Thermodynamics for Nonlinearity in Canonical Ensemble

Koretaka Yuge

I. INTRODUCTION

When we consider classical discrete system under constant composition, expectation value of structure along chosen coordination \( p \) under given coordination \( \{ q_1, \cdots, q_f \} \) in thermodynamic equilibrium is given by

\[
\langle q_p \rangle_Z = Z^{-1} \sum \langle q_p \rangle \exp \left( -\beta U(i) \right),
\]

where \( \langle \cdot \rangle \) denotes canonical average, \( \beta = (k_B T)^{-1} \) inverse temperature, \( Z = \sum \exp(-\beta U_i) \) partition function, and summation is taken over all possible configuration. Potential energy \( U \) for any configuration \( k \) is then exactly expressed using e.g., complete orthonormal basis (COB) for generalized Ising model (GIM) namely

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

where \( \langle \cdot \mid \cdot \rangle \) denotes inner product on configuration space. When we introduce two \( f \)-dimensional vectors of \( q_Z = (\langle q_1 \rangle_Z, \cdots, \langle q_f \rangle_Z) \) and \( U = (U_1, \cdots, U_f) \) (\( U_p = (U \mid q_p) \)), it is clear from Eqs. (1) and (2) that generally, \( q_Z \) is a complicated nonlinear function of \( U \), i.e., thermodynamic (here, canonical) average \( \phi_{th} \) is a nonlinear map.

Whereas various approaches have been developed including Metropolis algorithm, entropic sampling and Wang-Landau sampling for effective exploration of configuration merged from the nonlinear map to determine equilibrium properties\(^{12,14}\) 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 well addressed so far. Our recent theoretical study reveal that nonlinearity can be reasonably treated through introduced vector field \( A \) of anharmonity in s.d.f. (ASDF) depending only on configurational geometry\(^{12,14}\) where \( A \) can be naturally treated as time-evolution of discrete dynamical system. We quantitatively formulate bidirectional stability (BS) character of thermodynamic average between equilibrium structure and potential energy surface in terms of their hypervolume correspondence, by divergence and Jacobian for \( A \) and we further examine the origin of nonlinearity based on tropical geometry and information geometry with dually flat Riemannian manifold, which clarifies how spatial constraint to individual s.d.f., entanglement between s.d.f. and nonadditivity of the entanglement dominate the nonlinearity\(^{15,16}\).

Although these studies provide deeper geometric interpretation of origin for the nonlinearity, their information are restricted to average, i.e., all higher-order moment information about nonlinearity, which should play essential role for small systems, has been lack. Furthermore, the geometric studies so far does not provide sufficient information about how nonlinearity is globally evolved from disordered to ordered states. To overcome the problems, we here establish formulation for nonlinearity including previously-missing information, by transforming deterministic dynamical system for evolution of nonlinearity to stochastic Markovian system, to explicitly introduce its forward and backward transition probability with thermodynamic functions, in analogy with stochastic thermodynamics\(^{110}\). The details are shown below.

II. DERIVATION AND CONCEPT

Stochastic Description of Nonlinearity

We first briefly explain the basic concept of the ASDF. When structure \( \bar{q} \) is interpreted as \( f \)-dimensional vector \( \bar{q} = (q_1, \cdots, q_f) \) under, e.g., the GIM orthonormal basis, ASDF is defined as the following vector field at \( \bar{q} \):

\[
A(\bar{q}) = \left\{ \phi_{th}(\beta) \circ (-\beta \cdot \Gamma)^{-1} \right\} \cdot \bar{q} - \bar{q},
\]

where \( \circ \) denotes composite map, and \( \Gamma \) is \( f \times f \) real symmetric covariance matrix of configurational density of states (CDOS). Note that here and hereinafter, without lack of generality, structure \( \bar{q} \) is measured from center of gravity of CDOS. Important points here are that (i) \( \Gamma \) is taken before applying many-body interaction to the system, (ii) when \( \phi_{th} \) is a linear map, \( A \) takes zero-vector, and (iii) image of the composite map is independent of temperature and of many-body interaction: Therefore, we can know vector field of ASDF without any information about temperature or energy, i.e., it can be \textit{a priori} known depending only on configurational geometry. Therefore, ASDF in Eq. (3) is a natural measure of nonlinearity in \( \phi_{th} \) defined on individual configuration \( \bar{q} \).

