

An improved sampling strategy for global energy minimization of multi-component systems



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ARTICLE INFO

Article history:

Received 6 August 2016

Received in revised form 21 December 2016

Accepted 13 January 2017

Available online 2 February 2017

Keywords:

CALPHAD

Thermodynamics

Energy minimization

Miscibility gap

ABSTRACT

Effective initial sampling plays an important role in capturing key details about the energy surfaces of multi-component, multi-sublattice phases for the purposes of accurate convergence toward the global minimum energy configuration of a given system. It is shown that, when using the appropriate statistical distribution, both quasi-random and pseudo-random sampling methods compare well with the standard uniform grid-based technique. Moreover, the combination of random sampling with uniform grid points, while maintaining sampling performance for equilibrium calculations in the Al-Co-Cr system, significantly increases performance for a fictive 10-component system.

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1. Introduction

Miscibility gap detection is a crucial feature in thermodynamic calculation software to accurately calculate the energy of phases containing regions of compositional instability and is commonly handled through global minimization (GM) of the Gibbs energy. The cause of miscibility gaps in non-ideal solutions is the presence of energetically unfavorable interactions between components that overwhelm the entropically-driven ideal mixing contribution to the Gibbs energy.

To fix notations, let G^i represent the molar Gibbs energy of a particular phase i within the system, with $i = 1, \dots, K$. Furthermore, assume that T is temperature, P is pressure, f^i is the fraction of phase i and y_{kj}^i is the site occupation fraction of component j in sublattice k of phase i . In vector form, let $\vec{y} = \{y_{kj}^i\}_{j=1, \dots, J, k=1, \dots, M_i}^{i=1, \dots, K}$, where K stands for the total number of phases, J for the total number of system components and M_i for the number of sublattices in phase i . Similarly, denote $\vec{f} = \{f^i\}$ for all $i = 1, \dots, K$.

The isothermal-isobaric total molar Gibbs energy minimization problem for a closed system can be stated in the following way:

$$\min_{\vec{f}, \vec{y}} \left(G_m(T, P, \vec{f}, \vec{y}) = \sum_i f^i G^i(T, P, \vec{y}) \right) \quad (1)$$

$$\text{s.t. } c_n(T, P, \vec{f}, \vec{y}) = 0 \quad (2)$$

where $c_n, n = 1, \dots, C$ represent all possible equality constraints including mass balance constraint. Sublattice site fractions are related to mole fractions by the relation

$$x_j^i = \frac{\sum_k b_k y_{kj}^i}{\sum_k b_k (1 - y_{k,va}^i)}, \quad (3)$$

where b_k is the number of sites on sublattice k and $y_{k,va}^i$ is the fraction of vacancies on sublattice k .

Site fraction balance constraints, $\sum_k y_{kj}^i - 1 = 0$, are always present for each sublattice. This problem is equivalent to solving the following unconstrained minimization problem for the Lagrangian \mathcal{L} :

$$\min_{\vec{f}, \vec{y}} \left(\mathcal{L}(T, P, \vec{f}, \vec{y}, \vec{\lambda}) = G_m(T, P, \vec{f}, \vec{y}) - \sum_{n=1}^C \lambda_n c_n(T, P, \vec{f}, \vec{y}) \right), \quad (4)$$

where the notation $\vec{\lambda} = \{\lambda_n\}_{n=1, \dots, C}$ is used for the vector of Lagrange multipliers. The Lagrangian is closely related to the thermodynamic driving force function by the equality of the chemical potentials to the values of λ_n for the mass balance constraints. For further details,

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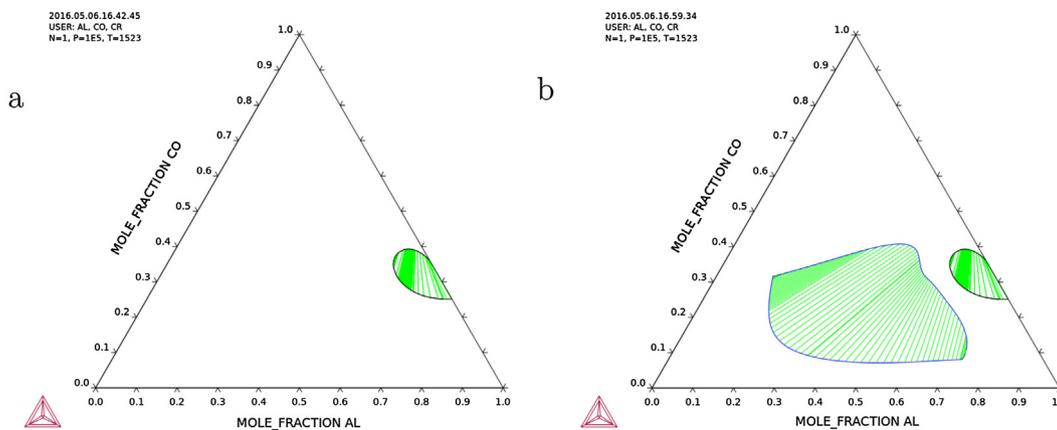


Fig. 1. Two Al-Co-Cr metastable phase diagrams, including only the bcc phase, are shown at 1523 K. Using the default settings in Thermo-Calc version 2015a, an incorrect diagram missing the ternary miscibility gap is produced (a). Increasing the global minimization point density or explicitly adding equilibrium points in the miscibility gap region produces the correct metastable diagram (b).

