Efficient, Systematic Estimation of Alloy Free Energy from Special Microscopic States

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For classical discrete systems under constant composition typically referred to substitutional alloys, we propose a new free energy calculation method so that a set of representative configurations can reasonablly predict composition-dependence of free energy above the transition temperature for alloys with many-body interactions.

I. INTRODUCTION

In order to achieve suitable alloy design, Helmholtz free energy should be central and fundamental information to construct e.g., their phase diagrams. For classical discrete system under constant composition typically referred to multicomponent alloys, free energy can be given by

\[ F = -\beta^{-1} \ln Z \]
\[ Z = \sum_d \exp \left( -\beta U^{(d)} \right) \]  

where \( \beta \) denotes inverse temperature, \( Z \) partition function, and summation is taken over possible microscopic states on configuration space (i.e., possible configurations). It is clear from Eq. (1) that with increase of system size, the number of possible configurations exponentially increases, making the direct estimation of \( F \) practically intractable. Therefore, various calculation techniques have been amply developed, including entropic sampling with Monte Carlo (MC) simulation the cluster variation method and thermodynamic integration with Frenkel method. Basically, the existing calculation method explore a set of configurations that dominantly contributes to estimation of \( F \), where these configurations should in principle depend on temperature and energy through Eq. (1).

Another important point for \( F \) calculation is accurate estimation of the potential energy \( E \) for each configuration, where first-principles (FP) total-energy calculation should be employed. However, direct estimation of \( E \) for possible configurations requires huge amount of computational cost. One of the most effective approaches to overcome the problem is to combine FP calculation with generalized Ising model (GIM) where energy for any given configuration \( d \) can be exactly expressed as

\[ U^{(d)} = \sum_{r=1}^{f} \langle U \mid q_r \rangle q_r^{(d)} \]  

where summation is taken over structural degree of freedoms (SDFs), \( \{ q_r \} \) denotes a set of complete basis functions of GIM, and \( \langle \cdot \mid \cdot \rangle \) represent inner product, i.e., trace over possible configurations. Since \( \{ q_r^{(d)} \} \), corresponding to multisite correlations, can be determined from configuration and \( \langle U \mid q_r \rangle \) is independent of configuration, we should know optimal values of \( \{ \langle U \mid q_r \rangle \} \) for given alloy system through FP calculation, typically requires at least several hundreds of total-energy calculations for representative configurations. Although the procedure of how to select a set of the representative configurations has been amply improved through several theoretical studies, it still remains difficult to apply the GIM-based procedure with FP calculation when we systematically change conditions including the constituent elements for multicomponent systems: This is because a set of representative configurations should depend on alloy system, which cannot be known a priori without any thermodynamic information.

In order to overcome the above practical problem, here we propose a new free energy calculation method so that a set of representative configuration is independent of energy and temperature: This can be achieved by rewriting semi-grand canonical average of composition in terms of multivariate moments based on GIM basis functions, and applying suitable dimensionality reduction. We confirm that the proposed method can reasonably predict composition-dependence of free energy above the transition temperature, by comparing with conventional thermodynamic simulation. Details of the concept, the derivation, and related discussion are shown in the following.

II. DERIVATION AND APPLICATIONS

Let us first briefly explain GIM basis functions used in the present work, which describes configuration and corresponding energy. We here focus on binary A-B system up to 3-body correlation, where occupation of given lattice site \( i \) is specified by spin variable \( \sigma_i = 1 \) for A and \( \sigma_i = -1 \) for B. Then, \( k \)-th basis function for configuration \( d \) is given by

\[ q_k^{(d)} = \left\langle \prod_{i \in S_k} \sigma_i \right\rangle_d \]  

where \( \langle \cdot \rangle_d \) denotes taking linear average for configuration \( d \), and the product is taken over a set of symmetry-equivalent figure \( S_k \) of \( k \). Hereinafter, without lack of generality, we describe configuration \( d \) measured from center of gravity for configurational density of states (CDOS), which is the density of states for possible configurations before applying many-body interaction to the system.
Under this preparation, we next consider semi-grand canonical average of point cluster \( q_1 \) (i.e., on-site correlation):

\[
\langle q_1 \rangle_Y = Y^{-1} \sum_d q_1^{(d)} \exp \left\{ -\beta \left( U^{(d)} - \Delta \mu N_A^{(d)} \right) \right\},
\]

where \( Y \) denotes semi-grand partition function defined as

\[
Y = \sum_d \exp \left\{ -\beta \left( U^{(d)} - \Delta \mu N_A^{(d)} \right) \right\}.
\]

