1.1} + v^0_{2.2}\right) - 2v^0_{3.2} \\
v^0_{(3.1)\xi} &= v^0_{3.1}\left(-\frac{17}{2} + 8v^0_{1.1} + 3v^0_{2.1} + 2v^0_{2.2} - \frac{2v^0_{3.1} + v^0_{3.2}}{v^0_{1.1}} - \frac{v^0_{3.1}}{2v^0_{2.1}}\right) - v^0_{4.1} \\
v^0_{(3.2)\xi} &= v^0_{3.2}\left(-\frac{17}{2} + 8v^0_{1.1} + 2v^0_{2.1} + 3v^0_{2.2} - \frac{v^0_{3.1} + 2v^0_{3.2}}{v^0_{1.1}} - \frac{v^0_{3.2}}{2v^0_{2.2}}\right) - v^0_{4.1} \\
v^0_{(4.1)\xi} &= v^0_{4.1}\left(-14 + 12v^0_{1.1} + 4v^0_{2.1} + 4v^0_{2.2} - 2\frac{v^0_{3.1} + v^0_{3.2}}{v^0_{1.1}} - \frac{v^0_{4.1}}{v^0_{3.1}} - \frac{v^0_{4.1}}{v^0_{3.2}}\right)
\end{aligned}
\tag{2.32}
$$

A similar methodology can be used to obtain limiting values of higher order derivatives of the CFs.

Using Eq. (2.23), the limiting values of the CFs at $u_0 = 0$ and $\xi = 1$, $u^0_{i.j}$ are found to be

$$\begin{aligned} u^0_{1.1} &= -1; & u^0_{2.1} &= 1; & u^0_{2.2} &= 1 \\ u^0_{3.1} &= 1; & u^0_{3.2} &= -1; & u^0_{4.1} &= 1 \end{aligned} \tag{2.33}$$

Considering the total derivative of CFs in the orthogonal basis with respect to u_0 and ξ, the limiting first derivatives of the CFs (with respect to u_0 and ξ), $u^0_{(i.j)0}$ and $u^0_{(i.j)\xi}$ respectively, are calculated as

$$\begin{aligned} u^0_{(1.1)0} &= 0; & u^0_{(2.1)0} &= -2; & u^0_{(2.2)0} &= 2 \\ u^0_{(3.1)0} &= -1; & u^0_{(3.2)0} &= -1; & u^0_{(4.1)0} &= 0 \\ u^0_{(1.1)\xi} &= -2; & u^0_{(2.1)\xi} &= 2; & u^0_{(2.2)\xi} &= 2 \\ u^0_{(3.1)\xi} &= 3; & u^0_{(3.2)\xi} &= -3; & u^0_{(4.1)\xi} &= 4 \end{aligned} \tag{2.34}$$

Similarly, the limiting values of second derivatives of the CFs in the orthogonal basis with respect to u_0 and ξ, $u^0_{(i.j)00}$ and $u^0_{(i.j)\xi\xi}$, and the mixed derivatives $u^0_{(i.j)\xi 0}$ respectively, are found to be

$$\begin{aligned} u^0_{(1.1)00} &= 2v^0_{1.1}; & u^0_{(2.1)00} &= 2v^0_{2.1} \\ u^0_{(2.2)00} &= 2v^0_{2.2}; & u^0_{(3.1)00} &= -4v^0_{1.1} + 2v^0_{2.1} \\ u^0_{(3.2)00} &= 4v^0_{1.1} - 2v^0_{2.2}; & u^0_{(4.1)00} &= -8v^0_{1.1} + 2v^0_{2.1} + 2v^0_{2.2} \end{aligned} \tag{2.35}$$

$$\begin{aligned} u^0_{(1.1)\xi 0} &= 0; & u^0_{(2.1)\xi 0} &= -2v^0_{2.1} \\ u^0_{(2.2)\xi 0} &= 2v^0_{2.2}; & u^0_{(3.1)\xi 0} &= -2v^0_{2.1} \\ u^0_{(3.2)\xi 0} &= -2v^0_{2.2}; & u^0_{(4.1)\xi 0} &= -2v^0_{2.1} + 2v^0_{2.2} \end{aligned} \tag{2.36}$$

