

A Novel Numerical Framework based on gPC to Compute Phase Diagrams

Phase diagrams are of significant importance in materials science as they provide relationship between phases in a system as a function of temperature, pressure and composition. CALculation of PHase Diagram (CALPHAD) is used as a reliable method to address the difficulty in determining multicomponent phase diagrams experimentally. But the classic description of excess Gibbs energy by RedlichKister polynomials requires excessive knowledge of the nature of α phase and m - n system. In this paper, we propose a novel numerical framework based on the generalized polynomial chaos expansion (gPC) method, to describe excess Gibbs energy based on mathematical methods, which requires just a few experimental data and hence saves much work to obtain various phase diagrams. We demonstrate the accuracy and efficiency of the proposed method by estimating Cu-Ni binary system.

It is self-evident that phase diagrams are of significant importance in materials science. In the early stage, phase diagrams were determined with experimental methods such as X-ray diffraction analysis, electron probing analysis, thermal analysis, etc. With the increase of the difficulty in determining multicomponent phase diagrams experimentally and the development of computer technology, CALculation of PHase Diagram (CALPHAD), which was first described by Kaufman and Bernstein in 1970[1], has become a reliable and widely used method to obtain various phase diagrams.

The Calphad method means the use of all available experimental and theoretical data to assess the parameters of the Gibbs energy models selected for different phases[2]. The key to an appropriate description of a phase lies in the excess Gibbs energy, which is mostly expressed by RedlichKister polynomials[3] (R-K polynomials for short) or their variants. For example, the form of R-K polynomials for α phase in the binary system consisting of components m and n is shown as below.

$$G^{ex} = x^{(m)}x^{(n)}L_{mn} \quad (1)$$

where G^{ex} is the excess Gibbs energy of α phase; $x^{(m)}$ and $x^{(n)}$ are the mole fraction of component m and n ; L_{mn} is interaction parameter of component m and n in α phase. The parameter L_{mn} has the form shown below.

$$L_{mn} = \sum_{\nu=1}^z (x^{(m)} - x^{(n)})^{\nu} \cdot {}^{\nu}L_{mn} \quad (2)$$

where the parameter ${}^{\nu}L_{mn}$ is linear temperature-dependent in most cases and only when heat-capacity data are available a higher term after the linearly temperature-dependent one is needed:

$${}^{\nu}L_{mn} = a_{\nu} + b_{\nu}T \quad (3)$$

where the parameter a_{ν} and b_{ν} are to be determined based on experimental data of α phase.

However, there exists a problem. The number of parameter ${}^{\nu}L_{mn}$, that is, the parameter z in Equation (2), varies with the model selected for α phase. For example,

ν takes 0 for regular solution model[4] and 1 for subregular solution model[5]. For sublattice model[6], the expression of excess Gibbs energy contains the similar form of Equation(2) and the parameter z differs from the sublattices with different nature. Therefore, it takes much work to determine the expression of excess Gibbs energy because sufficient knowledge of the nature of α phase and m - n system is necessary to select an appropriate model.

In this paper, we propose a formula to describe excess Gibbs energy based on mathematical methods, which requires just a few experimental data and hence saves much work to obtain various phase diagrams.

To address the challenges above, a novel numerical framework which owns high precision has been proposed. Our method is based on generalized polynomial chaos(gPC)[7] which is essential to uncertainty quantification. T refers to the temperature whose unit is Kelvin. We construct an approximation $\widetilde{G_{ex}}(x^{(m)}, T)$ by Legendre polynomials $P_{i_1}(x^{(m)})$ and $P_{i_2}(T)$ to replace traditional R-K polynomials:

$$\begin{aligned} G^{ex}(x^{(m)}, T) &\approx \widetilde{G^{ex}}(x^{(m)}, T) \cdot x^{(m)} \cdot x^{(n)} \\ &= x^{(m)} \cdot x^{(n)} \cdot \sum_{|\mathbf{i}| \leq 0} c_{\mathbf{i}} P_{i_1}(f_1(x^{(m)})) P_{i_2}(f_2(T)) \end{aligned} \quad (4a)$$

