Grand Projection State: A Single Microscopic State to Determine Free Energy

Tetsuya Taikei, Tetsuya Kishimoto, Kazuhito Takeuchi, and Koretaka Yuge
Department of Materials Science and engineering, Kyoto University, Kyoto 606-8501, Japan

Recently, we clarify connection of spatial constraint and equilibrium macroscopic properties in disordered states of classical system under the fixed composition; namely few special microscopic states, independent of constituent elements, can describe macroscopic properties. In this study, we extend our developed approach to composition-unfixed system. Through this extension in binary system, we discover a single special microscopic state to determine not only composition but also Helmholtz free energy measured from unary system, which has not been described by a single state.

I. INTRODUCTION

It has been more than 130 years since Hermann von Helmholtz defined free energy $F$. $F$ is very useful concept when we can consider the system to be under constant volume, like crystalline solid and liquid. $F$ has the member of entropy, which is a measure of the number of possible microscopic states. Therefore, $F$ has not been described by a single state in classical system. In statistical mechanics, free energy and macroscopic physical properties ($\bar{C}$) can be given by

$$F = -k_B T \ln Z,$$

$$\bar{C} = Z^{-1} \sum \langle C \rangle \exp \left( -\frac{E^{(d)}(q)}{k_B T} \right) \cdot$$ (1)

Here, $d$ is a microscopic state on phase space, $k_B$ is Boltzmann constant, $T$ is temperature, and $Z$ is partition function. $Z$ takes sum over possible microscopic state, thus $F$ cannot be described by a single state from Eq. [1] It is obvious that with increase of system, the number of possible states increases exponentially. This fact makes direct estimation of $F$ practically impossible. Therefore, several calculation techniques have been developed and widely utilized, such as entropic sampling [1] with Monte Carlo (MC) simulation [2][3], cluster variation method[4][5], and Frankel method[6].

Recently, we clarify relation between spatial constraint (viz. lattice for crystalline solids, volume and density for liquid) and equilibrium macroscopic properties in disordered states of classical system under the fixed composition[7][8][9]. Here, we do not need temperature, elements constituent, or interactions. This approach relies on that density of state for $C$ on configuration space can be well characterized by multidimensional Gaussian distribution. This important characteristic of distribution of $C$ is proven by combination of a theory and an approximation.

The theory is that microscopic states on configuration space can be described by complete basis functions $\{q_1, q_2, ..., q_s\}$. By using basis functions, $C$ for any microscopic state $d$ can be expressed as

$$C^{(d)} = \sum_{r=1}^{s} \langle C|q_r \rangle q_r^{(d)},$$ (3)

where $\langle C|q_r \rangle$ means inner product. Thus, when $C$ is energy and $q_r$ is cluster function[10][11][12], $\langle C|q_r \rangle$ denotes effective cluster interaction, called ECI. The approximation is that the density of states for $q_r$ on non-interacting system is expressed by Gaussian distribution. The validity of this approximation is confirmed by random matrix research; this means vanishment of statistical interdependence of $q_r$. These two points shows that density of state for $C$, linear combination of $q_r$, is well characterized by multidimensional Gaussian distribution. This developed approach enable us to estimate free energy directly, and to get few special microscopic states, which determine $\bar{C}$ and $\bar{C}$. However, we have not been successful in considering composition and describing free energy by one state even with our approach.

In the present study, we extend our developed approach under fixed composition (canonical approach) to composition-unfixed system (semi-grand canonical approach). In semi-grand canonical approach, we consider the system with the framework of semi-grand canonical ensemble, thus chemical potential is needed. Unlike grand canonical ensemble, semi-grand one needs number of all atoms. This extension is suggested by additional research with random matrix. Through this study, we get a single special microscopic state in binary system of disordered states under classical system, which is derived only from spatial constraint. We call this state “Grand Projection State” (GPS). GPS give us not only composition in the system, but also Helmholtz free energy $F$ measured from unary system, which has not been represented by a single state in classical system. We explain additional random matrix research, and introduce present approach to get composition and free energy with GPS.

