

# Chapter 1

## Introduction

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### 1.1 Computational thermodynamics of alloys

Phase diagrams play an important role in alloy development by providing the regions of thermodynamic stability for different phases present in a chosen materials system, depicted as a function of composition, temperature ( $T$ ) and pressure. The number of experiments required to determine these diagrams or these stability regions increases significantly with the number of components present in the system. Thus, determination of phase diagrams exclusively by conventional methods is a very cumbersome and tedious process. However, the efforts required to determine these diagrams can be considerably reduced with the help of computational thermodynamics (CT). In CT, the Gibbs energy or any other thermodynamic state property of each phase is represented using appropriate thermodynamic models. Physically based models can predict the thermodynamic properties even in the meta-stable regions in a fairly reliable manner. Once such physically based models are developed for each phase in a (multicomponent) system by optimizing the various types of data available for the system, the phase diagrams and thermodynamic properties can be readily computed and plotted as a function of the chosen set of variables.

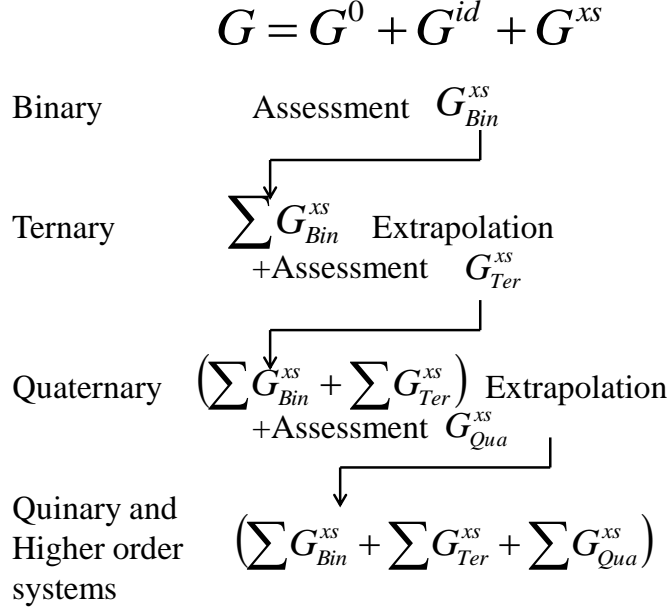
The so-called CALPHAD (calculation of phase diagrams) methodology is widely used in CT of alloys (Kaufman and Bernstein, 1970; Lukas *et al.*, 2007; Saunders and Miodownik, 1998; Sundman *et al.*, 2018). In this methodology, a sequential modelling is carried out starting from the unary- to binary- to ternary- subsystems, etc. up to the required multicomponent- system of interest (Kattner, 1997). For example, Gibbs energies of phases present in a binary system are modelled using the standard

representation for unary phases given in the unary system database, namely, the SGTE database (Dinsdale, 1991) such that the available thermodynamic properties and the phase diagram data are reproduced to the level of desired accuracy. Such an exercise is usually called as thermodynamic assessment. Using these models for all the three binary subsystems corresponding to a chosen ternary system, phase diagram of the ternary system is predicted/ computed initially by assuming that the ternary interactions are negligible. The phase diagram and thermodynamic data thus computed are compared with the available ternary system data. If ternary system data are not available, careful experiments could be conducted in the regions of critical interest in the predicted phase diagram. Based on the agreement between the predicted and the actual phase diagrams (and thermodynamic data), the ternary system is reassessed to determine the hitherto neglected ternary interactions, keeping the already determined binary interactions intact. If required, the lower order systems are also reassessed to readjust the binary interactions. This procedure can be extended to model any multicomponent materials system. This procedure is quite feasible due to the fact that interactions beyond quaternary level are negligible in metallic materials due to which, phase diagrams of systems beyond quaternary can be computed purely by extrapolation. Further, this methodology becomes indispensable for multicomponent systems, especially for visualization and graphical representation of different views and sections of phase diagrams and property diagrams, as per the requirement. A graphical illustration of this methodology is given in Figure 1.1.

