Generic thermodynamic model for solutions in various configurations: 
Part I. Ternary system with single sublattice and unique ordered pairs

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Abstract: In current paper serials, a generic thermodynamic model for solutions will be successively put forward no matter what kinds of short-range ordering configurations occur (or if they exist) in the solutions and no matter how to select geometric interpolation methods. This paper is demonstrating the derivation process of the model for use in ternary alloy systems as well as ternary common-ion ionic systems with single sublattice and unique ordered pairs. The model is formulated by extensions of the Modified Quasichemical Model (MQM) in the pair approximation 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 present model is eventually validated by the real Li-Cu-Sn liquid with complicated solution configurations over the entire composition zone to exhibit its effectiveness and accuracy. The future papers will be organized to show the generic thermodynamic model for use in multicomponent reciprocal solutions with two sublattices and distinguishable ordered pairs in various configurations.

Keywords: Thermodynamics; Geometrical interpolation; Quasichemical 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.

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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 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 (SRO). 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 [5]. The mathematical models based upon the Bragg-Williams point approximations [6-7] 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 SRO and unreasonable prediction of thermodynamic properties of ternary solutions using the symmetrical interpolation.

The current paper serials are organized to show the development of a generic thermodynamic model for solutions in various configurations. The present work is the first in serials to demonstrate the derivation process of the model for ternary alloy systems as well as ternary common-ion ionic systems with single sublattice and unique ordered pairs. The present model is derived on the basis of the MQMPA and an unbiased geometrical interpolation approach. The MQMPA [8] is widely used in the Factsage community to treat binary solutions no matter whether they appear SRO. 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 [9] 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 parameters which can be adjusted using experimental data from ternary solutions. If ternary experimental data are unavailable, usually these parameters could be reasonably calculated by the Chou model [10]. These interpolation parameters 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 [11], Toop [12], Muggianu [13] and Chou [10] schemes. Therefore, it has been used to successfully interpolate the pair energies in ternary solutions from sub-binaries in terms of either the “coordination-equivalent” fractions or 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 solutions no matter if SRO appears and without empirical selection of interpolation models. The Li-Cu-Sn liquid solution is selected to validate the present model in section 4 since complicated solution configurations occur over the entire composition zoon. The complex configurations result from the Li-Sn liquid with strong SRO and completely different Li-Cu and Cu-Sn liquids with respective positive repulsion and weak interaction for alloy atoms. In subsequent papers, the generic thermodynamic model for solutions will be successively put forward for use in: (II) multicomponent systems with single sublattice and unique ordered pairs; (III) multicomponent reciprocal systems with two sublattices and unique ordered quadruplets; (IV) binary systems with single sublattice and distinguishable ordered pairs; (V) ternary systems with single sublattice and distinguishable ordered pairs; (VI) multicomponent systems with single sublattice and distinguishable ordered pairs; (VII) ternary reciprocal systems with two sublattices and distinguishable ordered quadruplets; (VIII) multicomponent reciprocal systems with two sublattices and distinguishable ordered quadruplets.

2. The Model

For the A-B-C ternary solution, the generic thermodynamic model inheriting the MQMPA has the formalism as,

\[ G = (n_A g_A^0 + n_B g_B^0 + n_C g_C^0) + RT \left( n_A \ln(x_A) + n_B \ln(x_B) + n_C \ln(x_C) + n_{AA} \ln(Y_{AA}^\gamma) + n_{BB} \ln(Y_{BB}^\gamma) + n_{CC} \ln(Y_{CC}^\gamma) + n_{AB} \ln(Y_{AB}^{\gamma A}) + n_{AC} \ln(Y_{AC}^{\gamma A}) + n_{BC} \ln(Y_{BC}^{\gamma A}) \right) + \left( n_{AB} \Delta g_{AB} + n_{AC} \Delta g_{AC} + n_{BC} \Delta g_{BC} \right) \]

(1)

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 of mixing, and the last term stands for the summation of the nonconfigurational Gibbs 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,

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

(2)

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 \( m-n \) solution, \( \Delta g_{mn} \) can be expressed either in terms of the coordination-equivalent fraction as,

\[ \Delta g_{mn} = \Delta g_{mn}^0 + \sum_{i+j=1} \gamma_{ij} m_{i} n_{j} \]