II. DERIVATION AND CONCEPT

A. Random Matrix

Let us first explain our random matrix (RM) approach. This approach is introduced for confirming the characteristic of density of microscopic states, and we show that statistical interdependence of $q_r$ becomes disappeared as the scale of spatial constraint becomes large[13]. Here, we take $m \times n$ matrix $K$, where $m$ is the number
of sampling point on configuration space, and \( n \) is the
number of basis functions considered. With this defi-
tion, the normalized covariance matrix \( J \) for \( q_r \) can be
calculated as

\[
J = \frac{1}{m} K^T K, \tag{4}
\]

where \( K^T \) means transposed matrix of \( K \). When we con-
sider an ideal system where statistical interdependence is
disappeared (viz. \( K \) is RM, \( K_{RM} \)), all elements is inde-
pendently consisted of normal random numbers, with its
average and variance respectively taking 0 and 1, lead-
ing to all diagonal elements for RM, \( J_{RM} \), to be 1. The
validity of constructed RM in this research with finite
size is guaranteed, comparing with Marchenko-Pastur
distribution \([14]\). Meanwhile, when we consider practical
system, we first uniformly sample \( m \) microscopic states
using MC simulation. Then, we calculate and normalize
the value of \( n \) basis functions in each microscopic state
so that average and variance of each column of \( J \) re-
spectively should be 0, and \( 1/m \) for comparison. When
the statistical interdependence of \( q_r \) is disappeared, the
elements of matrix \( J \) is regarded to be consisted inde-
pendently, which is same as RM. Therefore, we check the
difference of matrices using their eigenvalues, as density
of eigenvalues (DOE) of covariance matrix \( J \). For setting
practical system, we have two choices; composition-fixed
method and composition-unfixed method (see appendix
A).

In this study, we consider an example for equiatomic A-B
binary system on FCC lattice. In order to get basis func-
tion, we employ generalized Ising-like spin of \( \sigma = \pm 1 \), and
\( q_r \) can be defined by \( q_r = \langle \prod_{i \in k} \sigma_i \rangle_{\text{lattice}} \), where \( \sigma_i \) is spin
at site \( i \), \( \langle \cdot \rangle_{\text{lattice}} \) is average over all sites on the lattice,
and \( k \) is the index indicating cluster type, such as empty,
point, 1st nearest neighbor (1NN) pair. Advantage of ap-
plying Ising-model is that the interdependent of \( q_r \) has
already been none-zero with taking limit of the number of
atoms in the system without a change of basis \([9]\). Here,
clusters considered are pair clusters up to 6NN, triplet
clusters consisting of up to 6NN pairs, resulting in 29
basis functions(i.e. \( n = 29 \)). We sample 500,000 micro-
scopic states (i.e. \( m = 500,000 \)), and perform 500,000
MC steps for 1152-atom MC-cell for getting one micro-
scopic state. We can see that statistical interdependence is
more vanished in composition-unfixed practical system
(CUFS) than in composition-fixed practical system
(CFS).

Figure 1 shows DOEs for CFS, CUFS, and RM. Although
difference between CFS and RM is gradually disappeared
when number of atoms increases \([13]\), they still have
quantitative differences: DOE for RM has single sharp
peak, while CFS does not have. Meanwhile for CUFS,
under the same number of atoms, it is easily realized
that the landscape of DOE is much more similar to RM
than CFS in terms of shape and location of the peak.
To make further quantitative comparison, we estimate
moments (from 2nd to 4th) of DOEs, defined by

\[
M_1 = \frac{\sum_{i=1}^{N_d} x_i}{N_d},
\]

\[
M_L = \frac{\sum_{i=1}^{N_d} (x_i - M_1)^L}{N_d}, \tag{6}
\]