Eq. (3)
The r.h.s. of Eq. (6) is defined as

\[ \tilde{q}_{t+1} = \tilde{q}_t + A(\tilde{q}_t), \tag{4} \]

which includes average information of nonlinearity along its time evolution.

We here extend the above ideas to further treat higher-order moment information for nonlinearity, by transform the dynamical system to the following stochastic Markovian process with master equation for probability \( P \) of

\[ \frac{d}{dt} P(\tilde{q}_n) = \sum_m \{ P(\tilde{q}_m) g_m(\tilde{q}_n) - P(\tilde{q}_n) g_n(\tilde{q}_m) \} \tag{5} \]

under given initial distribution, where transition probability \( P(\tilde{q}_K|\tilde{q}_J) \) is given for instance by

\[ P(\tilde{q}_B|\tilde{q}_A) = P(\tilde{q}_A; t, \tilde{q}_B; t + 1) = g_A(\tilde{q}_B). \tag{6} \]

The r.h.s. of Eq. (6) is defined as

\[ g_J(\tilde{q}_K) := g(\tilde{q}_K) \exp \left[ -\beta \left( \tilde{q}_K \cdot \tilde{V}_J \right) \right] \sum_{\tilde{q}_B \tilde{q}} \exp \left[ -\beta \left( \tilde{q} \cdot \tilde{V}_J \right) \right]. \tag{7} \]

where free energy \( F_J \) is defined as

\[ F_J := -\beta^{-1} \ln Z_J, \tag{12} \]

and

\[ \Delta S := \ln \frac{P(\tilde{q}_B|\tilde{q}_A)}{P(\tilde{q}_A|\tilde{q}_B)} \]

\[ \Delta S_0 := \ln \frac{g(\tilde{q}_A)}{g(\tilde{q}_B)} = -\ln g(\tilde{q}_B) - ( - \ln g(\tilde{q}_A)) \]

\[ : = S_{B0} - S_{A0} \]

\[ \sigma' := \Delta S + \Delta S_0. \tag{13} \]

which means that the following corresponds to stochastic relative entropy \( d_{KL} \):

\[ \sigma := \Delta S + \Delta S_{sys} = d_{KL}(P_+(\tilde{q}_A,\tilde{q}_B) : P_-(\tilde{q}_A,\tilde{q}_B)). \tag{16} \]

When we interpret above introduced functions in terms of thermodynamics, \( \sigma \) can be viewed as entropy change for whole system thermally isolated, since we obtain from Eq. (16) that ensemble average of \( \sigma \) always satisfies

\[ \langle \sigma \rangle_{P_+} \geq 0, \tag{17} \]
which corresponds to the second law of thermodynamics, and thereby $\Delta S$ can be viewed as entropy change in thermal bath.

Based on $S_0$, we can define another type of ensemble average with the following probability distributions:

$$
P_\ast (\tilde{q}_A, \tilde{q}_B) = P (\tilde{q}_B | \tilde{q}_A) g (\tilde{q}_A)
$$

$$
P'_\ast (\tilde{q}_A, \tilde{q}_B) = P (\tilde{q}_A | \tilde{q}_B) g (\tilde{q}_B).
$$

(18)

Since $g (\tilde{q})$ is CDOS itself, $\langle H \rangle_{P_\ast}$ represents average of changes in $H$ over randomly chosen configuration through a single transition. Therefore, $\langle H \rangle_{P_\ast}$ can be considered as special case of $\langle \iiint \rangle_{P_\ast}$, which corresponds to average through a single transition, from natural choice for initial state of $g (\tilde{q})$ to subsequent state. Hereinafter, we thus call $\Delta S_0$ as initial entropy change for the system, which will play essential role for evolution of nonlinearity. Further insight and physical interpretation for introduced thermodynamic functions are addressed later.