$$\begin{aligned} u^0_{(1.1)\xi\xi} &= -2v^0_{1.1}; & u^0_{(2.1)\xi\xi} &= 2v^0_{2.1} \\ u^0_{(2.2)\xi\xi} &= 2v^0_{2.2}; & u^0_{(3.1)\xi\xi} &= 4v^0_{1.1} + 2v^0_{2.1} \\ u^0_{(3.2)\xi\xi} &= -4v^0_{1.1} - 2v^0_{2.2}; & u^0_{(4.1)\xi\xi} &= 8v^0_{1.1} + 2v^0_{2.1} + 2v^0_{2.2} \end{aligned} \tag{2.37}$$

Calculation of the third derivatives of the CFs in the orthogonal basis involves first derivative of the CFs in the sublattice solvent bases, which are given in Eqs. (2.30) and (2.32).

2.5 Analytical solutions for the CFs of $L1_0$ phase

The tetrahedron cluster used in the formulation for $L1_0$ phase is shown in Figure 2.3. This structure consists of two sublattices, α and β. The details of the distinct clusters, the corresponding ordered CFs and their distribution over the sublattices, multiplicities and the K-B coefficients are given in Table 2.2.

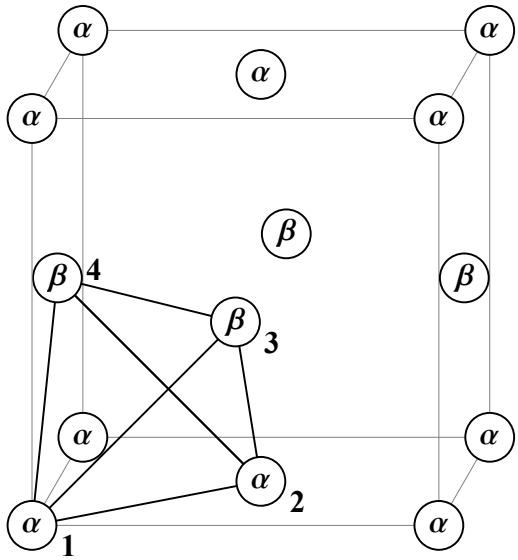

Figure 2.3: The regular tetrahedron basic cluster [1-2-3-4] in the $L1_0$ phase along with the sublattice sites designated α and β.

Table 2.2: The clusters, their designations $(i.j)$, multiplicities $(m_{i.j})$, number of sub-clusters $k.l$ present in each cluster $i.j$ $(n_{i.j}^{k.l})$ and K-B coefficients $(\gamma_{i.j})$ for the $L1_0$ phase using T approximation.

Cluster	Ordered $L1_0$ cluster	$i.j$	$m_{i.j}$	$n_{i.j}^{3.1}$	$n_{i.j}^{2.2}$	$n_{i.j}^{2.1}$	$n_{i.j}^{1.3}$	$n_{i.j}^{1.2}$	$n_{i.j}^{1.1}$	$n_{i.j}^{0.2}$	$n_{i.j}^{0.1}$	$\gamma_{i.j}$
Tetrahedron	$\alpha\alpha\beta\beta$ (1,2,3,4)	3.1	2	1	2	2	1	4	1	2	2	1
Equilateral triangle	$\alpha\beta\beta$ (1,3,4)	2.2	4	0	1	0	1	2	0	2	1	0
	$\alpha\alpha\beta$ (1,2,3)	2.1	4	0	0	1	0	2	1	1	2	
I-n pair	$\beta\beta$ (3,4)	1.3	1	0	0	0	1	0	0	2	0	-1
	$\alpha\beta$ (1,3)	1.2	4	0	0	0	0	1	0	1	1	
	$\alpha\alpha$ (1,2)	1.1	1	0	0	0	0	0	1	0	2	
Point	β (3)	0.2	1/2	0	0	0	0	0	0	1	0	5
	α (1)	0.1	1/2	0	0	0	0	0	0	0	1	

Using these data, the configurational energy and the entropy of mixing for the $L1_0$ phase are written based on Eqs. (2.15) and (2.16) in the orthogonal basis. Subsequently, the Helmholtz energy expression is obtained using Eq. (2.18).

