Chapter 3

Correlation between entropy and glass-forming ability of Cu-Zr and Cu-Zr-Al alloys

3.1 Introduction

Bulk glass formation in multicomponent metallic liquids is a complex process that is governed by several inter-related factors such as the topological and chemical short-range order, thermodynamic drive force, enthalpy of mixing etc. As the glass-forming ability (GFA) of these alloys depends on its composition, it is a challenging task to identify the compositions with high GFA. Three empirical rules proposed by Inoue [168] for achieving high GFA in metallic alloys guided the discovery of many new families of metallic glass-forming alloys. One of these rules emphasizes the requirement of atomic size difference greater than 12% between the atoms of constituent elements of the alloy. It suggests that the dense random-packing of different-sized atoms in the multicomponent liquid alloys and the resultant topological short-range order (TSRO) plays an important role in stabilizing the liquid against crystallization during the rapid cooling. The significance of the atomic-size difference for existence of a particular type of TSRO (typically icosahedral) in an alloy and its connection with GFA has been demonstrated in the three-dimensional

structural models [21, 23, 50, 169]. The packing of local structural units (coordination polyhedra) characterizing the TSRO and the subsequent evolution of medium-range order are the central features of these models. The packing fraction for the liquid mixtures of hard-spheres has also served as a useful parameter in the theoretical formulation proposed by Mansoori et al. [96] where the excess entropy and the Gibbs free energy have been derived in terms of the packing fraction. The total entropy considered in this formulation includes a term (also called a misfit term) for the effect of atom size mismatch-often referred to as the mismatch entropy [97] and is used for mapping the glass-forming composition region in multicomponent alloys [97, 170, 171]. However, these studies assumes a uniform value of the packing fraction equal to 0.64 for all the compositions.

In a recent investigation on Cu_xZr_{100-x} metallic glasses over a broad composition range $46 \leq x \leq 70$, it has been reported that the atomic packing efficiency strongly correlates with the GFA [52]. The availability of atomic packing efficiency data for Cu-Zr alloys over a wide composition range motivated us to use the theoretical model proposed by Mansoori et al [96] and a semi-empirical model [97] to obtain the excess entropy, mismatch entropy and; check whether these thermodynamic quantities are correlated with the GFA. Further, we have also carried out classical molecular dynamics simulations for $Cu_{50}Zr_{50-x}Al_x$, $(5 \leq x \leq 40)$ alloys to understand the effect of Al addition on the atomic packing efficiency, its correlation with the mismatch and excess entropies and; GFA.

3.2 Simulation details and Methods

Molecular dynamics simulations for $Cu_{50}Zr_{50-x}Al_x$ $(5 \leq x \leq 40)$ alloys have been carried out using the LAMMPS code [164]. An embedded-atom model (EAM) potential [169] is utilized. The simulation protocol for all the alloys is as follows: A total of 13500 atoms in a cubic simulation box subject to the periodic boundary conditions were considered. Verlet algorithm in the velocity form with a timestep of 2

fs was used to integrate the equations of motion. After obtaining an equilibrated liquid configuration at 2000 K by melting and homogenizing for 2 ns, the liquid was quenched to 300 K at a rate of 10^{11} K/s under zero pressure condition in NPT ensemble.

To obtain the atomic packing efficiency, it is necessary to obtain the details of three-dimensional local structure. For this production runs were performed for all the alloys at 300 K and 25 independent atomic configurations were recorded. These configurations were utilized to extract the inherent structures using energy minimization procedure employing the conjugate gradient algorithm to bring the system to a local minimum in the potential-energy surface. Voronoi analysis [94, 172] has been performed to obtain the information about the different polyhedra types present in the three-dimensional local structure of the system. n this method the neighborhood of an atom is characterized by a polyhedron with designated Voronoi index $\langle n_3, n_4, n_5, n_6, ..., n_i \rangle$ being the number of i-edged faces of the Voronoi polyhedron. Based on the definition of atomic-packing efficiency, the detailed geometrical information of different polyhedra types present in the system is analyzed to calculate the atomic packing efficiency which is defined as [27]

$$\xi = V_a / V_u \tag{3.1}$$

where, V_a is the volume of the atoms embedded inside a polyhedron and V_u the volume of the polyhedron. For further details the readers are referred to ref. [52].