where \( L \) is an order of the moment, \( N_d \) is number of data and \( x_i \) is each data of index \( i \). Figure 2 shows mo-
ments in CFS, CUFS, RM. 2nd-order moment of CUFS
successfully agree with that of RM. In addition to 2nd-
order, compared to CFS, 3rd and 4th-order is vanished
in CUFS, which shows excellent agreement with RM.
These fact shows that CUFS is much more similar to
RM, namely statistical interdependence is more vanished
in CUFS than in CFS. Therefore, composition should be
considered in setting practical system, and this suggests

\[
\begin{array}{c}
\text{Left: The value is unnormalized.} \\
\text{Right: The value is normalized for comparison so that the}
\text{magnitude of each order moment for CFS is 1.}
\end{array}
\]
that our established approach in disordered states should be extended to composition-unfixed system; semi-grand canonical ensemble. We show concept and derivation of the extension in binary system.

B. Grand Projection State (GPS)

In canonical ensemble, we have shown that canonical average of basis function \( q_r \), \( Q_r \), can be expressed by

\[
Q_r(T) \simeq \langle q_r \rangle_1 + \sqrt{\frac{\pi}{2}} \langle q_r \rangle_2 \cdot \frac{E^{\text{proj}}_{r \pm}}{k_B T},
\]

(7)

\[
E^{\text{proj}}_{r \pm} = \sum_{t=1}^{s} \langle E|q_t\rangle|q_t\rangle^{(\pm)},
\]

(8)

where, \( \langle \cdot \cdot \cdot \rangle_1 \) and \( \langle \cdot \cdot \cdot \rangle_2 \) respectively denotes average and standard deviation over all microscopic state [8](and see Appendix B). \( \langle \cdot \cdot \cdot \rangle^{(+)} \) and \( \langle \cdot \cdot \cdot \rangle^{(-)} \) is a partial average over all microscopic states respectively under \( q_r \geq \langle q_r \rangle_1 \) and \( q_r \leq \langle q_r \rangle_1 \). Then, \( E^{\text{proj}}_{r \pm} \) respectivley can be described by a single microscopic state, \( \{ \langle q_1 \rangle^{(\pm)}, \langle q_2 \rangle^{(\pm)}, ..., \langle q_s \rangle^{(\pm)} \} \), which is deriving only from the information of spatial constraint (e.g., lattice). We call this state projection state, and \( E^{\text{proj}}_{r \pm} \) projection energy along coordination \( r \). It is notable that Eq. (7) is derived from the fact that density of states on configuration space for non-interacting system can be well characterized by multidimensional Gaussian distribution. Two representation of \( Q_r(T) \) comes from this approximation, and when density of states completely matches Gaussian distribution, two values are same.

In semi-grand canonical ensemble, instead of \( E \), we consider \( \Delta \mu \) and \( I \) defined as

\[
\Delta \mu = \mu_A - \mu_B,
\]

(9)

\[
I = E - \Delta \mu N x_A,
\]

(10)

with Legendre transformation; \( E \) to \( I \). Here, \( \mu_A \) and \( x_A \) respectively means chemical potential energy and composition of A atoms, and \( N \) means number of all atoms (constant in semi-grand canonical). Then in semi-grand canonical ensemble, we can write the ensemble average like Eq. (1) as

\[
\langle \cdot \cdot \cdot \rangle_{1G} = AZ_G^{-1} \sum_d C^{(d)} \exp\left(-\frac{I^{(d)}}{k_B T}\right),
\]

(11)

where \( A = \exp\left(\frac{\mu_A N x_A}{k_B T}\right) \), and \( Z_G \) is semi-grand partition function. We take care about a possible microscopic state \( d \) including composition, and we respectively define \( \langle \cdot \cdot \cdot \rangle_{1G} \) and \( \langle \cdot \cdot \cdot \rangle_{2G} \) as average and standard derivation including composition. Now in binary system, we define coordination for composition, \( q_{\text{comp}} = x_A \). With this definition \( \Delta \mu N x_A \) can be described by coordination for composition; therefore same as \( E \), we can express \( I \) with inner product like Eq. (3):

\[
I^{(d)} = \sum_{t=1}^{s} \langle E|q_t\rangle q_t^{(d)} - \Delta \mu N q_{\text{comp}}
\]