**Derivation for Evolution of Nonlinearity**

In order to clarify the relationships between nonlinearity change through the transition $A \rightarrow B$ and entropy changes in Eq. (11), we should measure the entropy changes from those for linear system, i.e., system where $\phi_0$ becomes globally linear: Our recent work clarify that CDOS providing global linearity is restricted to Gaussian distribution with the same $\Gamma$ as CDOS for practical system. When CDOS takes discretized Gaussian of $g_G (\tilde{q})$, we can obtain corresponding bath and initial entropy changes as

$$
\sigma_G := \Delta S_G + \Delta S_{G_{\text{sys}}}
$$

$$
\sigma'_G := \Delta S_G + \Delta S_{G_0}
$$

$$
\Delta S_{G_{\text{sys}}} (\tilde{q}_B | \tilde{q}_A) := \ln \frac{P_G (\tilde{q}_A)}{P_G (\tilde{q}_B)}
$$

$$
\Delta S_G := \ln \frac{P_G (\tilde{q}_B | \tilde{q}_A)}{P_G (\tilde{q}_A | \tilde{q}_B)}
$$

$$
\Delta S_{G_0} := \ln \frac{g_G (\tilde{q}_A)}{g_G (\tilde{q}_B)} := S_{G_{B0}} - S_{G_{A0}}
$$

$$
\Delta S_G + \Delta S_{G_0} = -\beta (F_G - F_{G_{A}})
$$

$$
P_{G_+} (\tilde{q}_A, \tilde{q}_B) := P_G (\tilde{q}_B | \tilde{q}_A) P_G (\tilde{q}_A).
$$

(19)

Here, $P_G$ denotes taking transition probability of Eqs. (6) and (7) by using $g_G$ instead of practical CDOS of $g$, and $F_{G_J}$ ($J = A, B$) denote free energy of Eq. (12) with CDOS of $g_G$ instead of $g$, where subscript $G$ will be used for corresponding linear system throughout the paper. To clarify character of the nonlinearity for original dynamical system, based on dually flat Riemannian manifold, our recent study reveal that nonlinearity in $\phi_0$ at state $J$ can be geometrically given by Kullback-Leibler divergence of $D_{KL} (g_J : g_{GJ})$, which can be further decomposed into sum of three contributions from deviation in spatial constraint from Gaussian, entanglement in s.d.f., and nonadditivity in entanglement.

With these preparations, our first goal is therefore to bridge deterministic nonlinearity in dually flat Riemannian manifold and stochastic entropy changes of Eq. (11) containing information about fluctuation of the nonlinearity. When we measure entropy changes from those of linear system, we simply obtain

$$
\Delta \tilde{S} = \Delta S - \Delta S_G,
$$

$$
\Delta \tilde{S}_0 = \Delta S_0 - \Delta S_{G0},
$$

(20)

and we also define

$$
\Delta F := (F_B - F_A) - (F_{GB} - F_{GA}),
$$

(21)

where tilde is always used for functions measured from linear system throughout the paper. Then we define vicinity average of quantity $M (\tilde{q}_A, \tilde{q}_B)$ for transition $A \rightarrow B$ as

$$
\langle M \rangle_{AB} := \sum_{\tilde{q}_A} g_A (\tilde{q}_A) \cdot M + \sum_{\tilde{q}_B} g_B (\tilde{q}_B) \cdot M
$$

$$
:= \langle M \rangle_A + \langle M \rangle_B.
$$

(22)

Then we can straightforwardly get the followings by applying the vicinity average to bath entropy change $\Delta \tilde{S}$, namely

$$
\langle \Delta \tilde{S} \rangle_{AB} = D_{KL} (g_A : g_{GA}) - D_{KL} (g_B : g_{GB}) - \Delta \tilde{S}_0 - \beta \left( \langle \Delta F \rangle_{AB} - \Delta F \right),
$$

