

Nonequilibrium Bound for Canonical Nonlinearity Under Single-Shot Work

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For classical discrete systems under constant composition (specifically substitutional alloys), canonical average acts as a map from a set of many-body interatomic interactions to a set of configuration in thermodynamic equilibrium, which is generally nonlinear. In terms of the configurational geometry (i.e., information about configurational density of states), the nonlinearity has been measured as special vector on configuration space, which is extended to Kullback-Leibler (KL) divergence on statistical manifold. Although they successfully provide new insight into how the geometry of lattice characterizes the nonlinearity, their application is essentially restricted to thermodynamic equilibrium. Based on the resource theory (especially, thermo-majorization), we here extend the applicability of the nonlinearity to nonequilibrium states obtained through single-shot work on Gibbs state. We derive the bound for the extended nonlinearity in nonequilibrium state, characterized by the nonlinearity in equilibrium state, Renyi ∞ -divergence between equilibrium and nonequilibrium distribution, temperature and work.

I. INTRODUCTION

For classical discrete systems with f structural degrees of freedom (SDFs) on given lattice, specifically substitutional alloys under a *constant* composition, the expectation for configuration under a given coordination $\{q_1, \dots, q_f\}$ in thermodynamic equilibrium can be provided by the following canonical average

$$\langle q_p \rangle_Z = Z^{-1} \sum_i q_p^{(i)} \exp(-\beta U^{(i)}), \quad (1)$$

where $\langle \cdot \rangle_Z$ represents the canonical average, β the inverse temperature, $Z = \sum_i \exp(-\beta U^{(i)})$ the partition function, with the summation over all possible configurations i : e.g., coordinate q_k as k th multisite correlation function defined by the generalized Ising model,¹ forming complete basis functions. Then the potential energy $U^{(k)}$ for configuration k is given by

$$U^{(k)} = \sum_{j=1}^f \langle U | q_j \rangle q_j^{(k)}, \quad (2)$$

where $\langle \cdot | \cdot \rangle$ denotes the inner product in the configuration space, e.g., $\langle a | b \rangle = \rho^{-1} \sum_k a^{(k)} \cdot b^{(k)}$ (ρ is normalization constant). When we introduce two f -dimensional vectors of $\vec{Q}_Z = (\langle q_1 \rangle_Z, \dots, \langle q_f \rangle_Z)$ and $\vec{U} = (\langle U | q_1 \rangle, \dots, \langle U | q_f \rangle)$, the former and latter respectively correspond to the configuration in thermodynamic equilibrium and many-body interatomic interactions in the inner-product form. Subsequently, the canonical average of Eq. (1) can be interpreted as a map ϕ_{th} of

$$\phi : \vec{U} \mapsto \vec{Q}_Z, \quad (3)$$

which is generally nonlinear.

In alloy configurational thermodynamics, due to the complex nonlinearity in ϕ_{th} , many theoretical approaches have been proposed to capture alloy equilibrium properties: e.g., The Metropolis algorithm was devised for effective exploration of the configuration space, followed by advanced techniques including the multihistogram method, multicanonical

ensemble, and entropic sampling.²⁻⁵ In terms of another aspect to ascertain many-body interatomic interactions, they employ the generalized Ising model, augmented with optimization techniques like cross-validation, genetic algorithms, and regression in machine learning.⁶⁻¹¹ Although they yield accurate predictions of alloy equilibrium properties, they do not essentially elucidate the nature of the canonical average for alloys as a nonlinear map, which holds particularly true from the perspective of “configurational geometry” informed by the density of states in the configuration space (CDOS’) independently determined from thermodynamic variables such as temperature or energy.