(3)

or in terms of the pair fraction as,

\[ \Delta g_{mn} = \Delta g_{mn}^0 + \sum_{i \geq 1} \gamma_{mn}^i m_{i} + \sum_{j \geq 1} \gamma_{mn}^j n_{j} \]

(4)

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

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

\[ X_m = \frac{n_m}{\sum n_m} \]

(5)

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

(6)
\[
X_{mn} = \frac{n_{mn}}{\sum_{m}n_{mn}} = \frac{2n_{mn}}{\sum_{m}Z_{m}n_{mn}}
\]

(7)

\[
Y_{m} = \frac{Z_{m}n_{m}}{\sum_{m}Z_{m}n_{m}} = \frac{Z_{m}X_{m}}{Z_{m}n_{m}} = X_{mn} + \frac{1}{2}\sum_{m \neq n}X_{mn}
\]

(8)

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 [8]. In the current MQM, \(Z_{m}\) has been permitted to vary with composition as follows,

\[
\frac{1}{Z_{m}} = \frac{1}{Z_{m}^{\text{mm}}}n_{mn} + \frac{1}{Z_{m}^{\text{mn}}}n_{mn}
\]

(9)

where \(Z_{m}^{\text{mm}}\) and \(Z_{m}^{\text{mn}}\) 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,

\[
n_{mn} = \frac{2n_{mn}}{Z_{m}^{\text{nn}}} + \sum_{m \neq n}n_{mn}Z_{m}^{\text{mn}}
\]

(10)

which is the true mass balance between the overall composition of \(m\) and the number of pairs \((m-m), (n-n)\) and \((m-n)\) in the ternary solution if these pairs are formally treated as the fractional associates of \(m_{1/2}^{m}, m_{1/2}^{n}, n_{1/2}^{m}, n_{1/2}^{n}\). In this regard, equation (1) can be reshaped as,

\[
G = (n_{AA}g_{AA}^{0} + n_{BB}g_{BB}^{0} + n_{CC}g_{CC}^{0}) + RT(n_{A}ln(x_{A}) + n_{B}ln(x_{B}) + n_{C}ln(x_{C}) + n_{AA}ln(X_{AA}) + n_{BB}ln(X_{BB}) + n_{CC}ln(X_{CC}) + n_{AB}ln(X_{AB}) + n_{AC}ln(X_{AC}) + n_{BC}ln(X_{BC})) - RT(n_{AA}ln(Y_{A}^{2}) + n_{BB}ln(Y_{B}^{2}) + n_{CC}ln(Y_{C}^{2}) + n_{AB}ln(2Y_{A}Y_{B}) + n_{AC}ln(2Y_{A}Y_{C}) + n_{BC}ln(2Y_{B}Y_{C})) + \left(n_{AB}\frac{\Delta g_{AB}^{0} - \Delta g_{AB}^{0}}{2} + n_{AC}\frac{\Delta g_{AC}^{0} - \Delta g_{AC}^{0}}{2} + n_{BC}\frac{\Delta g_{BC}^{0} - \Delta g_{BC}^{0}}{2}\right)
\]

(11)

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

\[
g_{mm}^{0} = \frac{2}{Z_{m}^{\text{mm}}}g_{m}^{0}
\]

(12)

\[
g_{mn}^{0} = \frac{1}{Z_{m}^{\text{mn}}}g_{m}^{0} + \frac{1}{Z_{m}^{\text{mn}}}g_{n}^{0} + \frac{\Delta g_{mn}^{0}}{2}
\]

(13)

where \(\Delta g_{mn}^{0}\) is the binary parameter from equations (3) or (4). Comparing to the associate solution model, the quasichemical model just has an extra entropy term that is the third part in equation (11). Hence, the same existing algorithms and computer subroutines commonly used for the associate solution model can be applied conveniently to the quasichemical model with minor alterations.