(23)

which is further transformed into

$$
\langle \Delta \tilde{S} + \beta \Delta F \rangle_{AB} = D_{KL} (g_A : g_{GA}) - D_{KL} (g_B : g_{GB}) + \beta \Delta F - \Delta \tilde{S}_0.
$$

(24)
From Eqn. (11), (19) and (20), we also obtain the equality of
\[ \Delta S + \Delta S_0 = -\beta \Delta F. \]  
(25)

By combining Eqs. (24) and (25), we finally obtain the desired relationships:

\[ \Delta D_{KL}^{A \rightarrow B} := D_{KL}(g_B : g_GB) - D_{KL}(g_A : g_GA) = -\{\Delta \tilde{S} + (2\Delta \tilde{S}_0 - \langle \Delta \tilde{S}_0 \rangle_{AB})\}. \]  
(26)

Physical interpretation of Eq. (26) is that through the transition \( A \rightarrow B \), information gain for nonlinearity (l.h.s.) is given by negative of the sum of the entropy change in thermal bath (first term of r.h.s.) and fluctuation of initial entropy change in system (second term of r.h.s.), whose intuitive interpretation is illustrated in Fig. 1.

![Intuitive interpretation for fluctuation of initial entropy change](image)

**Fig. 1:** Intuitive interpretation for fluctuation of initial entropy change, \( 2\Delta \tilde{S}_0 - \langle \Delta \tilde{S}_0 \rangle_{AB} = 2\Delta \tilde{S}_0 - \langle \Delta \tilde{S}_0 \rangle_A - \langle \Delta \tilde{S}_0 \rangle_B \).

This intuition of fluctuation for entropy change certainly tells us another important aspect of nonlinearity for large systems: When

\[ B = \{\phi_{th} \circ (-\beta \Gamma)^{-1}\} \cdot A \]  
(27)

is satisfied, we get from Eq. (26) that

\[ \Delta D_{KL}^{A \rightarrow B} \simeq -\{\Delta \tilde{S} + \langle \Delta \tilde{S}_0 \rangle_A - \langle \Delta \tilde{S}_0 \rangle_B\}, \]  
(28)

which means that stochastic information about initial entropy change can be typically vanished.

**Generalization to Multiple Transitions**

Up to above discussions, we confine ourselves to a single discrete transition, \( A \rightarrow B \). Generalization of the relationships between nonlinearity and entropy functions of Eq. (26) to those for multiple transitions, i.e., from initial time \( t = 0 \) to final time \( t = t \), is straightforward. Let \( \Delta \tilde{S}(k) \) and \( \Delta \tilde{S}_0(k) \) respectively denotes changes in thermal bath and the initial entropy at a transition from time \( t = (k - 1) \) to \( t = k \), i.e., from configuration \( \tilde{q}_{k-1} \) to \( \tilde{q}_k \), we can obtain

\[ \sum_{k=1}^{t} D_{KL}(g_k : g_{Gk}) - D_{KL}(g_{k-1} : g_{G(k-1)}) = -\sum_{k=1}^{t} \left\{\Delta \tilde{S}(k) + \left(2\Delta \tilde{S}_0(k) - \langle \Delta \tilde{S}_0 \rangle_{(k-1)k}\right)\right\}. \]  
(29)

When we generalize *vicinity average* to multiple transitions as

\[ \langle M \rangle_t := \sum_{k=1}^{t} \left\{\sum_{\tilde{q}_k} g_{k-1}(\tilde{q}_k) \cdot M(k) + \sum_{\tilde{q}_{k-1}} g_k(\tilde{q}_{k-1}) \cdot M(k)\right\}, \]  
(30)

where \( M \) is now a separable function at individual time \( k \), i.e.,

\[ M = \sum_{k=1}^{t} M(k), \]  
(31)

we finally get generalized relationships between nonlinearity information gain and entropy:
where
\[ \Delta S_{\text{tot}}^0 = \sum_{k=1}^{t} \Delta \tilde{S}(k) \]
\[ \Delta S_{\text{tot}}^0 = \sum_{k=1}^{t} \Delta \tilde{S}_0(k) = S(t) - \tilde{S}_0(0). \] (33)

**Thermodynamic Properties**

Up to the above discussion, we do not provide physical insight into the system and thermal bath. Here we show that major properties for introduced entropy, free energy and internal energy can be naturally interpreted in the context of standard thermodynamics.