The CFs in the orthogonal basis can be expressed in terms of those in the sublattice solvent bases in a manner similar to that followed for the $B2$ phase and are given below.

$$
\begin{aligned}
u_{1.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{1.1} \\
u_{1.2} &= -1 + 2x_{\mathrm{B}}^{\alpha} + 2x_{\mathrm{A}}^{\beta} - 4x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta} v_{1.2} \\
u_{1.3} &= 1 - 4x_{\mathrm{A}}^{\beta} + 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{1.3} \\
u_{2.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} - 2x_{\mathrm{A}}^{\beta} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{1.1} + 8x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta} v_{1.2} - 8\left(x_{\mathrm{B}}^{\alpha}\right)^2 x_{\mathrm{A}}^{\beta} v_{2.1} \\
u_{2.2} &= -1 + 2x_{\mathrm{B}}^{\alpha} + 4x_{\mathrm{A}}^{\beta} - 8x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta} v_{1.2} - 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{1.3} + 8x_{\mathrm{B}}^{\alpha}\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{2.2} \\
u_{3.1} &= 1 - 4x_{\mathrm{B}}^{\alpha} - 4x_{\mathrm{A}}^{\beta} + 4\left(x_{\mathrm{B}}^{\alpha}\right)^2 v_{1.1} + 16x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta} v_{1.2} + 4\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{1.3} \\
&\quad - 16\left(x_{\mathrm{B}}^{\alpha}\right)^2 x_{\mathrm{A}}^{\beta} v_{2.1} - 16x_{\mathrm{B}}^{\alpha}\left(x_{\mathrm{A}}^{\beta}\right)^2 v_{2.2} + 16\left(x_{\mathrm{B}}^{\alpha}x_{\mathrm{A}}^{\beta}\right)^2 v_{3.1}
\end{aligned}
\tag{2.38}
$$

As in the case of $B2$ phase, a dimensionless ratio $K = x_{\mathrm{A}}^{\beta}/x_{\mathrm{B}}^{\alpha}$ is introduced such that K remains a finite non-zero number, even in the limit $x_{\mathrm{B}}^{\alpha} \to 0$ and $x_{\mathrm{A}}^{\beta} \to 0$ and is used to eliminate x_{A}^{β} from the equilibrium equations. The transformed energy expression is used to write the equilibrium equations as given in Eq. (2.24). The equilibrium equations can be significantly simplified after making this substitution and can be solved for the limiting values of the CFs at the stoichiometric composition at $u_0 = 0$ and $\xi = 1$. The limiting values of the CFs thus obtained are as follows.

$$
\begin{aligned}
v_{1.1}^0 &= \eta_1\eta_2^2\sqrt{\eta_3}; & v_{1.2}^0 &= \frac{\sqrt{\eta_3}}{\eta_1}; & v_{1.3}^0 &= \frac{\eta_1\sqrt{\eta_3}}{\eta_2^2} \\
v_{2.1}^0 &= \frac{\eta_2\eta_3}{\eta_1}; & v_{2.2}^0 &= \frac{\eta_3}{\eta_1\eta_2}; & v_{3.1}^0 &= \frac{\eta_3^2}{\eta_1^2}
\end{aligned}
\tag{2.39}
$$

The limiting values of first derivatives of the CFs with respect to u_0 and ξ respectively are evaluated using Eqs. (2.29) and (2.31) in terms of limiting values of the transformed CFs given in Eq. (2.39). These are given by