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 \(\Delta g_{mn}^{0}\) expressions given in terms of either “coordination-equivalent” fractions or pair fractions are generally interpolated by the unbiased geometrical solution model to characterize the \(m-n\) pair energy for use in the ternary solution. The general ternary \(\Delta g_{mn}^{0}\) 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 model; (c) Kohler-Toop model; (d) Muggianu model](image)

### 3.1 The unbiased interpolation

Suppose $\Delta g_{AB}$ in the A-B binary subsystem has been expressed as a polynomial in 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

\[
\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{(i+j) \geq 1} q_{AB}^{ij} (Y_A + \delta_{AB} Y_C)^{i} (Y_B + (1 - \delta_{AB}) Y_C)^{j}) + \sum_{i \geq 0} g_{AB}^{i} (Y_A + \delta_{AB} Y_C)^i (Y_B + (1 - \delta_{AB}) Y_C)^j (1 - \delta_{AB}) Y_C^j
\]

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 keeps constant
along the 1-0 line. The position of “1” is chosen according to the interpolation parameter \( \delta^A_{AB} \). It can be function of temperature and its value is within the range from 0 to 1. The codomain of \( \delta^C_{AB} \) enables the unbiased model to be ergodic over all the existed geometrical solution models. \( \delta^B_{CA} \) can be calculated by the Chou model [10] and further fine-tuned by experimental ternary data. Similar schemes can be used for \( \delta^A_{BC} \) and \( \delta^B_{CA} \). 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 \( q^{ijr}_{AB(C)} \) can also be 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,

\[
\Delta g_{CA} = (\Delta g^0_{CA} + \sum_{i+j=1} q^{ij}_{CA} (Y_C + \delta^B_{CA} Y_B)(Y_A + (1 - \delta^B_{CA}) Y_B)^i (Y_A + (1 - \delta^B_{CA}) Y_B)^j) + \sum_{i+j=1} q^{ijr}_{CA(B)} (Y_C + \delta^B_{CA} Y_B)^i (Y_A + (1 - \delta^B_{CA}) Y_B)^j (1 - \delta^B_{CA}) Y_B)^k
\]

\[
\Delta g_{BC} = (\Delta g^0_{BC} + \sum_{i+j=1} q^{ij}_{BC} (Y_B + \delta^B_{BC} Y_A)^i (Y_C + (1 - \delta^B_{BC}) Y_A)^j) + \sum_{i+j=1} q^{ijr}_{BC(A)} (Y_B + \delta^B_{BC} Y_A)^i (Y_C + (1 - \delta^B_{BC}) Y_A)^j Y_B^k
\]

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 \( q^{ij}_{CA(B)} \) and \( q^{ij}_{BC(A)} \) 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 [15] that the functional form for the ternary terms is preferable to traditional expressions such as \( Y_A^i Y_B^j Y_C^k \).

Suppose \( \Delta g_{AB} \) in the A-B binary subsystem has the functional form as equation (4) written 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,

\[
\Delta g_{AB} = \Delta g^0_{AB} + \sum_{i+j=1} q^{ij}_{AB} (X_{AA} + \delta^C_{AB} X_{CC} + \delta^C_{AB} X_{AC})(X_{BB} + (1 - \delta^C_{AB}) X_{BC})^i (X_{BB} + (1 - \delta^C_{AB}) X_{BC})^j
\]

\[
+ \sum_{i+j=1} q^{ijr}_{AB(C)} (X_{AA} + \delta^B_{AB} X_{BB} + \delta^B_{AB} X_{BC})(X_{BB} + (1 - \delta^B_{AB}) X_{BB} + (1 - \delta^B_{AB}) X_{BB})^k
\]

where \( \Delta g^0_{AB} \) and \( q^{ij}_{AB} \) are obtained by optimization of experimental binary data, and \( q^{ijr}_{AB(C)} \) 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 \( X_{AA} + \delta^C_{AB} X_{CC} + \delta^C_{AB} X_{AC} \rightarrow (Y_A + \delta^B_{AB} Y_C)^2 \) and \( X_{BB} + (1 - \delta^B_{AB}) X_{BB} \rightarrow (1 - \delta^B_{AB}) X_{BB} \rightarrow (1 - \delta^B_{AB}) X_{BB} \rightarrow (1 - \delta^B_{AB}) X_{BB} \rightarrow (Y_B + (1 - \delta^B_{AB}) Y_C)^2 \) are realized.