We first see the following term as
\[ \beta^{-1} (\Delta S_0 - \Delta S_{\text{sys}}) = \delta W, \] (34)
where \( \delta W \) denotes work done by the system. This can be naturally accepted since its ensemble average satisfy the principle of maximum work derived from Eq. (17), namely,
\[ - \langle F_B - F_A \rangle_{p_e} \geq \langle \delta W \rangle_{p_e}. \] (35)

The definition of work in Eq. (34) means that the system evolves under potential energy surface \( U_p(\bar{q}) \) of
\[ U_p(\bar{q}) = \beta^{-1} \{ \ln P(\bar{q}) - \ln g(\bar{q}) \}, \] (36)
which corresponds to difference between logarithm of state probability and CDOS. With this preparation, from Eq. (11), heat gain for thermal bath \( \Delta Q \) during transition \( A \to B \) of the system is given by \( \Delta Q = \beta^{-1} \Delta S \), which means that heat gain for the system \( \Delta Q_{\text{sys}} \) becomes \( \Delta Q_{\text{sys}} = -\beta^{-1} \Delta S \). We then obtain from the first-law of thermodynamics that internal energy change \( \Delta E \) in the system satisfies
\[ -\beta^{-1} \Delta S = \Delta E + \delta W, \] (37)
which leads to the relationships:
\[ \Delta E = \Delta F + \beta^{-1} \Delta S_{\text{sys}}. \] (38)

Next, we examine “thermodynamic equilibrium” (ES) for the present evolution of nonlinearity. At steady state (SS), we obtain the following relationship from Eq. (5) that
\[ \sum_{m,n} \{ P(\bar{q}_m) g_n(\bar{q}_n) - P(\bar{q}_n) g_n(\bar{q}_m) \} = 0, \] (39)
and thus at ES, following detailed balance should be satisfied:
\[ \forall A, B : \frac{P_{\text{ES}}(\bar{q}_A)}{P_{\text{ES}}(\bar{q}_B)} = \frac{g_B(\bar{q}_A)}{g_A(\bar{q}_B)}. \] (40)

This immediately indicates that at ES for nonlinearity,
\[ \Delta S_{\text{sys}}^{\text{ES}} = -\Delta S \] (41)
is satisfied (i.e., entropy production \( \sigma \) takes zero). Therefore, at thermodynamic equilibrium, we can obtain several relationships for evolution of nonlinearity and thermodynamic functions:
\[ \Delta D_{\text{KL}}^{A \to B} = \Delta S_{\text{sys}}^{\text{ES}} - (2 \Delta \tilde{S}_0 - \langle \Delta \tilde{S}_0 \rangle_{\text{AB}}) \] (42)
and
\[ T \Delta S_0 = \Delta Q_{\text{sys}} + \delta W. \] (43)

We then see how the second law of thermodynamics is modified for entropy production measured from that for linear system, \( \tilde{\sigma} \). From above equations, we first obtain that
\[ \tilde{\sigma} = \ln \frac{P_+(\bar{q}_A, \bar{q}_B) P_{G-}(\bar{q}_A, \bar{q}_B)}{P_-(\bar{q}_A, \bar{q}_B) P_{G+}(\bar{q}_A, \bar{q}_B)}. \] (44)

Its ensemble average for the forward transition \( P_+ \) is then given by
\[ -\langle \tilde{\sigma} \rangle_{p_+} = \ln \left\{ \frac{P_{G+} P_+}{P_{G-} P_+} \right\}_{p_+} \leq \ln \left\{ \frac{P_{G+}}{P_{G-}} \right\}_{p_+}, \] (45)
where we employ Jensen’s inequality. Since value of summation in Eq. (45) is invariant w.r.t. exchange of \( \bar{q}_A \) and \( \bar{q}_B \), we further get
\[ -\langle \tilde{\sigma} \rangle_{p_+} \geq -\ln \sum_{\bar{q}_A, \bar{q}_B} P_+ \frac{P_G}{P_{G+}} = - \ln \left\{ \frac{P_G}{P_{G+}} \right\}_{p_+}. \] (46)

