Information-geometric dual affine coordinate systems for chemical thermodynamics

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We construct information-geometric dual affine coordinate systems for chemical thermodynamics, which are generalizations of our recent preprint on information-geometric dual affine coordinate systems for stochastic thermodynamics [N. O. and S. I., arXiv:2112.11008] [1].

I. INTRODUCTION

Information geometry is a differential geometry for information theory [2, 3], which introduces two coordinate systems called the dual affine coordinate systems. The dual affine coordinate systems are connected via the Legendre transformation of two convex functions. The dual affine coordinate systems and two convex functions provide the Bregman divergence [4]. The Bregman divergence induces a geometric structure of a differential geometry, namely dually flat geometry.

In chemcal thermodynamics [5–7], the Gibbs free energy and chemical free energy are given by the generalized Kullback-Leibler divergence [8, 9], and information geometry for chemical thermodynamics is naturally introduced based on the generalized Kullback-Leibler divergence [10]. The generalized Kullback-Leibler divergence is also regarded as the Lyapunov function [11, 12], and the second law of thermodynamics is given by the monotonicity of the Lyapunov function. Since the generalized Kullback-Leibler divergence is an example of the Bregman divergence, the Gibbs free energy and chemical free energy might induce a geometric structure of dually flat geometry. However, such a structure has not been explicitly constructed so far.

On the other hand, stochastic thermodynamics has been recently discussed as a framework of a stochastic description of chemical thermodynamics [13, 14]. Several analogies between stochastic thermodynamics and chemical thermodynamics for deterministic rate equation has been figured out [8, 15–21]. In stochastic thermodynamics, a relation between information-geometric quantities such as the Kullback-Leibler divergence and thermodynamic quantities such as the free energy has been well discussed [22–33] as a generalization of differential geometry for thermodynamics and statistical mechanics [34–43]. In stochastic thermodynamics, we have introduced information-geometric dual affine coordinate systems [1] based on the Kullback-Leibler divergence, and show the usefulness of this geometric description in the stochastic process of relaxation to equilibrium.

In this paper, we construct information-geometric dual affine coordinate systems for chemical thermodynamics in parallel with Ref. [1], based on information geometry for chemical thermodynamics [10]. We discuss the dual affine coordinate systems for both closed and open chemical reaction networks. For open chemical reaction networks, the dual affine coordinates provides the description of the steady-state thermodynamics for chemical thermodynamics.

II. DUALLY FLAT GEOMETRY

A. Dual affine coordinates

Dually flat geometry is a mathematical framework which introduces two different coordinate systems \( \eta \) and \( \theta \) into one space (manifold) and provides a geometry unifying the two coordinates [3]. Let \( K \) be the dimensionality of the space. One of the coordinate systems called \( \eta \)-coordinate are denoted by \( \eta \equiv (\eta_\rho)_{\rho=1}^K \equiv (\eta_1, \ldots, \eta_K) \) with its range \( \eta \in \mathcal{V} \subseteq \mathbb{R}^K \). The other system called \( \theta \)-coordinate are denoted by \( \theta \equiv (\theta_\rho)_{\rho=1}^K \equiv (\theta_1, \ldots, \theta_K) \) with \( \theta \in \mathcal{U} \subseteq \mathbb{R}^K \) [44]. The two coordinate systems together are called the dual affine coordinate systems.

In dually flat geometry, the coordinates \( \theta \) is related to \( \eta \) through a twice-differentiable function \( \varphi(\eta) \) as

\[ \theta^\rho(\eta) = \frac{\partial \varphi}{\partial \eta_\rho} \tag{1} \]

To ensure the one-to-one correspondence between the two coordinates, the function \( \varphi(\eta) \) must be strictly convex with respect to \( \eta \)-coordinates, namely the \( K \times K \) matrix \( \partial^2 \varphi / \partial \eta_\rho \partial \eta_\sigma \) must be positive definite for all \( \eta \in \mathcal{V} \). We introduce another function through the Legendre transformation:

\[ \psi(\theta) := \sum_{\rho=1}^K \theta^\rho \eta_\rho(\theta) - \varphi(\eta(\theta)) \tag{2} \]

It is convex with respect to \( \theta \)-coordinates and satisfies the Legendre duality

\[ \eta_\rho(\theta) = \frac{\partial \varphi}{\partial \theta_\rho}, \tag{3} \]
\[ \varphi(\eta) = \sum_{\rho=1}^K \eta_\rho \theta^\rho(\eta) - \psi(\theta(\eta)) \tag{4} \]

The quadruplet \( (\eta, \varphi(\eta), \theta, \psi(\theta)) \) suffices to designate all the geometric structures of a dually flat geometry as follows.
B. Bregman divergence

We introduce a two-point function called the Bregman divergence based on the quadruplet \((\eta, \varphi(\eta), \theta, \psi(\theta))\), which plays a central role in dually flat geometry. Let \(P\) and \(Q\) be two points on the manifold. Corresponding coordinates of \(P\) and \(Q\) in the \(\eta\)-coordinate system is denoted by \(\eta\) and \(\eta'\), and those in the \(\theta\)-coordinate systems is denoted by \(\theta\) and \(\theta'\). The Bregman divergence is defined as

\[
D(P\|Q) := \varphi(\eta) + \psi(\theta') - \sum_{\rho} \theta' \rho \eta_{\rho} \tag{5}
\]

\[
= \varphi(\eta) - \varphi(\eta') - \sum_{\rho} \theta' \rho (\eta_{\rho} - \eta'_{\rho}) \tag{6}
\]

\[
= \psi(\theta') - \psi(\theta) - \sum_{\rho} \eta_{\rho}(\theta'_{\rho} - \theta_{\rho}). \tag{7}
\]

Since \(f(\eta) := \varphi(\eta') + \sum_{\rho} \theta' \rho (\eta_{\rho} - \eta'_{\rho})\) gives the tangent plane of \(\varphi\) at the contact point \(Q\), the equation (6) implies that \(D(\cdot\|Q) = \varphi - f\) is the difference between \(\varphi\) and the tangent plane \(f\). Because \(\varphi\) is the strictly convex function, the value of \(\varphi\) is always larger than the value of the point in the tangent plane. Therefore, the following properties

\[
D(P\|Q) \geq 0, \tag{8}
\]

\[
D(P\|Q) = 0 \iff P = Q. \tag{9}
\]

are valid. We can also interpret the Bregman divergence as a difference between \(\psi\) and its tangent plane in a similar way based on (7). As discussed later, the Bregman divergence can be interpreted as a generalization of the squared distance, but it is not necessarily the square of a distance function because the axiom of symmetry is not generally satisfied, i.e., \(D(P\|Q) \neq D(Q\|P)\).

