

Preface

A vast majority of the structural alloys are multi-component alloys. Development of these alloys involves careful selection of alloying elements and processing routes to craft the phases and their distribution in the material to ensure desired set of properties and performance of the engineering component in service. This requires knowledge of the phases and their stability with respect to the composition, temperature (T) and pressure. In this process, phase diagrams play a vital role by providing the thermodynamic conditions required to stabilize desired phases and/or destabilize harmful or undesired phases. Determination of the phase diagrams solely by experimental techniques for a multi-component system over a wide range of composition and temperature is very laborious, expensive and impractical.

With the development of less expensive computing power, many of the theoretical models could be tested and implemented. Using different principles and approximations, many models have been developed to approximate the Gibbs energy of a phase. These models are validated using the available experimental data and databases are developed such that they reproduce phase diagrams, thermodynamic and other properties of interest. This resulted in the evolution of the subject called “computational thermodynamics” (CT). The models used in CT are such that they are able to calculate thermodynamic properties of the phases even in the regions outside the stability regions of these phases. Thus, metastable phase diagrams also can be calculated.

CALPHAD (calculation of phase diagrams) methodology introduced by Kaufman (1970) is extensively used in CT of alloys (Lukas *et al.*, 2007; Saunders and Miodownik, 1998). Redlich-Kister polynomials (Redlich and Kister, 1948) are used in this methodology to approximate the excess Gibbs energy of disordered solution phases while more complex models such as the Gorsky-Bragg-Williams approximation,

quasi-chemical method, compound energy formalism, *etc.* are required to represent the excess Gibbs energy of ordered phases. Even though these models are very successful in computation of phase diagrams, they do not provide any direct estimate of the chemical or configurational short range order (SRO), which is always present in materials systems and can be measured by various experimental techniques.

Cluster variation method (CVM) introduced by Kikuchi (1951) together with cluster expansion (CE) method introduced by Sanchez *et al.* (1984) offers a solution to the problem of describing SRO. In the CE method, configurational energy of a phase is expressed as a trilinear sum of the products of adjustable model parameters called cluster expansion coefficients (CECs), multiplicities and microscopic state variables called correlation functions (CFs). The configurational entropy of the phase is expressed using CVM in terms of the Boltzmann summations of configuration probabilities of the selected cluster and its subclusters, such that all the cluster- and subcluster- configurations present in the structure are counted only once by the use of Kikuchi-Barker overlap correction coefficients. The probabilities of occurrence of the cluster- and subcluster- configurations are called the cluster variables (CVs) and are linear functions of the CFs. These CFs can be used to describe the SRO of the system in a reliable manner. The accuracy of the method generally increases with the size of the cluster, which is associated with an increase in the number of CFs. The number of CFs also increases significantly due to lowering of symmetry on ordering or due to increase in the number of components in the phases. Such an increase in the number of CFs leads to increased algebraic complexity and computational burden.

For a chosen system, equilibrium values of the CFs have to be determined by minimization of Gibbs energy of the phase with respect to the CFs at the selected composition and T . This involves solving a non-linear system of equations, referred to as equilibrium equations, by numerical methods such as Newton-Raphson method. Sluiter (1994) introduced rescaling method to reduce the computational burden in which the CFs determined by minimization of Gibbs energy of smaller clusters are used to predict the higher order CFs. Sanchez and Mohri (2016) have set higher order CFs to '0' in variable basis CE and minimized the Gibbs energy with respect to the other CFs. Transformation of CFs from variable basis to orthogonal basis results in non-zero values for CFs. Even though this method can reduce the computational burden, the

phase boundaries calculated by this method are poorly reproduced. These two methods still require minimization of Gibbs energy. Tamerabet *et al.* (2018) proposed a method based on genetic algorithm to optimize grand potential of the selected system. Thus, different kinds of efforts are made to get the approximate/accurate values of the SRO parameters (CFs) with reduced computational burden.

In the present study, two different approaches are discussed that can reduce the computational burden without loss of SRO information. The first approach is to approximate the CFs as polynomials of composition (and also LRO parameter(s) for the ordered phases) that can eliminate solving the equilibrium equations for the selected approximation. The second approach is to obtain the accurate results corresponding to a larger cluster approximation, by using a smaller cluster approximation with reduced computational burden.

Sarma *et al.* (2012) have considered solvent basis and re-expressed the disordered phase CFs as a product of the random value of the CFs and its departure. It is observed in these calculations that limiting value at infinite dilution and the first derivative of the CFs with respect to the composition, in the orthogonal basis, are independent of the CECs and temperature. In Chapter 2 a new basis, referred to as sublattice solvent bases, is considered for the ordered phases for which the CVs that are exclusively occupied by solute atoms on the respective sublattices become the CFs. Further, these CFs are expressed as a product of the random value on the respective sublattices and its departure. This leads to cancellation of random values of the CFs from the equilibrium equations with respect to which the first derivative is considered to obtain the equilibrium equation. The new basis thus results in simplified equilibrium equations which do not underflow even in the limit of perfect ordering and accordingly the equilibrium value of the CFs can be calculated to much lower temperature than that can be accomplished by using orthogonal basis. At the stoichiometric composition and in the limit of perfect ordering, the equilibrium equations can be analytically solved to obtain the limiting values of the CFs in the sublattice solvent bases. The limiting values of the orthogonal CFs and their first derivatives with respect to composition and the order parameter calculated based on the relation between the orthogonal basis and sublattice solvent bases CFs are independent of the CECs and T . However, the second derivatives are dependent on CECs and T . The results of Sarma *et al.* (2012) and

those from sublattice solvent bases are used to obtain the form of the polynomials for the CFs of disordered and ordered phases respectively. These polynomials are used to obtain the approximate values of the CFs for the chosen thermodynamic state without having to solve nonlinear system of equilibrium equations.