(12)

\[
= \sum_{t=1}^{s} \langle I|q_t\rangle q_t^{(d)}.
\]

(13)

In addition to this, density of states along \( q_{\text{comp}} \) shows Gaussian distribution, because it is from binomial distribution. Therefore, we can write \( I \) as multidimensional Gaussian distribution; thus, we can apply our canonical approach to semi-grand canonical one with minor change. Just we should do is to replace \( E \) by \( I \); Equations (7) and (8) can be extended:

\[
\dot{Q}_r(T) \simeq \langle q_r \rangle_{1G} + \sqrt{\frac{\pi}{2}} \langle q_r \rangle_{2G} \cdot \frac{I^{\text{proj}}_{r \pm} - \langle I \rangle_{1G}}{k_B T},
\]

(14)

\[
I^{\text{proj}}_{r \pm} = \sum_{t=1}^{s} \langle I|q_t\rangle |q_t\rangle^{(\pm)}
\]

(15)

= \sum_{t=1}^{s} \langle E|q_t\rangle |q_t\rangle^{(\pm)} - \Delta \mu N \langle q_{\text{comp}} \rangle^{(\pm)}.
\]

(16)

Here, \( \langle \cdot \cdot \cdot \rangle^{(\pm)} \) denotes partial average including composition, \( E \) denotes projection energy in semi-grand canonical ensemble, and \( \dot{Q}_r \) denotes semi-grand canonical average of basis function \( q_r \). When we think coordination \( r \) to be composition, we can get special information and advantage. We call this special projection state for \( q_{\text{comp}}, \) Grand Projection State (GPS). First, GPS determine composition in the system. From symmetry of binomial distribution, which leads density of states along \( q_{\text{comp}} \), we can easily introduce \( \langle q_{\text{comp}} \rangle_{1G} = 1/2 \). In addition, \( I^{\text{proj}}_{\text{comp}+} \) and \( I^{\text{proj}}_{\text{comp}-} \) is calculated respectively based on A-rich, B-rich composition. Therefore, from Eq. (14), we get two representation of ensemble average of composition (for the sake of simplicity, hereinafter \( \langle I \rangle_{1G} = 0 \));

\[
x_{\text{A}}(T) \simeq \frac{1}{2} - \sqrt{\frac{\pi}{2}} \langle q_{\text{comp}} \rangle_{2G} \frac{I^{\text{proj}}_{\text{comp}+}}{k_B T}.
\]

(17)

\[
x_{\text{B}}(T) \simeq \frac{1}{2} - \sqrt{\frac{\pi}{2}} \langle q_{\text{comp}} \rangle_{2G} \frac{I^{\text{proj}}_{\text{comp}-}}{k_B T}.
\]

(18)

Here, we get composition in the system from a single state, GPS, \( \{ q_1^{(+G)}, q_2^{(+G)}, ..., q_s^{(+G)} \} \), or \( \{ q_1^{(-G)}, q_2^{(-G)}, ..., q_s^{(-G)} \} \), which depends only on
With Eqs. (15)-(17), Eqs. (21) and (22) can be developed; energy, composition and temperature shows in appendix between disorder states like fig. 3. The connection of free energy, this two representation indicate phase separation comparison to A and B unary system. In addition to this, Eqs. (23) and (24) respectively tells stability with F cause both efficient even though their differences. It is because we define \( \langle \alpha \rangle \) \( \equiv \langle I \rangle_1 = 0 \) after Eq. (17). These development successfully shows that Helmholtz free energy \( F \) can be described only by GPS (projection energy and \( \langle q_{\text{comp}} \rangle_{\text{comp}} \)) even though \( F \) has entropy term depending on all possible microscopic states. Here, we have two representation based on A-rich and B-rich system. Difference of these value comes from approximation of density of states (explained above). However, these two types of representation are both efficient even though their differences. It is because \( F \) has introduced for value comparison of stability, and Eqs. (23) and (24) respectively tells stability with comparison to A and B unary system. In addition to this, this two representation indicate phase separation between disorder states like fig. 5. The connection of free energy, composition and temperature shows in appendix.