3.3 Theoretical formulation and calculation

3.3.1 Excess Entropy

The Percus-Yevick equation for a hard-sphere mixture of m components has been solved by Lebowitz [173] and two forms of equation of state have been obtained as

given below [96]:

$$Z^c = [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi)](1 - \xi)^{-3} \tag{3.2}$$

$$Z^v = Z^c - 3\xi^2 y_2 (1 - \xi)^{-3} \tag{3.3}$$

where,

$$Z = PV/Nk_BT$$

$$\xi = \sum_{i=1}^{m} \xi_i$$

$$\xi_i = \frac{1}{6}\pi\rho d_i^3 x_i$$

$$\sum_{i=1}^{m} X_i = 1$$

ρ is the number density, d_i and x_i are the hard-sphere diameter and the mole fraction of the i^{th} component in the mixture. The superscripts v and c are assigned to the virial and compressibility forms respectively. y_1, y_2 and y_3 are the dimensionless parameters defined as [96]

$$y_1 = \sum_{j>i=1}^{m} \Delta_{ij}(d_i + d_j)(d_i d_j)^{-1/2} \tag{3.4}$$

$$y_2 = \sum_{j>i=1}^{m} \Delta_{ij} \sum_{k=1}^{m} \left(\frac{\xi_k}{\xi}\right)(d_i d_j)^{-1/2}/d_k \tag{3.5}$$

$$y_3 = \left[\sum_{k=1}^{m} \left(\frac{\xi_k}{\xi}\right)^{2/3} x_k^{1/3}\right]^3 \tag{3.6}$$

$$\Delta_{ij} = [(\xi_i\xi_j)^{1/2}][(d_i - d_j)^2/d_i d_j](x_i x_j)^{1/2} \tag{3.7}$$

Two results in Eqs. 3.2 and 3.3 have been combined by an averaging process to obtain the equation of state as [96]

$$\begin{aligned} Z^{cv} &= \frac{1}{3}(2z^c + Z^v) \\ &= [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - \xi^3 y_3](1 - \xi)^{-3} \end{aligned} \tag{3.8}$$

The excess entropy, S^E of the system over that of an ideal gas is defined as

$$-S^E/Nk_B = (F - F^{id})/Nk_BT - \ln Z \tag{3.9}$$

Using Eq. (3.8) for Z, the first term in Eq. (3.9) is given by

$$\begin{aligned}(F - F^{id})/Nk_BT = &-\frac{3}{2}(1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)(1 - \xi)^{-1} \\ &+ \frac{3}{2}\left(1 - y_1 - y_2 - \frac{1}{3}y_3\right)(1 - \xi)^{-2} + (y_3 - 1)\ln(1 - \xi)\end{aligned} \tag{3.10}$$

The change in the excess entropy due to the mixture of hard spheres at constant reduced densities is given as

$$\Delta S^E/Nk_B = S^E/Nk_B - (3 - 2\xi)(1 - \xi)^{-2} + 3 - \ln[(1 + \xi + \xi^2 - \xi^3)^{-3}] \tag{3.11}$$

3.3.2 Mismatch and Configurational Entropy

The effect of the atomic size mismatch in a mixture of hard-spheres on the entropy of the system has been included as a so-called misfit term [97] in the analytical approach given by Mansoori et al [96]. This term has been re-derived in terms of a parameter $\xi = 1/(1 - \xi)$ where, ξ is the packing fraction. The mismatch entropy (S_σ) is given by [97]

$$S_\sigma = k_B\left[\frac{3}{2}(\xi^2 - 1)y_1 + \frac{3}{2}(\xi - 1)^2 y_2 - \left(\frac{1}{2}(\xi - 1)(\xi - 3) + \ln\xi\right)(1 - y_3)\right] \tag{3.12}$$

where, k_B is the Boltzmann constant. The parameters y_1, y_2 and y_3 are dimensionless and are given as follows:

$$y_1 = \frac{1}{\sigma^3}\sum_{i>j=1}^{n}(d_i + d_j)(d_i - d_j)^2 C_i C_j \tag{3.13}$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2}\sum_{j\geq i=1}^{n} d_i d_j (d_i - d_j)^2 C_i C_j \tag{3.14}$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2} \tag{3.15}$$

$$\sigma^k = \sum_{i=1}^{n} C_i d_i^k, (k = 2, 3) \tag{3.16}$$

where, d_i and d_j are the atomic diameters of atom type i and j respectively. C_i and C_j are the concentrations of the atoms of type i and j respectively. The configurational entropy can be calculated by using the following equation

$$S_{config} = -R \sum_{i=1}^{n} x_i \ln C_i \tag{3.17}$$

where, x_i is the atomic percent and R is the universal gas constant.

3.4 Results and Discussion

To calculate the entropies for Cu_xZr_{100-x} alloys mentioned in Sec.3.3, the values of atomic packing efficiency ξ are obtained from ref. [52]. (ξ) in these alloys has been found to be correlated to the GFA and suggests highest GFA for two compositions with Cu 50% and 60% which is in very good agreement with experimental [70, 174] and simulation results [27]. The values of ξ have been utilized to calculate the excess entropy, change in the excess entropy, configurational entropy and mismatch entropy. Fig. 3.1 shows the variation of $-S^E/Nk_B$ and S_{config}/R. None of the two exhibits any definite correlation with the packing efficiency. On the other hand, the compositional dependence of S_σ/k_B and $\Delta S^E/Nk_B$ [Fig. (3.2)] is similar to that observed for ξ [52].

The peaks in S_σ/k_B correspond to the best glass-forming compositions. It suggests that higher is the mismatch entropy, higher will be the GFA. It can be observed that while $-S^E/Nk_B$ does not point out a specific glass-forming composition region, $\Delta S^E/Nk_B$ does indicate anti-correlation with S_σ/k_B and GFA. Therefore, the change in the excess entropy on mixing of the two atom types should be minimum to achieve higher GFA. Although the values of S_σ/k_B for most of the alloys reported in the literature are less than 1, $S_\sigma/k_B > 1$ obtained in the present work is within the range 0.001 to 5.7 [97].

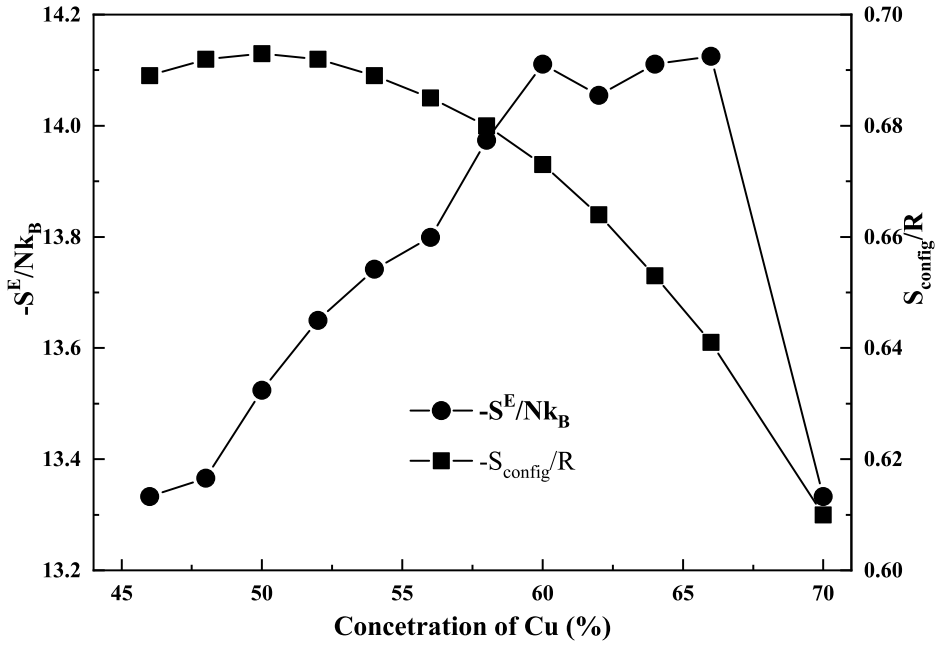

Figure 3.1: Compositional dependence of excess entropy and configuration entropy in Cu_xZr_{100-x} alloys