$$
\begin{aligned}
v_{(1.1)0}^0 &= v_{1.1}^0\left(-1 - v_{1.1}^0 + 4v_{1.2}^0\right) - 2v_{2.1}^0 \\
v_{(1.2)0}^0 &= v_{1.2}^0\left(-v_{1.1}^0 + v_{1.3}^0\right) + v_{2.1}^0 - v_{2.2}^0 \\
v_{(1.3)0}^0 &= v_{1.3}^0\left(1 - 4v_{1.2}^0 + v_{1.3}^0\right) + 2v_{2.2}^0 \\
v_{(2.1)0}^0 &= v_{2.1}^0\left(-1 - 2v_{1.1}^0 + 3v_{1.2}^0 - \frac{3}{2}v_{1.3}^0 - \frac{v_{2.1}^0}{v_{1.1}^0} + \frac{v_{2.1}^0 - v_{2.2}^0}{v_{1.2}^0}\right) - \frac{v_{3.1}^0}{2} \\
v_{(2.2)0}^0 &= v_{2.2}^0\left(1 + \frac{3}{2}v_{1.1}^0 - 3v_{1.2}^0 + 2v_{1.3}^0 + \frac{v_{2.1}^0 - v_{2.2}^0}{v_{1.2}^0} + \frac{v_{2.2}^0}{v_{1.3}^0}\right) + \frac{v_{3.1}^0}{2} \\
v_{(3.1)0}^0 &= v_{3.1}^0\left(-3v_{1.1}^0 + 3v_{1.3}^0 - \frac{v_{2.1}^0}{v_{1.1}^0} + 2\frac{v_{2.1}^0 - v_{2.2}^0}{v_{1.2}^0} + \frac{v_{2.2}^0}{v_{1.3}^0}\right)
\end{aligned}
\tag{2.40}
$$

and

$$
\begin{aligned}
v^0_{(1.1)\xi} &= v^0_{1.1}\left(-3 + v^0_{1.1} + 4v^0_{1.2}\right) - 2v^0_{2.1} \\
v^0_{(1.2)\xi} &= v^0_{1.2}\left(-3 + v^0_{1.1} + 3v^0_{1.2} + v^0_{1.3}\right) - v^0_{2.1} - v^0_{2.2} \\
v^0_{(1.3)\xi} &= v^0_{1.3}\left(-3 + 4v^0_{1.2} + v^0_{1.3}\right) - 2v^0_{2.2} \\
v^0_{(2.1)\xi} &= v^0_{2.1}\left(-7 + 2v^0_{1.1} + 7v^0_{1.2} + \frac{3}{2}v^0_{1.3} - \frac{v^0_{1.2}}{v^0_{1.1}} - \frac{v^0_{2.1} + v^0_{2.2}}{v^0_{1.2}}\right) - \frac{v^0_{3.1}}{2} \\
v^0_{(2.2)\xi} &= v^0_{2.2}\left(-7 + \frac{3}{2}v^0_{1.1} + 7v^0_{1.2} + 2v^0_{1.3} - \frac{v^0_{2.1} + v^0_{2.2}}{v^0_{1.2}} - \frac{v^0_{2.2}}{v^0_{1.3}}\right) - \frac{v^0_{3.1}}{2} \\
v^0_{(3.1)\xi} &= v^0_{3.1}\left(-12 + 3v^0_{1.1} + 12v^0_{1.2} + 3v^0_{1.3} - \frac{v^0_{2.1}}{v^0_{1.1}} - 2\frac{v^0_{2.1} + v^0_{2.2}}{v^0_{1.2}} - \frac{v^0_{2.2}}{v^0_{1.3}}\right)
\end{aligned}
\tag{2.41}
$$

Using the relations among the CFs in the sublattice-solvent bases and those in the orthogonal basis, the limiting values, the first and the second derivatives of the CFs with respect to u_0 and ξ are evaluated and are given in Table 2.3.

Table 2.3: The limiting values and the limiting derivatives of the orthogonal CFs for $L1_0$ phase using T approximation.

$i.j$	$u^0_{i.j}$	$u^0_{(i.j)0}$	$u^0_{(i.j)\xi}$	$u^0_{(i.j)00}$	$u^0_{(i.j)\xi 0}$	$u^0_{(i.j)\xi\xi}$
1.1	1	-2	2	$2v^0_{1.1}$	$-2v^0_{1.1}$	$2v^0_{1.1}$
1.2	-1	0	-2	$2v^0_{1.2}$	0	$-2v^0_{1.2}$
1.3	1	2	2	$2v^0_{1.3}$	$2v^0_{1.3}$	$2v^0_{1.3}$
2.1	1	-1	3	$2v^0_{1.1} - 4v^0_{1.2}$	$-2v^0_{1.1}$	$2v^0_{1.1} + 4v^0_{1.2}$
2.2	-1	-1	-3	$4v^0_{1.2} - 2v^0_{1.3}$	$-2v^0_{1.3}$	$-4v^0_{1.2} - 2v^0_{1.3}$
3.1	1	0	4	$2v^0_{1.1} - 8v^0_{1.2} + 2v^0_{1.3}$	$-2v^0_{1.1} + 2v^0_{1.3}$	$2v^0_{1.1} + 8v^0_{1.2} + 2v^0_{1.3}$