The expression for molar Gibbs energy ( $G$ ) of a phase typically contains terms corresponding to contributions from mechanical mixture of the components ( $G^0$ ), the configurational entropy of ideal mixing ( $G^{id}$ ) apart from an excess Gibbs energy term ( $G^{xs}$ ). In general, for a binary phase  $\alpha$  in an alloy system we have

$$G_{Bin}^{\alpha} = \sum_{i=1}^2 x_i^{\alpha} G_i^{0,\alpha} + RT \sum_{i=1}^2 x_i^{\alpha} \ln x_i^{\alpha} + G_{Bin}^{xs,\alpha} \quad (1.1)$$

The excess Gibbs energy term contains contributions from different effects such as configurational, vibrational, electronic, *etc.* The former is very dominant, but contributions from, say, vibrational effects can significantly affect the quantitative details such as critical temperatures in phase diagrams. Additional terms such as  $G^{phys}$  are also included in the expression for  $G$  in order to account for specific physical phenomena such as ferromagnetism. Thermodynamic models of varying degrees of



**Figure 1.1:** CALPHAD methodology for assessment of multicomponent systems (Kattner, 1997).

sophistication are available in literature for representing these effects (Lukas *et al.*, 2007). The standard CALPHAD methodology uses Redlich-Kister polynomials (Redlich and Kister, 1948) for the disordered phases, Gorsky-Bragg-Williams (Bragg and Williams, 1934, 1935; Gorsky, 1928; Williams, 1935) or compound energy formalism (Sundman and Ågren, 1981; Sundman *et al.*, 2018) for the ordered phases or compounds. In addition, cluster/site approximation (CSA) (Chang *et al.*, 2004); cluster expansion–cluster variation method (CE–CVM) (de Fontaine, 1994; Inden, 2005; Kikuchi, 1951; Sanchez *et al.*, 1984), *etc.* are also occasionally used. Some of these models are implemented in software packages such as Thermo-Calc (Andersson *et al.*, 2002), OpenCalphad (OC) (Sundman *et al.*, 2015), PANDAT (Cao *et al.*, 2009; Chen *et al.*, 2002), FactSage (Bale *et al.*, 2016), CaTCalc (Shobu, 2009), *etc.*

Another important class of techniques is the Monte-Carlo simulations (MCS) (Bichara and Inden, 1991; Binder and Heermann, 2010; Binder *et al.*, 1981; Inden, 2005; Lanzini and Romero, 2015). In MCS, a virtual crystal is defined in computer as a 3D array of memory spaces, in which, each memory space is assumed to correspond to a specific atomic site in the corresponding real crystal. A variable, say  $\sigma_i$ , is associated with each site  $i$  in the crystal. In a binary system,  $\sigma_i$ , can take the values  $-1$  and  $+1$  for representing say, A and B atoms respectively. The evolution of the atomic configuration in the structure is simulated by considering interchange between an atom

which is randomly chosen in the structure and one of its nearest neighbours. The atom exchanges in the structure are accepted or rejected by following the Metropolis algorithm (Metropolis *et al.*, 1953). The difference in energy of the system is computed by using an appropriate ‘Hamiltonian’ or ‘energy function’. Quite frequently, only pair-wise interactions are considered up to second neighbour distances, to limit the computational burden. This procedure is repeated for each atom in the structure. Due to its kinetic nature, it is difficult to attain strict equilibrium, especially close to critical points. However, well-simulated Monte-Carlo results are treated as accurate, against which, different approximations of methods like CE-CVM are judged (Finel, 1989, 1994).

Availability of quality experimental data is always critical for validating the models. However, such data are often not available. Due to the rapid progress made in the recent past in the computation of thermophysical properties using the first-principles quantum mechanical methods based on density functional theory (Calderon *et al.*, 2015; Mardirossian and Head-Gordon, 2017; Toher *et al.*, 2018), these data are being increasingly used in the CALPHAD methodology (Enoki *et al.*, 2020; Shi *et al.*, 2020; Yen *et al.*, 2020). Thus, CT, first-principles computations and experiments can go hand in hand supporting one another in accelerated design and development of novel materials.