C. Geometry induced from a Bregman divergence

Based on the Bregman divergence, we introduce the differential geometry on the manifold. We consider the situation that two points \(P\) and \(Q\) are infinitesimally close. The corresponding coordinates of two points \(P\) and \(Q\) in the \(\eta\)-coordinate systems are \(\eta\) and \(\eta + d\eta\), and those in the \(\theta\)-coordinate systems are \(\theta\) and \(\theta + d\theta\), respectively. In this case, the Bregman divergence between \(P\) and \(Q\) is symmetric \(2D(Q\|P) = 2D(P\|Q) = \sum_{\rho} d\theta'_{\rho} d\eta_{\rho}\) up to the second order of \(d\eta\) and \(d\theta\). We write this quantity as \(ds^2\),

\[
d s^2 := \sum_{\rho} \sum_{\sigma} \frac{\partial^2 \varphi}{\partial \eta_{\rho} \partial \eta_{\sigma}} d\eta_{\rho} d\eta_{\sigma} \tag{10}
\]

\[
= \sum_{\rho,\sigma} \frac{\partial^2 \varphi}{\partial \eta_{\rho} \partial \eta_{\sigma}} d\eta_{\rho} d\eta_{\sigma}
\]

\[
= \sum_{\rho,\sigma} \frac{\partial^2 \psi}{\partial \theta'_{\rho} \partial \theta'_{\sigma}} d\theta'_{\rho} d\theta'_{\sigma},
\]

and discuss the Riemannian geometry of the manifold by interpreting \(ds^2\) as the square of the line element.

We show some examples of dually flat geometry:

**Example 1.**—We set \(V = \mathbb{R}^K\) and

\[
\varphi(\eta) = \frac{1}{2} \sum_{\rho} (\eta_{\rho})^2. \tag{11}
\]

In this case, the dual coordinates and convex function are given by

\[
\theta'(\eta) = \eta_{\rho}, \quad \psi(\theta) = \frac{1}{2} \sum_{\rho} (\theta'_\rho)^2, \tag{12}
\]

with \(U = \mathbb{R}^K\), and the Bregman divergence is calculated as

\[
D(P\|Q) = \frac{1}{2} \sum_{\rho} (\eta_{\rho} - \eta'_{\rho})^2. \tag{13}
\]

This is the case of the self-duality, where the \(\theta\)-coordinate is same as the \(\eta\)-coordinate, and \(\psi\) is equal to \(\varphi\). The Bregman divergence is proportional to the square of the Euclidean distance. Thus, geometry induced from this Bregman divergence is the Euclidean geometry, that is \(ds^2 = \sum_{\rho} (d\eta_{\rho})^2 = \sum_{\rho} (d\theta'_{\rho})^2\).

**Example 2.**—We set \(V = \mathbb{R}^K\) and

\[
\varphi(\eta) = \sum_{\rho} [\eta_{\rho} \ln \eta_{\rho} - \eta_{\rho}]. \tag{14}
\]

In this case, the dual coordinates and convex function are given by

\[
\theta'(\eta) = \ln \eta_{\rho}, \quad \psi(\theta) = \sum_{\rho} \exp(\theta'_\rho), \tag{15}
\]

with \(U = \mathbb{R}^K\), and the Bregman divergence is calculated as

\[
D(P\|Q) = \sum_{\rho} \left[ \eta_{\rho} \ln \frac{\eta_{\rho}'}{\eta_{\rho}} - \eta_{\rho} + \eta_{\rho}' \right]. \tag{16}
\]

This Bregman divergence is called the generalized Kullback–Leibler divergence, which is well used in information geometry [3], that is the dually flat geometry for the set of the probability distributions. If \(\eta_{\rho}\) and \(\eta'_{\rho}\) are the probability distributions which satisfies the normalization of the probability distributions \(\sum_{\rho} \eta_{\rho} = \sum_{\rho} \eta'_{\rho} = 1\), this Bregman divergence reduces to the Kullback–Leibler divergence [45]. As discussed later, this Bregman divergence (16) is well used in chemical thermodynamics, where \(\eta_{\rho}\) and \(\eta'_{\rho}\) denote the particle numbers of \(\rho\)th chemical species in two different states.

D. Invariance under affine transformations

We show that the geometric structure of dually flat geometry is invariant under an affine transformation. Let \(A_{\rho}^{\sigma}\) and \((A^{-1})_{\rho}^{\rho}\) be a \(K \times K\) invertible matrix and its inverse matrix, respectively, with the matrix product \(\sum_{\rho} (A^{-1})_{\rho}^{\sigma} A_{\rho}^{\lambda}\).
giving the Kronecker delta $\delta_{\sigma^j} = \sum_{\rho} (A^{-1})_{\rho^j} A_{\rho^j}$. Let $(b_\rho^j)^K_{j=1}$ and $(d_\rho^j)^K_{j=1}$ be two sets of constants. By using these quantities $A_{\rho^j}^\sigma$, $(A^{-1})_{\rho^j}^\sigma$, $(b_\rho^j)^K_{j=1}$, and $(d_\rho^j)^K_{j=1}$, we introduce two new coordinate systems $\tilde{\eta}$ and $\tilde{\theta}$ by the following affine transformation,

\begin{equation}
\begin{aligned}
\tilde{\eta}_\rho(\eta) &= \sum_{\sigma} A_{\rho^\sigma}^\sigma \eta_\sigma + b_\rho, \\
\tilde{\theta}(\theta) &= \sum_{\sigma} (A^{-1})_{\rho^\sigma}^\sigma \theta_\sigma + d_\rho.
\end{aligned}
\end{equation}

By using a constant $C$, two new strictly convex functions $\tilde{\varphi}(\tilde{\eta})$ and $\tilde{\psi}(\tilde{\theta})$ are also introduced by

\begin{equation}
\begin{aligned}
\tilde{\varphi}(\tilde{\eta}) &= \varphi(\eta(\tilde{\eta})) + \sum_{\rho} d^\rho \tilde{\eta}_\rho + C, \\
\tilde{\psi}(\tilde{\theta}) &= \psi(\theta(\tilde{\theta})) + \sum_{\rho} b_\rho \tilde{\theta}^\rho - \sum_{\rho} b_\rho d^\rho - C.
\end{aligned}
\end{equation}

