Where Nonlinearity in Thermodynamic Average Comes from?
Configurational Geometry Revisited

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For classical discrete system under constant composition, we theoretically examine origin of nonlinearity in thermodynamic (so-called canonical) average w.r.t. many-body interactions, in terms of geometrical information in configuration space. We clarify that nonlinearity essentially comes from deviation in configurational density of states (CDOS) before applying many-body interactions to the system, from multidimensional gaussian distribution. The present finding strongly suggest the significance to investigate how the deviation in CDOS bridges bidirectional stability relationships between equilibrium structure and potential energy in thermodynamic average.

I. INTRODUCTION

For classical discrete system under constant composition typically referred to substitutional alloys, expectation value of energy, when we assume that partial differentiation of lnZ is typically difficult to exactly determine temperature dependence of the nonlinearity. Due to the nonlinear character, it is usually constructed by generalized Ising model (GIM), which is typically constructed by generalized ising model (GIM) with which is considered in the present case. When we employ such COB, potential energy U for microscopic structure k is exactly given by

\[ U(k) = \sum_j \langle U \mid Q_j \rangle Q_j^{(k)} \]

where \( \langle U \mid Q_j \rangle \) denotes inner product, i.e., trace over possible states on configuration space. When we introduce two f-dimensional vectors of \( Q = \{ Q_1, \cdots, Q_f \} \) and \( U = \{ U_1, \cdots, U_f \} U = \{ U \mid Q \} \), it is clear from Eqs. (1) and (2) that generally, Q and U are not a linear function of U, i.e., thermodynamic (here, canonical) average is a nonlinear map w.r.t. potential energy. Due to the nonlinear character, it is typically difficult to exactly determine temperature dependence of \( \langle Q \mid \rangle \) for given potential energy. Thus, various approaches have been developed including Metropolis algorithm, entropic sampling and Wang-Landau sampling for efficient exploration of important microscopic states to determine equilibrium properties. We recently, we quantitatively formulate bidirectional stability (BS) character of thermodynamic average between equilibrium structure and potential energy surface in terms of their hypervolume correspondence, where the nonlinearity plays essential role to break the BS character.

Despite such significance, origin of the nonlinearity in terms of configurational geometry, i.e., geometric information in configuration space without requiring any thermodynamic information such as temperature or energy, has not been addressed so far. We here show that the nonlinearity comes from any deviation in configurational density of states before applying many-body interaction to the system, from ideal Gaussian distribution. The details are shown below.

II. DERIVATION AND APPLICATION

A. Derivation for condition of thermodynamic average as a linear map

Hereinafter for simplicty (without loss of generality), structure (value of Qs) are measured from that at center of gravity of configurational density of states (CDOS), given by \( \{ \langle Q_1 \rangle, \cdots, \langle Q_f \rangle \} \), where \( \langle \cdots \rangle \) denotes taking linear average for all possible microscopic states. If the thermodynamic average is a linear map, it should be given by

\[ Q \beta = \beta \cdot \Lambda \cdot U, \]

where \( \Lambda \) is temperature-independent \( f \times f \) matrix, and \( \beta \) in r.h.s. should be required from dimensional analysis between \( Q \) and \( U \). On the other hand, Mclaughlin expanion of \( \langle Q \beta \rangle \) at \( \beta = 0 \) up to g-th order is given by

\[ M \left[ \langle Q \beta \rangle \right] = \frac{\partial \ln Z}{\partial (-u_p)} \bigg|_{\beta=0} + \sum_{n=1}^g \left[ \frac{1}{n!} \sum_{k_1, \cdots, k_n=1}^f (-u_{k_1}) \cdots (-u_{k_n}) \left\{ \frac{\partial}{\partial (-u_{k_1})} \cdots \frac{\partial}{\partial (-u_{k_n})} \ln Z \right\} \bigg|_{\beta=0} \right], \]

where \( u_p = \beta \cdot \langle U \mid Q \rangle \). For the Mclaughlin expansion, when we assume that partial differentiation of \( \ln Z \) by \( \{ -u_{k(1,1)}, \cdots, -u_{k(1,m_1)}, \cdots, -u_{k(n,m_n)} \} \) takes one of
\[ \{ u_1, \ldots, u_f \} \] where duplicate selection is allowed is given by the following products for canonical average
\[ \langle Q_{k_1} \ldots Q_{k_{(1,m)}} \rangle_Z \cdots \langle Q_{l_{(n,0)}} \rangle_Z. \] \tag{5}

