Generic thermodynamic model for ternary solutions in various configurations

Kun Wang\textsuperscript{1}, Xingli Zou\textsuperscript{1}, Hongwei Cheng\textsuperscript{1}, Chonghe Li\textsuperscript{1}, Xionggang Lu\textsuperscript{1}

\textit{State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China}

Abstract: A generic thermodynamic model for ternary solutions has been derived regardless of whether the solutions contain short-ranger ordering configurations or how to select geometric interpolation methods. The model is formulated by extensions of the Modified Quasichemical Model in the Pair Approximation (MQMPA) into ternary solutions using an unbiased interpolation scheme which might be ergodic over all reported geometric solution models, such as Kohler, Toop, Muggianu and Chou models, with changeable interpolation parameters. The interpolation is practically conducted to express the pair interaction energies in ternary solutions by employing the counterparts in their constituent binary solutions. The pair energies could be expanded in terms of either the “coordination-equivalent” fractions (composition-dependent) or the pair fractions (configuration-dependent). The generic thermodynamic model is eventually validated by the real Li-Cu-Sn liquid to demonstrate its effectiveness and accuracy.

Keywords: Thermodynamics; Geometrical interpolation; Quasichemcial model; Short-range ordering

1. Introduction

Phase diagrams entangled with thermodynamics have provided strict laws and methods [1] to understand and investigate the interrelationship among compositions, properties, phase equilibria, microstructures, and process conditions. They are thus metaphorized as the “GPS” navigation system for materials exploration, design and preparation. Nowadays, the research paradigm for phase diagrams has been greatly shifted from pure experimental measurements to theoretical predictions incorporating key experimental validations, especially for multicomponent systems. This transformation indeed stimulates the boom of phase diagram investigations since from now on researchers unnecessarily conduct purely experimental determinations which are expensive and time-consuming.

The currently prevailing theoretical framework to predict phase diagrams is the so-called Calphad (Calculation of phase diagrams) method [2-4]. The Calphad method employs thermodynamic information from sub-binary and sub-ternary solutions to predict thermodynamic properties of multicomponent solutions and then calculate multicomponent phase diagrams. In the foreseeable future, the Calphad method is considered as the sole way to efficiently and speedily compute multicomponent multi-phase equilibria since thermodynamic information is experimentally or theoretically available for most binary solutions while atomistic simulations are hugely expensive.

\textsuperscript{*}Corresponding author.

E-mail address: wangkun0808@shu.edu.cn
in terms of computational resources. The accuracy of the Calphad method depends largely upon the reliability of thermodynamic models for multicomponent solutions. The reliability involves two aspects. Firstly, the thermodynamic model must be reliable enough for characterizing the Gibbs energy of each constituent binary solution no matter whether the solution configuration presents short-range ordering. Secondly, the thermodynamic model must have an unbiased geometrical interpolation scheme which is general, changeable and system-dependable to predict thermodynamic properties of multicomponent solutions from all the constituent binary solutions. However, it seems that the two aspects are not well respected in the Calphad community and commercial software except the CRCT group and Factsage software. The mathematical models based upon the Bragg-Williams or point approximations [5-6] are overused for almost all binary solutions regardless of their solution configurations. The Muggianu model is also widely abused to symmetrically interpolate thermodynamic properties of all sub-binaries into ternary and higher-order solutions regardless of the similarity and difference among components in chemistry. Although the thermodynamic model featuring the point approximation and Muggianu interpolation are simply taken and conveniently implemented into software, its deficiency is obvious for the incapable reproduction of experimental thermochemical data of binary solutions having strong short-range ordering and unreasonable prediction of thermodynamic properties of ternary solutions using the symmetrical interpolation.

The present paper is devoted to the development of a generic thermodynamic model for ternary liquid solutions. The model is developed on the basis of the MQMPA and an unbiased geometrical interpolation approach. The MQMPA [7] is widely used in the Factsage community to treat binary solutions no matter whether they appear short-range ordering. It is thought to be the right response to the first remark of the model reliability. The MQMPA is also extended by Pelton et.al [8] for use in multicomponent solutions by means of a combined Kohler-Toop formalism. However, it requires human interference to arrange components to three apexes in the Kohler-Toop triangle according to some empirical rules, such as chemical properties of components, locations of elements in a periodic table, or valences of compounds. The unbiased interpolation model never requires human interference to conduct the arrangement and will introduce interpolation coefficients which can be adjusted using experimental data from ternary solutions. If experimental data are unavailable for ternary solutions, these coefficients could be approximately calculated by the Chou model [9]. These interpolation coefficients are temperature dependent and within the range from 0 to 1. The codomain enables the unbiased interpolation model to be general and ergodic over all the Kohler [10], Toop [11], Muggianu [12] and Chou [9] schemes. Therefore, it has been used to successfully interpolate the pair energies in ternary solutions from sub-binaries in terms of the “coordination-equivalent” fractions or in terms of the pair fractions. This comes to the well response to the second remark of the model reliability. The generic thermodynamic model is thus derived to characterize ternary liquid solutions no matter if short-range ordering appears and without empirical selection of interpolation models. The Li-Cu-Sn liquid solution is selected to validate this generic model in section 4 since there exists strong short-range ordering in the Li-Sn subsystem, which are completely different from the Li-Cu and Cu-Sn subbinaries. In an accompanying paper [13], the MQMPA will be extended for use in multicomponent solutions by the general unbiased interpolation model.

2. The Model

For the A-B-C ternary solution, the generic thermodynamic model has the formalism as,
\[
G = (n_A g_A^0 + n_B g_B^0 + n_C g_C^0) + R T \left( n_A \ln(x_A) + n_B \ln(x_B) + n_C \ln(x_C) + n_{AA} \ln \left( \frac{x_A}{x_A} \right) + n_{BB} \ln \left( \frac{x_B}{x_B} \right) + n_{CC} \ln \left( \frac{x_C}{x_C} \right) + n_{AB} \ln \left( \frac{x_{AB}}{2x_A x_B} \right) + n_{AC} \ln \left( \frac{x_{AC}}{2x_A x_C} \right) + n_{BC} \ln \left( \frac{x_{BC}}{2x_B x_C} \right) \right) + \left( n_{AB} \Delta g_{AB} + n_{AC} \Delta g_{AC} + n_{BC} \Delta g_{BC} \right)
\]

where \( g_m, n_m, x_m \) and \( Y_m \) are the molar Gibbs energy, number of moles, mole fraction and “coordination-equivalent” fraction of component \( m \) (\( m = A, B, C \)), respectively. \( R \) and \( T \) refer to the gas constant and temperature in kelvin. \( \Delta g_{mn}, n_{mn} \) and \( X_{mn} \) refer to the nonconfigurational Gibbs energy change for the formation of one mole, the number of moles and the pair fraction of the \( m-n \) (equivalent to \( n-m \)) pair (\( m, n = A, B, C \)), respectively. In equation (1), the first term is the linear summation of Gibbs energies from pure components, the second term refers to the Gibbs energy contributed from the configurational entropy, and the last term stands for the summation of the nonconfigurational Gibss energy change for the formation of one mole of A-B, A-C and B-C pairs. The pair exchange reaction can be schematically shown as,

