Compositional asymmetry of disordered structure: Role of spatial constraint

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When spatial constraint for the constituents (e.g., atom or particle) of system is once given, disordered structure for *non-interacting* system in equilibrium states is symmetric with respect to equiatomic composition. Meanwhile, when the interaction between constituents is introduced, this symmetry is typically broken, naturally appearing compositional asymmetry. Although this asymmetry, depending on temperature, comes from multibody interactions in the system, we here clarify that the asymmetry near equiatomic composition can be universally well-characterized by two specially selected microscopic structure, which can be known *a priori* without any information about interactions or temperature: The key role is the class of spatial constraint. Based on the facts, we provide analytical expression of temperature dependence of disordered structure, and demonstrate its validity and applicability by predicting short-range order parameters of practical alloys compared with full thermodynamic simulation.

Key words: Statistical physics, Theory, Short-range order

1. INTRODUCTION

In classical systems in equilibrium states, when temperature increases, the system can undergo from ordered to disordered structures due to the competition between interactions and (configurational) entropy. When we prepare set of complete orthonormal basis $\{q_1, \dots, q_g\}$ to describe microscopic structures on configuration space under fixed composition x , their expectation value along q_r at temperature T can be typically obtained through canonical average, given by $Q_r(x, T) = Z^{-1} \sum_d q_r^{(d)} \exp(-\beta E^{(d)})$, where summation is taken over all microscopic states at composition x on phase space. Since number of possible microscopic states astronomically increases, potential energy surface should be described by corresponding high-dimensional configuration space. Therefore, a variety of calculation techniques have been developed to overcome the practical difficulty, including Monte Carlo (MC) simulation with Metropolis algorithm, multicanonical ensembles and entropic sampling to effectively sampling possible microscopic states for predicting macroscopic properties. Although the developed approaches have successfully provided accurate prediction of disordered structures in equilibrium states, the role of spatial constraints on composition and temperature dependence of the disordered structures does not get sufficient attention so far.

Very recently, we develop a theoretical approach, enabling to provide new insight into how equilibrium properties (including structures and free energy) connects with spatial constraint on the system.[1–4] Through this approach, we find a few special microscopic states, called "Grand Projection states" (GP states), that can be constructed without any information about energy or temperature, can characterize the macroscopic properties. In the present study, we extend the approach to investigating composition dependence of disordered structures in equilibrium states near equiatomic composition (i.e., which we call "compositional asymmetry"). Through the extension, we provide analytical representation for temperature and composition

dependence of disordered structure in terms of the condition of spatial constraint, which can be determined by energy of GP states.

2. DERIVATION AND DISCUSSIONS

Let us here consider a binary system (for simplicity), but our derivation can be straightforwardly extended to multicomponent system as seen below. In classical system under potential energy as a function of spatial positions of constituents, we have found that grand-canonical average of structure can be universally given by[4]

$$Q_r(T) \simeq \langle Q_r \rangle_{1G} \mp \sqrt{\frac{\pi}{2}} \langle Q_r \rangle_{2G} \frac{I_{GP}^{(Q_r \pm)} - \langle I \rangle_{1G}}{k_B T} \quad (1)$$

where $\langle \cdot \rangle_{1G}$ and $\langle \cdot \rangle_{2G}$ respectively denotes taking average and standard deviation over all microscopic states on configuration space (including compositions) without weight of Boltzmann factor $\exp(-\beta E)$. I s are respectively defined as

$$I = E - \Delta \mu N x \quad (2)$$

and

$$\begin{aligned} I_{GP}^{(Q_r \pm)} &= E_{GP}^{(Q_r \pm)} - \Delta \mu N \langle x \rangle_{GP}^{(Q_r \pm)} \\ &= \sum_{t=1}^s \langle E | Q_t \rangle \langle Q_t \rangle_{GP}^{(Q_r \pm)} - \Delta \mu N \langle x \rangle_{GP}^{(Q_r \pm)} \end{aligned} \quad (3)$$