The new quadruplet $(\tilde{\eta}, \tilde{\theta}, \tilde{\varphi}, \tilde{\psi})$ satisfies the structure of the Legendre transformation in Eqs. (1)–(4) with replacement of $(\eta, \theta, \varphi, \psi)$ by $(\tilde{\eta}, \tilde{\theta}, \tilde{\varphi}, \tilde{\psi})$. Moreover, the Bregman divergence between two points $P$ and $Q$ is given by

\begin{equation}
D(P|Q) = \varphi(\eta) + \psi(\theta') - \sum_{\rho} \theta'^\rho \eta_\rho = \tilde{\varphi}(\tilde{\eta}(\eta)) + \tilde{\psi}(\tilde{\theta}(\theta')) - \sum_{\rho} \tilde{\theta}'(\theta') \tilde{\eta}_\rho(\eta),
\end{equation}

where $\eta$ and $\eta'$ are the corresponding $\eta_1$-coordinates of the points $P$ and $Q$, and $\theta$ and $\theta'$ are the corresponding $\theta$-coordinates of the points $P$ and $Q$, respectively. Thus, the Bregman divergence between two points $P$ and $Q$ is invariant under an affine transformation between two coordinate systems. Since the structure of the dually flat geometry is induced from the Bregman divergence, the geometric structure of the dually flat geometry is invariant under an affine transformation.

### III. Chemical Thermodynamics

#### A. Thermodynamic quantities

Consider a system of $N$ chemical species $X_1, \ldots, X_N$ (including solvent species) undergoing chemical reactions. The system is immersed in a reservoir to keep the temperature $T$ and pressure $P$ constant. We assume that the system is uniform and with no hydrodynamic flows. In other words, the degrees of freedom other than chemical reactions, such as diffusion, mixing, heat conduction, and hydrodynamic motion, are assumed to relax very fast compared to chemical reactions. Therefore, the state of the system is completely specified by the particle numbers of the species $n \equiv (n_i)_{i=1}^N \equiv (n_1, \ldots, n_N)$.

The Gibbs free energy of the system $G$ is a function of $n$. It admits the extensivity $G(\lambda n) = \lambda G(n)$ for an arbitrary constant $\lambda > 0$. We define the chemical potential of $X_i$ by $\mu^i := \partial G/\partial n_i$. They satisfy the Euler relations

\begin{equation}
G(n) = \sum_i \mu^i(n)n_i
\end{equation}

due to the extensivity of the Gibbs free energy.

**Ideal dilute solution.** An important class of chemical reaction systems is the ideal dilute solution [8, 9, 46]. In this paper, we do not necessarily assume the ideal dilute property. Nevertheless, we will write down our main results for the case of ideal dilute solutions explicitly as an example.

Consider that $X_1$ is the solvent species accounting for most of the total particle number of the system, and $X_2, \ldots, X_N$ are the small amount of solutes dissolved in it. We further assume the ideal dilute property, i.e., that there is no interaction between solute molecules, that the free energy change due to dissolving the solutes into the solvent is linearly proportional to the particle number of the solutes, and that we can approximate the Gibbs free energy up to the first order in $n_i/n_1$ ($i = 2, \ldots, N$). Under these assumptions, we obtain

\begin{equation}
G(n) = \sum_{i=2}^N \left[ \frac{\mu^i_0 + RT \ln \frac{n_i}{n_1}}{n_i} n_i - RT n_i \right] + \mu^1_0 n_1,
\end{equation}

where $\mu^i_0$’s are constants depending only on $T$ and $P$, and $R$ is the gas constant. Therefore, the chemical potentials are

\begin{equation}
\mu^i = \mu^i_0 + RT \ln \frac{n_i}{n_1} (i = 2, \ldots, N),
\end{equation}

\begin{equation}
\mu^1 = \mu^1_0 - RT \sum_{i=2}^N \frac{n_i}{n_1}.
\end{equation}

The assumption of ideal dilute property is phenomenologically equivalent to that, when the solution is in vapor-liquid equilibrium with its vapor, the solute vapor behaves as an ideal gas and the vapor-liquid equilibrium obeys Henry’s law.

We further assume that the solvent $X_1$ does not react with the solutes in ideal dilute solutions for simplicity. Therefore, $n_1$ is constant, and the chemical potentials of the solutes $\mu^i (i = 2, \ldots, N)$ depends only on the particle numbers of respective solute species.

#### B. Closed chemical reaction systems

We introduce $M$ chemical reactions taking place in the system,

\begin{equation}
v_{1}^\rho X_1 + \cdots + v_{N}^\rho X_N \rightleftharpoons k_{1}^\rho X_1 + \cdots + k_{N}^\rho X_N,
\end{equation}

for $\rho = 1, \ldots, M$. Here, $v_{\rho}^\rho$ and $k_{\rho}^\rho$ are nonnegative constants called stoichiometric coefficients. We assume that all the reactions are reversible (at least in a very small rate). We define the stoichiometric matrix by $S \equiv (S_{\rho}^i)_{i=1}^N \equiv (S_{\rho}^i)_{i=1}^N M$. 


with $S_i^\rho := \nu_i^\rho - v_i^\rho$. When the $\rho$th reaction proceeds by $d\xi_{\rho}$, the particle numbers change by

$$dn_{i} = \sum_{\rho} S_i^\rho d\xi_{\rho}. \quad (25)$$

This equation implies that states reachable from a reference state $n^{\text{ref}}$ are confined in

$$\left\{ \left( n^{\text{ref}}_i + \sum_{\rho} S_i^\rho \xi_{\rho} \right)_{i=1}^N \in \mathbb{R}^M \right\} \cap \mathbb{R}_{\geq 1}^N. \quad (26)$$

We call this set the stoichiometric compatibility class corresponding to $n^{\text{ref}}$. We also define the linear space called stoichiometric subspace by

$$\left\{ \sum_{\rho} S_i^\rho \xi_{\rho} \right\}_{i=1}^N = \mathbb{R}^M. \quad (27)$$

We discuss the Gibbs free energy on the stoichiometric compatibility class. The Gibbs free energy $G(n)$ is always a convex function with respect to $n$, but it is not strictly convex because of the extensivity. Nevertheless, if we restrict ourselves to $n$ in a stoichiometric compatibility class, we often recover the strict convexity. Exceptions are the systems with phase separations or phase transitions. Systems with a ‘birth’ reaction, i.e., a reaction with $v_i^1 = v_i^2 = \cdots = v_i^\rho = 0$ may also be an exception. We exclude such systems and assume the convexity of the Gibbs free energy in the stoichiometric compatibility class.