It is important to recognise that CT forms the foundation for modern-day alloy design and component development. This is increasingly being performed using the so-called integrated computational materials engineering (ICME) approach. The ICME consists of many computational tools and has been proven to hasten the development of both the product and processes. The ICME involves study of materials from atomic level using techniques such as *ab initio* calculations, molecular dynamics to crafting of microstructures involving design of heat treatment and mechanical working processes to obtain the desired set of properties and performance in the materials and the engineering components. In ICME, at first, a desired set of properties of the component to be developed is identified. Then, by integrating the information from all the materials databases, physical metallurgy expertise and modelling information available across different length scales, suitable materials are selected and processing schedules designed to fulfill the engineering requirements of the components

(Gong *et al.*, 2017; Olson and Kuehmann, 2014; Xiong and Olson, 2015) and the successful cases published in the world congress reports published by TMS such as (Mason *et al.*, 2017). Clearly, integration of models across the length scales from quantum mechanical- to statistical mechanical- to classical/macrosopic levels is of paramount importance. This is being done by bridging the gaps, if necessary, even by primitive models at present, all the way to engineering applications (National Academies of Sciences, Engineering, and Medicine, 2019). The 6th world congress by TMS on ICME is going to be held in April, 2021.

On the other hand, it is also vital to improve the models at different length scales that form part of the ICME, such that they have sound physical basis, yet remain algebraically simple, mathematically tractable and computationally efficient. This thesis presents the details of such an effort, in which, a direct solution of the correlation functions is obtained in a binary phase using polynomial expressions, which in turn represent the often neglected configurational short range order (SRO).

A brief account of some of the important thermodynamic models, which are used to describe disordered and ordered binary substitutional solid solutions, is presented below. Accordingly, phases such as interstitial solutions, oxides and other compounds with ionic constituents, topologically close packed (TCP) phases, amorphous phases, liquids, *etc.* will not be included in the following summary.

## 1.2 Thermodynamic models

Any model has advantages as well as limitations depending on the set of assumptions and approximations made. Based on the limitations, the models are modified from time to time. In this section the details of the formalism, limitations and advantages and some of the improvements that have taken place in the modelling of thermodynamics of alloys, which are directly relevant to the thesis are discussed.

An important structural feature which is generally neglected in most of the modelling efforts is the chemical or configurational SRO, which is always present in materials and accordingly influences the properties. In addition to the configurational SRO, the topological SRO is also present in amorphous materials and liquids. A quantitative description of the configurational SRO in crystalline materials is commonly represented by using Cowley-Warren parameters (Cowley, 1950, 1960,

1965), which, in a binary system characterize the departure of the probability of occurrence of unlike pairs from ideal/random distribution (see Chapter 4, Eq. (4.53)). A generalized representation of configurational SRO in materials is difficult, but can be accomplished by the CE-CVM in terms of the microscopic state variables called multi-site correlation functions as calculated and shown in Chapter 4. Even though some thermodynamic models provide quantitative description of long range chemical order (LRO), many models tend to neglect the important contributions of SRO. The SRO can be measured by using experimental techniques such as X-Ray, electron and neutron diffraction studies. Owen *et al.* (2016) have recently introduced a new method to obtain the information of SRO from X-Ray powder diffraction. A comprehensive review on the influence of SRO and LRO on surface segregation and related phenomena is presented by Polak and Rubinovich (2000). The role of SRO on the properties of the materials can be found in Abe and Sundman (2003), Owen *et al.* (2016) and in the references therein.

In a disordered substitutional solid solution, atoms of different components occupy the same set of atomic sites. In the presence of LRO, a phase would have several distinct sublattices in the structure, while some of the sublattices may be preferred by certain components. Two distinct types of LRO are observed in alloys. In the most common case of LRO, the sublattices are crystallographically different. For example, the  $\sigma$  phase has 5 different sublattices while the Laves phase can have two or more sublattices. The other type of LRO occurs in phases which undergo order/disorder transformation in certain ranges of  $T$  and composition. They are usually based on simple structures like FCC ( $A1$ ), BCC ( $A2$ ) or HCP ( $A3$ ), e.g.,  $B2$  ordering in Al-Fe system. The transformation can be of first order which is associated with a two-phase region in the corresponding phase diagram, or it can also be of second order without exhibiting any two-phase region in the phase diagram. Modelling both the ordered and disordered states using the same Gibbs energy function makes it theoretically sound to describe the order/disorder transformations of first order, while it is mandatory for describing those of second order.