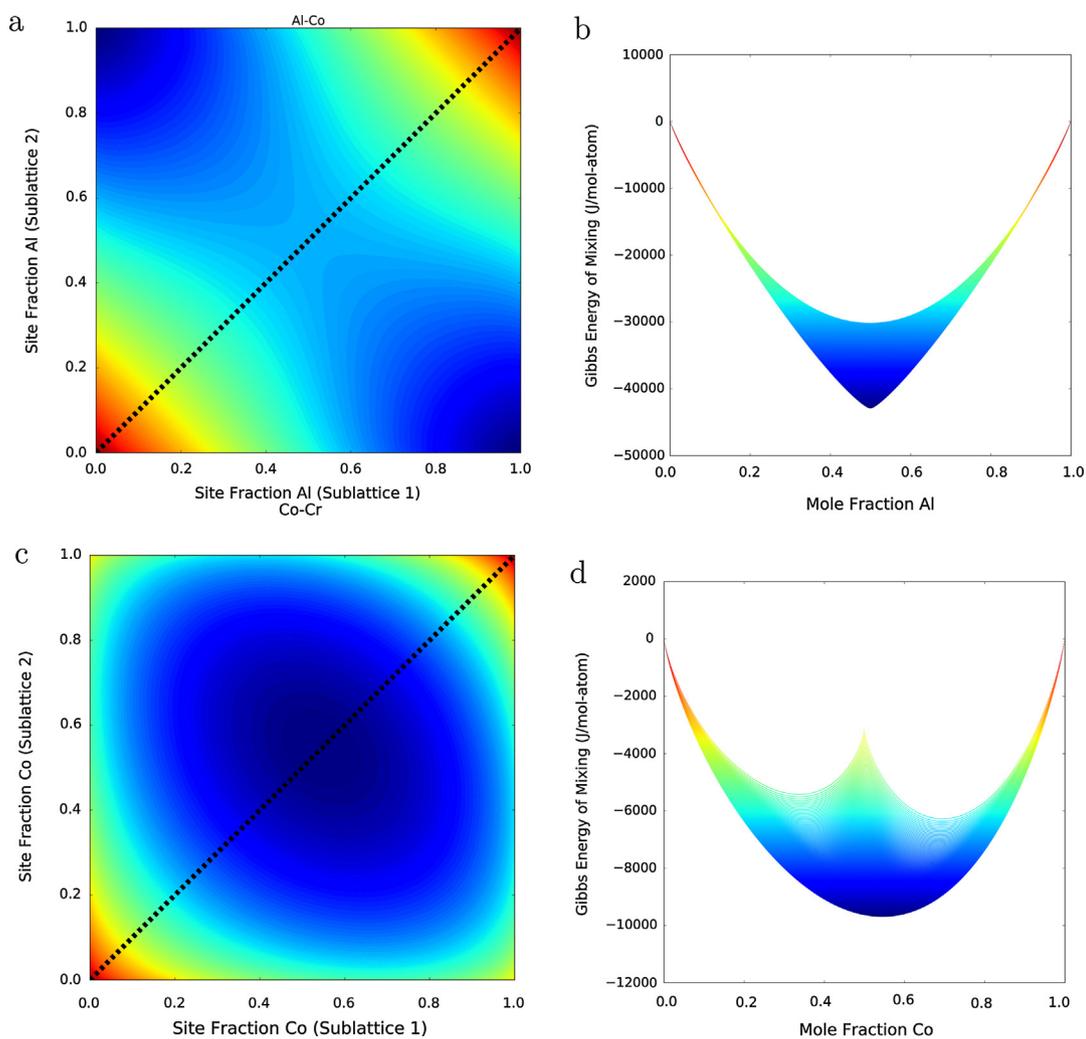


Fig. 2. The Al-Co (a, b) and Co-Cr (c, d) systems are shown with their internal energy surfaces (a, c) and those configurations mapped to the overall composition space (b, d). Multiple internal configurations map to the same overall composition, but only the low-energy configurations are relevant to equilibrium. For the Al-Co system, low-energy configurations are located at the Al:Co and Co:Al end-members, corresponding to the ordered bcc configuration of the phase near 50% Al. Due to crystallographic symmetry, Al:Co and Co:Al have the same energy, but this is not a requirement of sublattice models in the general case. The disordered bcc configuration, corresponding to the black dashed line across the diagonal, has higher energy in the composition region near 50% Al. Conversely, in the Co-Cr system, the ordered B2 end-members Co:Cr and Cr:Co are both much higher in energy than the disordered configuration of the same overall compositions, and that this holds true everywhere in that system at this temperature. This means B2 will not be observed at that temperature. The Al-Cr system (not shown) has a similar energy surface to the Co-Cr system.

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