To address these issues, we recently introduced a metric for local nonlinearity at a given configuration as a vector field \vec{H} on the configuration space,^{12,13} which clarifies that the magnification of ϕ_{th} can be quantified by the divergence and Jacobians of the vector field.¹⁴ We also propose an additional metric for nonlinearity by expanding the concept of \vec{H} to the statistical manifold, which enables the inclusion of further nonlocal information of nonlinearity, as Kullback-Leibler (KL) divergence.¹⁵ We observe a strong positive correlation between the averaged partial contribution to nonlocal nonlinearity across all configurations, and the geometric distance in configurational polyhedra (i.e., convex polyhedra determined from correlation functions range) between practical binary alloys and ideally separable systems in terms of SDFs.¹⁶

Although these works have successfully introduced metrics for the nonlinearity, they do not provide any information about nonequilibrium state, i.e., their original consideration is essentially restricted to thermodynamic equilibrium. To overcome the problem, we first introduce the concept of the nonlinearity for nonequilibrium state as a natural extension from that for thermodynamic equilibrium. Then, based on the resource theory, we derive bound for the nonequilibrium nonlinearity, which is characterized by the nonlinearity for thermodynamic equilibrium, Renyi divergence between equilibrium and nonequilibrium state, temperature and work. The details are shown below.

II. CONCEPT AND DERIVATION

Nonlinearity Measure

First, we briefly explain the basic concept of locality on configuration space as a vector field \vec{H} .¹² we read the configuration as an f -dimensional vector (q_1, \dots, q_f) , \vec{H} is given by

$$\vec{H}(\vec{q}) = \left\{ \phi(\beta) \circ (-\beta \cdot \Gamma)^{-1} \right\} \cdot \vec{q} - \vec{q},$$

where \circ denotes the composite map and Γ is an f symmetric covariance matrix of CDOS, $g(\vec{q})$ that is mentally independent of many-body interatomic interactions and temperature. We have shown that ϕ_{th} exhibits a linear map iff the CDOS assumes a multidimensional Gaussian form,¹⁵ which reveals that the local nonlinearity can be decomposed into linear and nonlinear contributions, with the former as the invertible map of $(-\beta \cdot \Gamma)$. Therefore, (i) when ϕ_{th} is locally linear at configuration \vec{q} , $\vec{H}(\vec{q})$ takes a zero-vector, and (ii) the image of the composite map $\phi_{\text{th}}(\beta) \circ (-\beta \cdot \Gamma)^{-1}$ is essentially independent of temperature and interatomic interactions. These certainly suggest that \vec{H} can be *a priori* determined based solely on CDOS, $g(\vec{q})$.

Then, we extend the concept of \vec{H} to the statistical manifold to capture additional nonlocal nonlinearity information at configuration \vec{q} . The corresponding nonlocal nonlinearity at a given configuration \vec{q}' , D_{NOL} , is defined by the KL divergence D of:¹⁵

$$D_{\text{NOL}} = D(P^{\text{E}} : P^{\text{G}}). \quad (5)$$

The probability distributions P^{E} and P^{G} are given by

$$\begin{aligned} P^{\text{E}}(\vec{q}) &= z'^{-1} \cdot g(\vec{q}) \exp \left[-\beta (\vec{q} \cdot \vec{V}') \right] \\ P^{\text{G}}(\vec{q}) &= z'^{\text{G}} \cdot g^{\text{G}}(\vec{q}) \exp \left[-\beta (\vec{q} \cdot \vec{V}') \right], \end{aligned} \quad (6)$$

where $g(\vec{q})$ corresponds to the CDOS of practical system with covariance matrix Γ , $g^{\text{G}}(\vec{q})$ corresponds to the CDOS of synthetically linear system, given by multidimensional Gaussian with the same Γ , and

$$\begin{aligned} z' &= \sum_{\vec{q}'} g(\vec{q}') \exp \left[-\beta (\vec{q}' \cdot \vec{V}') \right] \\ V' &= (-\beta \cdot \Gamma)^{-1} \cdot \vec{q}'. \end{aligned} \quad (7)$$

Hereafter, we employ the superscript G as a function of the linear system, as defined for P^{G} and g^{G} . Note that D_{NOL} is independent of the temperature and many-body interactions, which is a common characteristic with \vec{H} .