\[
(m - m) + (n - n) = 2(m - n) - 2\Delta g_{mn}
\]

and there are six kinds of pairs participating in three types of such reactions. All these represent the first-nearest-neighbor (FNN) pairs. In the binary \( i - j \) solution, \( \Delta g_{ij} \) can be expressed either in terms of the coordination-equivalent fraction as,

\[
\Delta g_{mn} = \Delta g_{mn}^0 + \sum_{i \neq j \neq 1} g_{ij}^0 x_{m}^i x_{m}^j
\]

or in terms of the pair fraction as,

\[
\Delta g_{mn} = \Delta g_{mn}^0 + \sum_{i \neq 1} g_{m}^{i0} X_{m}^i m_{m} + \sum_{j \neq 1} g_{n}^{0j} X_{n}^j n_{n}
\]

where \( \Delta g_{mn}^0, g_{m}^{i0}, g_{m}^{0j} \) and \( g_{n}^{0j} \) are the model parameters that can be functions of temperature.

The interrelations among those substance quantities in equation (1) can be defined as,

\[
X_m = \frac{n_m}{\sum_{m} n_m}
\]

\[
Z_m n_m = 2n_{mn} + \sum_{m \neq n} n_{mn}
\]

\[
X_{mn} = \frac{Z_m n_m}{\sum_{m} Z_m n_m} = \frac{Z_m n_m}{\sum_{m} Z_m n_m} = X_{mn} + \frac{1}{2} \sum_{m \neq n} X_{mn}
\]

where \( Z_m \) is the overall coordination number of component \( m \). For an earlier version of the MQM, \( Z_m \) is a constant value and independent of composition. However, it brought a number of drawbacks [7]. In the current MQM, \( Z_m \) has been permitted to vary with composition as follows,

\[
\frac{1}{Z_m} = \frac{1}{2n_{mn} + \sum_{m \neq n} n_{mn}} \left( \frac{Z_m n_m}{Z_m n_m} + \sum_{m \neq n} \frac{n_{mn}}{Z_m n_m} \right)
\]

where \( Z_{mn}^m \) and \( Z_{mn}^n \) are the values of \( Z_m \) when all the nearest neighbors of an \( m \) are \( m(s) \) and when all the nearest neighbors of an \( m \) are \( n(s) \), respectively. Substituting equation (9) into equation (6) gives,

\[
n_m = \frac{2n_{mn}}{Z_m n_m} + \sum_{m \neq n} \frac{n_{mn}}{Z_m n_m}
\]

which is the true mass balance between the overall composition of \( m \) and the number of pairs \( (m-m), (n-n) \) and \( (m-n) \)s in the ternary solution if these pairs are formally treated as the fractional associates of \( m_1/z_{mn}^m, m_1/z_{mn}^n \), \( n_1/z_{mn}^n, n_1/z_{mn}^m \) and \( m_1/z_{mn}^n, n_1/z_{mn}^m \). In this regard, equation (1) can be reshaped as,
\[ G = (n_{AA}g_{AA}^0 + n_{BB}g_{BB}^0 + n_{CC}g_{CC}^0) + RT \left( n_A \ln(x_A) + n_B \ln(x_B) + n_C \ln(x_C) + n_{AA} \ln\left(\frac{x_A}{y_A^A}\right) + n_{BB} \ln\left(\frac{x_B}{y_B^B}\right) + n_{CC} \ln\left(\frac{x_C}{y_C^C}\right) + n_{AB} \ln\left(\frac{x_{AB}}{2y_{AB}^A}\right) + n_{AC} \ln\left(\frac{x_{AC}}{2y_{AC}^A}\right) + n_{BC} \ln\left(\frac{x_{BC}}{2y_{BC}^C}\right) \right) + (n_{AB}(\Delta g_{AB} - \Delta g_{AB}^0) + n_{AC}(\Delta g_{AC} - \Delta g_{AC}^0) + n_{BC}(\Delta g_{BC} - \Delta g_{BC}^0)) \]  

(11)

where \( g_{mn}^0 \) and \( g_{mn}^0 \) are the standard Gibbs energies. They can be defined according to the mass-balance principle as,

\[ g_{mn}^0 = \frac{2}{z_{mm}} g_m^0 \]  

(12)

\[ g_{mn}^0 = \frac{1}{z_{mm}} g_m^0 + \frac{1}{z_{mn}} g_n^0 + \Delta g_{mn}^0 \]  

(13)

where \( \Delta g_{mn}^0 \) is the binary parameter from equation (3) or (4).

The coefficients of equations (3-4) are obtained by fitting the experimental data of thermochemistry and phase equilibria. Equations (3-4) only apply in the binary subsystems. It is now required to derive expressions of \( \Delta g_{mn}^0 \) in terms of either “coordination-equivalent” fractions or pair fractions within the ternary system for use in equation (11). This will be discussed thoroughly in the next section.

3. The interpolation schemes

At the beginning of this section, the binary \( \Delta g_{ij} \) expressions in terms of either “coordination-equivalent” fractions or pair fractions are generally interpolated by the unbiased geometrical solution model to characterize the \( i-j \) pair energy for use in the ternary solution. The general ternary \( \Delta g_{ij} \) expressions are then explored for some special conditions under which they are equivalent to those interpolated by the Kohler, Toop, Muggianu and Chou models. Last but not the least, pros and cons among all the interpolation models are fully discussed and the possible implementations into software are envisaged.
Fig. 1 Some geometrical interpolation methods: (a) generic model; (b) Kohler-Toop model; (c) Toop model; (d) Muggianu model

3.1 The unbiased interpolation

Suppose $\Delta g_{AB}$ in the A-B binary subsystem has been expressed as a polynomial in terms of the coordination-equivalent fractions $Y_A$ and $Y_B$ by equation (3). We now want to interpolate an $\Delta g_{AB}$ expression for use in the ternary A-B-C solution. With the unbiased model illustrated in Fig. 1a, $\Delta g_{AB}$ in the ternary solution is given by

$$\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j=1} q_{ij}^{AB} (Y_A + \delta_{AB} Y_C)^i (Y_B + (1 - \delta_{AB}) Y_C)^j) + \sum_{k=1}^\infty q_{ABC}^{jk} (Y_A + \delta_{AB} Y_C)^k (Y_B + (1 - \delta_{AB}) Y_C)^j$$

where the first term on the right-hand side of equation (14) is constant along the line $1-O$ in Fig. 1a and is equal to $\Delta g_{AB}$ in the A-B side at point 1 (where $Y_A + Y_B = 1$). This means the binary A-B interaction energy keep constant along the $1-O$ line. The position of “1” is chosen according to the interpolation parameter $\delta_{AB}$ can be function of temperature and its value is within the range from 0 to 1. The codomain of $\delta_{AB}$ enables the unbiased model to be ergodic over all the existed geometrical solution models. $\delta_{AB}$ can be calculated by the Chou model [9] and further fine-tuned by experimental ternary data. Similar schemes are used for $\delta_{BC}$ and $\delta_{CA}$. The second summation in equation (14) contains “ternary term” that all zero in the A-B binary, and which give the effect of the presence of component C upon the energy $\Delta g_{AB}$ of the A-B pair interactions. The empirical ternary coefficients $q_{ABC}^{jk}$ can also obtained by optimization of experimental ternary data. Actually, ternary coefficients could be very small if the interpolation parameters are appropriate enough.