2.6 Discussion and conclusions

The CVM configurational entropy of mixing (ΔS^{mix}) expression contains terms such as $x^\alpha_{\mathrm{B}} \ln x^\alpha_{\mathrm{B}}$, which underflow in numerical computations for $x^\alpha_{\mathrm{B}} \leq 10^{-14}$ (in standard double precision calculations), corresponding to nearly perfect order. The choice of sublattice solvent bases makes the CFs in these bases identical to the CVs corresponding to clusters whose sites are occupied exclusively by solute atoms on the respective sublattice sites. Transformation of these CFs as products of random and non-random parts (as given in Eq. (2.21)) results in cancellation of terms such as

$x_{\mathrm{B}}^{\alpha} \ln x_{\mathrm{B}}^{\alpha}$ from the equilibrium equations. The equilibrium equations thus simplified do not underflow even in the limits of perfect order and stoichiometric composition. This offers a significant advantage in numerical computations. The limiting values of equilibrium CFs and their derivatives with respect to u_0 and ξ can then be easily found. These provide a set of good initial values for the CFs for chosen values of CECs, temperature and composition close to the state of perfect order and stoichiometric composition.

These equilibrium equations in the simplified form when used with initial values of transformed CFs estimated using the limiting values become amenable to numerical solutions to much lower temperatures compared to the conventional procedures using CFs in the orthogonal basis. An illustration of the above for $B2$ and $L1_0$ phases under T approximation is given below.

For $B2$ phase the equilibrium values of CFs are calculated as follows. At first, the limiting values of the vs, namely $v_{i.j}^0$, are substituted into the Helmholtz energy expression and the equilibrium equation with respect to ξ is obtained. The value of ξ obtained by solving this equation (ξ') and the random values ($v_{rnd}, v_{i.j} = 1$) or $v_{i.j}^0$ can be considered as two different sets of initial values to obtain the equilibrium values of ξ and the other CFs. The calculations are carried out for first neighbour pair interactions for $u_0 = 0$ at two different η_1 values, namely $\eta_{1,\mathrm{c}}^2$ $(T/T_{\mathrm{c}} = 1/2)$ and η_1 corresponding to $\xi_{eq} = 0.999999$ ($\eta_{1,min}$). The details of the calculations such as condition number of the Hessian matrix for the initial (κ_i) and the converged (κ_{c}) values of the CFs, number of iterations, *etc.* are given in Table 2.4.

Table 2.4: Comparison of condition number of the Hessian matrices, number of iterations to convergence and the equilibrium value of ξ at two different temperatures $\eta_{1,min}$ and $\eta_{1,\mathrm{c}}^2$ for the random values of CFs in orthogonal basis (u_{rnd}), CFs in the sublattice solvent bases (v_{rnd}) and the limiting values ($v_{i.j}^0$) for $B2$ phase using T approximation.

	at $\eta_{1,min}, \xi' = 0.999999$			at $\eta_{1,\mathrm{c}}^2, \xi' = 0.983254$		
Initial values	u_{rnd}*	v_{rnd}	$v_{i.j}^0$	u_{rnd}	v_{rnd}	$v_{i.j}^0$
κ_i	-	2.25×10^6	2.03×10^{12}	5.91×10^8	1.22×10^2	2.83×10^4
Number of iterations	-	13	3	8	9	4
ξ_{eq}	-	0.999999		0.983209		
κ_{c}	-	2.04×10^{12}		3.49×10^6	2.62×10^4	

* Due to accumulated round off errors, the calculations could not be carried out at $\eta_{1,min}$.