### 1.2.1 CALPHAD methodology

The CALPHAD methodology proposed by Kaufman (1970) is widely used to represent the Gibbs energy of the phases. In this methodology, the Gibbs energies of the disordered phases are represented using Redlich-Kister polynomials (Redlich and Kister, 1948) and those of the ordered phases are represented using compound energy formalism which is reviewed by Sundman *et al.* (2018).

#### Redlich-Kister polynomials

The Redlich-Kister (R-K) polynomials are used along with the ideal entropy of mixing to represent the excess Gibbs energy of a disordered phase. For a binary phase having components A and B, the excess Gibbs energy is expressed in the form of R-K polynomial as

$$G^{xs} = x_A x_B \sum_{i=0}^n L_i (x_B - x_A)^i \quad (1.2)$$

In this expression, the index  $i$  usually takes the values '0' to  $n$  such that the resulting expression of Gibbs energy represents the available experimental data in a satisfactory manner. The interaction parameters,  $L_i$ , are written as linear functions in  $T$   $L_i = a_i + b_i T$  where  $a_i$  and  $b_i$  are parameters to be determined for each phase. This is referred to as linear model. It was reported by Chen *et al.* (2001) that many of the phase diagrams optimized using experimental and/or theoretical data with this model exhibit formation of inverted miscibility gaps in the liquid phase region above the liquidus boundary and/or stabilization of low temperature solid solution phases in the liquid phase at high temperatures.

Kaptay (2004) considered  $G^{xs}$  with  $i = 1$  and analysed the parameters in  $L_1$  obtained for different binary systems in the literature. A constraint on the values of  $(a_i/b_i)$  is obtained to avoid high temperature artefacts such as inverted miscibility gaps for a chosen phase. Further, a new form for the interaction parameter has been suggested with an exponential function as

$$L_i = a_i \exp\left(-\frac{T}{\tau_i}\right) \quad (1.3)$$

where  $a_i$  and  $\tau_i$  are the parameters to be determined by optimization of experimental data. Unlike the linear model, this model could retain the values of  $G^{xs}$  finite even in

the limit of  $T \rightarrow \infty$ . However, this model may sometimes result in the low-temperature artefact of re-stabilization of liquid phase at low temperature.

An additional model is also proposed by Kaptay (2014), which is a combination of linear and exponential functions, known as linear-exponential function, defined as

$$L_i = (a_i - b_i T) \exp\left(-\frac{T}{\tau_i}\right) \quad (1.4)$$

For this linear-exponential function, Kaptay suggested a methodology to be followed to obtain the model parameters for alloy systems that are thermodynamically distinct.

Kaptay (2017) has further suggested a piecewise fit to the liquid phase considering two different functional forms. For temperatures less than  $T^*$  (the lowest temperature in the solidus boundary for the chosen alloy system), a functional form similar to the one used to represent the standard Gibbs energy by Dinsdale (1991) is used. However, for the higher temperatures, exponential or linear-exponential forms given in Eqs. (1.3) and (1.4) can be used. It must be ensured that both the functions and their derivatives with respect to  $T$  up to third order are equal.

Even though the modified  $L_i$  forms can satisfy all the thermodynamic limits for  $T = 0$  and  $T \rightarrow \infty$  without resulting in any artefacts in the phase diagrams assessed, this model cannot describe the SRO present in the alloys.

## Compound energy formalism

In this formalism, compounds with a specific constituent on each sublattice are considered to be the end members instead of the individual components, as a general case, since it may not always be possible to separate the properties of individual components in a phase. The Gibbs energy expression is obtained in terms of these end member compounds and hence the name compound energy formalism (CEF). The general form of the Gibbs energy expression for an ordered phase is given by Sundman and Ågren (1981) and Hillert (2001), based on the formalism used earlier by Hillert and Staffansson (1970) for an interstitial solid solution of C in Fe. The configurational entropy of the given ordered phase is written in terms of constitutional variable,  $y_i^\lambda$  (for the constituent  $i$  on the sublattice  $\lambda$ ) as

$$S^{conf} = -R \sum_{\lambda} a^{\lambda} \sum_j y_j^{\lambda} \ln y_j^{\lambda} \quad (1.5)$$



where  $a^\lambda$  is the number of sites on the sublattice  $\lambda$  and  $y_j^\lambda$  is the fraction of sites of sublattice  $\lambda$  occupied by constituent  $j$ . These constitutional variables,  $y_j^\lambda$ , are related to the average composition of the phase as

$$x_i = \frac{\sum_\lambda a^\lambda \sum_j b_{ij} y_j^\lambda}{\sum_\lambda a^\lambda \sum_j \sum_k b_{jk} y_j^\lambda} \quad (1.6)$$

where  $b_{ij}$  is the stoichiometric factor of component  $i$  in the constituent  $j$ .