Similar equations give $\Delta g_{CA}$ and $\Delta g_{BC}$ as,

$$\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j=1} q_{iCA}^{j} (Y_C + \delta_{CA} Y_B)^i (Y_A + \delta_{CA} Y_B)^j) + \sum_{k=1}^\infty q_{CA}^{jk} (Y_C + \delta_{CA} Y_B)^k (Y_A + \delta_{CA} Y_B)^j$$

$$\Delta g_{BC} = (\Delta g_{BC}^0 + \sum_{i+j=1} q_{iBC}^{j} (Y_B + \delta_{BC} Y_A)^i (Y_C + \delta_{BC} Y_A)^j) + \sum_{k=1}^\infty q_{BC}^{jk} (Y_B + \delta_{BC} Y_A)^k (Y_C + \delta_{BC} Y_A)^j$$
where the binary term in $\Delta g_{CA}$ and $\Delta g_{BC}$ is equal to its value at point “2” and “3”, respectively, in Fig.1a. The ternary coefficients $q_{CA(b)}^{ijk}$ and $q_{BC(c)}^{ijk}$ give effect of the presence of component B upon the pair energy $\Delta g_{CA}$ and of component A upon $\Delta g_{BC}$, respectively. It has been considered [14] that the ternary term in the equations is preferable to traditional expressions such as $Y_A^{(y)} Y_B^{(k)}$.

Suppose $\Delta g_{AB}$ in the A-B binary subsystem has a functional form as equation (4) expressed in pair fractions $X_{AA}$ and $X_{BB}$. We also want to interpolate an $\Delta g_{AB}$ expression for use in the ternary A-B-C solution. The $\Delta g_{AB}$ expression can be formulated as,

$$
\Delta g_{AB} = \Delta g_{AB}^0 + \sum_{(i+j) \geq 1} q_{AB}^{ij}(X_{AA} + \delta_{AB}^2X_{CC} + \delta_{AB}X_{AC})^j(X_{BB} + (1 - \delta_{AB})^2X_{CC} + (1 - \delta_{AB})X_{BC})^i
$$

$$+ \sum_{k \geq 0} q_{AB(c)}^{ik}(X_{AA} + \delta_{AB}^2X_{CC} + \delta_{AB}X_{AC})^i(X_{BB} + (1 - \delta_{AB})^2X_{CC} + (1 - \delta_{AB})X_{BC})^jY_k^c
$$

(17)

where $\Delta g_{AB}^0$ and $q_{AB}^{ij}$ are obtained by optimization of experimental binary data, and $q_{AB(c)}^{ik}$ is done by ternary data. The formalism is derived by considering the following facts. As $\Delta g_{AB}$, $\Delta g_{BC}$ and $\Delta g_{CA}$ become small, the solution approaches ideality, and $X_{AA} \rightarrow Y_A^2$, $X_{BB} \rightarrow Y_B^2$, $X_{CC} \rightarrow Y_C^2$, $X_{AB} \rightarrow 2Y_A Y_B$, $X_{AC} \rightarrow 2Y_A Y_C$ and $X_{BC} \rightarrow 2Y_B Y_C$. In this case, equation (17) approaches equation (14) since $X_{AA} + \delta_{AB}^2X_{CC} + \delta_{AB}X_{AC} \rightarrow (Y_A + \delta_{AB}Y_C)^2$ and $X_{BB} + (1 - \delta_{AB})^2X_{CC} + (1 - \delta_{AB})X_{AC} \rightarrow (1 - Y_A - \delta_{AB}Y_C)^2$ are realized.

Following the similar route, $\Delta g_{BC}$ and $\Delta g_{CA}$ can be derived as,

$$
\Delta g_{CA} = \Delta g_{CA}^0 + \sum_{(i+j) \geq 1} q_{CA}^{ij}(X_{CC} + \delta_{CA}^2X_{BB} + \delta_{CA}X_{BC})^j(X_{AA} + (1 - \delta_{CA})^2X_{BB} + (1 - \delta_{CA})X_{AB})^i
$$

$$+ \sum_{k \geq 0} q_{CA(b)}^{ik}(X_{CC} + \delta_{CA}^2X_{BB} + \delta_{CA}X_{BC})^i(X_{AA} + (1 - \delta_{CA})^2X_{BB} + (1 - \delta_{CA})X_{AB})^jY_k^b
$$

(18)

$$
\Delta g_{BC} = \Delta g_{BC}^0 + \sum_{(i+j) \geq 1} q_{BC}^{ij}(X_{BB} + \delta_{BC}^2X_{AA} + \delta_{BC}X_{AB})^j(X_{CC} + (1 - \delta_{BC})^2X_{AA} + (1 - \delta_{BC})X_{AC})^i
$$

$$+ \sum_{k \geq 0} q_{BC(c)}^{ik}(X_{BB} + \delta_{BC}^2X_{AA} + \delta_{BC}X_{AB})^i(X_{CC} + (1 - \delta_{BC})^2X_{AA} + (1 - \delta_{BC})X_{AC})^jY_k^c
$$

(19)

where equations (18-19) approach equations (15-16), respectively, since $X_{BB} + \delta_{BC}^2X_{AA} + \delta_{BC}X_{AB} \rightarrow (Y_B + \delta_{BC}Y_A)^2$ along with $X_{CC} + (1 - \delta_{BC})^2X_{AA} + (1 - \delta_{BC})X_{AC} \rightarrow (Y_C - \delta_{BC}Y_B)^2$ , and $X_{CC} + \delta_{CA}^2X_{BB} + \delta_{CA}X_{BC} \rightarrow (Y_C + \delta_{CA}Y_B)^2$ together with $X_{AA} + (1 - \delta_{CA})^2X_{BB} + (1 - \delta_{CA})X_{AB} \rightarrow (1 - Y_C - \delta_{CA}Y_B)^2$ are envisaged.

From equations (14) and (17), it can be seen [8] that in the ternary terms the factor $Y_C$ is equal to $X_{CC} + (X_{CA} + X_{BC})/2$ as referred to equation (8). In principle, the effect of these three terms upon $\Delta g_{AB}$ could easily be represented by three independent ternary coefficients. However, it may be not necessary to have this additional complexity. The similar reason is for keeping the factor $Y_A$ in equations (16, 19) and $Y_B$ in equations (15, 18).