Partial differentiation of Eq. (5) by \(-u_k\) becomes
\[
\begin{align*}
\left. \frac{\partial \ln Z}{\partial (-u_k)} \right|_{Z} &= \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,m)}} \rangle_Z \\
&+ \cdots \\
&+ \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z \\
&- \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z \langle Q_{k_{(1,1)}} \rangle_Z. \\
&\left. \frac{\partial \ln Z}{\partial (-u_k)} \right|_{Z} &= \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z + \cdots + \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z - \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z \langle Q_{k_{(1,1)}} \rangle_Z. \\
&\left. \frac{\partial \ln Z}{\partial (-u_k)} \right|_{Z} &= \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z + \cdots + \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z - \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z \langle Q_{k_{(1,1)}} \rangle_Z. \\
&\left. \frac{\partial \ln Z}{\partial (-u_k)} \right|_{Z} &= \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z + \cdots + \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z - \langle Q_{k_{(1,1)}} \rangle_Z \cdots \langle Q_{k_{(1,1)}} \rangle_Z \langle Q_{k_{(1,1)}} \rangle_Z.
\end{align*}
\tag{6}

When we apply partial differentiation of \( \ln Z \) by \(-u_k\), we get
\[
\left. \frac{\partial \ln Z}{\partial (-u_k)} \right|_{Z} = \langle Q_{k} \rangle_Z. \\
\tag{7}
\]

From Eqs. (5)-(7), we can see that \( \ln Z \) can be partial differentiated by any times for \(-u_k\), which leads to that we can take \( g \to \infty \) in Eq. (4). We here focus on the condition where
\[
\lim_{g \to \infty} \text{M} \left[ \langle Q_p \rangle_Z \right] = \langle Q_p \rangle_Z
\tag{8}
\]
is satisfied. Then, by comparing Eqs. (5) and (4), we can immediately see that when thermodynamic average is a linear map, coefficients for \( \beta' \) (\( r \geq 2 \)) in Eq. (3) should be all zero. From Eqs. (5)-(7), it is clear that partial derivatives of \( \ln Z \) in Eq. (4) by combination of \( \{-u_{k_1}, \ldots, -u_{k_m}\} \) should always results in summation of multiple terms consisting of products for canonical average, where each term contains every single \( \{Q_{k_1}, \ldots, Q_{k_m}\} \). For instance, terms for \( \beta \) is given by
\[
- \sum_{k_1} u_{k_1} \langle Q_p Q_{k_1} \rangle,
\tag{9}
\]
and those for \( \beta^2, \beta^3 \) and \( \beta^4 \) in Eq. (4) respectively becomes
\[
\begin{align*}
\sum_{k_1,k_2} u_{k_1} u_{k_2} \frac{1}{2} \left\langle Q_p Q_{k_1} Q_{k_2} \right\rangle, \\
\sum_{k_1,k_2,k_3} u_{k_1} u_{k_2} u_{k_3} \frac{1}{6} \left( \left\langle Q_p Q_{k_1} Q_{k_2} Q_{k_3} \right\rangle - \sum_{[j]} \left\langle Q_j Q_{j_1} \right\rangle \left\langle Q_{j_1} Q_{j_2} \right\rangle \right), \\
\sum_{k_1,k_2,k_3,k_4} u_{k_1} u_{k_2} u_{k_3} u_{k_4} \left( \left\langle Q_p Q_{k_1} Q_{k_2} Q_{k_3} Q_{k_4} \right\rangle - \sum_{[j]} \left\langle Q_j Q_{j_1} Q_{j_2} Q_{j_3} \right\rangle \left\langle Q_{j_2} Q_{j_3} \right\rangle \right).
\end{align*}
\tag{10}
\]