From Eq. (19), we obtain the lower bound for entropy production of
\[ -\langle \tilde{\sigma} \rangle_{p_+} \geq - \ln \langle e^{-\sigma_G} \rangle_{p_+}, \] (47)
which can be viewed as the second law of thermodynamics for the present system. In a similar fashion, we obtain integral fluctuation theorem for evolution of the nonlinearity by taking ensemble average for \( e^{-\tilde{\sigma}} \):
\[ -\langle e^{-\tilde{\sigma}} \rangle_{p_+} = \langle e^{-\sigma_G} \rangle_{p_+}, \] (48)
which means that average entropy production in exponential form is always conserved for linear and nonlinear systems. The above relationships naturally include the special case of initial probability distribution given by CDOS itself, namely
\[ -\langle e^{-\tilde{\sigma}} \rangle_{p'_+} = \langle e^{-\sigma_G} \rangle_{p'_+}. \] (49)
We finally see how the nonlinearity information gain is bounded for entire transition process. In a similar fashion to the derivation of the above second law, we obtain the following by employing the average of $\langle \tilde{\sigma}' \rangle_{P_{t}}$

$$\langle \tilde{\sigma}' \rangle_{P_{t}} = \langle \tilde{\mathcal{S}} + \mathcal{S}_0 \rangle_{P_{t}} \geq -\ln \left( e^{-\sigma'_G} \right)_{P_{t}} .$$

(50)

Substituting the above relationship to Eq. (26), we obtain the ensemble average of upper bound for evolution of nonlinearity:

$$\langle \Delta D^{\text{A} \rightarrow \text{B}}_{\text{KL}} \rangle_{P_{t}} \leq \ln \left( e^{-\sigma'_G} \right)_{P_{t}} + \langle \langle \Delta \tilde{\mathcal{S}}_0 \rangle_{\text{AB}} - \Delta \tilde{\mathcal{S}}_0 \rangle_{P_{t}} .$$

(51)

This equation indicates that in order to design nonlinearity for given system in terms of s.d.f., exponential average of entropy production for linear system, fully determined by covariance matrix for CDOS of practical system, plays significant role.

### III. CONCLUSIONS

By transforming discrete dynamical system for vector field providing nonlinearity in thermodynamic average to stochastic Markovian process, we see that evolution of nonlinearity including higher-order moments information can be naturally viewed in terms of total entropy production in analogy to stochastic thermodynamics. We reveal that through the transition, information gain about the nonlinearity is identical to sum of entropy change in thermal bath and fluctuation of entropy change in the system. We finally derive lower bound of total entropy production for evolution of nonlinearity, corresponding to the second law of thermodynamics.

### IV. ACKNOWLEDGEMENT

The author expresses cordial thanks to Yoshikazu Tabata at Kyoto University for fruitful discussions. This work was supported by Grant-in-Aids for Scientific Research on Innovative Areas on High Entropy Alloys through the grant number JP18H05453 and a Grant-in-Aid for Scientific Research (16K06704) from the MEXT of Japan, Research Grant from Hitachi Metals·Materials Science Foundation, and Advanced Low Carbon Technology Research and Development Program of the Japan Science and Technology Agency (JST).

---

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, J. Phys. Soc. Jpn. **86**, 104802 (2018).
6 K. Yuge, J. Phys. Soc. Jpn. **85**, 024802 (2016).
7 K. Yuge and S. Ohta, J. Phys. Soc. Jpn. **88**, 104803 (2019).
8 K. Yuge and S. Ohta, J. Phys. Soc. Jpn. **89**, 084802 (2020).
9 K. Yuge, [arXiv:1811.09612 [cond-mat.stat-mech]] (2021).
10 U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).