$$|\mathbf{i}| = i_1 + i_2, \quad \dim = C_{N+2}^N \quad (4b)$$

Where N refers to the degree of gPC basic functions, $\mathbf{i} = (i_1, i_2)$ is a multi-index with $|\mathbf{i}| = i_1 + i_2$ and $c_{\mathbf{i}}$ is the expansion coefficient of the index \mathbf{i} yet to be determined. Notice that we must translate the variables $x^{(m)}$ and T of Legendre polynomials from the domain $[p^m, q^m]$ and domain $[p_T, q_T]$ into a reference domain $[-1, 1]$ which is required by Chebyshev points method[8]. It means that the variables of Legendre polynomials must come from Chebyshev points. Then we define f_1 and f_2 as the corresponding mapping functions. And for convenience, we denote $f x^{(m)}$ and $f T$ as the variables of Legendre polynomials after mapping. Legendre polynomials which are orthogonal Wiener-Askey polynomial can be defined as followed:

$$P_{-1} = 0, \quad (5a)$$

$$P_0(V) = 1, \quad (5b)$$

$$(i+1)P_{i+1}(V) = (2i+1)V P_i(V) - i P_{i-1}(V). \quad (5c)$$

we listed a few orders of the Legendre polynomials In Table I. For more details ,readers can refer to Xius works[9].

i	$P_i(x^{(m)})$
0	1
1	$x^{(m)}$
2	$\frac{1}{2}(3(x^{(m)})^2 - 1)$
3	$\frac{1}{2}(5(x^{(m)})^3 - 3(x^{(m)}))$
4	$\frac{1}{8}(35(x^{(m)})^4 - 30(x^{(m)})^2 + 3)$
5	$\frac{1}{8}(63(x^{(m)})^5 - 70(x^{(m)})^3 + 15(x^{(m)}))$
6	$\frac{1}{16}(231(x^{(m)})^6 - 315(x^{(m)})^4 + 105(x^{(m)})^2 - 5)$

Table I. The first few orders of Legendre polynomials $P_i(x^{(m)})$.

Now we need to determine the gPC expansion coefficient c_i in order to complete the approximation. The number of c_i is C_{N+2}^N . After selecting a dataset $(x_1^{(m)}, T_1, G_1^{le}), (x_2^{(m)}, T_2, G_2^{le}), \dots, (x_M^{(m)}, T_M, G_M^{le})$, we let $\mathbf{G}^{le} = (G_1^{le}, G_2^{le}, \dots, G_M^{le})'$, $\mathbf{c} = (c_{0,0}, c_{0,1}, \dots, c_{C_{N+2}^N, 0})'$. And we define \mathbf{P} as followed :

$$\begin{bmatrix} P_0(fx_1^{(m)})P_0(fT_1) & P_0(fx_1^{(m)})P_1(fT_1) & \dots & P_{C_{N+2}^N}(fx_1^{(m)})P_0(fT_1) \\ P_0(fx_2^{(m)})P_0(fT_2) & P_0(fx_2^{(m)})P_1(fT_2) & \dots & P_{C_{N+2}^N}(fx_2^{(m)})P_0(fT_2) \\ \vdots & \vdots & \ddots & \vdots \\ P_0(fx_M^{(m)})P_0(fT_M) & P_0(fx_M^{(m)})P_1(fT_M) & \dots & P_{C_{N+2}^N}(fx_M^{(m)})P_0(fT_M) \end{bmatrix} \quad (6)$$

Then we use least-square method[10] to solve the following linear system of equation:

$$\mathbf{P} * \mathbf{c} = \mathbf{G}^{le} \quad (7)$$

Once the approximation $\tilde{G}^{le}(x^{(m)}, T)$ is constructed for the binary system, we can determine corresponding Gibbs energy:

$$G^{liquid}(x^{(m)}, T) = RT(x^{(m)} \ln(x^{(m)}) + x^{(n)} \ln(x^{(n)})) + (x^{(m)} G_m^{liquid} + x^{(n)} G_n^{liquid}) + G_{liquid}^{ex}(x^{(m)}, T) \quad (8a)$$

$$x^{(m)} + x^{(n)} = 1 \quad (8b)$$

$$G^{solid}(x^{(m)}, T) = RT(x^{(m)} \ln(x^{(m)}) + x^{(n)} \ln(x^{(n)})) + (x^{(m)} G_m^{solid} + x^{(n)} G_n^{solid}) + G_{solid}^{ex}(x^{(m)}, T) \quad (9a)$$

$$x^{(m)} + x^{(n)} = 1 \quad (9b)$$

Where R refers to gas volume constant, G_m^{liquid} and G_m^{solid} refer to Gibbs energy of component m in liquid state and solid state correspondingly. G_n^{liquid} and G_n^{solid} refer to Gibbs energy of component n in liquid state and solid state as well.

