

Chapter 6

Summary and scope for future work

In the framework of CE-CVM, the presence of the CFs can be considered as a strength since they represent the SRO information in a reliable manner up to the maximal cluster considered. The accuracy of the results calculated increases with increase in the size of the maximal cluster considered in these calculations. To obtain the values of the CFs that result in lowest energy for the chosen thermodynamic state of the system, the non-linear equilibrium equations have to be solved using numerical methods. The number of the equilibrium equations to be solved explodes significantly with increase in the size of the system. In the present work, the CFs, that represent the SRO, are approximated (i) that can avoid solving the equilibrium equations for *A2-B32* phases (ii) improve the accuracy of the approximation for FCC phases under tetrahedron approximation.

By considering the sublattice solvent bases, the CVs that are exclusively occupied by solute atoms on the respective sublattices become CFs. These CFs are re-expressed as a product of the random value of the CF on the respective sublattices and its departure from the random value. This results in factoring and cancellation of the random value from the CVs in the equilibrium equations. Further, the equilibrium equations considered in these bases are simplified for the case of perfect ordering. Using these equilibrium equations the limiting values of the CFs and their derivatives with respect to the point CF and ξ are calculated analytically at the stoichiometric composition for various binary ordered phases. It is observed that the equilibrium values of the CFs in this new basis can be obtained to much lower temperature than the conventional orthogonal basis for the compositions and temperatures where the degree of ordering is high. Further, the extrapolated polynomials obtained by Taylor

series expansion for the CFs are used to approximate the configurational energy of the system. The order parameter obtained by minimizing this approximated energy expression is in good agreement with that found by conventional CVM. Thus these extrapolated polynomials can be used to get the values of the CFs as well as the order parameter for the regions around the stoichiometric composition where ξ value is high. Further, the limiting values and the first derivatives of the CFs in the orthogonal basis are independent of system specific parameters. These results are used to approximate the ordered CFs as polynomials in terms of the point CFs.

A few special cases exist where the analytical solution for the equilibrium values of the CFs can be obtained, in general at the equi-atomic composition. In the present work, two special cases, one for the BCC based phases ($A2-B32$), another for FCC based phases ($A1-L1_1$), are presented where the analytical solution for the equilibrium values of the CFs are presented for exclusive second neighbour pair as a function of both composition and T (and ξ also in the case of ordered phases). This assisted in obtaining the analytical expression for the phase boundaries like miscibility gap boundary, spinodal and order-disorder boundaries. Further, analytical expressions for some of the thermodynamic quantities are also calculated.

Guided by the solvent basis results of Sarma *et al.* and the sublattice solvent bases CF results, the general forms of polynomials to approximate the disordered and ordered CFs are obtained as a function of point CFs. The analytical solutions obtained for the CFs show that the CFs can be represented with rational functions of CECs and T for a fixed composition. Directed by these results, coefficients of these polynomials are approximated as rational functions. A methodology is proposed to obtain the parameters of these rational functions for the exclusive second neighbour pair interactions of $A2-B32$ system. The phase boundaries obtained for the phase separating as well as ordering system are reproduced well by this approximation that does not require solving the nonlinear equilibrium equations except for ξ for the ordered phase. Further, the agreement between the CFs and the SRO parameters obtained by CVM and the polynomials is also good.

The same methodology or a similar methodology can be applied to approximate the CFs for the other phase of the BCC system for the I-n pair interactions. The combined expressions of I-n pair and the II-n pair interactions with selected range

of triangle and tetrahedron interactions can eliminate the requirement of solving the nonlinear equilibrium equations for tetrahedron approximation of BCC system, which can be considered as part of future work.

The modification of multiplicities (and thereby the K-B coefficients) for the FCC phases ($A1$, $L1_0$ and $L1_2$) with tetrahedron approximation is able to reproduce the triple point and the corresponding ordering temperatures well. However, the requirement of the modifications of multiplicities is opposite for improving the phase separating system. Yet, the phase separating system can be made accurate by modification of CECs like the case of optimizing CECs for a real system. In this methodology, though the modification of multiplicities is carried out to improve the phase diagram topology, there is improvement of thermodynamic properties with respect to both temperature and composition.

Thus, this methodology has reduced the computational burden and improved the accuracy. The Au–Cu phase diagrams calculated using this modified CVM could reproduce only some of the invariant reactions. It is expected that vibrational contributions and the atomic size effects can lead to improvement of the phase diagram, which are significant for the selected system. Further, since tetrahedron approximation contains only first neighbour pairs, this model cannot be used for the phases stabilized by II-n pair (interactions). So, other cluster approximations larger than tetrahedron cluster and smaller than TO clusters may have to be considered if the phases stabilized by second neighbour pairs have to be studied.

It is important to note that, the contributions from vibrational and electronic effects have been included through the temperature dependence of the CECs for a model system. Similarly, contributions from elastic interactions and volume changes as well as truncation of terms in cluster expansion have been included through composition dependence of the CECs. The specific values of the CECs for a real system are usually determined by optimizing different types of data available for the system. In recent times, the experimental data are also being supplemented by those obtained from the first principles computations. The accuracy of these results can be tested by computation of phase diagrams and thermophysical quantities as well as integrated intensity of diffuse scattering, which is related to the SRO present in the system. The results from these calculations can be combined with approximate solutions of the

equilibrium equations as well as the modified CVM suggested in this thesis. This can result in reduction of computational burden along with improved accuracy.