where summation \( \{j\} \) takes all possible combination including index \( p \) and the rest from \( \{k\} \) where duplicate selection is not allowed. Generally, terms for \( \beta' \) corresponds to polynomial for \( \{u_{k_1}, \ldots, u_{k_m}\} \), where its coefficient is given by linear combination of \((r+1)\)-th order multivariate moment \( \langle Q_p Q_{k_1} \cdots Q_{k_r} \rangle \) and products of lower-order moments, as seen in Eq. (10). Therefore, if thermodynamic average is a linear map w.r.t. any given set of \( u_k \), \( t \)-th (\( t \geq 3 \)) multivariate moments should either take zero or be given by linear combination of lower-order moments. For instance with \( t = 4 \), we obtain
\[
\forall p, \quad \left\langle Q_p Q_{k_1} Q_{k_2} Q_{k_3} \right\rangle = \sum_{\{j\}} \left\langle Q_{j_1} Q_{j_2} \right\rangle \left\langle Q_{j_3} Q_{j_4} \right\rangle.
\tag{11}
\]

We have recently clarified that when CDOS is exactly given by multidimensional Gaussian distribution, thermodynamic average exactly becomes linear map by the form of Eq. (3). This directly means that all \( t \)-th (\( t \geq 3 \)) multivariate moments of Gaussian satisfy terms for \( \beta'^{-1} \) taking zero, seen in Eq. (11). From above discussions, when provided CDOS leads to thermodynamic average as linear map, relationships between \( t \)-th (\( t \geq 3 \)) order multivariate moments and second-order moments of \( \{\langle Q_k Q_k \rangle | k = 1, \ldots, f\} \) (i.e., covariance matrix of \( \Gamma_{ik} = \langle Q_k Q_k \rangle \)) should be exactly same as the relationships for multidimensional Gaussian. Therefore, if a certain Gaussian can have the same covariance matrix \( \Gamma \), the provided CDOS should be nothing but Gaussian. Since covariance matrix is by definition real symmetric, any \( \Gamma \) can always be diagonalized with appropriate orthogonal orthogonal matrix \( P \) of
\[
C = P^{-1} \Gamma P,
\tag{12}
\]
with diagonal elements of \( \{c_1, \ldots, c_f\} \). Let us consider whether or not \( \{d_i\} \) includes zero value. When we choose linearly independent basis under constant composition, it always corresponds to including empty \( Q_E \) (i.e., independent of composition and of configuration) and multiser correlation: This leads to a set of basis function of \( \{Q_E, Q_1, \ldots, Q_f\} \). If \( \Gamma \) for \( \{Q_1, \ldots, Q_f\} \) has zero eigenvalue, one of the basis after orthogonal transformation (with fixing \( Q_E \)) is independent of configuration, i.e., it takes constant value. In this case, such a basis should clearly be linearly dependent with \( Q_E \), where such coordinatation should be omitted for basis under given constant composition. Therefore, for any practical CDOS under such basis, \( \Gamma \) should always be positive definite. Under this coordinatation, multidimensional Gaussian can be simply constructed by product of a set of single-variate Gaussian with variance of \( d_k \). These directly means that for classical discrete system with complete basis, we can always construct multidimensional Gaussian with any given \( \Gamma \) obtained from practical CDOS. Therefore, under the condition of Eq. (5), CDOS providing thermodynamic average as a linear map is restricted to multidimensional Gaussian with covariance matrix of \( \Gamma \).
B. Application to practical systems