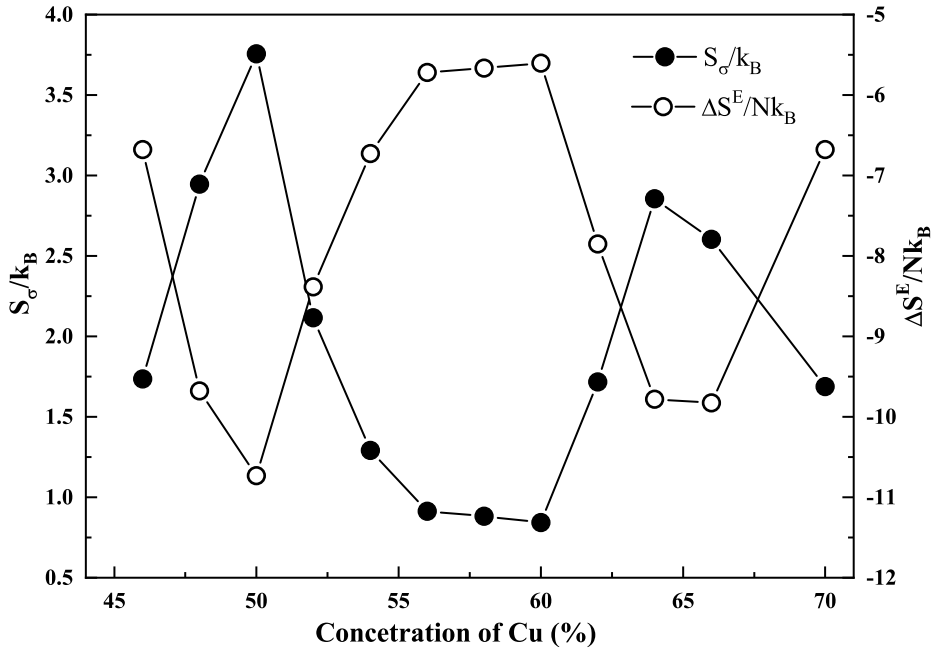

Figure 3.2: Mismatch entropy and the change in the excess entropy in Cu_xZr_{100-x} alloys

To obtain ξ for $Cu_{50}Zr_{50-x}Al_x$ alloys, the results of the Voronoi analysis were utilized to identify the dominant Cu-centered, Zr-centered and Al-centered polyhdedra types such as $< 0,0,12,0 >, < 0,2,8,2 >, < 02,8,6 >, < 0,1,10,5 >$ etc. Subsequently, ξ was obtained using a computational method using Eq. (3.1) As this ξ is a weighted average of the packing efficiencies for polytetrahedral clusters corresponding to various Voronoi polyhedra types, it would depend on which polyhedra types are considered. It might make its physical significance ambiguous. However as noted in ref. [52], insofar as it is ascertained that the majority of the polyhedra types (with reasonably well-defined geometry) are considered and the treatment is not biased by the choice of polyhedral types for all the alloy compositions, the values of ξ would still be physically meaningful as it gives a relative measure of packing efficiency for different alloy compositions.

The compositional dependence of the packing fraction in $Cu_{50}Zr_{50-x}Al_x$ is shown in Fig. 3.3. It can be observed that the variation in ξ for Cu-centered polyhedra is