where summation is taken over possible configurational degree of freedom including composition, $\langle \cdot \rangle_{GP}^{(Q_r \pm)}$ denotes partial average over microscopic states satisfying $Q_r \geq \langle Q_r \rangle_{1G}$ ($Q_r \leq \langle Q_r \rangle_{1G}$) for Q_r^+ (Q_r^-), and $\langle \cdot | \cdot \rangle$ represents inner product on configuration space. Here, we call $E_{GP}^{(Q_r \pm)}$ as grand projection (GP) energy along Q_r , and corresponding special microscopic structure given by $\{\langle Q_1 \rangle_{GP}^{(Q_r \pm)}, \dots, \langle Q_s \rangle_{GP}^{(Q_r \pm)}\}$ is called as GP state along Q_r , which is clearly independent of temperature and energy,

and depends only on the class of spatial constraint since $\langle Q_t \rangle_{\text{GP}}^{(Q_r \pm)}$ can be obtained by density of microscopic states on configuration space for *non-interacting* system. When we choose coordination Q_r as composition, corresponding energy and microscopic states are simply called as GP energy and GP state, which can provide relationship between chemical potential $\Delta\mu$ and grandcanonical average of composition, $x(T, \Delta\mu)$.

In the present study, we only focus on the GP energy and state for composition, and we do not derive explicit expression for grand canonical average of structures: The reason is treating numerator in Eq. (1). When we directly apply the previous expression for two dimensional configuration space of $g(x, Q_r)$ in analogy to our previous approach using characteristics of multidimensional gaussian (here, g denotes density of microscopic states, and Q_r corresponds to pair correlations), we can obtain for numerator as

$$E_{\text{GP}}^{(Q_r \pm)} - \langle E \rangle_{1G} + \Delta\mu N \cdot \text{cov}(x, Q_r) \quad (4)$$

where $\text{cov}(x, Q_r)$ denotes covariance for $g(x, Q_r)$. Since for even-order correlation should be symmetric at equiatomic composition, we obtain $\text{cov}(x, Q_r) = 0$, which should be only allowed at high temperature limit $T \rightarrow \infty$. Therefore, in order to apply Eq. (1) at non-infinite temperature, we should take other strategies. To include the asymmetry of $g(x, Q_r)$, in analogy to obtaining GP states, we should explicitly take composition-dependent partial average of x in $g(x, Q_r)$ space. Let $\langle x \rangle_{\text{GP}}^{(Q_r \pm)}$ be a function of composition x . From the constraint condition that $\langle x \rangle_{\text{GP}}^{(Q_r \pm)} = 0$ at $x = \langle x \rangle_{1G}$ and $Q_r(x, T)$ is a quadratic function of x at $T \rightarrow \infty$, [5] we can determine the composition-dependence, namely, $\langle x \rangle_{\text{GP}}^{(Q_r \pm)} = x \langle x \rangle_{x+}^{(Q_r \pm)} + (1-x) \langle x \rangle_{x-}^{(Q_r \pm)} - \langle x \rangle_{1G}$. Here, $\langle \cdot \rangle_{x+}^{(Q_r \pm)}$ ($\langle \cdot \rangle_{x-}^{(Q_r \pm)}$) denotes partial average $\langle \cdot \rangle^{(Q_r \pm)}$ for $x \geq \langle x \rangle_{1G}$ ($x \leq \langle x \rangle_{1G}$). In order to obtain composition dependence of disordered structure from Eq. (1), we should further determine the relationship between chemical potential $\Delta\mu$ and grand-canonical average of composition x . This can be easily performed by choosing coordination of Q_r in Eq. (1) as composition, x . [4]

Using the above results, we can give analytical expression for pair correlation near equiatomic composition:

$$Q_r(x, T) \simeq \langle Q_r \rangle_{1G} \mp \sqrt{\frac{\pi}{2}} \langle Q_r \rangle_{2G} \frac{E_{\text{GP}}^{(Q_r \pm)} - \langle E \rangle_{1G} \pm \zeta^{(x+/x-)}(T) C^{(Q_r \pm)}(x)}{k_B T} \quad (5)$$

where

$$\begin{aligned} \zeta^{(x+/x-)}(T) &= \pm \frac{1}{\langle x \rangle_{x+}^{(Q_r \pm)} - \langle x \rangle_{1G}} \left\{ k_B T \sqrt{\frac{2}{\pi}} \frac{1}{\langle x \rangle_{2G}} (x - \langle x \rangle_{1G}) \pm E_{\text{GP}}^{(x+/x-)} - \langle E \rangle_{1G} \right\} \\ C^{(Q_r \pm)}(x) &= x \langle x \rangle_{x+}^{(Q_r \pm)} + (1-x) \langle x \rangle_{x-}^{(Q_r \pm)} - \langle x \rangle_{1G}. \end{aligned} \quad (6)$$