Here, \( \Delta \mu = \mu_A - \mu_B \) denotes difference in chemical potential per atom for constituents A and B, and \( N_d \) denotes number of A in the system. When we know the relationships between chemical potential difference and semi-grand canonical average of \( q_1 \) given by Eq. (4), we can estimate corresponding system free energy through the conventional thermodynamic relation:

\[
F(T, x_A) = F(T, x_A = 0) + N \int_{x_A = 0}^{x_A^d} \Delta \mu dx_A,
\]

where \( x_A^d = N_A^d / N = (q_A^d + 1) / 2 \). In order to figure out a set of special configurations independent of energy and temperature, which can characterize behavior of \( F \), we first rewrite Eq. (4) as

\[
\langle q_1 \rangle_Y = \frac{2}{N} \frac{\partial}{\partial m} \ln \left\{ \sum_{N_A=0}^N \sum_c \exp \left( \sum_{i\neq 1} h_i q_i^c \right) e^{m v_A} \right\} - 1,
\]

where

\[
m = \beta \left( \Delta \mu - 2V_1 / N \right) = \beta (\Delta \mu - 2V_1)
\]

with \( V_1 = \langle U | q_i \rangle = N v_i, h_i = -\beta V_i \), and summation for \( c \) denotes possible configuration on given \( N_A \). Then we perform Maclaurin series expansion in terms of \( \{ h_i \} \) up to the second order and employ exact formulation of multivariate moments under constant composition leading to (see Appendix)

\[
\langle q_1 \rangle_Y = \tanh \frac{m}{2} - 2\beta \left[ \sum_i v_{2i} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^2 \right] + \beta^2 \left[ \sum_i \sum_j \frac{\delta_{ij}^{[2,3]}}{D_i} v_{2i} v_{3j} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^3 \right] + \beta^2 \left[ \sum_i \sum_j \left( 4 - 2\delta_{ij} \right) v_{2i} v_{2j} + \sum_i \sum_j \left( f_{ij}^{[3,3]} - 3\delta_{ij} \right) v_{3i} v_{3j} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^4 \right] + \beta^2 \left[ \sum_i \sum_j \left( 9 - 2f_{ij}^{[3,3]} + 3\delta_{ij} \right) v_{3i} v_{3j} - \sum_i \sum_j \left( 4 - \delta_{ij} \right) v_{2i} v_{2j} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^5 \right] - \beta^2 \left[ \sum_i \sum_j \left( 9 - f_{ij}^{[3,3]} + \delta_{ij} \right) v_{3i} v_{3j} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^6 \right],
\]

where \( v_{kn} \) denotes \( n \)-th figure of \( k \)-body (\( k = 2, 3 \)) figure, \( \delta_{ij} \) Kronecker delta, \( D_i \) (\( T_i \)) the number of \( i \)-th pair (\( j \)-th triplet) figure per site, and \( \delta_{ij}^{[2,3]} \) number of \( i \)-th pair included in a single \( j \)-th triplet figure. We here emphasize the technically important point in Eq. (9) is that we exclude variable of \( \beta \Delta \mu \) from the series expansion so that only special configuration-based information (as seen later) directly relates to the series expansion, which is a desirable condition: If we also include \( \beta \Delta \mu \) as variable for the expansion, we confirm that undesirable divergence for \( \Delta \mu - x \) relationships around equiatomic composition always appears even well above the transition temperature. When we individually define index for constituent pair in \( i \)-th (\( j \)-th) triplet as \( 2i_1, 2i_2 \) and \( 2i_3, 2j_1, 2j_2 \) and \( 2j_3 \), \( f_{ij}^{[3,3]} \) is given by

\[
f_{ij}^{[3,3]} = \sum_{m=1}^{3} \sum_{n=1}^{3} \frac{\delta_{mn} \beta}{D_{mn}}.
\]