\[
F = E - TS + \mu N = E - TS + \mu_B N + \Delta \mu N x_A. \tag{19}
\]

Therefore,
\[
\frac{\partial F}{\partial x_A} = \Delta \mu N, \quad \frac{\partial F}{\partial x_B} = -\Delta \mu N. \tag{20}
\]

Therefore, we get \( F \) measured from unary system;
\[
F = F_A + \int_1^{x_A(T)} \Delta \mu N dx_A. \tag{21}
\]
\[
F = F_B + \int_1^{x_B(T)} (-\Delta \mu N) dx_B. \tag{22}
\]

With Eqs. (15)-(17), Eqs. (21) and (22) can be developed;
\[
F \approx F_A + \frac{x_A^2}{\alpha \cdot \langle q_{\text{comp}} \rangle_{\text{comp}}^{(+G)}} + (\alpha \cdot \langle q_{\text{comp}} \rangle_{\text{comp}}^{(+G)} - 1) x_A - \alpha \cdot \langle \dot{E}_{\text{comp}}^{\text{proj}} \rangle_{\text{comp}}^{(+G)}. \tag{23}
\]
\[
F \approx F_B - \frac{x_B^2}{\alpha \cdot \langle q_{\text{comp}} \rangle_{\text{comp}}^{(-G)}} + (\alpha \cdot \langle q_{\text{comp}} \rangle_{\text{comp}}^{(-G)} - 1) x_B - \alpha \cdot \langle \dot{E}_{\text{comp}}^{\text{proj}} \rangle_{\text{comp}}^{(-G)}. \tag{24}
\]

Note that \( \langle q_{\text{comp}} \rangle_{\text{comp}}^{(-G)} \leq 0 \) because we define \( \langle I \rangle_1 = 0 \) after Eq. (17). This result suggest to us that our canonical approach should be extended to semi-grand canonical one. Then, we successfully discover a single microscopic state describing composition of one element. However for getting free energy, we need composition of all elements, thus we need \( (N-1) \) microscopic states. They are our future works.

\[\alpha = \frac{\sqrt{\pi} \langle q_{\text{comp}} \rangle_{\text{comp}}^{(G)}}{k_B T}. \tag{25}\]

III. CONCLUSION

In present study, we confirm that composition unfixed practical system is more similar to random matrix than composition-fixed system in terms of vanishment of interdependence of \( q_r \). This result suggest to us that our canonical approach should be extended to semi-grand canonical one. Then, we successfully discover a single special microscopic state (GPS) in binary system only from the information of spatial constraint. This GPS gives us composition in the system. Furthermore, GPS gives us Helmholtz free energy measured from unary system, which has not been described by a single state.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research (16K06704), and a Grant-in-Aid for Scientific Research on Innovative Areas Materials Science on Synchronized LPSO Structure (26109710) from the MEXT of Japan, Research Grant from Hitachi Metals-Materials Science Foundation, and Advanced Low Car-
In this section, we explain two method to set practical system in random matrix research: composition-fixed and composition-unfixed method. In the fixed method, we set the atom under fixed composition through MC simulation. In the unfixed method, we consider local system should have composition-fluctuation; probability $P_x$ that local system has $A$-composition $x$ in binary system is theoretically given by binomial distribution:

$$ P_x = N_l C_{xN_l} x_f^{xN_l} (1-x_f)^{N-N_l} \quad (A1) $$

Here, $N_l$ is number of local system, $x_f$ is composition of large system. In $m$ times sampling, $m \cdot P_x$ is the times sampled at composition $x$. Therefore, for getting matrix from local system, we set the atom $m \cdot P_x$ times under composition $x$, and do MC simulation. In this setting, we can consider local composition fluctuation of the large system.