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

\[
\Delta g_{BC} = \Delta g^0_{BC} + \sum_{i+j=1} q^{ij}_{BC} (X_{CC} + \delta^B_{BC} X_{BB} + \delta^B_{BC} X_{BC})(X_{CC} + \delta^B_{BC} X_{BB} + \delta^B_{BC} X_{BC})^i (X_{CC} + \delta^B_{BC} X_{BB} + \delta^B_{BC} X_{BC})^j
\]

\[
+ \sum_{i+j=1} q^{ijr}_{BC(A)} (X_{CC} + \delta^B_{BC} X_{BB} + \delta^B_{BC} X_{BC})(X_{CC} + \delta^B_{BC} X_{BB} + \delta^B_{BC} X_{BC})^k
\]

\[
(1 - \delta^B_{BC}) X_{BC}^j Y_C^k
\]
\[ \Delta g_{BC} = \Delta g_{BC}^0 + \sum_{i+j\geq 1} q_{BC}^{ij} (X_{BB} + \delta_{BC}^A X_{AA} + \delta_{BC}^B X_{AB})^{i}(X_{CC} + (1 - \delta_{BC}^A)^2 X_{AA} + (1 - \delta_{BC}^B) X_{AC})^{j} + \sum_{l \geq 0} q_{BC(A)}^{ij} (X_{BB} + \delta_{BC}^A X_{AA} + \delta_{BC}^B X_{AB})^{i}(X_{CC} + (1 - \delta_{BC}^A)^2 X_{AA} + (1 - \delta_{BC}^B) X_{AC})^{j}/y_A^l \]  

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

From equations (14, 17), it can be seen [9] 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 is defined as some special values. For the Kohler interpolation scheme \( \delta_{CA}^C = Y_A/(Y_A + Y_B) \) can be employed to realize such interpolation. Substituting it into equation (14) gives the \( \Delta g_{AB} \) expression in the coordination-equivalent fractions as,

\[ \Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j\geq 1} q_{AB}^{ij} (Y_A/Y_A+Y_B)^i(Y_B/Y_A+Y_B)^j) + \sum_{m \geq 0} q_{AB(C)}^{jm} (Y_A/Y_A+Y_B)^i(Y_B/Y_A+Y_B)^j/y_A^m \]  

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 energy which has already been well explained below equation (14).

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

\[ \Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j\geq 1} q_{CA}^{ij} (Y_C/Y_C+Y_A)^i(Y_A/Y_C+Y_A)^j) + \sum_{m \geq 0} q_{CA(B)}^{jm} (Y_C/Y_C+Y_A)^i(Y_A/Y_C+Y_A)^j/y_A^m \]  

\[ \Delta g_{BC} = (\Delta g_{BC}^0 + \sum_{i+j\geq 1} q_{BC}^{ij} (Y_B/Y_B+Y_C)^i(Y_C/Y_B+Y_C)^j) + \sum_{m \geq 0} q_{BC(A)}^{jm} (Y_B/Y_B+Y_C)^i(Y_C/Y_B+Y_C)^j/y_C^m \]  

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,
\[
\Delta g_{AB} = \left( \Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij} \left( \frac{X_{AA}}{X_{AA} + X_{BB} + X_{AB}} \right)^i \left( \frac{X_{BB}}{X_{AA} + X_{BB} + X_{AB}} \right)^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{AB}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{X_{AA} + X_{BB} + X_{AB}} Y_c^k
\]

(23)

\[
\Delta g_{CA} = \left( \Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij} \left( \frac{X_{CC}}{X_{CC} + X_{AA} + X_{CA}} \right)^i \left( \frac{X_{AA}}{X_{CC} + X_{AA} + X_{CA}} \right)^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{CA}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{X_{CC} + X_{AA} + X_{CA}} Y_c^k
\]

(24)

\[
\Delta g_{BC} = \left( \Delta g_{BC}^0 + \sum_{i+j \geq 1} q_{BC}^{ij} \left( \frac{X_{BB}}{X_{BB} + X_{CC} + X_{BC}} \right)^i \left( \frac{X_{CC}}{X_{BB} + X_{CC} + X_{BC}} \right)^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{BC}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{X_{BB} + X_{CC} + X_{BC}} Y_c^k
\]

(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., BeF$_2$-LiF-NaF, SiO$_2$-CaO-MgO, S-Fe-Cu, etc.), it is more appropriate to use the “asymmetric” model illustrated in Fig.1c, where A is selected as the asymmetric component.

### 3.3 The Toop interpolation

For the Toop interpolation scheme \(\delta_{AB}^C = 0\) 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,

\[
\Delta g_{AB} = \left( \Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij} \gamma^i_A(Y_A + Y_C)^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{AB}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{Y_A + Y_C}
\]

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,

\[
\Delta g_{CA} = \left( \Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij} \gamma^i_A(Y_A + Y_C)^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{CA}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{Y_A + Y_C}
\]

(27)

by taking \(\delta_{CA}^A = 1\) 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 \(\delta_{BC}^A = Y_B/(Y_B + Y_C)\) into equation (16).