### 3.2 The Kohler interpolation

As stated in aforementioned sections, the unbiased interpolation model might be ergodic over all reported geometric solution models when the interpolation parameter $\delta_{AB}$ is defined as some special values. For the Kohler interpolation scheme $\delta_{AB} = Y_A/(Y_A + Y_B)$ can be employed to realize such interpolation. Substituting it into equation (14) gives the $\Delta g_{AB}$ expression in the coordination-equivalent fractions as,
\[ \Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{i+j}^{AB} \left( \frac{Y_A}{Y_A+Y_B} \right)^i \left( \frac{Y_B}{Y_A+Y_B} \right)^j) + \sum_{m \geq 1} q_{AB(C)}^{jm} \left( \frac{Y_A}{Y_A+Y_B+C} \right)^i \left( \frac{Y_B}{Y_A+Y_B+C} \right)^j Y_C^m \]  

(20)

where the first term on the right-hand side of equation (20) is constant along the line 1-C in Fig.1b and is equal to \( \Delta g_{AB} \) in the binary at point “1” with the variables limiting to \( Y_A+Y_B=1 \). This means the binary A-B pair interaction energy is constant at a constant \( Y_A/Y_B \) ratio. The second term is regarding the ternary interaction energies which have already been well explained below equation (14).

If the Kohler model is also used for the interpolations in \( \Delta g_{CA} \) and \( \Delta g_{BC} \), \( \delta_{CA} = Y_C/(Y_C + Y_A) \) and \( \delta_{BC} = Y_B/(Y_B + Y_C) \) can be taken into equations (15-16), respectively, to give them as,

\[ \Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{i+j}^{CA} \left( \frac{Y_C}{Y_C+Y_A} \right)^i \left( \frac{Y_A}{Y_C+Y_A} \right)^j) + \sum_{m \geq 1} q_{CA(C)}^{jm} \left( \frac{Y_C}{Y_C+Y_A} \right)^i \left( \frac{Y_A}{Y_C+Y_A} \right)^j Y_A^m \]  

(21)

\[ \Delta g_{BC} = (\Delta g_{BC}^0 + \sum_{i+j \geq 1} q_{i+j}^{BC} \left( \frac{Y_B}{Y_B+Y_C} \right)^i \left( \frac{Y_C}{Y_B+Y_C} \right)^j) + \sum_{m \geq 1} q_{BC(C)}^{jm} \left( \frac{Y_B}{Y_B+Y_C} \right)^i \left( \frac{Y_C}{Y_B+Y_C} \right)^j Y_B^m \]  

(22)

where the binary term in \( \Delta g_{CA} \) and \( \Delta g_{BC} \) is constant along the line B-2 and C-3 with constant \( Y_C/(Y_C + Y_A) \) and \( Y_B/(Y_B + Y_C) \) ratio and is equal to its value at point “2” and “3” with the variable limiting to \( Y_C+Y_A=1 \) and \( Y_B+Y_C=1 \) in Fig.1(b), respectively. The second terms in equations (22-23) represent ternary interaction energies as explained detailedly underneath equations (15-16).

Suppose binary \( \Delta g_{AB}, \Delta g_{CA} \) and \( \Delta g_{BC} \) have been written as equation (4), then their expressions for use in the ternary solution are proposed,

\[ \Delta g_{AB} = \Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{i+j}^{AB} \left( \frac{X_A}{X_A+X_B+X_C} \right)^i \left( \frac{X_B}{X_A+X_B+X_C} \right)^j \]  

\[ + \sum_{k \geq 1} q_{AB(C)}^{jk} \left( \frac{X_A}{X_A+X_B+X_C} \right)^i \left( \frac{X_B}{X_A+X_B+X_C} \right)^j Y_C^k \]  

(23)

\[ \Delta g_{CA} = \left( \Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{i+j}^{CA} \left( \frac{X_A}{X_A+X_B+X_C} \right)^i \left( \frac{X_B}{X_A+X_B+X_C} \right)^j \right) \]  

\[ + \sum_{k \geq 1} q_{CA(C)}^{jm} \left( \frac{X_A}{X_A+X_B+X_C} \right)^i \left( \frac{X_B}{X_A+X_B+X_C} \right)^j Y_C^k \]  

(24)

\[ \Delta g_{BC} = \left( \Delta g_{BC}^0 + \sum_{i+j \geq 1} q_{i+j}^{BC} \left( \frac{X_B}{X_B+X_C+X_A} \right)^i \left( \frac{X_C}{X_B+X_C+X_A} \right)^j \right) \]  

\[ + \sum_{k \geq 1} q_{BC(C)}^{jk} \left( \frac{X_B}{X_B+X_C+X_A} \right)^i \left( \frac{X_C}{X_B+X_C+X_A} \right)^j Y_A^k \]  

(25)

by also considering those facts as stated below equation (17). Since the three components are treated in the same fashion, the interpolation scheme is the so-called symmetric Kohler model.

For certain systems, however, in which one component is chemically different from the other two (e.g., LiF-NaF-BeF₃, SiO₂-CaO-MgO, S-Fe-Cu, etc.), it is more appropriate to use the “asymmetric” Toop model illustrated in Fig.1c, where A is selected as the asymmetric component.
3.3 The Toop interpolation

For the Toop interpolation scheme $\delta_{AB} = 0$ can be used in the unbiased model to realize such interpolation. Substituting it into equation (14) gives the $\Delta g_{AB}$ expression in the polynomial of coordination-equivalent fractions as,

$$\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j \geq 2} q_{AB}^{ij} (Y_A + Y_B)^i (Y_C)^j) + \sum_{k \geq 1} q_{AB(C)}^{ijk} (Y_A + Y_B)^i (Y_C)^j (Y_C)^m$$

(26)

where the first term on the right-hand side of equation (26) is constant along the line “1-2” in Fig.1c and is equal to $\Delta g_{AB}$ in the binary at point “1”. The second term also represents the ternary interaction energy as detailedly explained below equation (14). A similar expression for $\Delta g_{CA}$ can be written as,

$$\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij} (Y_C + Y_B)^i (Y_A)^j) + \sum_{k \geq 1} q_{CA(B)}^{ijk} (Y_C + Y_B)^i (Y_A)^j (Y_B)^m$$

(27)

by taking $\delta_{CA} = 1$ into equation (15). Actually, the binary interaction energies in equations (26-27) are equivalent to each other since they are assumed to be constant at constant $Y_A$. $\Delta g_{BC}$ has the same interpolating formalism as equation (22) by substituting $\delta_{BC} = Y_B/(Y_B + Y_C)$ into equation (16).

Suppose the binary $\Delta g_{AB}$ and $\Delta g_{CA}$ are expressed in the polynomial of pair fractions, their formalism for use in the ternary solution can be given as,

$$\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij} X_{AA}^i (X_{BB} + X_{CC} + X_{BC})^j) + \sum_{k \geq 1} q_{AB(C)}^{ijk} X_{AA}^i (X_{BB} + X_{CC} + X_{BC})^j (Y_C)^k$$

(28)

$$\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij} (X_{BB} + X_{CC} + X_{BC})^i X_{AA}^j) + \sum_{k \geq 1} q_{CA(B)}^{ijk} (X_{BB} + X_{CC} + X_{BC})^i X_{AA}^j (Y_B)^k$$

(29)

by taking account of those facts as stated below equation (17). The expression for $\Delta g_{BC}$ has the same form as equation (25). In the limit of ideality, equations (28-29) reduce to equation (26-27), respectively, while equation (25) transforms to equation (22), which, in the limit, becomes the well-known Kohler-Toop model for asymmetrical ternary systems.