Since $-G(n)/T$ equals the total entropy of the system and the reservoir together up to an additive constant for a closed system, the entropy production $d\Sigma$ is related to the Gibbs free energy change by $Td\Sigma = -dG$. By using the definition of chemical potentials, we obtain

$$Td\Sigma = -dG = -\sum_{i} \mu_{i} dn_{i}. \quad (28)$$

We introduce the affinity (thermodynamic force) of the $\rho$th reaction by

$$F^\rho(n) := -\sum_{i} S_i^\rho \mu_{i}(n). \quad (29)$$

Using this definition and (25), we obtain the decomposition of entropy production into the reactions

$$Td\Sigma = \sum_{\rho} F^\rho(n)d\xi_{\rho}. \quad (30)$$

Therefore, the affinity of the $\rho$th reaction quantifies the entropy production due to the unit amount of occurrence of the $\rho$th reaction.

We call the state with $F^\rho = 0$ for all $\rho$ the equilibrium state. Let $n^{\text{eq}}$ denote the particle numbers at the equilibrium state. In the equilibrium, we have $dG = 0$ for any infinitesimal reaction due to (28) and (30). Therefore, the Gibbs free energy takes its minimum within the stoichiometric compatibility class at the equilibrium, since we assume that $G$ is strictly convex in the stoichiometric compatibility class. Moreover, the equilibrium state is unique due to this property.

The reactions follow a kinetics of the form

$$\frac{d\xi_{\rho}}{dt} = J_{\rho}(n), \quad (31)$$

or equivalently,

$$\frac{dn_i}{dt} = \sum_{\rho} S_i^\rho J_{\rho}(n), \quad (32)$$

where $t$ denotes the time and $J_{\rho}$ is a function of $n$. To the kinetics, we impose the consistency with thermodynamics; namely, the second law of thermodynamics $d\Sigma/dt \geq 0$ must hold. In addition, we often impose the second law of thermodynamics separately for each reaction: $F^\rho J_{\rho} \geq 0 (\rho = 1, \ldots, M)$. However, these constraints do not determine the kinetics uniquely from thermodynamics. In this paper, we do not use the specific form of kinetics.

**Ideal dilute solution.**—For example, the class of kinetics that is consistent with the thermodynamics of an ideal dilute solution is the mass action,

$$J_{\rho}(n) = k_+^{\rho} \prod_{i=1}^{N} \left( \frac{n_i^{\rho}}{V} \right)^{v_i^\rho} - k_-^{\rho} \prod_{i=1}^{N} \left( \frac{n_i^{\rho}}{V} \right)^{v_i^\rho}, \quad (33)$$

where $V$ is the closed volume of the system and $k_+^{\rho}, k_-^{\rho}$ are arbitrary positive rate constants. This kinetics leaves the freedom of choosing the rate constants.

**C. Open chemical reaction systems**

We can further generalize the above setup by allowing some chemical species exchanged with outside the system. Among the $N$ species, the first $N_{\text{cl}}$ species are closed species, i.e., those not exchanged with outside the system, and the other $N_{\text{op}} = N - N_{\text{cl}}$ species are open species, i.e., those exchanged with outside the system. Namely, $X_1, \ldots, X_{N_{\text{cl}}}$ are closed and $X_{N_{\text{cl}}+1}, \ldots, X_{N}$ are open. Dummy variables $i_{\text{cl}}, j_{\text{cl}}, \ldots$ are understood as changing over closed species only, while $i_{\text{op}}, j_{\text{op}}, \ldots$ are over open species only. We separate the particle numbers as $n_{\text{cl}} \equiv (n_{i_{\text{cl}}})_{i_{\text{cl}}=1}^{N_{\text{cl}}}$ and $n_{\text{op}} \equiv (n_{i_{\text{op}}})_{i_{\text{op}}=N_{\text{cl}}+1}^{N}$, which recovers $n \equiv (n_{\text{cl}}, n_{\text{op}})$.

We consider the situation where the chemical potentials $\mu_{i_{\text{op}}}$ of the open species are fixed at prescribed values $\mu_{i_{\text{op}}}$. This situation is physically realized by attaching the system with reservoirs containing the open species through semipermeable membranes that allow only the open species to pass, and assuming that the exchanges of the open species are much faster than chemical reactions.

Under this situation, the reactions still follow the kinetics of the form (31). Due to the kinetics, the particle numbers
of the closed species change by (32). On the other hand, the particle numbers of the closed species are determined by

$$\mu^{\text{op}}(n_{d1}, n_{op}) = \mu^{\text{pre}}_{\text{op}}.$$ \hspace{1cm} (34)

We assume the existence of a $n_{\text{op}}$ that solves (34) for each $n_{d1}$. This assumption is physically natural, since if we fix $\mu^{\text{op}}$ in the aforementioned protocol, we expect that $n_{\text{op}}$ settles down at a certain value. Since we assumed the strict convexity of the Gibbs free energy, the solution of (34) is unique for each $n_{d1}$. We denote the value as

$$n_{\text{op}} = \pi_{\text{op}}(n_{d1}).$$ \hspace{1cm} (35)

By defining the thermodynamic forces of reactions by (29), we still obtain the expression of the entropy production rate (30). However, the relation between the entropy production rate and the Gibbs free energy $Td\Sigma = -dG$ no longer holds.

*Ideal dilute solution.*—For ideal dilute solutions, $\pi_{\text{op}}$ for a solute is explicitly calculated using (22) as

$$n_{\text{op}} = \pi_{\text{op}}(n_{d1}) = n_1 \exp\left(\frac{\mu^{\text{op}}_{\text{pre}} - \mu^{\text{op}}_{\text{ref}}}{RT}\right)$$ \hspace{1cm} (36)

which is independent of $n_{d1}$ (recall that we assume $n_1$ to be constant). Therefore, for ideal dilute solutions, fixing chemical potentials of solutes is equivalent to fixing their particle numbers $n_{\text{op}}$.

**IV. DUALLY FLAT GEOMETRY FOR CLOSED CHEMICAL REACTION SYSTEMS**

We construct a dually flat geometry on a stoichiometric compatibility class using thermodynamic quantities. The resulting geometry reproduces the previously considered relationship between divergence and Gibbs free energy in ideal dilute solutions, and also reveals the underlying geometric structure, including the case of non-ideal solutions.