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

\[
\Delta g_{AB} = \left( \Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij} \gamma^i_A(X_{BB} + X_{CC} + X_{BC})^j \right) + \sum_{k \geq 2} \frac{\sum_{i+j \geq 1} q_{AB}^{ij} \gamma^i_k(Y_A + Y_C)^j(Y_C)^k}{X_{BB} + X_{CC} + X_{BC}}
\]

(28)
\[
\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij}(X_{BB} + X_{CC} + X_{BC})^iX_{AA}^j) + \sum_{\mathbb{Z}_{\geq 0}}^{\mathbb{Z}_{\geq 0}} q_{AB(C)}^{jk}(X_{BB} + X_{CC} + X_{BC})^jX_{AA}^k
\]

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

\[
\Delta g_{AB} = (\Delta g_{AB}^0 + \sum_{i+j \geq 1} q_{AB}^{ij}(Y_A + \frac{1}{2} Y_C)^i(Y_B + \frac{1}{2} Y_C)^j) + \sum_{\mathbb{Z}_{\geq 0}}^{\mathbb{Z}_{\geq 0}} q_{AB(C)}^{jk}(Y_A + \frac{1}{2} Y_C)^j(Y_B + \frac{1}{2} Y_C)^k
\]

(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 that 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 \(\delta_{AB}^C = 1/2\) and \(\delta_{BC}^C = 1/2\) into equations (15-16) gives,

\[
\Delta g_{CA} = (\Delta g_{CA}^0 + \sum_{i+j \geq 1} q_{CA}^{ij}(Y_C + \frac{1}{2} Y_A)^i(Y_A + \frac{1}{2} Y_B)^j) + \sum_{\mathbb{Z}_{\geq 0}}^{\mathbb{Z}_{\geq 0}} q_{CA(B)}^{jk}(Y_C + \frac{1}{2} Y_A)^j(Y_A + \frac{1}{2} Y_B)^k
\]

(31)

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

(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 formalisms for use in the ternary solution can be given as,

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

(33)

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

(34)

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

(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 [15], 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 may 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 scheme can be ergodic over all reported geometrical solution models. 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. With the Chou model [10], the challenge may be overcome. The interpolation parameters can be obtained by using the so-called “deviation sum of squares”.

The “deviation sum of squares” is defined as,

\[ \eta_A = \int_0^1 (\Delta G_{AB} - \Delta G_{AC})^2 d\eta_A \]  
\[ \eta_B = \int_0^1 (\Delta G_{BA} - \Delta G_{BC})^2 d\eta_B \]  
\[ \eta_C = \int_0^1 (\Delta G_{CA} - \Delta G_{CB})^2 d\eta_C \]

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. \( \eta_A, \eta_B \) and \( \eta_C \) 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),

\[ \delta_{AB}^C = \frac{\eta_A}{\eta_A + \eta_B} \]  
\[ \delta_{BC}^A = \frac{\eta_B}{\eta_B + \eta_C} \]  
\[ \delta_{CA}^B = \frac{\eta_C}{\eta_C + \eta_A} \]

where \( \delta \) is also termed as “similarity coefficient” [10]. This indicates that the similarity between the component C and the component B causes \( \eta_A = 0 \) and thus \( \delta_{AB}^C = 0 \), and the similarity between the component C and component A leads to \( \eta_B = 0 \) and thus \( \delta_{AB}^C = 1 \). Therefore, from the \( \delta_{AB}^C \) value one can judge if the component C is more familiar to the component A or B. Similar situations can be found for \( \delta_{BC}^A \) and \( \delta_{CA}^B \).

In order to obtain the interpolation parameters, the \( \eta \) values have to be firstly calculated using equations (36-38). Since \( \Delta G_{mn} \) 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 equilibrium pair fractions are initially
obtained by minimizing the Gibbs energy at required composition, temperature and pressure, and then they are taken back into the Gibbs energy expression. However, it is not sure if the equilibrium pair fractions could be taken into equations (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,

\[
F(n_A, n_{AB}, n_{AC}) = [\Delta G_{AB}(n_A, n_{AB}) - \Delta G_{13}(n_A, n_{AC})]^2
\]

and \( \eta_A \) will have the expression as,

\[
\eta_A = \int_0^1 F(n_A, n_{AB}, n_{AC}) \, dn_A
\]