From the first-order term in Eq. (9), we can clearly see that
when 2- and 3-body correlations for two special configurations \( Q_{g1} \) and \( Q_{g2} \) are given by

\[
\begin{align*}
Q_{g1} &= r_1 \cdot (q_2 = 1, \cdots, q_{n} = 1, q_3 = 0, \cdots, q_3 = 0) \\
Q_{g2} &= r_2 \cdot \{q_2 = 0, \cdots, q_2 = 0, q_3 = 1, \cdots, q_3 = 1\}
\end{align*}
\]

with arbitrary non-zero real number of \( r_1 \) and \( r_2 \), energy for each configuration satisfies

\[
\sum_i v_{2i} = r_1^{-1} \mathcal{E}_{g1}, \quad \sum_j v_{2j} = r_2^{-1} \mathcal{E}_{g2}.
\]

From Eq. (11), since configuration \( Q_{g1} \) and \( Q_{g2} \) can be known a priori without any thermodynamic information, the first-order term of Eq. (9) can be evaluated from energy of the two special configurations that are common for any constituents.

For the second-order terms in Eq. (9), we first define the following vector:

\[
v = (v_{21}, \cdots, v_{2i}, v_{31}, \cdots, v_{3k}).
\]

Then Eq. (9) can be rewritten as the following form:

\[
\angle q_1 \rangle_\gamma = \tanh \frac{m}{2} - 2\beta \left[ \sum_{k=1}^{2} \left\{ r_k^{-1} \mathcal{E}_{gk} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^{k+1} \right\} \right] + \beta^2 \sum_{n=1}^{6} b_n \cdot v^T A_n \cdot \left\{ \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^n \right\},
\]

where \( b_n \) take +1 for \( n = 1, 2, 3, 4 \) and -1 for \( n = 5, 6 \), and \( A_n \) is \((s + r) \times (s + r)\) real symmetric matrix whose elements correspond to each coefficient of \( v_{2i} v_{3j} \) in Eq. (9). To obtain a set of special configurations for the second-order term, we perform singular value decomposition (SVD) for \( A_n \), namely

\[
A_n = \sum_{i=1}^{a} \lambda_i^{(n)} \cdot u_i^{(n)} \cdot u_i^{(n)T}
\]

where \( \lambda_i^{(n)} \) and \( u_i^{(n)} \) correspond to the \( i \)-th singular value and singular vector for \( A_n \), and \( a \) denotes effective rank of \( A_n \). Therefore, we can specify a set of specialized configuration \( Q_{fi}^{(n)} \), satisfying

\[
Q_{fi}^{(n)} = r_i^{(n)} \cdot u_i^{(n)}
\]

with arbitrary non-zero real number of \( r_i^{(n)} \), Eq. (14) can be further rewritten by using energy for the additional special configurations:

\[
\angle q_1 \rangle_\gamma = \tanh \frac{m}{2} - 2\beta \left[ \sum_{k=1}^{2} \left\{ r_k^{-1} \mathcal{E}_{gk} \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^{k+1} \right\} \right] + \beta^2 \sum_{n=1}^{6} b_n \cdot \left\{ \frac{\partial}{\partial m} \left( \tanh \frac{m}{2} \right)^n \right\},
\]

From Eq. (16), since configurations \( \{Q_{fi}^{(n)}\} \) can also be known a priori without any thermodynamic information, Eq. (17) can be evaluated from energy of the two and additional special configurations that are common for any constituents. Eq. (17) can be effectively expressed by a few number of special configurations particularly for low-rank \( A_n \), and we confirm that this can typically hold for representative lattices including fcc and bcc.

We finally demonstrate applicability of the proposed approach for estimation of free energy, preparing two artificial fcc-based equiatomic system with many-body interactions shown in Fig. 1, respectively exhibit order structure and phase separation for the ground state.
vide reasonable agreement with thermodynamic simulation, where the proposed method employs information only about energy of special configurations common for the two systems and does not require explicit information about many-body interaction or not require sampling across configuration space, while the conventional one should require both information. The significant difference in free energy around transition temperature mainly comes from lack of higher-order moment information, which should be addressed in our future study.

III. CONCLUSIONS

We propose a new estimation method of Helmholtz free energy from information about energy of special configuration, which can be known a priori without any thermodynamic information, and can be determined only from lattice geometry. The proposed method demonstrates reasonable agreement in free energy prediction compared with conventional thermodynamic simulation above the transition temperature, indicating that the proposed method can effectively provide systematic prediction of alloy phase stability for various combination of constituents.

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