**A. Reduced stoichiometric matrix**

In preparation for the construction, we introduce what we call the reduced stoichiometric matrix. Let $K (\leq M)$ denote the dimensionality of the stoichiometric subspace (27), i.e., the number of independent reactions, and let $(\tilde{S} \rho)^{\text{ref}}_{\text{op}}$ for $\rho = 1, \ldots, K$ form a linear independent basis of the stoichiometric subspace. We call the $N \times K$ matrix $\tilde{S} \equiv (\tilde{S} \rho)^{\text{ref}}_{\text{op}}$ a reduced stoichiometric matrix. Since we have the freedom of changing the basis of stoichiometric subspace, $\tilde{S}$ is not unique. A simple way to construct $\tilde{S}$ is to eliminate $M - K$ columns of $S$ that are linear dependent to the remaining $K$ columns from $S$. Our construction of dually flat geometry below is valid regardless of the choice of the matrix $\tilde{S}$.

In the following, we no more use $S$ and only deal with $\tilde{S}$. Intuitively, the use of $\tilde{S}$ amounts to considering a virtual reaction system with the reactions corresponding to the columns of $\tilde{S}$. We call the reaction

$$\tilde{\nu}_i \rho X_1 + \cdots + \tilde{\nu}_N \rho X_N \rightleftharpoons \tilde{k}_1 \rho X_1 + \cdots + \tilde{k}_N \rho X_N$$ \hspace{1cm} (37)

the $\rho$th virtual reaction, where $\tilde{\nu}_i \rho$ and $\tilde{k}_i \rho$ are defined by $\tilde{\nu}_i \rho := \max(-\tilde{S} \rho, 0)$ and $\tilde{k}_i \rho := \max(\tilde{S} \rho, 0)$ so that we have $\tilde{S} \rho = \tilde{k}_i \rho - \tilde{\nu}_i \rho$.

**B. Coordinates and the convex functions**

Let us construct the $\eta$-coordinate system as the extent of the virtual reactions. First, we choose an arbitrary point on the stoichiometric compatibility class as the reference point $n^{\text{ref}}$. Since the possible variations of $n$ are represented by a linear combination of the columns of $\tilde{S}$, for any point $n$ on the stoichiometric compatibility class, there exists a unique $\eta \equiv (\eta_\rho)_{\rho=1}^K$ such that

$$n_\rho = n^{\text{ref}}_\rho + \sum_{\rho} \tilde{S} \rho \eta_\rho.$$ \hspace{1cm} (38)

This is the definition of the coordinates $\eta$. Namely, $\eta_\rho$ is the extent of the $\rho$th virtual reaction, measured with respect to $n^{\text{ref}}$. The range of $\eta$ is taken so that the corresponding particle numbers (38) are nonnegative. We have the one-to-one correspondence between $\eta$ and the states $n$ in the stoichiometric compatibility class.

We take the Gibbs free energy as the convex function $\varphi$ and construct $\theta$ and $\psi$ from the definitions (1)–(2). As a result, we obtain the following quadruplet of dually flat geometry:

$$\begin{cases} 
\eta_\rho(n) = \sum_i (\tilde{S}^-)_{\rho i} (n_i - n_i^{\text{ref}}), \\
\varphi(\eta) = G(n(\eta)) = \sum_i \mu^i (n(\eta)) n_i, \\
\theta(\eta) = \sum_i \tilde{S} \rho \mu^i (n), \\
\psi(\theta) = -\sum_i \mu^i (n(\theta)) n_i^{\text{ref}},
\end{cases}$$ \hspace{1cm} (39)

This quadruplet completely characterizes the dually flat geometric structure we construct. This quadruplet is in analogy with the quadruplet in stochastic thermodynamics [1]. Here, (39a) is obtained by inverting the definition (38), and $(\tilde{S}^-)_{\rho i}$ is a pseudo-inverse matrix of $\tilde{S} \rho$, defined by an arbitrary matrix satisfying

$$\sum_{\rho, j} \tilde{S} \rho (\tilde{S}^-)_{\rho j} \tilde{S} \rho \sigma = \tilde{S} \rho \sigma.$$ \hspace{1cm} (40)

Psuedo-inverse matrices of $S$ are not unique, but the right-hand side of (39a) does not depend on this ambiguity.
Comparing the obtained \( \theta \)-coordinates (39c) with Eq. (29), \( \theta^\rho \) is interpreted as the negative of the affinity of the \( \rho \)th virtual reaction. Thus, \( \theta^\rho = 0 \) holds in equilibrium for all \( \rho \). From the general theory of information geometry, \( \theta \) is in one-to-one correspondence with \( \eta \). Since \( \eta \) has in turn one-to-one correspondence with the particle number \( n \) in the stoichiometric compatibility class, we obtain the one-to-one correspondence between \( n \), \( \eta \), and \( \theta \). We denote these relations as \( \theta(\eta) \), \( \eta(\theta) \), \( \theta(n) \), and \( n(\theta) \), the last one being non-trivial. Therefore, we can use these affinities to specify a state on the stoichiometric compatibility class.

We have left some arbitrariness in the above constructed quadruplet. These arbitrariness are understood as the freedom of the affine transformation (17)–(18), and therefore do not affect the induced geometric structures. The arbitrariness in the construction of a reduced stoichiometric matrix \( \hat{S} \), i.e., the choice of the virtual reactions, corresponds to the freedom of transformations by the regular matrix \( (A_v^\rho) \) in (17). The arbitrariness in the choice of the reference point \( n^\text{ref} \) in the \( \eta \)-coordinates corresponds to the transformation by \( (b_v) \) in (17)–(18).

**Ideal dilute solution.**—For the case of ideal dilute solutions, we obtain the quadruplet

\[
\eta_{\rho}(n) = \sum_{i=2}^{N} (S^{-1})_{\rho i} (n_i - n_i^\text{ref}), \\
\phi(\eta(n)) = \sum_{i=2}^{N} \left[ \left( \mu^\rho + RT \ln \frac{n_i}{n_i^\text{ref}} \right) n_i - RT n_i \right] + \mu^\rho n_i^\text{ref}, \\
\theta^\rho(n) = \sum_{i=2}^{N} \hat{S}_{i\rho} (\mu^\rho + RT \ln \frac{n_i}{n_i^\text{ref}}), \\
\psi(\theta(n)) = -\sum_{i=2}^{N} \left[ \left( \mu^\rho + RT \ln \frac{n_i}{n_i^\text{ref}} \right) n_i^\text{ref} - RT n_i \right] - \mu^\rho n_i^\text{ref}.
\]

Here, we exploit the assumption that the solvent \( X_d \) does not react with the solutes, and therefore \( \hat{S}_{i\rho} = 0 \) and \( n_1 = n_1^\text{ref} \). The constant \( \mu^\rho n_i^\text{ref} \) in \( \phi \) and \( \psi \) can be dropped using the freedom of an affine transformation (18).