Minimizing \( \eta_A \) at fixed composition, the following equation yields,

\[
\frac{\partial \eta_A}{\partial n_{AB}} = \int_0^1 x = f(n_{AB}, n_{AC}) \frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AB}} \, dn_A + \left[ \frac{\partial g}{\partial n_{AB}} - \frac{\partial f}{\partial n_{AB}} \right] F(n_A, n_{AB}, n_{AC}) = 0
\]

\[
\frac{\partial \eta_A}{\partial n_{AC}} = \int_0^1 x = f(n_{AB}, n_{AC}) \frac{\partial F(n_A, n_{AB}, n_{AC})}{\partial n_{AC}} \, dn_A + \left[ \frac{\partial g}{\partial n_{AC}} - \frac{\partial f}{\partial n_{AC}} \right] F(n_A, n_{AB}, n_{AC}) = 0
\]

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

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

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

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,

\[
\frac{\partial \Delta G_{AB}(n_{AB}, n_A)}{\partial n_{AB}} = 0
\]

\[
\frac{\partial \Delta G_{AC}(n_{AC}, n_A)}{\partial n_{AC}} = 0
\]

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 \( \eta_A \), can be approximated by its closely related sum,

\[
\eta_A = \int_0^1 (\Delta G_{AB} - \Delta G_{AC})^2 \, dn_A \equiv \sum_{i=1}^{1/\Delta h - 1} \Delta h \left[ \Delta G_{AB}(i \Delta h, \tilde{n}_{AB}) - \Delta G_{AC}(i \Delta h, \tilde{n}_{AC}) \right]^2
\]

where \( \tilde{n}_{AB} \) and \( \tilde{n}_{AC} \) 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 prevalingly used in thermodynamic software is convenient to implement the generic 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 pair interaction energies expressed in the polynomial of pair fractions. The optimized model parameters are then taken into the generic thermodynamic model to demonstrate various predicted results using different interpolation parameters ($\delta_{\text{LiCu}}^{\text{Sn}}, \delta_{\text{SnLi}}^{\text{Cu}}$ and $\delta_{\text{CuSn}}^{\text{Li}}$). 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,

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

(51)

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

(52)

$$\Delta g_{\text{SnLi}} = \Delta g_{\text{SnLi}}^{0} + q_{\text{SnLi}}^{10}X_{\text{SnSn}}$$

(53)

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. 2 shows the calculated enthalpy of mixing in the Li-Sn system along with the experimental data [16]. The calculated curve shows a deep minimum located at the Li,Sn position, indicating Li and Sn atoms form strong SRO in their liquid alloy. The ratio $Z_{\text{LiSn}}^{\text{Sn}}/Z_{\text{LiSn}}^{\text{Li}} = 4$ is thus defined to address the composition of maximum SRO. The calculated enthalpies of mixing in the Li-Cu and Cu-Sn systems along with the experimental data [16-18] is respectively presented in Fig.3 and Fig.4 where both of the two curves display similar “S” shape profiles. The two liquids are close to regular solutions with atoms approximately in randomly mixing. The same coordination numbers are thus defined for all the atoms.

| Systems   | Li-Sn | Cu-Sn | Li-Cu |
|-----------|-------|-------|-------|
| Coordination numbers | $Z_{\text{LiSn}}^{\text{Li}} = 1.5$ | $Z_{\text{SnLi}}^{\text{Sn}} = 6$ | $Z_{\text{CuSn}}^{\text{Cu}} = 6$ | $Z_{\text{CuLn}}^{\text{Cu}} = 6$ | $Z_{\text{LiSn}}^{\text{Li}} = 6$ | $Z_{\text{SnLi}}^{\text{Sn}} = 6$ | $Z_{\text{CuSn}}^{\text{Cu}} = 6$ | $Z_{\text{CuLn}}^{\text{Cu}} = 6$ |
| Model parameters | $\Delta g_{\text{LiSn}}^{0} = -65000$ | $\Delta g_{\text{CuSn}}^{0} = 356.9 - 0.8504T$ | $\Delta g_{\text{CuSn}}^{0} = 9834.27 - 8T$ | $q_{\text{LiSn}}^{10} = -14527.57 + 0.1230T$ | $q_{\text{CuSn}}^{10} = -2713.6 + 1.0T$ | $q_{\text{LiSn}}^{10} = -146.77 - 3.3516T$ | $q_{\text{CuSn}}^{10} = -16703.2$ |