Table 2.5: Comparison of condition number of the Hessian matrices, number of iterations to convergence and the equilibrium value of ξ at two different temperatures $\eta_{1,min}$ and $\eta^2_{1,c}$ for the random values of CFs in orthogonal basis (u_{rnd}), CFs in the sublattice solvent bases (v_{rnd}) and the limiting values ($v^0_{i.j}$) for $L1_0$ phase using T approximation.

	at $\eta_1 = \eta_{1,min}$, $\xi_{min} = 0.9999995, \xi_{init} = 0.9999999$			at $\eta_1 = \eta^2_{1,c}$, $\xi_{min} = 0.9998, \xi_{init} = 0.9999$		
Initial values	u_{rnd}*	v_{rnd}	$v^0_{i.j}$	u_{rnd}	v_{rnd}	$v^0_{i.j}$
κ_i	-	2.25×10^7	1.94×10^{14}	1.02×10^{15}	2.25×10^4	1.67×10^9
Number of iterations	-	17	9	12	13	9
ξ_{eq}	-	0.999999		0.999513		
κ_c	-	1.69×10^{15}		2.93×10^8	5.80×10^9	

* Due to accumulated round off errors, the calculations could not be carried out at $\eta_{1,min}$.

It can be observed from Table 2.4 that the condition number of the Hessian matrix in the orthogonal basis in both the cases, namely, initial and converged CFs at $\eta^2_{1,c}$, is higher than that for all the cases of the sublattice solvent bases. However, in the case of sublattice solvent bases, the condition number of the Hessian matrix with the random initial values is less than that with $v^0_{i.j}$ as initial values. The number of iterations required to convergence is reduced when $v^0_{i.j}$ are used as initial values.

For $L1_0$ phase under T approximation with first neighbour pair interactions, it is found that the Helmholtz energy approximated by substituting $v^0_{i.j}$ does not have a minimum with respect to ξ at $u_0 = 0$ within the physically permitted configuration space defined by $-1 \leq u_0 \leq 1$, $-1 \leq \xi \leq 1$ and $0 \leq y^{i.j}_x \leq 1$. Hence, the value of ξ corresponding to the smallest possible value of the Helmholtz energy within the physically permitted configuration space can be found in the following manner. The $v^0_{i.j}$ are substituted in the equations corresponding to CVs being equal to 0 or 1 and are solved for ξs. Among these, the maximum value of ξ corresponds to the lower bound of possible ξs and is given by $\xi_{min} = 1 + 2\eta_1\left(\sqrt{1-\eta_1} - 1\right)$. The initial value for ξ (ξ_{init}) is chosen to be slightly greater than ξ_{min} using which the equilibrium state of the system is found at two different values of ξ as given in Table 2.5.

For $B2$ phase using T approximation, the limiting values of the CFs of the ordered phase, v^0, are used to approximate the CFs. By substituting these into the Helmholtz energy expression, the equilibrium equation corresponding to ξ is obtained. By solving this equation, the approximate value of ξ (ξ') is obtained at equiatomic composition as

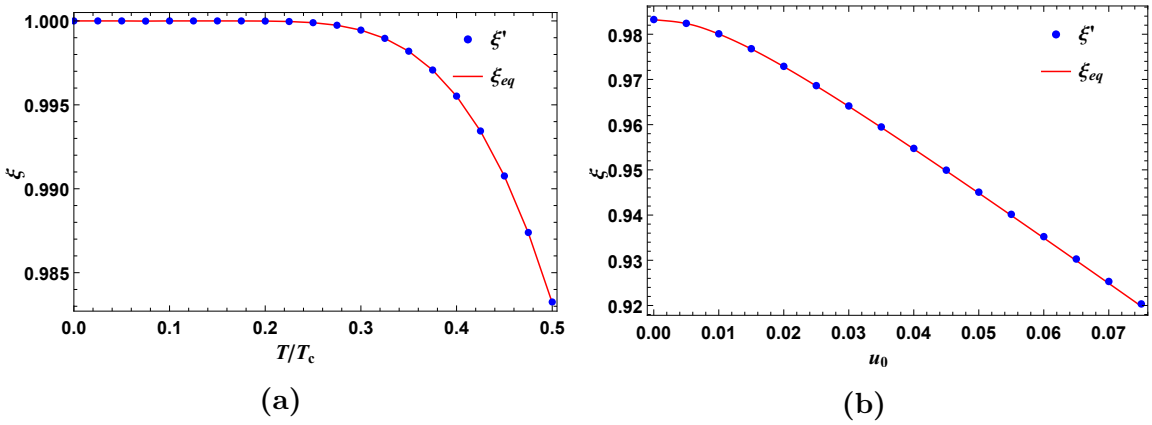

Figure 2.4: Comparison of the ξ calculated using the approximated Helmholtz energy expression (a) (ξ') at equiatomic composition and (b) (ξ') at T/T_c = 0.5 with CVM (ξ_{eq}) for $B2$ phase with exclusive I-n pair interactions using T approximation.