### C. Bregman divergence and differential geometry

Using the quadruplet constructed in the previous section, the Bregman divergence between arbitrary two points with particle numbers \( n, n' \) is given by

\[
D(n|n') = G(n) - G(n') - \sum_{\rho} \mu^\rho(n') S^\rho (\eta_{\rho}(n) - \eta_{\rho}(n'))
\]

where we used the definition (6) and the Euler relation (20). In particular, the divergence between an arbitrary state \( n \) and the equilibrium state \( n^\text{eq} \) is

\[
D(n|n^\text{eq}) = G(n) - G(n^\text{eq}),
\]

where we used \( \phi(\eta(n)) = G(n) \) and \( \theta(n^\text{eq}) = 0 \) in the original definition of the divergence (6).

Based on this quadruplet, the second law of thermodynamics are given by

\[
- \frac{d}{dt} D(n|n^\text{eq}) = -\frac{dG(n)}{dt} = T \frac{d}{dt} (\sum_{\rho} \theta^\rho \frac{dn^\rho}{dt}) \geq 0.
\]

or

\[
- \frac{dG(n)}{dt} = -\frac{d\varphi}{dt} = -\sum_{\rho} \theta^\rho \frac{dn^\rho}{dt} \geq 0,
\]

where we used the definition of \( \theta \)-coordinates (1). Thus, the second law of thermodynamics implies that \( \varphi \) and \( D(n|n^\text{eq}) \) are Lyapunov functions.

The information-geometric line element, namely the squared distance between two infinitesimally close points, is calculated from the definition (10) as

\[
ds^2 = \sum_{\rho} d\theta^\rho d\eta_{\rho} = \sum_{i} d\mu^i d\eta_i = \sum_{i,j} \chi_{ij} d\eta_i d\eta_j
\]

where \( \chi_{ij} = \partial \mu^i / \partial \eta_j \) denotes the susceptibility. The idea of using the Hessian of thermodynamic potentials \( \chi_{ij} \) as a thermodynamic metric dates back to the Riemannian geometry of classical equilibrium thermodynamics [34–36]. Our dually flat geometry provides modern concepts such as dual coordinates and the divergence that are consistent with the metric in those historical works.

**Ideal dilute solution.**—For the case of ideal dilute solutions, the divergence (42) is explicitly given by

\[
D(n|n') = RT \sum_{i=2}^{N} \left[ \ln \frac{n_i}{n_i'} - n_i + n_i' \right],
\]

where we used (22)–(23). This expression coincides with the generalized Kullback–Leibler divergence (16) between the particle numbers of the solutes by ignoring the factor of \( RT \). This expression has been already pointed out, for example, in Refs. [8–12]. Our result for general cases (42) is a natural generalization of this expression. Moreover, our result reveal the underlying geometric structure represented by the quadruplet (39a)–(39d).

### V. Dually flat geometry for open chemical reaction systems

We generalize the construction of dually flat geometry in the previous section for open chemical reaction systems. For open reaction systems, entropy production rate is not solely determined by the changes in the particle numbers. Therefore, we consider a wider space in which we can track all the entropy production.
A. Reduced stoichiometric matrix

We construct a reduced stoichiometric matrix similarly to the closed cases, but with an additional specification on the selection of basis of the stoichiometric subspace. First, we use the same procedure as the closed case to construct a reduced stoichiometric matrix $\tilde{\mathbf{S}} \equiv (\tilde{\mathbf{S}}_\rho)^N_{\rho=1}$ with an arbitrary choice of the basis. Although all of the $K$ columns of $\tilde{\mathbf{S}}$ are linearly independent due to its construction, if we look at the closed species only $(\tilde{\mathbf{S}}_\id^\rho)^N_{\rho=1}$, there might be a linear dependence among the columns.

Let $K'$ ($K' \leq K$) be the number of linear independent columns of $(\tilde{\mathbf{S}}_\id^\rho)^N_{\rho=1}$. We construct a new reduced stoichiometric matrix $\tilde{\mathbf{S}}' \equiv (\tilde{\mathbf{S}}'_\rho)^N_{\rho=1}$ as follows. For the first $K'$ columns of $\tilde{\mathbf{S}}'$, we collect arbitrary $K'$ columns of $\tilde{\mathbf{S}}$ that are linearly independent when looked at the closed species only. We construct the remaining $(K - K')$ columns of $\tilde{\mathbf{S}}'$ based on the unused $(K - K')$ columns of $\tilde{\mathbf{S}}$, but we add or subtract the already used $K'$ columns from the unused $(K - K')$ columns to cancel out the entries corresponding to closed species. Therefore, the latter $(K - K')$ columns of $\tilde{\mathbf{S}}'$ satisfy $\tilde{S}_\id^\rho = 0$ for all closed species $\id$. Of course, all of the $K'$ columns of $\tilde{\mathbf{S}}'$ are linear independent when we look at all the species. Hereafter, we use a thus constructed reduced stoichiometric matrix $\tilde{\mathbf{S}}'$ and omit the prime symbol to write it simply as $\tilde{\mathbf{S}}$.

To summarize, the constructed reduced stoichiometric matrix $\tilde{\mathbf{S}}$ satisfies

$$ (\tilde{\mathbf{S}}_\id^\rho)^N_{\rho=1} \quad \text{for } \rho = 1, \ldots, K' \text{ are linear independent}, $$

$$ \tilde{\mathbf{S}}_\id^\rho = 0 \quad (\id = 1, \ldots, N_\id, \rho = K' + 1, \ldots, K). $$

When we consider the interpretation of $\tilde{\mathbf{S}}$ as virtual reactions (37), the first $K'$ virtual reactions independently change the particle numbers of the closed species. The remaining $(K - K')$ virtual reactions only involves open species, and may produce steady flows of reactions even if the particle numbers in the system is constant in time.