3.4 The Muggianu interpolation

For the Muggianu interpolation scheme $\delta_{AB} = 1/2$ can be used in the unbiased model to achieve such interpolation. Taking it into equation (17) gives,

$$\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij} (Y_A + \frac{1}{2} Y_B)^i (Y_B + \frac{1}{2} Y_C)^j) + \sum_{k \geq 1} q_{AB(C)}^{ijk} (Y_A + \frac{1}{2} Y_C)^j (Y_B + \frac{1}{2} Y_C)^i (Y_C)^k$$

(30)

where the first term on the right-hand side of equation (30) is constant along the line “1-O” in Fig.1d and is equal to $\Delta g_{AB}$ in the binary at point “1". This indicates the binary A-B pair interaction energy is constant when $Y_A - Y_B$ is constant. The second term is regarding the ternary interaction energy similar to the aforementioned statement below equation (14). Substituting $\delta_{CA} = 1/2$ and $\delta_{BC} = 1/2$ into equations (15-16) gives,

$$\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij} (Y_C + \frac{1}{2} Y_B)^i (Y_A + \frac{1}{2} Y_B)^j) + \sum_{k \geq 1} q_{CA(B)}^{ijk} (Y_C + \frac{1}{2} Y_B)^j (Y_A + \frac{1}{2} Y_B)^i (Y_B)^k$$

(31)
\[ \Delta g_{BC} = (\Delta g_{BC}^0 + \sum_{(i+j) \geq 1} q_{BC}^{ij}(Y_B + \frac{1}{2} Y_A)(Y_C + \frac{1}{2} Y_A)^j) + \sum_{i \geq 1} q_{BC(A)}^{i+j}(Y_B + \frac{1}{2} Y_A)^i(Y_C + \frac{1}{2} Y_A)^j Y_A^k \]  

(32)

where the first term on the right-hand side of equations (31-32) is constant along the line “2-O” and “3-O” in Fig.1d and is equal to \( \Delta g_{CA} \) and \( \Delta g_{BC} \) in the binary at point “2” and “3”, respectively. This indicates the binary C-A and B-C pair interaction energies are constant when \( Y_C - Y_A \) and \( Y_B - Y_C \) are constant. The second summations refer to the ternary interaction energies.

Suppose all the binary pair interaction energies are formulated in the polynomial of pair fractions, their formalism for use in the ternary solution can be given as,

\[ \Delta g_{AB} = \Delta g_{AB}^0 + \sum_{(i+j) \geq 1} q_{AB}^{ij}(X_{AA} + \frac{1}{4} X_{CC} + \frac{1}{2} X_{AC})^i(X_{BB} + \frac{1}{4} X_{CC} + \frac{1}{2} X_{BC})^j \]

\[ + \sum_{i \geq 1} q_{AB(C)}^{i+j}(X_{AA} + \frac{1}{4} X_{CC} + \frac{1}{2} X_{AC})^i(X_{BB} + \frac{1}{4} X_{CC} + \frac{1}{2} X_{BC})^j Y_C^k \]  

(33)

\[ \Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{(i+j) \geq 1} q_{CA}^{ij}(X_{CC} + \frac{1}{4} X_{BB} + \frac{1}{2} X_{BC})^i(X_{AA} + \frac{1}{4} X_{BB} + \frac{1}{2} X_{AB})^j) \]

\[ + \sum_{i \geq 1} q_{CA(B)}^{i+j}(X_{CC} + \frac{1}{4} X_{BB} + \frac{1}{2} X_{BC})^i(X_{AA} + \frac{1}{4} X_{BB} + \frac{1}{2} X_{AB})^j Y_B^k \]  

(34)

\[ \Delta g_{BC} = (\Delta g_{BC}^0 + \sum_{(i+j) \geq 1} q_{BC}^{ij}(X_{BB} + \frac{1}{4} X_{AA} + \frac{1}{2} X_{AB})^i(X_{CC} + \frac{1}{4} X_{AA} + \frac{1}{2} X_{CA})^j) \]

\[ + \sum_{i \geq 1} q_{BC(A)}^{i+j}(X_{BB} + \frac{1}{4} X_{AA} + \frac{1}{2} X_{AB})^i(X_{CC} + \frac{1}{4} X_{AA} + \frac{1}{2} X_{CA})^j Y_A^k \]  

(35)

by taking into account those facts as stated below equation (17). In the limit of ideality, equations (33-35) reduce to equations (30-32), respectively, which, in the limit, becomes the well-known Muggianu model for symmetrical ternary systems.

It has been shown that, for systems with large composition-dependent deviations from ideality, the choice of a symmetric or asymmetric model can often give very different results. An incorrect choice can even give rise to spurious miscibility gaps.

### 3.5 Determining interpolation parameters

With the changeable interpolation parameters ranging from 0 to 1, the unbiased interpolation model can be ergodic over all reported geometrical solution model. In addition, it can also be applied to a ternary solution in case that all reported interpolation models are not appropriate to describe its thermodynamic properties. However, once experimental ternary data are unavailable for the ternary solution, it is a great challenge to use the unbiased model to perform accurate predictions since we have no idea on how to determine the interpolation parameters. Thanks to the Chou model [9], the challenge has been well overcome, and the interpolation parameters can now be quite reliably obtained by using the so-called “deviation sum of squares”.

The “deviation sum of squares” is defined as,

\[ \eta_A = \int_0^1 (\Delta G_{AB} - \Delta G_{AC})^2 d n_A \]  

(36)

\[ \eta_B = \int_0^1 (\Delta G_{BA} - \Delta G_{BC})^2 d n_B \]  

(37)

\[ \eta_C = \int_0^1 (\Delta G_{CA} - \Delta G_{CB})^2 d n_C \]  

(38)
where $\Delta G_{AB}$ (or $\Delta G_{BA}$), $\Delta G_{AC}$ (or $\Delta G_{CA}$) and $\Delta G_{BC}$ (or $\Delta G_{CB}$) represent the Gibbs energy of mixing for binary solution A-B, A-C and B-C, respectively. $n_A$, $n_B$ and $n_C$ refer to the number of moles of component A in the binary solution A-B and A-C, of component B in the binary solution B-C and B-A, and of component C in the binary solution C-A and C-B, respectively.