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

$$\Delta g_{\text{LiCu}} = \Delta g_{\text{LiCu}}^{0} + q_{\text{LiCu}}^{10}(X_{\text{LiLi}} + \delta_{\text{LiCu}}^{\text{Sn}}X_{\text{SnSn}} + \delta_{\text{LiCu}}^{\text{Li}}X_{\text{LiLi}}) + q_{\text{LiCu}}^{01}(X_{\text{CuCu}} + (1 - \delta_{\text{LiCu}}^{\text{Sn}})^{2}X_{\text{SnSn}} + (1 - \delta_{\text{LiCu}}^{\text{Li}})X_{\text{LiLi}})$$

(54)

$$\Delta g_{\text{CuSn}} = \Delta g_{\text{CuSn}}^{0} + q_{\text{CuSn}}^{10}(X_{\text{CuCu}} + \delta_{\text{CuSn}}^{\text{Cu}}X_{\text{CuCu}} + \delta_{\text{CuSn}}^{\text{Li}}X_{\text{LiLi}}) + q_{\text{CuSn}}^{01}(X_{\text{SnSn}} + (1 - \delta_{\text{CuSn}}^{\text{Cu}})^{2}X_{\text{LiLi}} + (1 - \delta_{\text{CuSn}}^{\text{Li}})X_{\text{SnSn}})$$

(55)
\[ \Delta g_{\text{SnLi}} = \Delta g_{\text{SnLi}}^0 + q_{\text{SnLi}}^{10} (X_{\text{SnSn}} + \delta_{\text{SnLi}}^{\text{Cu}} X_{\text{CuCu}} + \delta_{\text{SnLi}}^{\text{Cu}} X_{\text{CuSn}}) \]  