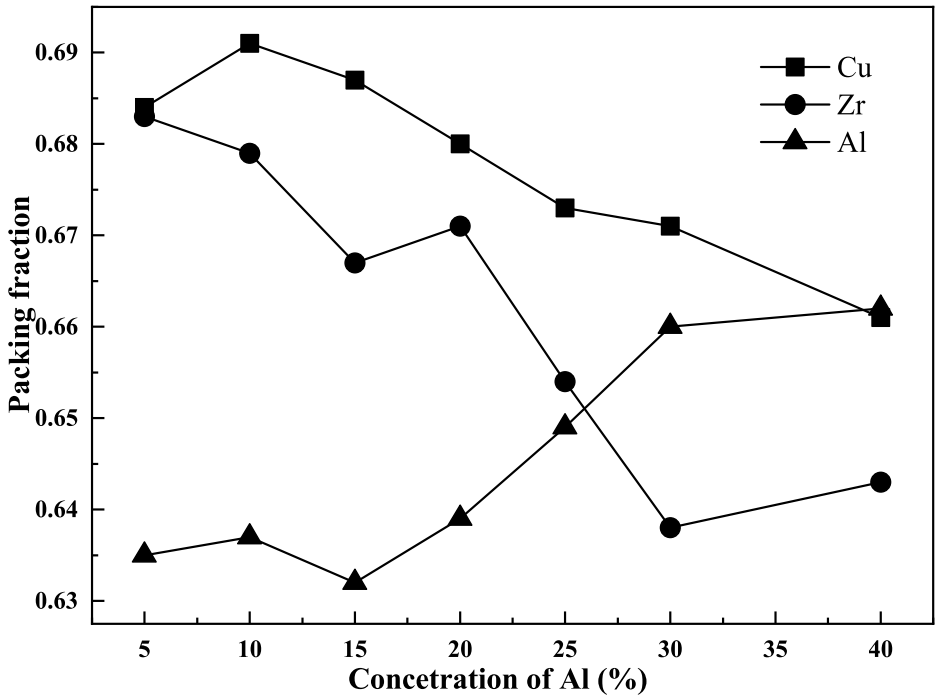

Figure 3.3: Atomic packing efficiency for Cu- centred, Zr-centred and Al-centered dominant polyhedra types in the $Cu_{50}Zr_{50-x}Al_x$ alloys

not as significant as the Zr-centered and Al-centered polyhedra. The decrease in ξ

indicates that the atoms are less densely packed in the various polyhedra i.e. the free volume is more. The converse is true for increasing ξ. To understand the packing of atoms in the polyhedra centered around the three constituent elements of the alloy, we should note that the hard-sphere diameters of Cu, Zr, Al are 2.56 Å, 3.32 Åand 2.86 Årespectively. It has been reported that the Zr-Cu, Zr-Al, Cu-Al interactions are the strongest and Cu-Al interatomic distance corresponding to the first neighbor shell is the shortest in these alloys [169]. It suggests that Cu and Al prefer each other as the nearest neighbors. Further, Al atom avoids another Al atoms in the first neighbor shell [169]. Thus, it can be primarily said that as the concentration of Al increases and that of Zr decreases, more and more number of Zr atoms will be replaced by Cu atoms in Al-centered polyhedra. With a view to the lesser size difference between Al and Cu atoms (0.3 Å) compared to that between Al and Zr atoms (0.46 Å) the increase in packing fraction for Al-centered polyhedra is discernible though this trend becomes dominant for Al % greater than 15. The variation in ξ with the composition does not pinpoint to the best glass-forming compositions as observed in case of the Cu-Zr alloys. However, the results of Cu-Zr alloys suggest that the best glass-forming compositions corresponds to the maximum value of ξ for all the atom types. In that sense, the values of ξ are highest in $Cu_{50}Zr_{50-x}Al_x$ alloys with Al concentration upto 10% and these compositions should possess highest GFA. It is also in agreement with the experimental and semi-empirical results [170, 171, 175].

$-S^E/Nk_B$ and S_{config}/R are plotted as a function of Al% in the alloy (Fig. 3.4). According to the results reported in the literature, the bulk glass-formation in Cu-Zr-Al alloys is favoured for the Al concentration range of 5 to 10% and for most of the compositions in this range, the values of S_{config}/R has been found to be between 0.8 and 1.0 [171]. Our results are in agreement with it and when correlated with the variation of $-S^E/Nk_B$ indicate that excess entropy should be higher for good GFA. The mismatch entropy is also found to be high for Al concentration of 5-10% (Fig.3.5).