Using this formalism, the phases which remain always ordered (such as line compounds, compounds that melt congruently), those which undergo order-disorder transformation, those containing defects, etc. can be modelled. It is stated that SRO also can be modelled in an approximate manner as a part of LRO contributions in this formalism (Sundman *et al.*, 2018), unlike Gorsky-Bragg-Williams approximation.

Thus, the R-K polynomials for the disordered phase and CEF for the ordered phases provide a useful framework in CT for expressing the configurational Gibbs energy of phases.

## 1.2.2 Cluster expansion–cluster variation method

### Cluster expansion method

Though cluster expansion (CE) method shares its roots with CVM, it was formally developed as an independent method by Sanchez *et al.* (1984). In this method the configurational energy of the system is expressed as a bilinear sum of the products of all the cluster functions and their system specific adjustable model parameters, called cluster expansion coefficients (CECs). The principle behind this series is that the contributions of the larger clusters are negligible, *i.e.* the series is convergent. The CECs introduced by Sanchez *et al.* (1984) are independent of composition. Later Asta *et al.* (1991) have shown that for a finite chosen cluster, the CECs should be composition dependent to have convergence. However, they have shown that for a grand canonical ensemble, the composition dependence of the CECs is taken care of by the cluster functions alone and in the case of canonical ensemble the composition dependence is taken care of by cluster functions as well as CECs together (Asta *et al.*, 1991; Wolverton *et al.*, 1991).

The CE has been widely used in conjunction with the CVM (Inden, 2005) as well as the DFT calculations (Chinnappan *et al.*, 2016) in order to predict and model

physical and thermodynamic properties in a variety of disordered systems. Several attempts have been made to reduce the computational burden from selection of clusters to methods to obtain a good fit discussing different aspects (Aldegunde *et al.*, 2016; Blum and Zunger, 2004). The CE has been used to predict the ground states of the system, determination of phase boundaries at low temperatures where the experimental phase boundaries could not be obtained (based on the ground states), band gap engineering, diffusion studies (Zhang and Sluiter, 2016), prediction of properties of surfaces, like chemisorption and physisorption properties (Sluiter and Kawazoe, 2003), as well as nano structures (Cao *et al.*, 2018).

Recently, Sanchez (Sanchez, 2017) has pointed out that the Connolly-Williams (C-W) method (Connolly and Williams, 1983) that approximates the energy by an Ising-like model forms the lowest level of a hierarchy of approximations provided by the CE method, while at the next level is the variable basis cluster expansion (VBCE) method proposed by Sanchez (2010) that incorporates only the concentration dependence of the CECs. Sanchez (2017) has also demonstrated with reference to the Mo-Ta system that the correct implementation of CE requires the determination of the CECs as a function of the full set of correlation functions, done in a self-consistent manner with the calculation of the configurational Gibbs energy of the system.

## **Cluster variation method**

Kikuchi (1951) introduced cluster variation method (CVM) as a systematic hierarchy of approximations for obtaining the configurational entropy of a phase by explicitly accounting for SRO to different degrees of accuracy. In this method, the configurational entropy of mixing is expressed in terms of Boltzmann summation of chosen maximal clusters and its overestimation due to overcounting of overlapping of smaller clusters is corrected such that all the (sub-)cluster configurations present in the structure are counted only once. A simplified method for obtaining these correction coefficients is provided by Barker (1953) and accordingly these are called Kikuchi-Barker (K-B) overlap correction coefficients. Schlijper (1983) showed that an appropriate sequence of clusters ensures that the entropy functional converges monotonically to the exact value in the thermodynamic limit.