Finally, we can get the phase diagram of m - n binary system based on Gibbs energy above. Then we would take Cu - Ni binary system as an example to compare

our model with R-K polynomials by using gPC method and lead to some conclusions .

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Since RK-polynomials have high accuracy in the phase diagram works of Cu - Ni binary system, we choose Cu - Ni binary system as an example to check our model and we regard the values of R-K polynomials as the actual results. In other words, we choose Chebyshev points G^{le} from R-K polynomials. In the case of Cu - Ni binary system, the formula of R-K polynomials is as followed:

$$G_{RK}^{ex} = \sum_{v=0}^{v=1} x^{(m)} * x^{(n)} * (x^{(m)} - x^{(n)})^v (a_v + b_v * T) \quad (10)$$

The coefficients of R-K polynomials in liquid and solid states are shown in Table II[11]. In the remainder of this letter, we would compare our model with R-K polynomials and get the phase diagram of this binary system.

	a_v	b_v
$v^{liquid} = 0$	12048.61	1.29093
$v^{liquid} = 1$	-1816.61	0.94201
$v^{fcc} = 0$	8047.72	3.42217
$v^{fcc} = 1$	-2041.30	0.99714

Table II. Coefficients of R-K polynomials in Cu - Ni binary system[11] .

The $\|\cdot\|_{\ell_2}$ norm between Legendre and R-K polynomials as error is computed by using 2000 equally distributed points in the domain $[p^{Cu}, q^{Cu}]$ and $[p_T, q_T]$. In the case of Cu - Ni binary system, we set $p^{Cu} = 0, q^{Cu} = 1$ and set $p_T = 1358.02K, q_T = 1728K$ which represent the melting point of Cu and Ni . Here the fact that the convergence rate is in tandem with the smoothness of actual relationship between the variables[9] must be noted. So we shall expect that for $N = 2$, sufficient accuracy could be achieved. And Fig. 1 shows the result which is in accordance with expectations: as N increased, we would obtain worse accuracy in our model. Based on this, we choose $N = 2$ to continue our works. And the error is $7.5832e-11$ at this time. Here we note that we ignore the case when $N = 1$ since $\|\cdot\|_{\ell_2}^{N=1} = 3.4889e+03$. As might have been expected, gPC polynomial would represent a line for $N = 1$ and linear case could not simulate a curve with high accuracy.

The Gibbs energy descriptions for copper and nickel are given in Table III and Table IV. We refer i to the component Cu or Ni and j to the liquid or solid state in G_i^j . We set $p_0 = 298.15K$. The description of the temperature dependence of the Gibbs energies of the pure components has been standardized as followed[11, 12] and all

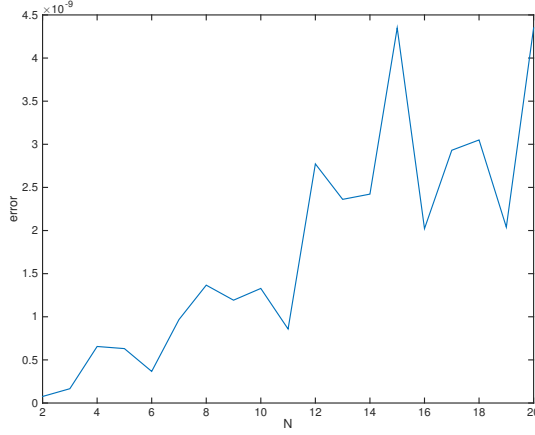


Figure 1. Error of excess Gibbs energy between gpc and R-K polynomials by choosing different order.

of the coefficients are shown in Table III and Table IV.

$$G_i^j(T) = a_{ij} + b_{ij} * T + c_{ij} * T * \ln(T) + d_{ij} * T^2 + e_{ij} * T^{-1} + f_{ij} * T^3 + t_{ij} * T^7 + k_{ij} * T^{-9} \quad (11)$$

	$Cu^{liquid}(T = [p_0, p_T])$	$Cu^{liquid}(T > p_T)$
a_{ij}	$5.194382E + 03$	$-4.693E + 01$
b_{ij}	$1.2097516E + 02$	$1.73883734E + 02$
c_{ij}	$-2.4112392E + 01$	$-3.138E + 01$
d_{ij}	$-2.65684E - 03$	0
e_{ij}	$5.2478E + 04$	0
f_{ij}	$1.29223E - 07$	0
t_{ij}	$-5.83932E - 21$	0
k_{ij}	0	$3.64643E + 29$
	$Cu^{fcc}(T = [p_0, p_T])$	$Cu^{fcc}(T > p_T)$
a_{ij}	$-7.770458E + 03$	$-1.354233E + 04$
b_{ij}	$1.30485403E + 02$	$1.83804197E + 02$
c_{ij}	$-2.4112392E + 01$	$-3.138E + 01$
d_{ij}	$-2.65684E - 03$	0
e_{ij}	$5.2478E + 04$	0
f_{ij}	$1.29223E - 07$	0
t_{ij}	0	0
k_{ij}	0	$3.64643E + 29$