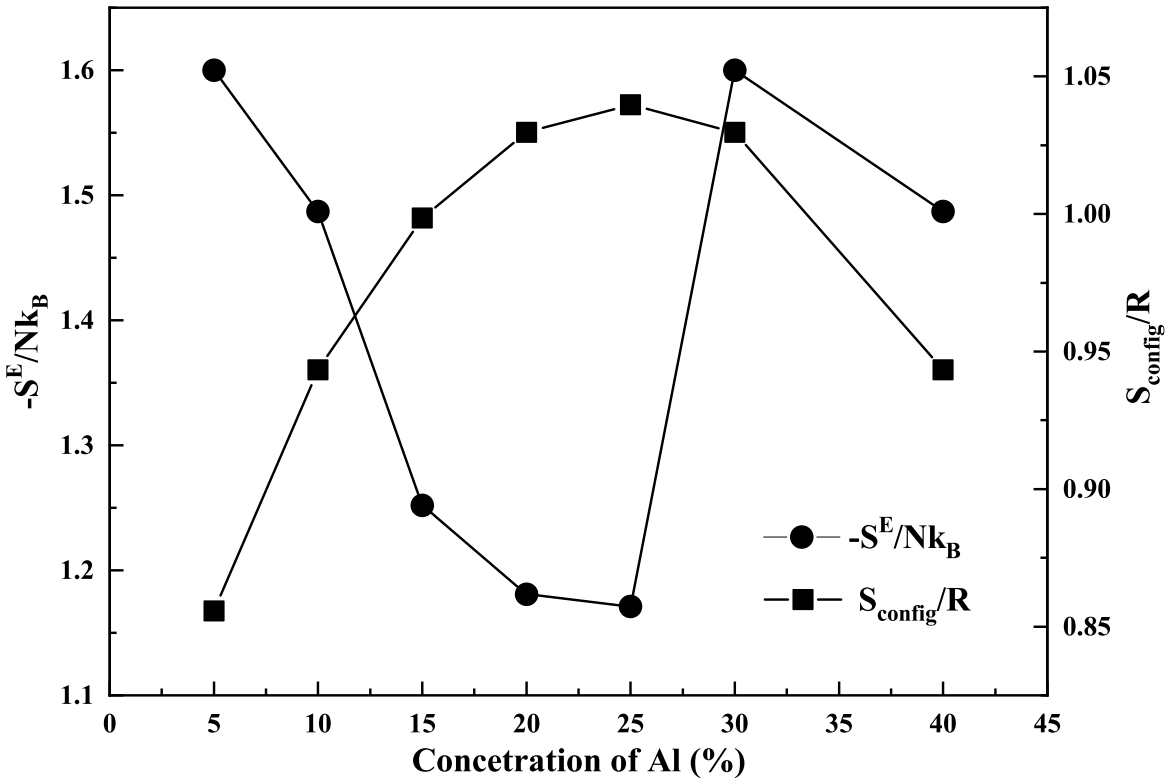

Figure 3.4: Compositional dependence of Excess entropy and configurational entropy in $Cu_{50}Zr_{50-x}Al_x$ alloys

The anti-correlation between $\Delta S^E/Nk_B$ and S_σ/k_B in the Al% range of 5-20% is similar to the case of Cu-Zr alloys and points to the minimization of $\Delta S^E/Nk_B$ and maximization of S_σ/k_B for better GFA. The compositional dependence of the three entropic terms and the change in the excess entropy (as shown in Figs. 3.4 and 3.5) for Al concentration greater than 25% suggests increase in the GFA. However, bulk glass-formation in Cu-Zr-Al alloys with Al % $>$ 20 is predicted to be less favourable as it would be thermodynamically unstable [169].