The equilibrium values of the CFs have to be obtained by solving equilibrium equations. However, in some special cases, analytical solutions for the CFs can be obtained. For example, analytical solutions can be found for CFs for the 2D close-packed net under triangle approximation at equiatomic composition. For 3D structures, analytical solutions for the CFs are obtained in Chapter 3 as functions of composition, T as well as CEC corresponding to exclusive second neighbor pair interactions in the cases of (i) $A2-B32$ phases under irregular tetrahedron cluster approximation and (ii) $A1-L1_1$ phases under tetrahedron-octahedron cluster (TO) approximation. Guided by the numerical solutions, the relation between the CFs is established and it is observed that the equilibrium equations satisfy these relations. Substituting these relations, analytical solutions for the CFs are obtained. In the case of ordered phases ($B32$ in BCC system and $L1_1$ in FCC system), analytical solutions for the CFs are functions of order parameter as well whereas analytical solution for the order parameter itself can be obtained only at 0 K. Using these results, analytical expressions for some of the thermodynamic quantities are obtained.

Based on the results of Sarma *et al.* (2012) and those of sublattice solvent bases, the general form for polynomial expressions for the disordered and ordered CFs are obtained in Chapter 4. For a chosen composition, analytical solutions obtained for the CFs of disordered as well as ordered phases reduce to a rational function of CEC and T . Based on this, coefficients of the polynomial functions are taken to be rational functions of T . For the case of exclusive second neighbor pair interactions, for $A2-B32$ system, a systematic procedure is developed to obtain the coefficients of the polynomials for selected values of CECs and T . The data thus obtained are fitted to the rational function forms, guided by the analytical forms of the CFs. Further, the coefficients of the rational functions obtained by the fit are optimized to ensure that the phase separating and order-disorder boundaries are well reproduced. Based on the results obtained by optimization, it is observed that along with the phase boundaries, the CFs are also well reproduced. For the chosen CEC, T and composition, these polynomials

can be directly evaluated to obtain the equilibrium values of the CFs without the necessity of numerically solving the nonlinear system of equilibrium equations. Thus, these polynomials lead to significant simplification of the CVM methodology and make it comparable to the CALPHAD methods, without loss of SRO information. The polynomials for the CFs can be generalized to any real system eliminating the necessity of solving the equilibrium equations.

In CVM, accuracy of the results can be improved by considering larger clusters at the expense of computational burden. Jindal *et al.* (2013; 2014) have considered modification of multiplicities of the basic cluster(s) and accordingly the K-B coefficients of tetrahedron-octahedron cluster in FCC system and tetrahedron cluster in BCC system. The phase diagrams and the thermodynamic data obtained by this modification are in good agreement with those of accurate larger clusters and Monte-Carlo simulation results. In the case of FCC system, tetrahedron cluster, a cluster smaller than TO cluster having fewer CFs, is considered to reproduce accurate results leading to further reduction in the computational burden. For the tetrahedron cluster, the tetrahedron and triangle multiplicities are such that the triangle K-B coefficient is '0'. In Chapter 5, the tetrahedron and triangle multiplicities are modified simultaneously along with pair multiplicity by keeping the triangle K-B equal to '0', thereby maintaining the entropy expression simple. It is observed that alloy systems exhibiting both ordering- and phase separating-tendencies could not be improved simultaneously with two parameters. Therefore, the multiplicities are modified to correct the ordering temperatures. For systems exhibiting phase separating tendency, the phase boundary is improved by modification of pair and tetrahedron CECs, which is similar to optimization of a phase diagram. For a real system, this will result in a slightly different values of CECs than those of conventional CVM. However, it is observed that this modification of multiplicities not only improved the phase boundaries but also improved the thermodynamic properties of the system.

Next, a thermodynamic assessment of Au–Cu phase diagram is carried out using these modified multiplicities by considering only the configurational contributions. With this modified methodology, one of the invariant reactions could not be reproduced. It is expected that consideration of elastic interaction and/or vibrational contributions and/or lattice distortions with composition, which are significant for the selected

system, may reproduce the correct topology.

In summary, in this thesis, approximations have been developed for CE-CVM which permit (i) direct evaluation of the SRO parameters for A_2B_3 phases, without having to solve the non-linear equilibrium equations and (ii) improving the accuracy of the method for FCC phases under tetrahedron approximation.

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