Here, superscript $(x+/x-)$ denotes disordered structure for higher x phase ($x+$) or for lower x phase ($x-$), where their

coexistence can be determined from GP energy along x , i.e., $E_{\text{GP}}^{(x+/x-)}$. [4]

From the above equations, we can clearly see that composition dependence of disordered structures can be characterized by five special microscopic states (whose energy corresponds to $E_{\text{GP}}^{(Q_r \pm)}$, $E_{\text{GP}}^{(x+/x-)}$ and $\langle E \rangle_{1G}$), whose structure can be known *a priori* when spatial constraint on the constituents is given. From Eq. (5), we can also see that compositional asymmetry around equiatomic composition is dominated by the asymmetry of GP energy along composition, where such asymmetry can be reasonably vanished at high temperature limit of $T \rightarrow \infty$. This can be schematically shown in Fig. 1, which shows the temperature and composition dependence of difference in structure, $Q_r(x+\langle x \rangle_{1G}, T) - Q_r(x-\langle x \rangle_{1G}, T)$, for the case of $\Delta E > 0$ and $\Delta E < 0$, where ΔE denotes absolute difference in grand projection energy along composition for $(x+)$ and $(x-)$ (energy is measured from $\langle E \rangle_{1G}$).

Fig. 1 Schematic illustration for temperature and composition dependence of difference in structure, $Q_r(x+\langle x \rangle_{1G}, T) - Q_r(x-\langle x \rangle_{1G}, T)$. ΔE denotes absolute difference in grand projection energy along composition for $(x+)$ and $(x-)$.

In order to confirm the tendency of compositional asymmetry, we compare the results given in Fig. 1 with those obtained by full thermodynamic simulation: We artificially prepare effective multibody interactions in terms of generalized Ising model on fcc lattices with binary elements, which provides well-known ordered structure of "40" at the ground state with order-disorder transition temperature is around 150 K. [2] We estimate difference in short-range order (SRO) parameter ΔQ for the system between $x = 0.46$ and $x = 0.54$, which is symmetric with respect to equiatomic composition of $x = 0.5$. Temperature dependence of SRO is quantitatively estimated by applying the multibody interactions to Monte Carlo (MC) statistical simulation under canonical ensemble, where the MC cell contains 2048 atoms (i.e., $8 \times 8 \times 8$ expansion of conventional fcc unit cell) with 8000 MC step per site to take ensemble average. The predicted ΔQ by the present theory and MC simulation is shown in Fig. 2 together with the multibody interaction used. We can clearly see that at

high temperature above ~ 800 K, SRO by the present theory exhibit excellent agreement with that by MC, while it shows deviation with decrease of temperature. This deviation can be reasonably interpreted since our theory is based on the configurational density of states (CDOS) for *non-interacting* system well-characterized by multidimensional gaussian, whose deviation from practical CDOS should be naturally enhanced by Boltzmann factor $\exp(-\beta E)$ at low temperature with the foot of the CDOS from its center of gravity where effect of spatial constraint on CDOS, especially information about landscape of higher order moment (typically, greater than two), plays significant role, which has already been confirmed by our previous studies. Inclusion of information about higher-order moments of CDOS into the proposed Eq. (5) therefore should be our future study.

Fig. 2 Difference in SRO parameter ΔQ as a function of temperature, predicted by the present theory and MC simulation. ΔQ is normalized by value of Q that can take maximum under the given spatial constraint, i.e., fcc lattice in this case. Multibody interactions used for MC simulation is given together.

4. CONCLUSIONS

By focusing on the role of spatial constraint on equilibrium properties, we propose analytical representation for compositional asymmetry of disordered structure in binary system, which is dominated by energy of two specially selected microscopic states whose structures can be known a priori without any information about energy or temperature. We demonstrate the validity of the proposed representation by predicting the short-range order tendency on fcc lattice, compared with full thermodynamic simulation based on generalized Ising model: While deviation is enhanced with decrease of temperature, we find excellent agreement at high temperature region.

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