Clearly, if the component B is similar to the component C thermodynamically, the value of $\eta_A$ is supposed to be zero otherwise it is expected to be a positive nonzero. Similar scenario is found for $\eta_B$ and $\eta_C$. The interpolation parameters can be obtained via equations (39-41),

$$\delta_{AB}^C = \frac{\eta_A}{\eta_A + \eta_B} \quad (39)$$

$$\delta_{BC}^A = \frac{\eta_B}{\eta_B + \eta_C} \quad (40)$$

$$\delta_{CA}^B = \frac{\eta_C}{\eta_C + \eta_A} \quad (41)$$

where $\delta$ is also termed as “similarity coefficient” [9]. This indicates that the similarity between the component C and the component B causes $\eta_A = 0$ and thus $\delta_{AB} = 0$, and the similarity between the component C and component A leads to $\eta_B = 0$ and thus $\delta_{AB} = 1$. Therefore, from the $\delta_{AB}$ value one can judge if the component C is more familiar to the component A or B. Similar situations can be found for $\delta_{BC}$ and $\delta_{CA}$.

In order to obtain the interpolation parameters, the $\eta$ values have to be firstly calculated using equations (36-39). Since $\Delta G_{ij}$ is now expressed in the quasichemical formalism, it is infeasible to analytically solve the integral due to the existing internal variables (pair fractions). In binary systems, the pair fractions are initially obtained by minimizing the Gibbs energy at required compositions, temperature and pressure, and then they are taken into the Gibbs energy expression. However, it is not sure if the pair fractions could be taken into equation (36-38) to obtain the minimal $\eta$ values. This uncertainty could be well clarified by considering the following expressions. Let $F(n_A, n_{AB}, n_{AC})$ be the integrand as,

$$F(n_A, n_{AB}, n_{AC}) = [\Delta G_{AB}(n_A, n_{AB}) - \Delta G_{AC}(n_A, n_{AC})]^2 \quad (42)$$

and $\eta$ will have the expression as,

$$\eta_I = \int_0^1 F(n_A, n_{AB}, n_{AC}) \, dn_A \quad (43)$$

Minimizing $\eta$ at fixed composition, the following equation yields,

$$\frac{\partial \eta_I}{\partial n_{AB}} = \int_0^1 g(n_{AB}, n_{AC}) \left( \frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AB}} \right) \, dn_A + \left( \frac{\partial g}{\partial n_{AB}} - \frac{\partial f}{\partial n_{AB}} \right) F(n_A, n_{AB}, n_{AC}) = 0 \quad (44)$$

$$\frac{\partial \eta_I}{\partial n_{AC}} = \int_0^1 g(n_{AB}, n_{AC}) \left( \frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AC}} \right) \, dn_A + \left( \frac{\partial g}{\partial n_{AC}} - \frac{\partial f}{\partial n_{AC}} \right) F(n_A, n_{AB}, n_{AC}) = 0 \quad (45)$$

where the second terms on the right-hand side are always zero. This indicates that the following equations must result,

$$\frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AB}} = 2[\Delta G_{AB}(n_A, n_{AB}) - \Delta G_{AC}(n_A, n_{AC})] \left[ \frac{\partial \Delta G_{AB}(n_{AB}, n_{AC})}{\partial n_{AB}} \right] = 0 \quad (46)$$

$$\frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AC}} = 2[\Delta G_{AC}(n_A, n_{AC}) - \Delta G_{AB}(n_A, n_{AB})] \left[ \frac{\partial \Delta G_{AC}(n_{AC}, n_{AB})}{\partial n_{AC}} \right] = 0 \quad (47)$$

since $n_A$ is an arbitrary value ranging from 0 to 1 in equations (46-47). In general, the deviation between $\Delta G_{AB}$ and $\Delta G_{AC}$ should not always disappear, and the following expressions are thus generated,
It is evident that equations (48-49) are the right minimization condition to obtain the equilibrium pair fractions for the binary A-B and A-C systems. This indicates that the $\eta$ values could be calculated by just taking the equilibrium pair fractions obtained from binary subsystems into the integral equations. The integral equations, such as $\eta_1$, can be approximated by its closely related sum,

$$\eta_1 = \int_0^1 (\Delta G_{AB} - \Delta G_{AC})^2 d\bar{n}_A \approx \sum_{i=1}^{1/\Delta h - 1} \Delta h [\Delta G_{AB}(i\Delta h, \bar{n}_{AB}) - \Delta G_{AC}(i\Delta h, \bar{n}_{AC})]^2$$

where $\bar{n}_{AB}$ and $\bar{n}_{AC}$ are the equilibrium number of moles of pairs A-B and A-C in the binary A-B and A-C subsystems at compositions $i\Delta h$, respectively. After numerous tests, it is found that $\Delta h$ equal to 0.1 could generally yield good approximations. The similar approximations could be used for calculating $\eta_B$ and $\eta_C$. All three interpolation parameters are thus determined. It is obvious that $\delta$ can be function of temperature since $\eta$ may be changeable against temperature. Like other thermodynamic parameters, such as Gibbs energy of pure components, interaction parameters between components, magnetic parameters, etc., the interpolation parameters can also be placed in the thermodynamic database so that the current algorithm prevailing used in thermodynamic software is convenient to implement the present thermodynamic model.

4 Case study

In this section, thermodynamic properties of the Li-Cu-Sn liquid solution are investigated using the generic thermodynamic model which is developed based upon the MQMPA and the unbiased interpolation model. We firstly performed thermodynamic optimizations of the Li-Cu, Li-Sn and Cu-Sn binary liquids with the pair interaction energies expressed in the polynomial of the pair fractions. The optimized model parameters are then taken into the generic thermodynamic model to demonstrate various predicted results using different interpolation parameters ($\delta_{CuLi}^{Sn}$, $\delta_{SnLi}^{Cu}$ and $\delta_{CuSn}^{Li}$). Actually, the unbiased interpolation model has evolved into the Kohler, Toop, Muggianu and Chou methods. The optimal interpolation parameters are eventually obtained to better reproduce all experimental thermodynamic data for the Li-Cu-Sn ternary liquid solution.

According to equation (4), the three pair interaction energies in their binary solutions can be derived as,

$$\Delta g_{LiCu} = \Delta g_{LiCu}^0 + q_{LiCu}^{10}X_{LiLi} + q_{LiCu}^{01}X_{CuCu}$$
$$\Delta g_{CuSn} = \Delta g_{CuSn}^0 + q_{CuSn}^{10}X_{CuCu} + q_{CuSn}^{01}X_{SnSn}$$
$$\Delta g_{SnLi} = \Delta g_{SnLi}^0 + q_{SnLi}^{10}X_{SnSn}$$

where the optimized model parameters are listed in Table 1 along with the defined coordination numbers. Thermodynamic properties of all the binary liquids can thus be calculated based upon the model parameters and coordination numbers. Fig.1 shows the calculated enthalpy of mixing in the Li-Sn system along with the experimental data [15]. The calculated curve shows a deep minimum located at the Li$_4$Sn position, indicating Li and Sn atoms have strong short-range ordering in their liquid alloy. The ratio $Z_{LiSn}^{Sn}/Z_{LiSn}^{Li} = 4$ is thus defined to address the composition of maximum short-range ordering. The calculated enthalpy of mixing in the Li-Cu and Cu-Sn
system along with experimental data [15-17] is respectively presented in Fig.2 and Fig.3 where both of the two curves display similar “S” shape profiles. The two liquids are close to regular solutions with atoms approximately being ideally mixing. The same coordination numbers are thus defined for all the atoms.