As pointed out earlier, CE-CVM together offer a systematic hierarchy of approximations for expressing the configurational contributions to the Gibbs energy of a phase, by explicitly accounting for the configurational SRO present in the system. The zeroth level of the approximation corresponds to the ideal solution model for disordered phases and to the Gorsky-Bragg-Williams approximation for the phases exhibiting LRO, while the first level approximation corresponds to quasichemical model in the pairwise approximation, *etc.* In general, the same cluster approximation is used for the disordered phase and the corresponding ordered phases, such that a single Gibbs energy expression represents SRO and LRO states of different symmetries. Finel *et al.* (1989; 1994) have considered a larger cluster for the disordered phase (quadruple tetrahedron (QT) or 13-14 pt) but smaller cluster(s) for ordered phase(s) (tetrahedron - octahedron clusters (TO)) and computed prototype phase diagrams for FCC ordering systems which are in good agreement with the MCS results computed using the same first neighbour pair interactions. Such an approximation is referred to as mixed CVM. Further, the values of the correlation functions obtained from the MCS are used along with the CVM and transition temperatures and other thermodynamic properties such as enthalpy and entropy are obtained. Such calculations are referred to as MCS-CVM in literature.

For the chosen cluster, the configurational energy is in general written using CE with CECs independent of composition while the configurational entropy is expressed using CVM to obtain the Gibbs energy of the chosen alloy. This energy expression has to be minimized for a chosen thermodynamic state of the system with respect to the microscopic state variables. Kikuchi introduced natural iteration method (NIM) (Kikuchi, 1974) to minimize the grand potential of the selected system. The other methods involve solving a non-linear system of equations by using numerical techniques such as Newton-Raphson, conjugate gradient method, *etc.* (Mebane and Wang, 2010; Yuille, 2002).

The first iso-energy phase diagram with non-vanishing multi-site interactions is calculated using CVM by van Baal (1973). Following van Baal, Au-Cu phase diagram is calculated by Kikuchi and de Fontaine (1978). Many binary and ternary phase diagrams of real systems have been calculated using CVM in combination with data from MCS, *ab initio* DFT methods (Bourgeois *et al.*, 2019; Colinet, 2001; Eleno *et al.*,

2014; Inden, 2005; Kiyokane *et al.*, 2017; Sodr e *et al.*, 2009; Yamada and Mohri, 2020; Zarkevich *et al.*, 2008). The first principles data along with CVM coupled with phase field modelling is used to study microstructures (Mohri *et al.*, 2007; Wang *et al.*, 2007). A few other applications can be found in Finel (1994) and Mohri (2017), among others. This methodology is also reviewed from time to time (de Fontaine, 1979, 1994; Inden, 2005; Pelizzola, 2005).

A methodology, called simultaneous optimization using CE-CVM, is introduced by Sarma (2000) and Lele and Sarma (2009) to obtain the values of CECs of the selected system by minimizing a merit function defined using thermodynamic, structural and phase diagram data. This methodology is applied for the systems Sc–Zr, Ti–Zr, Hf–Zr and Sc–Ti. They have also included the often neglected vibrational mixing contributions to the Gibbs energy by using high temperature expansion of Debye model. In order to have good estimates for the initial CECs in simultaneous optimization, empirical polynomials are derived as functions of temperature and composition of the consolute point and congruent point by Gupta *et al.* (2008; 2005). Such estimates ensure correct topology of the phase diagram in the beginning itself and are critical for the success of optimization. Further, they lead to significant reduction in the computational burden involved in optimization.

Further, a new method, called overlap and rescaling method, was introduced by Sluiter (1994) to obtain distant interactions with smaller clusters and the accuracy of the CFs obtained in this method is good. Further, Jindal *et al.* (2013; 2014) have considered modification of the number of clusters per site (multiplicity) such that the phase diagrams calculated using the accurate MCS or that of larger cluster approximations can be obtained with smaller clusters with a reduction in the computational burden. In this modification, improvement in the thermodynamic properties is also observed. Sanchez and Mohri (2016) have given the relation between the orthogonal basis and the variable (composition) basis. They have considered some of the variable basis cluster functions to be ‘0’ and calculated the equilibrium value for the remaining cluster functions. Transformation of these variable basis cluster functions to the orthogonal basis results in non-zero values. It is shown that the values of the CFs obtained by this method are in good agreement with those obtained directly from CVM. Tamerbet *et al.* (2018) have applied genetic algorithm to optimize

the grand potential of the system under CVM framework.