The state of the system $(\mathbf{n}_\id, \mathbf{\pi}(\mathbf{n}_\id))$ reachable from a reference state $(\mathbf{n}_\id^{\text{ref}}, \mathbf{\pi}(\mathbf{n}_\id^{\text{ref}}))$ is limited to the states whose $\id$ is in the following set:

$$ \left\{ \mathbf{n}_\id^{\text{ref}} + \sum_{\rho=1}^{K'} \tilde{\mathbf{S}}_\id^\rho \mathbf{\xi}_\rho \mid \mathbf{\xi} \in \mathbb{R}^{K'}, \mathbf{n}_\id \geq 0 \right\}. $$

This set is of $K'$-dimensional.

B. Coordinates and the convex functions

We construct the $\eta$-coordinates $\eta \equiv (\eta_\rho)^{K'}_{\rho=1}$ as the extent of reactions of the virtual reactions. Although the extent of reactions of the actual reactions are well-defined from the kinetics (31), those of the virtual reactions must be newly defined. We define them as follows. Since the columns of reduced stoichiometric matrix $\tilde{\mathbf{S}}$ form a basis of the stoichiometric subspace (27), each of the columns of the original stoichiometric matrix $\mathbf{S}$ is uniquely expressed as a linear combination of the columns of $\tilde{\mathbf{S}}$:

$$ \mathbf{S}_i^\rho = \sum_{\rho=1}^{K} \tilde{\mathbf{S}}_i^\rho \mathbf{c}_\rho^\sigma. $$

Put in the language of virtual reactions, each of the actual reactions is uniquely interpreted as a combination of virtual reactions. Therefore, given the extent of each actual reaction $d\xi_\rho$, we can unambiguously define the extent of virtual reactions $d\eta_\rho$ by

$$ d\eta_\rho = \sum_{\sigma=1}^{M} \mathbf{c}_\rho^\sigma d\xi_\sigma, $$

so that we have

$$ \sum_{\rho=1}^{K} \mathbf{S}_i^\rho d\xi_\rho = \sum_{\rho=1}^{K} \tilde{\mathbf{S}}_i^\rho d\eta_\rho $$

for all $i$ including both closed and open species. The change in the closed species are related to the coordinates by

$$ d\mathbf{n}_\id = \sum_{\rho=1}^{K'} \tilde{\mathbf{S}}_\id^\rho d\eta_\rho, $$

where we used (25) and (53).

We are left with integrating (52) to define $\eta_\rho$. By choosing an arbitrary reference state $(\mathbf{n}_\id^{\text{ref}}, \mathbf{\pi}(\mathbf{n}_\id^{\text{ref}}))$, the first $K'$ coordinates are defined by integrating (54) as

$$ n_{\id}(\eta) = n_{\id}^{\text{ref}} + \sum_{\rho=1}^{K'} \tilde{\mathbf{S}}_\id^\rho \eta_\rho. $$

Since $(\tilde{\mathbf{S}}_\id^\rho)^N_{\rho=1}$ for $\rho = 1, \ldots, K'$ are linear independent (48), $(\eta_\rho)^{K'}_{\rho=1}$ that satisfy (55) for a given $\mathbf{n}_\id$ is unique. Therefore, Eq. (55) unambiguously defines $\eta_\rho$ for $\rho = 1, \ldots, K'$. Inverting this definition, we obtain

$$ \eta_\rho(\mathbf{n}) = \sum_{\id} (\tilde{\mathbf{S}}_\id^{\rho})_{\id} (\mathbf{n}_\id - n_{\id}^{\text{ref}}) \quad (\rho = 1, \ldots, K'), $$

where $((\tilde{\mathbf{S}}_\id^{\rho})_{\id})^{N_\id}_{\id=1}$ is a pseudo-inverse matrix of $(\tilde{\mathbf{S}}_\id^{\rho})^{N_\id}_{\rho=1}$, and the right-hand side of (56) does not depend on the choice of the pseudo inverse. Eqs. (55)–(56) give the one-to-one correspondence between $\mathbf{n}_\id$ in the reachable space (50) and $(\eta_\rho)^{K'}_{\rho=1}$. Therefore, the whole $\eta$-coordinate space is of higher-dimensional and wider than the space of possible $\mathbf{n}_\id$’s (50) if $K' < K$.

On the other hand, the remaining coordinates $(\eta_\rho)^{K'}_{\rho=K'+1}$ are not related the particle numbers. Therefore, the above specification of the reference state cannot determine the
of the remaining coordinates. In fact, the choice of their origins is arbitrary and does not affect the following results. Therefore, we here simply write

$$\eta_\rho(t) = \sum_{\sigma} c_{\rho\sigma} \int_0^t d\tilde{\xi}_{\rho\sigma} \quad (\rho = K' + 1, \ldots, K). \quad (57)$$

by integrating (52). For example, we can specify \(\eta_\rho = 0\) at time \(t = 0\) for \(\rho = K' + 1, \ldots, K\).

We choose the following \(\varphi\) for the convex function:

$$\varphi(\eta) = \sum_{i_d} \mu^{i_d}(n(\eta))n_{i_d}(\eta) + \sum_{i_p} \sum_{\beta=1}^K \mu^{i_p}_{\text{pre}} \tilde{S}_{i_p \beta} \rho_\beta \eta_\rho. \quad (58)$$

This quantity will turn out to be \((-T)\) times the cumulative entropy production, as verified shortly. This choice of \(\varphi\) for open reaction systems is regarded as a natural generalization of the choice for closed systems in (39b), because the \(\varphi\) for closed systems, i.e., the Gibbs free energy, is also \((-T)\) times the cumulative entropy production in closed systems (see (28)).

The defined function \(\varphi(\eta)\) is convex, but not necessarily strictly convex, since \(\eta_\rho\), for \(\rho = K' + 1, \ldots, K\) are linearly related to \(\varphi(\eta)\). Therefore, strictly speaking, this choice of \(\varphi\) is outside of the scope of dually flat geometry. Nevertheless, we can formally follow the definitions (1)–(2) to construct \(\theta\) and \(\psi\):

$$\theta'(n) = \sum_i \tilde{S}_i \rho \mu_i(n), \quad (59)$$

$$\psi(\theta) = -\sum_{i_d} \mu^{i_d}(n(\theta))n_{i_d}^{\text{ref}}. \quad (60)$$

Eqs. (56)–(60) constitute the quadruplet of dually flat geometry for open reaction systems. The resulting \(\theta\)-coordinates represents the negative of the affinities of the virtual reactions, as in the closed cases. Since the strict convexity of \(\varphi\) does not hold, the one-to-one correspondence between \(\eta\) and \(\theta\) is violated. From (59) and (49), we easily see that each \(\theta_\rho\) for \(\rho = K' + 1, \ldots, K\) takes only a single value, \(\sum_{i_p} \tilde{S}_{i_p \beta} \rho \mu^{i_p}_{\text{pre}}\), despite that each \(\eta_\rho\) for these \(\rho\)'s takes an arbitrary real value.