Setup for Nonequilibrium State

In order to extend the above concept of the nonlinearity for equilibrium state to nonequilibrium state (NS), we here consider that the NS is prepared from equilibrium state contacting

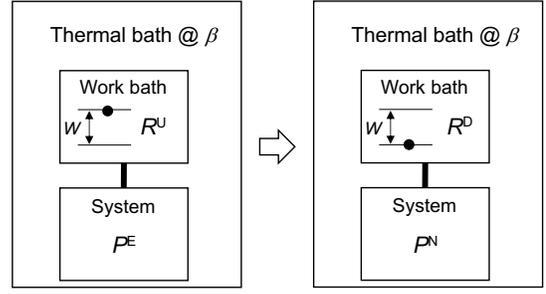


FIG. 1: Present setup for preparation of the nonequilibrium state from equilibrium state through the single-shot work.

with thermal bath (at inverse temperature β) and with work bath. The detailed setup is illustrated in Fig. 1, where (i) at the initial time, system takes P^{E} of thermodynamic equilibrium and that for work bath takes the energy level of $+W \geq 0$ (defined as R^{U}), and (ii) at the final time, system takes nonequilibrium of P^{N} and the energy level of the work bath of 0 (defined as R^{D}), corresponding to the single-shot work.

Under this setup, we consider the Gibbs preserving map Λ for the composite of system and work bath, which provides the condition for transferability between initial and final states with thermo-majorization:

$$P^{\text{N}} \otimes R^{\text{D}} \prec_{P^{\text{E}} \otimes R^{\text{E}}} P^{\text{E}} \otimes R^{\text{U}}, \quad (8)$$

with

$$\Lambda(P^{\text{E}} \otimes R^{\text{E}}) = P^{\text{E}} \otimes R^{\text{E}}. \quad (9)$$

From the Lorentz curve of the composite system, necessary and sufficient condition for Eq. (8) is given by¹⁷

$$W \geq \beta^{-1} S_{\infty}(P^{\text{N}} : P^{\text{E}}), \quad (10)$$

where S_{∞} denotes Renyi α -divergence $S_{\alpha}(\alpha \rightarrow \infty)$ of

$$S_{\alpha}(p : q) = \frac{1}{\alpha - 1} \ln \left(\sum_i \frac{p_i^{\alpha}}{q_i^{\alpha-1}} \right). \quad (11)$$

We note that

$$\lim_{\alpha \rightarrow 1} S_{\alpha}(p : q) = D(p : q). \quad (12)$$

To address the nonlinearity for nonequilibrium state, we first divide the canonical average as the following composite of canonical map Φ and taking average for probability distribution $\langle \cdot \rangle_1$:

$$\phi = \langle \cdot \rangle_1 \circ \Phi(g), \quad (13)$$

where

$$\Phi(g) : \vec{V} \mapsto P^{\text{E}} \quad (14)$$

under CDOS of g . Based on these maps, we show in Fig. 2 the relationship between the previously-introduced nonlinearity D_{NOL} for equilibrium state and nonequilibrium state obtained through the Gibbs preserving map Λ . From the figure,

in analogy to the equilibrium state, nonlinearity for nonequilibrium state can be naturally introduced as the nonlinear character for map Ω :

$$\Omega : \vec{v}' \mapsto \vec{q}^N, \quad (15)$$

where

$$\Omega = \langle \cdot \rangle_1 \circ \Lambda \circ \Phi(g). \quad (16)$$

We can now clearly see that when

$$P^N = P^G \quad (17)$$

is satisfied,

$$\Omega = -\beta\Gamma \quad (18)$$

holds on. Therefore, Eq. (17) is a sufficient condition where Ω becomes locally linear map in terms of the configurational geometry. With these considerations, we here naturally define the nonlinearity for the nonequilibrium state given by

$$D_{\text{NOL}}^N = S_\alpha(P^N : P^G), \quad (19)$$

which has the common end-point for KL divergence of D_{NOL} . The present purpose is therefore to reveal relationship between equilibrium and nonequilibrium nonlinearity of D_{NOL} and D_{NOL}^N , under the condition of work bound in Eq (10).

