1. Objective

Cluster expansion and cluster variation methods (CE-CVM) accounts for the short range order (SRO) in terms of correlation functions (CFs), which describe the microscopic state of the material system.

For the chosen thermodynamic state, the equilibrium CFs have to be determined by solving set of non-linear equations.

The number of CFs increases with (i) the size of the cluster (ii) the number of components of the system and/or (iii) reduction in the symmetry of the cluster/structure.

Approximation of the CFs (or G) without losing SRO can be a solution for the above problem.

2. CE-CVM Formalism for A2-Tetrahedron Cluster

- **Cluster Algebra:**

<table>
<thead>
<tr>
<th>Correlation Function</th>
<th>Cluster type</th>
<th>Multiplicity (m_i)</th>
<th>No. of subclusters in cluster i</th>
<th>K_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>u_4</td>
<td>Tetrahedron</td>
<td>6</td>
<td>4 4 4 4</td>
<td>1</td>
</tr>
<tr>
<td>u_3</td>
<td>Triangle</td>
<td>12</td>
<td>1 1 2 3 -1</td>
<td></td>
</tr>
<tr>
<td>u_2</td>
<td>II-n pair</td>
<td>3</td>
<td>1 0 2 1</td>
<td>-1</td>
</tr>
<tr>
<td>u_1</td>
<td>I-n pair</td>
<td>4</td>
<td>0 0 1 2</td>
<td>1</td>
</tr>
<tr>
<td>u_0</td>
<td>Point</td>
<td>1</td>
<td>0 0 0 0</td>
<td>-1</td>
</tr>
</tbody>
</table>

- **Configurational Gibbs Energy of Mixing (G_0):**

\[
G_0^{mix} = H_0^{mix} - TS_0^{mix} = \sum_{i=1}^{n} e_i m_i u_i^{mix} + R T \sum_{i=1}^{n} m_i \gamma_i \sum_{j=1}^{n} z_i^j \ln z_i^j
\]

- **Equilibrium state of the system:**

For a chosen set of \( (e_i, T, u_0) \), CFs can be obtained by solving the set of non-linear equations, that corresponds to minimum in \( G_0 \):

\[
\left( \frac{\partial G_0}{\partial u_j} \right)_{u_0, T} = 0, \ i = 1 \ to \ n
\]

The more the number of CFs (e.g. for multi component systems), the more the computational burden in solving the non-linear equations!

3. CVM solutions for CFs of different approximations

- **Equilateral triangle approx.** (for close packed net):

\[
U_{i,j=0} = \left( \frac{1}{2} \left( \sqrt{3} \eta_i - 1 \right) \right) \left( \frac{3}{2} \left( \sqrt{3} \eta_i + 1 \right) \right)
\]

- **For pure II-n interactions:**

where \( \eta_i = \exp \left( -\frac{2^{1/2} r_i}{R \delta} \right) \) & \( r_i = \) no of points in the \( i^{th} \) cluster

4. Methodology

The form of polynomials satisfying the system independent limiting values are:

\[
U_i = u_i^{\text{II-n}} + u_i^{\text{II-n pair}}\left( \frac{1}{2} \left( 1 + \frac{1}{2} \right) \right) P(u_i)
\]

Based on the (anti-)symmetry of CFs, the terms of \( P \) are chosen.

Data selection:

\- u_0 range: -1 to 0, corresponding to spinodal or order-disorder boundary
\- \( y \) range: \( \eta \) corresponding to miscibility gap boundary at \( x = 0.05 \) to consolute temperature
\- \( \eta \) corresponding to 50% critical temperature to critical temperature

Procedure:

At the selected \( \eta \) obtain the coefficients of \( P \) for the CFs using constraints based on requirement.

Choose appropriate rational functions to represent temp. dep. of CFs.

Complete the rational function fits for \( c_1^0 = 0 \) and \( c_0 = 0 \) separately.

Choose the simplest combined rational functions and obtain the coefficients of RFs based on data at \( e_0/e_1 \times \sqrt{2} - 1, 0 \times \sqrt{2} + 1 \)

5. Results

\[
\begin{array}{ccc}
e_0/e_1 \times \sqrt{2} & \text{Relative error in } T_s(10^3) & \text{Relative error in } T_s(10^3) \\
0 & -4 & 1 & -31 \\
1/3 & -19 & \sqrt{3} & -30 \\
2/3 & -22 & \sqrt{2} + 1 & -26 \\
1/\sqrt{3} & -26 & 2 \times \sqrt{3} & -20 \\
2/\sqrt{3} & -28 & \infty & -2 \\
\end{array}
\]

6. References


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