In conventional CVM, the configurational entropy of mixing is expressed by permutation of atoms on the rigid lattice. In general, lattice distortions are caused due to atomic size differences, thermal lattice vibrations and elastic interactions. In conventional CVM, these effects are not considered. Considering the effects of atomic size differences accounting for displacement of atoms around their lattice points, continuous displacement CVM (CDCVM) is formulated (Finel, 1994; Kikuchi, 1998). The possible positions of the atoms due to displacement are taken around the lattice points and are referred to as quasi lattice points. The atoms on the quasi lattice points are treated as a different atom and the configurational entropy is calculated by mapping it into the entropy of the multi-component system. A comparison of CVM and CDCVM can be found in (Mohri, 2013, 2017).

The variation of CECs with change in atomic distance is estimated using different approximations such as Lennard-Jones potentials, Morse potential (Mohri, 2009; Mohri *et al.*, 2009). The calculations based on these show that the phase boundaries and transition temperatures are significantly affected due to atomic displacements. For pair interactions, a comparison of phase boundaries computed using CVM and CDCVM showed that the transition temperatures are decreased and the phase boundaries are shifted towards the side of smaller atoms. Using this methodology, properties such as thermal expansion (Mohri, 2008), displacive phase transformation (Kiyokane and Mohri, 2013, 2018; Mohri *et al.*, 2013), order-disorder transformations (Mohri, 2011) are also studied. Since the atoms occupying the quasi lattice points are treated as a different kind of atoms, the number of cluster variables increases significantly even for a simple approximation in 2D lattice. Since the number of variable with respect to which the energy function has to be minimized increases significantly, new algorithms are proposed to reduce the computational burden (Kiyokane and Mohri, 2011).

It is clear that the CE-CVM framework has a physically sound basis, but it involves significant algebraic complexity and prohibitively large amount of computational burden, especially for multicomponent systems. Therefore, several efforts have been made to reduce the computational burden, even by significantly undermining the accuracy of the method. One such method is the so-called cluster-site approximation (CSA).

### 1.2.3 Cluster-site approximation

The cluster-site approximation (CSA) is based on the generalized quasi-chemical method introduced by Yang and Li (Li, 1949; Yang, 1945). In this approximation, the configurational entropy is written for a chosen maximal cluster. The number of maximal clusters is chosen such that they share only points which ensures that the first neighbour pairs get counted accurately. However, this number is different from the actual number of clusters shared by the atoms in the structure. Thus, the correction to be made to the entropy of the maximal cluster ( $S^{clust}$ ) is only for removing the over counting of the points ( $S^{pt}$ ) shared by all the clusters. Hence the name cluster-site approximation. Accordingly, the configurational entropy expression for an  $n$ -site cluster becomes

$$S^{conf} = mS^{clust} - (m n - 1)S^{pt} \quad (1.7)$$

in which  $m$  is the number of energetically non-interfering clusters per site. This  $m$ , calculated using a value different from the geometrical value of the structure, is further modified by Oates *et al.* (1999) for the FCC system under tetrahedron approximation to improve the agreement between the phase diagrams calculated using CSA and MCS.

The CSA has advantages like (i) simplified form for the entropy expression, (ii) reduction in the number of independent variables to be considered (from  $C^n$  to  $Cn$  where  $C$  is number of components and  $n$  is number of lattice points in the cluster) to obtain the lowest energy state of the system. Such a reduction in the number of variables becomes very significant for multi-component systems. Using this methodology, many binary (Chang *et al.*, 2004), ternary (Cao *et al.*, 2005a,b, 2007) and quaternary (Zhu *et al.*, 2007) systems are assessed. In addition, CSA is coupled with first principles methods and phase diagrams are also calculated (Zereg and Bourki, 2009; Zhang *et al.*, 2008a,b, 2009). This method is also used to calculate the interphase boundary energy using sum-method (Cao *et al.*, 2006) and applied to study stability of Co-Cu nano-structures (Cao *et al.*, 2005c). The SRO parameters also can be calculated in this approach, but they are not as accurate as those of CVM obtained using the same cluster approximation or those obtained using MCS, since the number of clusters per site considered in CSA is different from that of the actual value.