Derivation of Nonequilibrium Bound for Nonlinearity

We here assume that

$$P^E, P^N, P^G \in \mathbb{P}_d \quad (20)$$

$$\forall p, q, r \in \mathbb{P}_d, \quad \exp[-D(p : ar + bq)] \geq a \cdot \exp[-D(p : r)] + b \cdot \exp[-D(p : q)], \quad (25)$$

where

$$\begin{aligned} 0 &\leq a, b \leq 1 \\ a + b &= 1. \end{aligned} \quad (26)$$

When we read

$$p = P^E, r = P^N, ar + bq = P^G, \quad (27)$$

$$\exp[-D(P^E : P^G)] \geq a \cdot \exp[-D(P^E : P^N)] + b \cdot \exp[-D(P^E : q)]. \quad (28)$$

We can always find the sufficient condition that there exists

are all full rank. When we consider

$$\exists m, M \in \mathbb{R} \quad \text{s.t.} \quad m \leq \frac{P_i^N}{P_i^E} \leq M, \quad (21)$$

the following is always satisfied:

$$D(P^E : P^N) \leq \frac{1}{m} D(P^N : P^E) \quad (22)$$

from the common characteristics in KL divergence. In Eq. (21), we can specifically choose m as

$$\frac{1}{m} = \max_i \frac{P_i^E}{P_i^N} = e^{S_\infty(P^E : P^N)}. \quad (23)$$

Substituting Eq. (22) into Eq. (10) with the condition of Eq. (23) and using the inequality for Renyi divergence of $S_\alpha \geq S_{\alpha'}$ for $\alpha \geq \alpha'$, we first obtain the inequality of

$$D(P^E : P^N) \leq e^{S_\infty(P^E : P^N)} \beta W. \quad (24)$$

To further include the information about P^G , we employ the following superadditive property for KL divergence:¹⁸

Eq. (25) can be rewritten as

$q \in \mathbb{P}_d$, holding the inequality of Eq. (28), namely,

$$\begin{aligned} 0 &\leq a \leq \frac{1}{J} \leq 1 \\ J &= \max_i \frac{P_i^N}{P_i^G} = e^{S_\infty(P^N : P^G)}. \end{aligned} \quad (29)$$

Therefore, when we specifically put $a = J^{-1}$, Eq. (28) can be further transformed into

$$\begin{aligned} \exp \left[-D \left(P^E : P^G \right) \right] &\geq J^{-1} \exp \left[-D \left(P^E : P^N \right) \right] + (1 - J^{-1}) \cdot \exp \left[-D \left(P^E : q \right) \right] \\ &\geq J^{-1} \exp \left[-D \left(P^E : P^N \right) \right] \\ &\geq J^{-1} \exp \left[-e^{S_\infty(P^E:P^N)} \beta W \right], \end{aligned} \quad (30)$$

where we employ Eq. (24) to obtain the last equation. Substituting Eq. (29) into Eq. (30) and taking logarithm for l.h.s and r.h.s, we finally obtained the desired nonequilibrium bound:

$$D_{\text{NOL}}^{\text{N}} = S_\infty \left(P^{\text{N}} : P^{\text{G}} \right) \geq D_{\text{NOL}} - e^{S_\infty(P^E:P^N)} \cdot \beta W, \quad (31)$$

where the equality holds *iff* $P^E = P^N = P^G$ (implicitly assuming $W = 0$). Eq. (31) certainly clarifies the lower bound for the nonlinearity for nonequilibrium state, which is characterized by the nonlinearity in equilibrium state, Ranyi ∞ -divergence between equilibrium and nonequilibrium state, temperature and the work.

III. CONCLUSIONS

Based on thermo-majorization and superadditive property for KL divergence, we derive lower bound for the extended

concept of canonical nonlinearity in the nonequilibrium state. The bound is characterized by the nonlinearity in equilibrium state, Ranyi ∞ -divergence between equilibrium and nonequilibrium state, temperature and the work.

IV. ACKNOWLEDGEMENT

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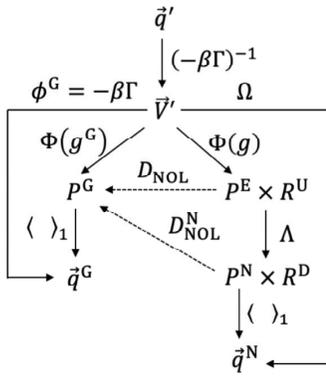


FIG. 2: Schematic relationships between nonlinearity for equilibrium state D_{NOL} and nonequilibrium state P^N obtained through Gibbs preserving map Λ . Solid arrows denote taking map, and dashed arrows represents taking difference in probability distributions through (appropriate) divergence.