| Systems | Li-Sn | Cu-Sn | Li-Cu |
|---------|-------|-------|-------|
| Coordination numbers | $Z_{LiSn}^L = 1.5$ | $Z_{CuSn}^L = 6$ | $Z_{LiCu}^L = 6$ | $Z_{LiSn}^S = 6$ | $Z_{CuSn}^S = 6$ | $Z_{LiCu}^S = 6$ |
| Model parameters | $\Delta g_{LiCu}^{0} = -65000$ | $\Delta g_{CuSn}^{0} = 356.9 - 0.8504T$ | $\Delta g_{LiCu}^{0} = 9834.27 - 8T$ | $q_{SnLi}^{10} = -17000$ | $q_{CuSn}^{10} = -14527.57 + 0.1230T$ | $q_{LiCu}^{10} = -2713.6 + 1.07T$ | $q_{LiSn}^{10} = -146.77 - 3.3516T$ | $q_{CuLi}^{10} = -16703.2$ |

According to equations (14-16), the three pair interaction energies in the ternary solutions can be expressed as

$$\Delta g_{LiCu} = \Delta g_{LiCu}^{0} + q_{LiCu}^{10} \left( X_{LiLi} + \delta_{LiCu}^{Sn} X_{SnSn} + \delta_{LiCu}^{Si} X_{LiSn} \right) + q_{LiCu}^{01} \left( X_{CuCu} + (1 - \delta_{LiCu}^{Sn}) X_{SnSn} \right) + \left( 1 - \delta_{LiCu}^{Si} \right) X_{LiSn} \quad (54)$$

$$\Delta g_{CuSn} = \Delta g_{CuSn}^{0} + q_{CuSn}^{10} \left( X_{CuCu} + \delta_{CuSn}^{Li} X_{LiLi} + \delta_{CuSn}^{Si} X_{CuLi} \right) + q_{CuSn}^{01} \left( X_{SnSn} + (1 - \delta_{CuSn}^{Li}) X_{LiLi} + (1 - \delta_{CuSn}^{Si}) X_{CuLi} \right) \quad (55)$$

$$\Delta g_{SnLi} = \Delta g_{SnLi}^{0} + q_{SnLi}^{10} \left( X_{SnSn} + \delta_{SnLi}^{Cu} X_{CuCu} + \delta_{SnLi}^{Cu} X_{CuLi} \right) \quad (56)$$

where the model parameters are the same as those in the binary expression and have already been listed in Table 1.

Based on the expressions and model parameters, one can predict thermodynamic properties of the Li-Cu-Sn ternary liquid. By varying the interpolation parameters, the unbiased interpolation scheme can be flexibly shifted among the Kohler, Toop, Muggianu and Chou methods to interpolate the ternary Gibbs energy from its subbinaries, and can thus render different predicted results. Fürtauer [15] has carefully measured the enthalpy of mixing in the Li-Cu-Sn liquid along various sections as Fig.4 shows. These experimental data are very useful to validate the predicted results from different interpolation models. Fig.5 displays the calculated and experimental enthalpy of mixing in the ternary liquid along five composition paths as marked in Fig.4. By employing $\delta_{LiCu}^{Sn} = Y_{Li}/(Y_{Li} + Y_{Cu})$, $\delta_{SnLi}^{Cu} = Y_{Sn}/(Y_{Sn} + Y_{Cu})$ and $\delta_{CuSn}^{Li} = Y_{Cu}/(Y_{Cu} + Y_{Sn})$, the unbiased interpolation scheme can be transformed to the symmetrical Kohler model. By using $\delta_{LiCu}^{Sn} = 1$, $\delta_{SnLi}^{Cu} = Y_{Sn}/(Y_{Li} + Y_{Sn})$ and $\delta_{CuSn}^{Li} = 0$, the unbiased interpolation scheme can be reduced to the asymmetrical Kohler-Toop model and hence Cu is chosen as the asymmetrical component. By assigning $\delta_{LiCu}^{Sn} = \delta_{SnLi}^{Cu} = \delta_{CuSn}^{Li} = 0.5$, the unbiased interpolation scheme can be changed to the symmetrical Muggianu model. By working out $\delta_{LiCu}^{sn} = 0.9989$, $\delta_{SnLi}^{Cu} = 0.4635$ and $\delta_{CuSn}^{Li} = 0.0012$ through equation (50), the unbiased interpolation scheme has now been shifted to the Chou model. By better reproducing the experimental data, $\delta_{LiCu}^{sn} = 0.5$, $\delta_{SnLi}^{Cu} = 0.9$ and $\delta_{CuSn}^{Li} = 0.1$ have been obtained and used in the present modeling within the framework of the unbiased interpolation scheme. Along composition paths (a), (b) and (c) in Fig.4, the calculated enthalpy of mixing is displayed in Fig.5 (a), Fig.5 (b) and Fig.5 (c), respectively. The curves are similar to that of the Li-Sn liquid where a deep minimum is observed. This is because Li was dropped into the Cu-Sn liquid. Along composition routes (d) and (e), the calculated enthalpy of mixing is shown in Fig.5 (d) and Fig.5 (e), respectively. The curves taken on an “S” shaped profile, which is similar to that in the Cu-Li and Cu-Sn liquids. This is because Cu was dropped into the Li-Sn liquid.
There existed similar analysis performed by Li et al. [18] who introduced the associate Li$_4$Sn species and employed the associate solution model to treat the Li-Sn liquid having strong short-range ordering, and used the substitutional solution model with the Redlich-Kister polynomials to thermodynamically describe the Cu-Sn and Li-Cu liquids. Li et al. [18] then calculated thermodynamic properties of the Li-Cu-Sn liquid without ternary interaction parameters and just employing the symmetric Muggianu model, the asymmetric Muggianu-Toop models and an interpolation model based on the calculation of the global Gibbs free energy minimum of the ternary system. However, a good reproduction of the experimental data could only be given by the global minimization which was not detaiely described in their work. We have tried to use their liquid model (Li, Li$_4$Sn, Sn, and Cu) and model parameters to reproduce their calculated results within the interpolation schemes of Muggianu and Muggianu-Toop. Large deviations appeared in the calculations. In particular, their liquid model cannot predict a potential liquid-liquid miscibility gap along the Cu-Li$_4$Sn direction. This is not abnormal [19] since Cu and Li$_4$Sn are randomly mixed in their liquid model. However, as shown in Fig. 5, excellent predictions can be achieved for the metastable liquid-liquid miscibility gap along the Cu-Li$_4$Sn direction by using the generic thermodynamic model. This is due to the fact that in the ternary liquid atom Li is strongly inclined to stay with atom Sn, which repulses atom Cu to form the liquid-liquid miscibility gap along the Cu-Li$_4$Sn direction. This fact can be well considered in the generic thermodynamic model since it has inherited the spirit of the MQMPA.