Very recently, we quantitatively formulate bidirectional stability relationships $B$ in thermodynamic average between equilibrium structure and potential energy, based on its non-linearity:

$$B = \log \left| 1 + \text{div} \mathbf{D} + \sum_F J_F \left[ \frac{\partial \mathbf{D}}{\partial \mathbf{Q}} \right] + J \left[ \frac{\partial \mathbf{D}}{\partial \mathbf{Q}} \right] \right|, \quad (13)$$

where $\mathbf{D}$ is called “anharmonicity in structural degree of freedom”, which is a vector field on configuration space defined as

$$\mathbf{D} (\mathbf{Q}) = (D_1 (\mathbf{Q}), \ldots, D_f (\mathbf{Q})),$$

$$D_i (\mathbf{Q}) = \left\{ \left( \phi_{\text{th}} (\beta) \circ (-\beta \cdot \Lambda)^{-1} \right) \cdot \mathbf{Q} - \mathbf{Q} \right\}_i. \quad (14)$$

Here, $\phi_{\text{th}}$ denotes canonical average, and $\{ \cdot \}_i$ represents $i$-th component of $\mathbb{R}^f$ vector. Since $\Lambda$ is a invertible linear map and image of composite map $\phi_{\text{th}} (\beta) \circ (-\beta \cdot \Lambda)^{-1}$ is exactly independent of energy and of temperature, $\mathbf{D}$ is a measure of non-linearity for $\phi_{\text{th}}$ depending only on configurational geometry before applying many-body interaction to the system, i.e., can be known a priori without any thermodynamic information. Therefore, from above discussions, it is fundamentally important to investigate how the deviation in CDOS from gaussian connects with vector field $\mathbf{D}$.

In order to qualitatively address this point, we first rewrite canonical average of Eq. (1) by using CDOS of $n (\mathbf{Q}_1, \ldots, \mathbf{Q}_f)$, namely

$$\langle Q_p \rangle_Z = \frac{\int n (\mathbf{Q}_1, \ldots, \mathbf{Q}_f) Q_p \exp \left( -\beta \sum_{j=1}^f \langle U | \mathbf{Q}_j \rangle \mathbf{Q}_j \right) d\mathbf{Q}}{\int n (\mathbf{Q}_1, \ldots, \mathbf{Q}_f) \exp \left( -\beta \sum_{j=1}^f \langle U | \mathbf{Q}_j \rangle \mathbf{Q}_j \right) d\mathbf{Q}}. \quad (15)$$

Therefore, $\langle Q_p \rangle_Z$ can be interpret as a functional of CDOS, $n (\mathbf{Q}_1, \ldots, \mathbf{Q}_f)$. Then, corresponding functional derivative is immediately given by

$$\frac{\delta \langle Q_p \rangle_Z}{\delta n} = \left( \langle Q_p \rangle_Z \right)^{(n)} \cdot \exp \left( -\beta \sum_{j=1}^f \langle U | \mathbf{Q}_j \rangle \mathbf{Q}_j \right) \frac{Z \langle Q_p \rangle_Z^{(n)}}{Z^{(n)}}, \quad (16)$$

where $Z^{(n)}$ and $\langle Q_p \rangle_Z^{(n)}$ respectively denotes partition function and canonical average of $Q_p$ for CDOS of $n (\mathbf{Q}_1, \ldots, \mathbf{Q}_f)$. To apply the functional derivative of Eq. (16) to investigating the behavior of vector field $\mathbf{D}$, we first numerically obtain exact CDOS on fcc equiatomic binary system with 32-atom ($2 \times 2 \times 2$ expansion of conventional 4-atom unit cell) along 1NN and 2NN pair correlation, $\mathbf{Q}_1$ and $\mathbf{Q}_2$, by constructing all possible $32 \mathrm{C}_{16}$ atomic configurations. Figure 1 shows the resultant CDOS measured from corresponding Gaussian with the same covariance matrix. We can clearly see the character around center of gravity: (i) CDOS at 1st and 3rd quadrants shows positive, and that at 2nd and 4th quadrants shows negative deviation, and (ii) CDOS at 1st and 4th quadrants have larger absolute deviation than at 2nd and 3rd quadrants. Figure 2 shows vector field $\mathbf{D}$ near center of gravity, using the information about the obtained exact CDOS.