Table III. Coefficients of Gibbs energy for Cu in liquid and fcc states [11]

Since all parts of Gibbs energy in Cu-Ni system have been determined, we could compute Gibbs energy and then check our model. Fig. 2 shows the surface of G^{le} by using gPC method and it shows R-K curve as well for comparison. We can see that R-K curve fits our surface perfectly. Then we compute Gibbs energy of both liquid

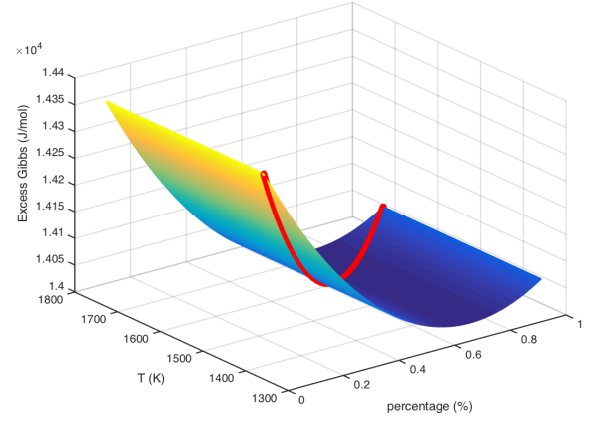


Figure 2. Legendre surface of excess Gibbs energy using least square method comparing with R-K curve.

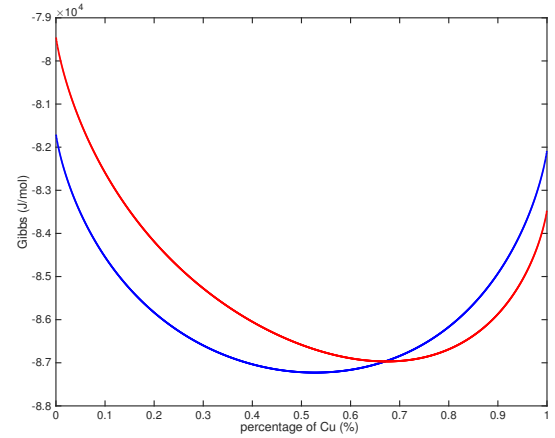


Figure 3. Gibbs energy of liquid and fcc phase when $T = 1500K$

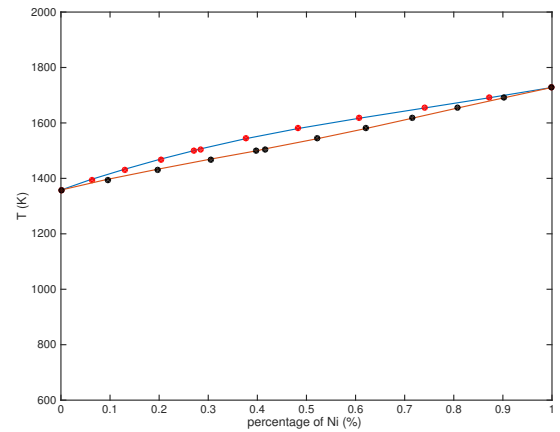


Figure 4. Phase diagram of Cu-Ni system.

	$Ni^{liquid}(T = [p_0, q_T])$	$Ni^{liquid}(T > q_T)$
a_{ij}	$1.1235527E + 04$	$-9.549775E + 03$
b_{ij}	$1.08457E + 02$	$2.68598E + 02$
c_{ij}	$-2.2096E + 01$	$-4.31E + 01$
d_{ij}	$-4.8407E - 03$	0
e_{ij}	0	0
f_{ij}	0	0
t_{ij}	$-3.82318E - 21$	0
k_{ij}	0	0
	$Ni^{fcc}(T = [p_0, q_T])$	$Ni^{fcc}(T > q_T)$
a_{ij}	$-5.179159E + 03$	$-2.7840655E + 04$
b_{ij}	$1.17854E + 02$	$2.79135E + 2$
c_{ij}	$-2.2096E + 01$	$-4.31E + 01$
d_{ij}	$-4.8407E - 03$	0
e_{ij}	0	0
f_{ij}	0	0
t_{ij}	0	0
k_{ij}	0	$1.12754E + 31$