There are still many ternary solutions absent for experimental data. The generic thermodynamic model can also be used to credibly predict their thermodynamic properties by appropriately defining the interpolation parameters. The appropriate definition can be well addressed by the Chou model. Since one model has included the features of the MQMPA and all the interpolation models, it can be conveniently implemented into thermodynamic software to perform freedom choice of different interpolation schemes. Various predictions can be flexibly realized by just changing the interpolation parameters. The predictive deviation is thus manifested and one may clearly notice the predictive range using the generic thermodynamic model. Once experimental data are available, the modification of the interpolation parameters is solely required to have better thermodynamic simulations for the ternary solutions. It has been demonstrated to be more effective and powerful in the simulation of multicomponent solutions [10]. Although the model has been developed mainly for liquid solutions, it can be certainly applied to treat solid solutions where all coordination numbers must be the same.
Fig. 1 Calculated enthalpy of mixing in the Li-Sn liquid along with experimental data [15, 16].

Fig. 2 Calculated enthalpy of mixing in the Li-Cu liquid along with experimental data [15-16].
Fig. 3 Calculated enthalpy of mixing in the Cu-Sn liquid along with experimental data [17].

Fig. 4 The composition paths selected for calculating the enthalpy of mixing in the Li-Cu-Sn liquid.
The present model

Chou
Kohler
Kohler-Toop
Muggianu
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(c) Enthalpy of mixing, kJ/mol vs. Mole Fraction of Li

Cu_{0.2}Sn_{0.8}

(d) Enthalpy of mixing, kJ/mol vs. Mole Fraction of Cu

Li_{0.2}Sn_{0.8}
Fig. 4 Enthalpy of mixing in the Li-Cu-Sn ternary liquid calculated using various interpolation methods.

Fig. 5 The predicted metastable liquid-liquid miscibility gap along the Cu-Li$_{0.5}$Sn$_{0.5}$ direction.
5 Concluding remarks

A generic thermodynamic model is proposed to describe thermodynamic properties of ternary solutions no matter whether the solutions contain short-range ordering configuration and no matter how to select geometric interpolation methods. The model is formulated by extensions of the Modified Quasichemical Model in the Pair Approximation (MQMPA) into ternary solutions using an unbiased interpolation scheme which might be ergodic over all reported geometric solution models, such as Kohler, Toop, Muggianu and Chou models, with changeable interpolation parameters. The practical formulation is to interpolate the pair interaction energies in ternary solutions by employing those from their constituent binary solutions within the framework of the MQMPA. The pair interaction energies could be expanded in the polynomial of either the “coordination-equivalent” fractions (composition-dependent) or the pair fractions (configuration-dependent). The generic thermodynamic model can be conveniently implemented into current thermodynamic software without alteration of the prevailing Gibbs energy minimization algorithm owing to all its analytical formalism.

The real Li-Cu-Sn liquid is selected to validate the generic thermodynamic model since the ternary solution contains various types of solution configurations over the entire composition range. The predicted deviation can be clearly exhibited by just changing the interpolation parameters and driving the interpolation to be freely shifted among various interpolation methods within the generic model. To the end, more appropriate interpolation parameters have been found to lead the calculated enthalpy of mixing to agree better with the experimental data. Since the generic thermodynamic model has inhibited the spirit of MQMPA, it can reasonably predict the potential liquid-liquid miscibility gap which, however, can hardly be described by the associate solution model without positive ternary interaction parameters. Although the present generic model has been developed primarily for liquid solutions, it can also be used to describe solid solutions with the same coordination numbers for all solution components.

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References

[1] Arthur D. Pelton, Phase diagrams and thermodynamic modeling of solutions, Elsevier, 2019.
[2] Mats Hillert, Phase Equilibria, Phase Diagrams and Phase Transformations, Cambridge University Press, 2008.
[3] Nigel Saunders and A. P. Miodownik, CALPHAD (Calculation of Phase Diagrams): A Comprehensive Guide, Pergamon, 1998
[4] Hans Lukas, Suzana G. Fries and Bo Sundman, Computational Thermodynamics: The Calphad Method, Cambridge University Press, 2007.
[5] William L. Bragg, Evan J. Williams, The effect of thermal agitation on atomic arrangement in alloys, Proceedings of the Royal Society of London. Series A, 1934, 145, 699-730.
[6] William L. Bragg, Evan J. Williams, The Effect of Thermal Agitation on Atomic Arrangement in Alloys II, Proceedings of the Royal Society of London. Series A, 1935, 151, 540-566.
[7] Arthur. D. Pelton, Sergey A. Degterov, Gunnar Eriksson, Christian Robelin, Yves Dessureault, The modified quasichemical model I—Binary solutions, Metallurgical and Materials Transactions B, 2000, 31, 651-659.

[8] Athur D. Pelton, The modified quasichemical model: Part II. Multicomponent solutions, 2001, 32A, 1355-1360.

[9] Kuo-chih Chou, A general solution model for predicting ternary thermodynamic properties, Calphad, 1995, 19, 315-325.

[10] Kun Wang, Xingli Zou, Hongwei Cheng, Chonghe Li, Xiaqin Zeng, Xionggang Lu, A generic thermodynamic model for multicomponent liquid solutions, in preparation.

[11] F. Kohler, Estimation of the thermodynamic data for a ternary system from the corresponding binary systems, Monatsh. Chem., 1960, 91, 738-740.

[12] G.W. Toop, Predicting ternary activities using binary data, Trans. Metal Soc AIME., 1965, 233, 850-855.

[13] Y.-M. Muggianu, M. Gambino, and J.-P. Bros, A new solution model, Journal of chemical physics, 1975, 72, 83-88.

[14] Patrice Chartrand, Arthur D. Pelton, On the choice of “Geometric” thermodynamic models, Journal of phase equilibria, 2000, 21, 141-174.

[15] S. Fürtäuer, E. Tserenjav, A. Yakymovych, H. Flandorfer, Calorimetric studies of Cu-Li, Li-Sn, and Cu-Li-Sn, The Journal of chemical thermodynamics, 2013, 61, 105-116.

[16] M.V. Mikhailovskaya, V.S. Sudavtseva, Ukr. Khim. Zh., 1989, 55, 1106-1108.

[17] H Flandorfer, C Luef, U. Saeed, On the Temperature Dependence of the Enthalpies of Mixing in Liquid Binary (Ag, Cu, Ni)-Sn Alloys, Journal of Non-Crystalline Solids, 2008, 354, 2953-2972.

[18] D. Li, S. Fürtäuer, H. Flandorfer, D.M. Cupid, Thermodynamic assessment of the Cu-Li system and prediction of enthalpy of mixing of Cu-Li-Sn liquid alloys, CALPHAD, 2016, 53, 105-115.

[19] Arthur D. Pelton, Youn-Bae Kang, Modeling short-range ordering in solutions, International Journal of materials research, 2007, 98, 907-917.