In present study, we set equiatomic large box in unfixed method and consider 1152-atom local system (i.e. $x_f = 0.5$ and $N_l = 1152$) for comparison to equiatomic fixed system. Figure [A1](#fig:A1) shows connection of composition and sampling number in unfixed method.

![Figure A1](#fig:A1) Sampling number for composition in composition-unfixed practical system. No plot point along composition does not be sampled in this trial because of the number of sampling.

### Appendix A: Effect of composition

#### 1. Composition-fixed/unfixed method

In this section, we explain two method to set practical system in random matrix research: composition-fixed and composition-unfixed method. In the fixed method, we set the atom under fixed composition through MC simulation. In the unfixed method, we consider local system should have composition-fluctuation; probability $P_x$ that local system has $A$-composition $x$ in binary system is theoretically given by binomial distribution:

$$ P_x = N_l C_{xN_l} x_f^{xN_l} (1-x_f)^{N-N_l} \quad (A1) $$

Here, $N_l$ is number of local system, $x_f$ is composition of large system. In $m$ times sampling, $m \cdot P_x$ is the times sampled at composition $x$. Therefore, for getting matrix from local system, we set the atom $m \cdot P_x$ times under composition $x$, and do MC simulation. In this setting, we can consider local composition fluctuation of the large system.

In present study, we set equiatomic large box in unfixed method and consider 1152-atom local system (i.e. $x_f = 0.5$ and $N_l = 1152$) for comparison to equiatomic fixed system. Figure [A1](#fig:A1) shows connection of composition and sampling number in unfixed method.

![Figure A1](#fig:A1) Sampling number for composition in composition-unfixed practical system. No plot point along composition does not be sampled in this trial because of the number of sampling.

### Appendix A: Effect of composition

#### 1. Composition-fixed/unfixed method

In this section, we explain two method to set practical system in random matrix research: composition-fixed and composition-unfixed method. In the fixed method, we set the atom under fixed composition through MC simulation. In the unfixed method, we consider local system should have composition-fluctuation; probability $P_x$ that local system has $A$-composition $x$ in binary system is theoretically given by binomial distribution:

$$ P_x = N_l C_{xN_l} x_f^{xN_l} (1-x_f)^{N-N_l} \quad (A1) $$

Here, $N_l$ is number of local system, $x_f$ is composition of large system. In $m$ times sampling, $m \cdot P_x$ is the times sampled at composition $x$. Therefore, for getting matrix from local system, we set the atom $m \cdot P_x$ times under composition $x$, and do MC simulation. In this setting, we can consider local composition fluctuation of the large system.

In present study, we set equiatomic large box in unfixed method and consider 1152-atom local system (i.e. $x_f = 0.5$ and $N_l = 1152$) for comparison to equiatomic fixed system. Figure [A1](#fig:A1) shows connection of composition and sampling number in unfixed method.

![Figure A1](#fig:A1) Sampling number for composition in composition-unfixed practical system. No plot point along composition does not be sampled in this trial because of the number of sampling.

### Appendix B: Another projection state

In reference [8], we have successfully introduce concept of projection state and energy;

$$ Q_r(T) \approx \langle q_r \rangle_1 - \frac{\sqrt{2}}{2} \langle q_r \rangle_2 \cdot \frac{E_{r+}^{proj} - \langle E \rangle_1}{k_B T} \quad (B1) $$

$$ E_{r+}^{proj} = \sum_{t=1}^* \langle E(q_t) | q_{r+} \rangle $$

In this approach, we have considered partial average of $q_r \geq \langle q_r \rangle_1$. However, when we consider that the approach relies on the approximation that density of state on configuration space for non-interacting system can be regarded as multidimensional Gaussian distribution, it is more natural that we consider another partial average; average under $q_r \leq \langle q_r \rangle_1$. Thus, we express $E_{r-}^{proj}$ below and introduce new projection energy $E_{r-}^{proj}$, partial average under $q_r \leq \langle q_r \rangle_1$;