Table IV. Coefficients of Gibbs energy for Ni in liquid and fcc states[11]

	error of x_T^{liquid}	error of x_T^{fcc}
$T = 1358$	0.00029	0.00039
$T = 1395$	0.00314	0.00512
$T = 1432$	0.00218	0.0039
$T = 1469$	0.00135	0.00276
$T = 1500$	0.00051	0.00161
$T = 1506$	0.00065	0.00168
$T = 1543$	0.00005	0.00072
$T = 1580$	0.00046	0.00001
$T = 1617$	0.00081	0.00044
$T = 1654$	0.00091	0.00064
$T = 1691$	0.00079	0.00062
$T = 1728$	0.00059	0.00047

Table V. Error of points of tangency between fcc and liquid Gibbs energy with the change of T .

and fcc states by adding our model in the formula after fixing a certain T . The results of these two curves are shown in Fig. 3 when $T = 1500K$. Based on the thermodynamics principle of Phase diagram, we find the common tangent line of these two curves and the corresponding two points of tangency. According to the abscissa of this two points, we can obtain the phase diagram with the change of T . Our phase diagram is showed in Fig. 4 and in order to check the accuracy, we add some points from Thermocalc software to the figure. We can see that all the points which come from Thermocalc are close to our phase diagram. To demonstrate the accuracy, we draw

a table to show the error of the abscissa which generate from x_T^{liquid} and x_T^{fcc} , the two points of tangency in different value of temperature. The results are shown in Table V.

In summary, we proposed a numerical framework to estimate Gibbs energy in a binary system by using generalized polynomial chaos expansion method (gPC method). gPC method is mathematically rigorous and versatile. In order to show the accuracy and efficiency of our model, we take $Cu-Ni$ binary system for example to compute Gibbs energy. And our analysis leads to the following conclusions:

1) The gPC method provides a good estimate of Gibbs energy in a binary system; 2) In contrast to the existing approaches, our method can show readers how to determine the coefficients of the polynomials; 3) Comparing to data size and sample spacing, the gPC method is found to be most sensitive to the data range and we could use a small number of samples to generate our model; 4) For a fixed binary system, small degree N of basic function are needed for the gPC method to achieve a desired accuracy.

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- [1] L. Kaufman and H. Bernstein. Computer calculation of phase diagrams with specific reference to refractory materials. 1970.
 - [2] Hans Lukas, Suzana G. Fries, and Sundman Bo. *Computational Thermodynamics: The Calphad Method*. Cambridge University Press, 2007.
 - [3] Otto Redlich and A. T. Kister. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. eng. chem.*, 40(2):345–348, 1948.
 - [4] Joel H. Hildebrand. Solubility. xii. regular solutions. *J. am. chem. soc.*, 51(1):66–80, 1929.
 - [5] H. K. Hardy. A sub-regular solution model and its application to some binary alloy systems. *Acta Metallurgica*, 1(2):202–209, 1953.
 - [6] M. Hillert and L. I. Staffansson. The regular solution model for stoichiometric phases and ionic melts. *Acta Chemica Scandinavica*, 24(10):3618–3626, 1970.
 - [7] Dongbin Xiu and George Em Karniadakis. The wiener–askey polynomial chaos for stochastic differential equations. In *SIAM J. SCI. COMPUT.*, pages 619–644, 2002.
 - [8] Anne M. Hofmeister. Interatomic potentials calculated from equations of state: Interatomic potentials calculated from equations of state: limitation of finite strain to moderate k' . *Geophys. Res. Lett.*, 20(7):635–638, 1993.
 - [9] Dongbin Xiu. *Numerical Methods for Stochastic Computations: A Spectral Method Approach*. Princeton University Press, 2010.
 - [10] R. Hill. The elastic behaviour of a crystalline aggregate. *Proc. Phys. Soc. London*, 65(5):350, 1952.
 - [11] Sabine An Mey. Thermodynamic re-evaluation of the cuni system. *Calphad computer Coupling of Phase Diagrams and Thermochemistry*, 16(3):255260, 1992.
 - [12] A. T. Dinsdale. Sgite data for pure elements. *Calphad computer Coupling of Phase Diagrams and Thermochemistry*, 15(4):317–425, 1991.