(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 thermodynamic properties from its subbinaries, and can thus render different predicted results. Fürtau [16] has carefully measured the enthalpy of mixing in the Li-Cu-Sn liquid along various sections as Fig.5 shows. These experimental data are very useful to validate the predicted results from different interpolation models. Fig.6 displays the calculated and experimental enthalpy of mixing in the ternary liquid along five composition paths as marked in Fig.5. By employing \( \delta_{\text{SnCu}}^{\text{SnCu}} = Y_{\text{Li}}/(Y_{\text{Li}} + Y_{\text{Cu}}), \delta_{\text{SnLi}}^{\text{Cu}} = Y_{\text{Sn}}/(Y_{\text{Sn}} + Y_{\text{Cu}}) \) and \( \delta_{\text{CuSn}}^{\text{Cu}} = Y_{\text{Cu}}/(Y_{\text{Cu}} + Y_{\text{Sn}}) \), the unbiased interpolation scheme can be transformed to the symmetrical Kohler model. By using \( \delta_{\text{SnCu}}^{\text{SnCu}} = 1, \delta_{\text{SnLi}}^{\text{Cu}} = Y_{\text{Sn}}/(Y_{\text{Li}} + Y_{\text{Sn}}) \) and \( \delta_{\text{CuSn}}^{\text{Cu}} = 0 \), the unbiased interpolation scheme can be reduced to the asymmetrical Kohler-Toop model and hence Cu is chosen as the asymmetrical component. By assigning \( \delta_{\text{SnCu}}^{\text{SnCu}} = \delta_{\text{SnLi}}^{\text{Cu}} = \delta_{\text{CuSn}}^{\text{Cu}} = 0.5 \), the unbiased interpolation scheme can be changed to the symmetrical Muggianu model. By working out \( \delta_{\text{SnCu}}^{\text{SnCu}} = 0.9989, \delta_{\text{SnLi}}^{\text{Cu}} = 0.4635 \) and \( \delta_{\text{CuSn}}^{\text{Cu}} = 0.0012 \) through equation (50), the unbiased interpolation scheme has now been shifted to the Chou model. By better reproducing the experimental data, \( \delta_{\text{SnCu}}^{\text{SnCu}} = 0.5, \delta_{\text{SnLi}}^{\text{Cu}} = 0.9 \) and \( \delta_{\text{CuSn}}^{\text{Cu}} = 0.1 \) 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.5, the calculated enthalpy of mixing is displayed in Fig.6 (a), Fig.6 (b) and Fig.6 (c), respectively. The curves are similar to that of the Li-Sn liquid where the 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.6 (d) and Fig.6 (e), respectively. The curves taken on the “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 exists similar analysis performed by Li et.al. [19] who introduced the associate LiSn species and employed the associate solution model to treat the Li-Sn liquid having strong SRO, and used the substitutional solution model with the Redlich-Kister polynomials to thermodynamically describe the Cu-Sn and Li-Cu liquids. Li et.al. [19] 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 detailedly described in their work. We have tried to use their liquid model (Li, LiSn, Sn, and Cu) and model parameters to reproduce their calculated results within the interpolation schemes of Muggianu or Muggianu-Toop. Large deviations appeared in the calculations. In particular, their liquid model cannot predict a potential liquid-liquid miscibility gap along the Cu-LiSn direction although they also estimated a possible miscibility gap in the center zoon of the Gibbs triangle (See Fig.S1 in the supplemental material). This is not abnormal [20] since Cu and LiSn were randomly mixed in their liquid model using the Muggianu or Muggianu-Toop methods. However, as shown in Fig.7, the reasonable prediction can be achieved for the stable/metastable liquid-liquid miscibility gap along the Cu-LiSn direction (the solid pink line) by using the present model within the generic interpolation scheme. The liquid-
liquid miscibility gap can be well predicted by the generic model without ternary interactions due to the fact that atom Li is strongly inclined to stay with atom Sn in the ternary liquid, 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. The present prediction can be well demonstrated by information from nine isopleth sections in the Cu-Li-Sn system. The nigh isopleth diagrams were measured by Fürtauer [21] and have been placed in the supplementary materials. Composition lines (a-i) in Fig.7 correspond to the measured isopleth sections of Figs.S2-S10, respectively. All the six dark dashed lines but line (a) pass through the liquid-liquid region, which is well consistent with the corresponding isopleth sections where the liquid-liquid miscibility gap may occur. For line (a), the Li$_{0.5}$Cu$_{0.5}$ side almost enters the two-liquid region. The two green dashed lines certainly have no possibility of entering the two-liquid zone, which also agrees well with the corresponding sections where no liquid-liquid miscibility gap appears. There is one exceptional inconsistence between the blue dashed line and Fig.S9 for the appearance of the liquid-liquid miscibility gap. It is hardly believed that the two-liquid region could be extended to the rich zone of copper since we have to roughly assign large a positive ternary interaction parameter $d_{LiSn(Cu)}^{011} = 15$kJ/mol in the present model to have such an extension. Fig.7 also displays different two-liquid zones predicted by other interpolation models. The predicted two-liquid zone by the present model seems remarkably smaller than those by the Kohler, Kohler-Toop, Muggianu and Chou models. This is not surprising since the calculated enthalpies of mixing by these models show obviously positive deviations from the experimental data and the present model.

There are still many ternary solutions absent for experimental data. The generic thermodynamic model can still be used to reasonably predict their thermodynamic properties by appropriately defining the interpolation parameters. The appropriate definition can be well addressed by the empirical rule in chemistry for components or the Chou model although the latter seems not excellent in treating the Li-Cu-Sn liquid. 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. 2 Calculated enthalpy of mixing in the Li-Sn liquid along with experimental data [15]
Fig. 3 Calculated enthalpy of mixing in the Li-Cu liquid along with experimental data [15-16]
Fig. 4 Calculated enthalpy of mixing in the Cu-Sn liquid along with experimental data [17]
Fig. 5 The composition paths selected for calculating the enthalpy of mixing in the Li-Cu-Sn liquid.
The present model
Fig. 6 Enthalpy of mixing in the Li-Cu-Sn ternary liquid calculated using various interpolation methods.
5 Concluding remarks

A generic thermodynamic model has been derived to treat solutions in various configurations. The model will be successively presented in subsequent papers. The present paper is the first in serials to demonstrate the derivation process of the model for use in ternary solutions no matter whether they contain SRO configurations 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 major alteration of the prevailing Gibbs energy minimization algorithm owning to its completely analytical formalism.

The real Li-Cu-Sn liquid is selected to validate the generic thermodynamic model since the ternary solution contains complicated 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 inherited the spirit of MQMPA, it can reasonably predict the potential liquid-liquid miscibility gap along the Li₄Sn-Cu direction which, however, can hardly be described by the associate solution model without positive ternary interaction parameters. Although the 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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