$$ E_{r-}^{proj} - \langle E \rangle_1 = 2 \int_0^\infty \int_{q_r \text{min}}^{\langle q_r \rangle_1} E \cdot g(E, q_r) dq_r dE $$

$$ = \sqrt{2 \pi} \Gamma_{12} \langle q_r \rangle_{2} - \exp \left[ -\frac{q_r \text{min}}{\sqrt{2 \langle q_r \rangle_2}} \right] - 1 \right]. \quad (B3) $$

With taking the limit of $N$, we can develop the equation same as $E_{r+}^{proj}$;

$$ Q_r(T) \approx \langle q_r \rangle_1 + \frac{\sqrt{2}}{2} \langle q_r \rangle_2 \cdot \frac{E_{r-}^{proj} - \langle E \rangle_1}{k_B T} \quad (B4) $$

It is described by a single state, $\{ (q_1)_r^{(-)}, (q_2)_r^{(-)} , \ldots , (q_{n_r})_r^{(-)} \}$, where $\cdot \cdot \cdot^{(-)}$ is a partial average under $q_r \leq \langle q_r \rangle_1$. Consequently, we get two
representation of $Q_r$;

$$Q_r(T) \simeq \langle q_r \rangle_1 \mp \sqrt{\frac{\pi}{2}} \langle q_r \rangle_2 \cdot \frac{E_{\text{proj}}}{k_B T} \cdot \frac{E_1}{E_2}.$$  \hfill (B5)

Two values of $Q_r$ can be different due to the approximation. When the density of states completely match Gaussian distribution, these values are same.

**Appendix C: The landscape of free energy, composition and temperature**

Figure. C1 shows connection of free energy, composition and temperature with Eq. (23) under constant projection energy. From Eq. (23) and Eq. (24) we realize that the system take minimum free energy at equiatomic composition with taking limit of thermodynamics; $T \rightarrow \infty$. It matches conventional thermodynamics.

![Graph](image)

**FIG. C1.** Image graph of free energy and composition and temperature under constant projection energy. Temperature and free energy is normalized.

[1] J. Lee, Phys. Rev. Lett. 71, 211 (1993).
[2] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A H and Teller E, J. Chem. Phys. 21 1087 (1953).
[3] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. 63, 1195 (1989).
[4] Kikuchi R, Phys. Rev. 81 988 (1951).
[5] Kikuchi R, J. Chem. Phys. 60 1071 (1974).
[6] B. J. Alder, S. P. Frankel and V. A. Lewis, J. Chem. Phys. 23, 417 (1955)
[7] K. Yuge, J. Phys. Soc. Jpn. 84, 084801 (2015).
[8] K. Yuge, J. Phys. Soc. Jpn. 85, 024802 (2016).
[9] K. Takeuchi, R. Tanaka and K. Yuge, J. Phys.:Condens. Matter 27, 385201 (2015).
[10] J. W. Connolly and A. R. Williams, Phys. Rev. 27, 5169 (1983).
[11] J. M. Sanchez, F. Ducastelle and D. Gratias, Physica 128A, 334 (1984).
[12] T. Mouri and Y. Chen, J. Japan Inst. Metals, 68, 996 (2004).
[13] K. Yuge, T. Kishimoto and K. Takeuchi, Trans. Mat. Res. Soc. Jpn. 41 213 (2016).
[14] V.A. Marchenko and L.A. Pastur, Math. USSR Sb. 1 457 (1967).
[15] D. de Fountain, in Solid State Physics, ed. H. Ehrenreich and D. Turnbull (Academic Press, Cambridge, MA, 1994) Vol. 47, p. 33.
[16] S.H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, Phys. Rev. B 42, 9622 (1990).
[17] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, Phys. Rev.Lett. 65, 353 (1990).