3.5 Conclusion

In the present work, the effect of topological packing on the excess entropy, the configurational entropy and the mismatch entropy in Cu-Zr and Cu-Zr-Al alloys have been investigated using an analytical approach based on the equation of state for the mixture of hard spheres. The essential input parameter for this approach,

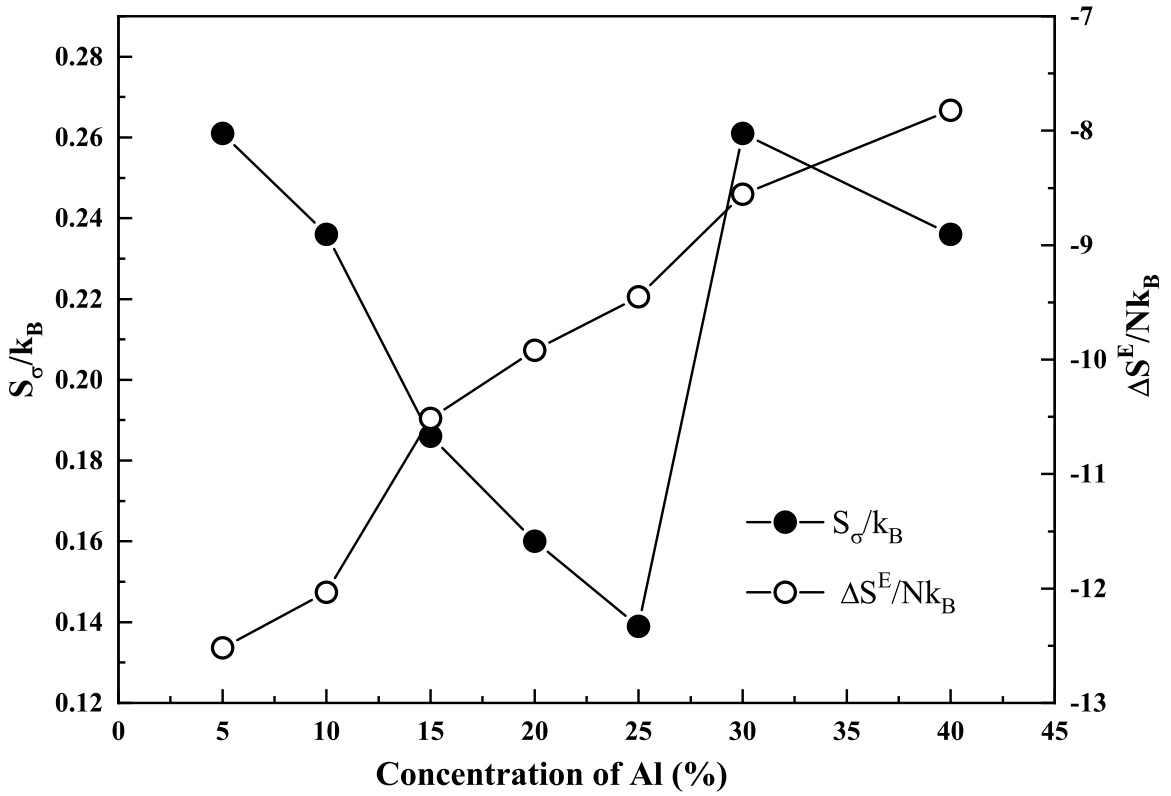

Figure 3.5: Mismatch entropy and the change in the excess entropy in $Cu_{50}Zr_{50-x}Al_x$ alloys

the atomic packing fraction, has been derived from the classical MD simulations and subsequent analysis of 3D atomic level structure.

As we have used composition dependent ξ, our results for the different entropic terms are much more realistic compared to similar studies on binary and ternary alloys where ξ is uniformly assumed to be equal to 0.64 for all the alloy compositions. The mismatch entropy and the change in the excess entropy of mixing show good correlation with the GFA in Cu-Zr alloy in a wide composition range. It suggests that the analytical approach based on hard sphere mixture model is appropriate for the description of the thermodynamic properties of Cu-Zr alloys. For Cu-Zr-Al alloys, however, this approach is effectively applicable in the limited composition range with Al $< 10\%$ due to dominant chemical-short range ordering on account of increasing Al%.

The composition dependence of the different entropic terms for both binary and ternary alloys, in general, indicates that the contributions of all the entropy terms

to the total entropy should be maximum for better GFA. It is consistent with the entropy maximization in process of glass formation.