a function of T/T_c for exclusive first neighbour pair interactions. The comparison of ξ obtained using CVM (ξ_{eq}) and that of ξ' is shown in Figure 2.4 (a). Similarly at T/T_c = 0.5, the approximate values of ξ (ξ') are obtained as a function of composition near to stoichiometric composition and are shown in Figure 2.4 (b). The same methodology is utilized for $L1_1$ phase using TO approximation to obtain the equilibrium values of ξ in the temperature - composition domain where the order parameter is significantly high. The corresponding plots are presented in Figure 2.5. From these two cases, it can be observed that the equilibrium values of ξ are reproduced well as functions of both T and composition around stoichiometric composition where the system is highly ordered. Hence, the approximate Helmholtz energy function utilized in the above calculation can be used as an alternative to the CVM expression in the regions where ξ_{eq} is high for these structures.

It is evident from the above calculations that transforming the CFs to sublattice solvent bases yields a set of equilibrium equations using which equilibrium CFs can be calculated to much lower temperatures in all the cases with proper selection of initial ξ value. Hence, the methodology presented here can serve as an alternative to the approximation of the grand potential of the ordered phases by series expansion at low temperatures suggested by Kohan *et al.* (1998). Further, the present methodology gives SRO estimates in terms of the CFs whereas the methodology followed by Kohan *et al.* can yield only macroscopic thermodynamic functions.

The limiting values of CFs in the orthogonal basis and their first derivatives with

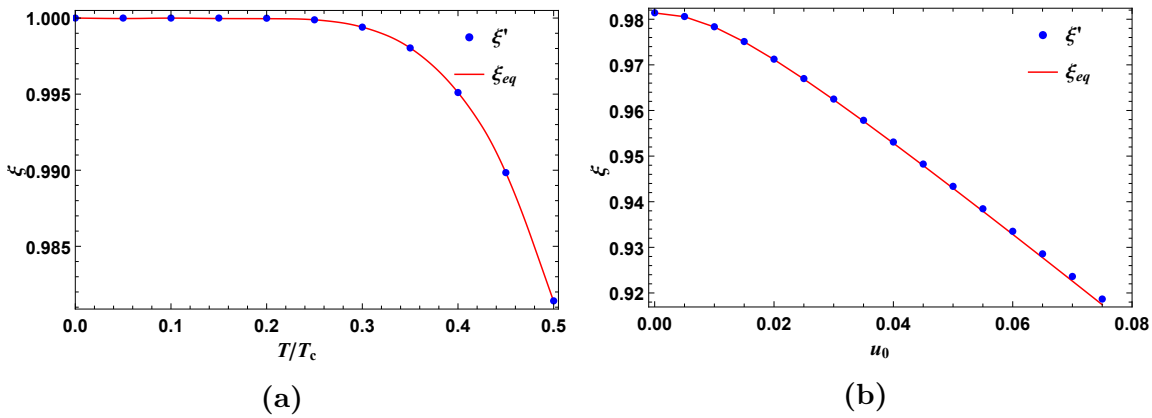

Figure 2.5: Comparison of the ξ calculated using the approximated Helmholtz energy expression (a) (ξ') at stoichiometric composition and (b) (ξ') at $T/T_c = 0.5$ with CVM (ξ_{eq}) for $L1_1$ phase with I-n pair interactions being 10% of II-n pair interactions using TO approximation.

respect to u_0 and ξ are independent of the system under consideration. However, the second derivatives of the CFs are functions of CECs and temperature. The results for disordered phases (Sarma *et al.*, 2012) and those obtained in this Chapter can be used for choosing appropriate forms of polynomials for approximating equilibrium values of CFs for disordered as well as ordered phases as shown in Chapter 4.