### 1.3 Scope of the thesis

Unlike R-K polynomials, both CSA and CVM approaches consist of a set of internal variables to be calculated for each thermodynamic state of the selected system by numerically solving a set of non-linear equations. Vul and de Fontaine (1992) have given hierarchy for selection of clusters for different two and three dimensional lattices. Sanchez and de Fontaine (1978) have reported that tetrahedron - octahedron, double tetrahedron and double tetrahedron - octahedron clusters have 10, 16 and 19 independent internal variables respectively for the binary FCC phase. The number of internal variables depends on the size and symmetry of the cluster chosen. For an ordered structure, due to loss of symmetry, this number is always higher than its disordered counterpart (refer to supplementary section for a comparison). It is apparent that increase in the size of the cluster can increase the accuracy of the results and make them comparable with those of MCS. But considering larger clusters results in increase in the number of internal variables. This number can be very significant for multi-component systems and can be as high as  $C^n$  where  $C$  is the number of components and  $n$  is the number of sites in the cluster chosen.

As a part of the present work, two aspects are discussed.

1. Approximating the CFs as a function of composition, temperature and the CECs so that solving the non-linear equations can be avoided for the selected cluster.
2. Improvement of accuracy of CE-CVM under tetrahedron (T) approximation for FCC phases such that results of the larger clusters or MCS results can be reproduced.

Sarma *et al.* (2012) have considered dilute solution basis with a transformation of CFs and calculated the limiting values and the derivatives with respect to compositions for BCC phase under T approximation as well as for FCC and CPH phases under TO approximation. In these calculations, it is found that the limiting values and their derivative with respect to composition are functions of CECs and temperature. However, the values of the CFs in orthogonal basis and their first derivatives with respect to composition are independent of both CECs and temperature. In Chapter 2, a methodology is discussed to obtain the limiting values and the derivatives of the CFs (expressed in newly defined *sublattice solvent bases*) with respect to composition and

order parameter for the ordered phases at the stoichiometric composition. Further, for the orthogonal basis CFs, the limiting values and the derivatives with respect to composition as well as order parameter are obtained. The specific advantages of the sublattice solvent bases and the applications of these results are also discussed.

For a three dimensional cluster, the analytical solutions for the CFs as a function of composition, temperature and CECs are usually not available for both disordered and ordered phases. In Chapter 3, the analytical solutions for the CFs are obtained for  $A2$  &  $B32$  and  $A1$  &  $L1_1$  phases for exclusive second neighbour pair interactions respectively under T and TO approximations. Using these solutions, analytical forms are calculated for the miscibility gap-spinodal boundary and order-disorder boundaries. Further, expressions are obtained for the difference in the heat capacity and thermodynamic stability function for order-disorder transformation.

In order to avoid solving the non-linear equations to obtain the equilibrium values of the CFs, polynomials are derived as a function of point CF, which is related to the composition of the system, for both disordered and ordered phases in Chapter 4. These polynomial forms are derived such that the results of Chapter 2 for the ordered phase and those obtained by Sarma *et al.* (2012), are satisfied. From the analytical solutions obtained in Chapter 3, it is observed that the CFs are rational functions of CECs and  $T$  for the selected composition. So, the coefficients of these polynomials are expressed as rational functions of CECs and  $T$ . Following this, a methodology is developed for obtaining the polynomials for the CFs of  $A2$ – $B32$  system for exclusive second neighbour pair interactions under T approximation. Thus, this avoids solving of non-linear equilibrium equations for all the second neighbour pair interactions under T approximation to obtain the estimates of SRO parameters.

Jindal *et al.* (2014) have approximated the entropy functional to improve the agreement between the prototype systems of FCC system of CVM under TO approximation and the accurate MC results. Even though the approximation is carried out only for the phase diagram data, it is observed that there is improvement even in the thermodynamic data. In the light of this improvement, the entropy of the T cluster, having a smaller number of correlation functions than TO cluster, is modified by adjusting the multiplicities of the tetrahedron, triangle and pair clusters in Chapter 5. In this approach also there is significant improvement in the prototype



phase diagrams as well as the thermodynamic data with reduction in computational burden than TO approximation. Using this modified entropy functional, Au–Cu phase diagram is also calculated. However, it must be concluded that the modified T approximation does not have sufficient flexibility/degrees of freedom to reproduce the topology of the Au–Cu phase diagram.

In Chapter 6, the summary and the scope for future work are discussed.