We now would like to know how the behavior of $\mathbf{D}$ in Fig. 2 and deviation in CDOS of Fig. 1 are bridged, based on func-
where $h$ is the functional derivative of Eq. (16). To achieve this, we apply singular value decomposition (SVD) to the deviation in CDOS, whose singular values are shown in Fig. 3. We can see that the deviation in CDOS can be approximated as low-rank discrete function.

We therefore simplify the deviation in CDOS from Gaussian to capture the above features as

$$h(Q_1, Q_2) \simeq h(Q_1)h(Q_2),$$

where

$$h(Q_1) = c_1 \delta(Q_1 - Q_{kl}) - c_1' \delta(Q_1 + Q_{kl}),$$

$$h(Q_2) = c_2 \delta(Q_2 - Q_{kl}) - c_2 \delta(Q_2 + Q_{kl}).$$

Here, $Q_{kl}$, $Q_{kl}$, $c_1$, $c_1'$ and $c_2$ are positive constants with $c_1 > c_1'$, and $\delta(Q)$ is a Dirac delta function. We perform inner product between the functional derivative and the deviation in CDOS to see the contribution from the simplified changes $h(Q_1, Q_2)$ contributes to $D_1$, namely

$$\delta D_{1}^{(h)}(Q_1, Q_2) = \left( \frac{\delta \langle Q_p \rangle}{\delta n} h(Q_1, Q_2) \right)_g$$

$$= -2c_2 \cdot \sinh \left( -\Lambda_{11}^{-1} Q_1 Q_2 \right) \left[ c_1 (Q_{kl} - Q_1) \exp (\Lambda_{11}^{-1} Q_1) + c_1' (Q_{kl} + Q_1) \exp (-\Lambda_{11}^{-1} Q_1) \right],$$

where

$$Z^g = \frac{1}{\sqrt{\Lambda_{11} \Lambda_{22}}} \exp \left( \frac{\Lambda_{11}^{-1} Q_1^2 + \Lambda_{22}^{-1} Q_2^2}{2} \right).$$

Here, $\langle \cdots \rangle_g$ means taking inner product with gaussian CDOS, and substitute the relationships in ASDF of $Q_1 \simeq -\beta \Lambda_{11} \langle U \mid Q_1 \rangle$ and $Q_2 \simeq -\beta \Lambda_{22} \langle U \mid Q_2 \rangle$ (approximation comes from neglecting off-diagonal elements of $\Lambda$ just for simplicity of Eq. (19), which does not provide significant effect in the present study). Figure 4 shows the resultant behavior of $\delta D_{1}^{(h)}$ with $c_1 = c_2 = 2c_1'$ and $Q_{kl} = Q_{kl} = 10e - 4$, which mimics the condition that slight changes in CDOS having the similar feature of Fig. 1 appears near the center of gravity. We can clearly see that behavior of $\delta D_{1}^{(h)}$ can qualitatively capture that of $D_1$ for the sign of each quadrants. Since landscape of $\delta D_{1}^{(h)}$ depend on $f(Q_1, Q_2)$, further investigation of vector field $D$ would require decomposition of $f(Q_1, Q_2)$ into low-rank functions, e.g., based on SVD.

III. CONCLUSIONS

We examine the origin of nonlinearity in thermodynamic average for classical discrete systems under constant composition, in terms of configurational geometry. We clarify that the nonlinearity comes from any deviation in configurational density of states before applying many-body interaction to the system, from ideal Gaussian distribution with the same covariance matrix as practical CDOS. The present results strongly indicate profound relationships between deviation in CDOS from Gaussian and bidirectional stability character in thermodynamic average.

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1 J.M. Sanchez, F. Ducastelle, and D. Gratias, Physica A **128**, 334 (1984).
2 N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Tellerand, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
3 J. Lee, Phys. Rev. Lett. **71**, 211 (1993).
4 F. Wang and D.P. Landau, Phys. Rev. Lett. **86**, 2050 (2001).
5 K. Yuge and S. Ohta, J. Phys. Soc. Jpn. (submitted).
6 K. Yuge, J. Phys. Soc. Jpn. **85**, 024802 (2016).