Since the \(\eta\)-coordinates are the extent of the virtual reactions and \(\theta\)-coordinates are the negative of the affinities of them, we obtain the following expression of the entropy production

$$T \frac{d\Sigma}{dt} = -\sum_\rho \theta_\rho \rho d\eta_\rho = -\frac{d\varphi}{dt} \geq 0, \quad (61)$$

as in the closed cases (45). The second equality is from the construction (1). Therefore, the function \(\varphi\) is \((-T)\) times the cumulative entropy production. A formal calculation of the first equality in (61) is as follows:

$$T d\Sigma = \sum_\rho F^\rho d\xi_\rho$$

$$= -\sum_\rho \mu^\rho \rho d\xi_\rho$$

$$= -\sum_\rho \mu^\rho \rho d\eta_\rho = -\sum_\rho \theta d\eta_\rho,$$

where we used the expression of entropy production (30), the definition of affinity (29), the relation (53), and the explicit expression of the \(\theta\)-coordinates (59) in order.

C. Bregman divergence and differential geometry

Although the convex function \(\varphi\) violates the strict convexity, we can formally calculate the Bregman divergence and the line element using their definitions (5)–(7) and (10). The resulting Bregman divergence is

$$D(n||n') = \sum_{i_d} (\mu^{i_d}(n) - \mu^{i_d}(n'))n_{i_d} \quad (63)$$

This is of a quite similar form to the closed case (42). This divergence is determined solely by the particle numbers \(n_{i_d}\) of the two states. Since \(n_{i_d}\) is completely determined by \((\eta_\rho)^{K'}\), the divergence only involves \((\eta_\rho)^K\) and does not depend on \((\eta_\rho)^{K+1}\). The divergence is zero if the two points differ only by their \(\eta\)'s with \(\rho = K' + 1, \ldots, K\).

The line element for open reaction systems is also similar to that in the closed systems (46), given by

$$d\Sigma^2 = \sum_{\rho=1}^{K'} \rho d\theta d\eta_\rho = \sum_{i_d} \rho d\mu^{i_d} d\eta_\rho. \quad (64)$$

Therefore, the virtual reactions involving no closed species amounts to zero in the length. In other words, the length associated with a change in \(\eta_\rho\)'s for \(\rho = K' + 1, \ldots, K\) is zero.

D. Affine transformation and steady-state thermodynamics

Here we present an application of the affine transformation (17)–(18) for dually flat geometry in open chemical reaction systems. Consider a system that admits a steady state \(n^d\), i.e., the state satisfying \(dn_i/dt = 0\) for all \(i\) with a given kinetics (32). We consider the case where the affinity of at least one reaction is nonzero in the steady state. If there are more than one such steady state, we focus on one of them.

Let us consider an affine transformation of the above constructed quadruplet \((\eta, \varphi(\eta), \theta, \psi(\theta))\) (56)–(60) so that the new \(\theta\)-coordinates vanish at the steady state. For this purpose, we take \(d' = -\sum_i \tilde{S}_i \mu(n^d)\), \(b_\rho = 0\), \(C = \)
\[ \bar{\eta} = \eta, \]
\[ \bar{\varphi}(\bar{\eta}) = \sum_{i_k} \mu^{i_k}(\mathbf{n}(\bar{\eta})) - \mu^{i_k}(\mathbf{n}^{\ast}) n_{i_k}(\bar{\eta}), \]
\[ \bar{\theta}(\mathbf{n}) = \sum_{i_k} \tilde{S}_i^{\ast}\left[\mu^{i_k}(\mathbf{n}) - \mu^{i_k}(\mathbf{n}^{\ast})\right], \]
\[ \bar{\psi}(\bar{\theta}) = -\sum_{i_k} \left[\mu^{i_k}(\bar{\mathbf{n}}(\bar{\theta})) - \mu^{i_k}(\mathbf{n}^{\ast})\right] n_{i_k}^{\ast}, \]
\[ \bar{\theta} = \bar{\theta} \quad \text{for } \rho = K' + 1, \ldots, K \]
\[ \bar{\psi} = \bar{\psi} \quad \text{for } \rho = K' + 1, \ldots, K \]

where \( \eta \) (65a) is given by (56)–(57). The \( \theta \)-coordinate \( \bar{\theta} \) is the affinely of the \( \rho \)-th virtual reaction relative to that value at the steady state, and vanishes at the steady state as expected. In particular, using (49) and \( \mu^{i_k} = \mu^{i_k}_{\text{pre}} \), we find that \( \bar{\theta} \) for \( \rho = K' + 1, \ldots, K \) are always zero. We remark that, although the above choice of \( \bar{\theta} \) in the affine transformation is essential for \( \tilde{\varphi}(\mathbf{n}^{\ast}) = 0 \), the choice of \( C \) is not. We choose the above \( C \) just for a simpler form of the transformed quadruplet. Different choices, such as \( C = 0 \), only cause additive constants in \( \bar{\varphi} \) and \( \bar{\psi} \), which does not affect the main points of the followings.

The new function \( \bar{\varphi}(\bar{\eta}) \) does not depend on \( \bar{\eta}_{\bar{\rho}}^{K'} \) as in (55) with \( \bar{\eta} = \eta \). Similarly, the new function \( \bar{\psi}(\bar{\theta}) \) does not depend on \( \bar{\theta}_{\bar{\rho}}^{K'} \), because \( \bar{\theta} \) for \( \rho = K' + 1, \ldots, K \) are identically zero and cannot affect the value of \( \bar{\psi} \). Therefore, by limiting the range of \( \rho \) to be \( 1, \ldots, K' \), we can reinterpret (65a)–(65d) as the quadruplet \( (\bar{\eta}_{\bar{\rho}}^{K'}, \bar{\varphi}, \bar{\theta}_{\bar{\rho}}^{K'}, \bar{\psi}) \). Since \( \bar{\eta}_{\bar{\rho}}^{K'} \) has the one-to-one correspondence with \( a_3 \) in the space (50) as discussed in (55)–(56), this limited quadruplet induces a dually flat geometry on the space (50).

The new function \( \bar{\varphi} \) is rewritten as
\[ \bar{\varphi}(\bar{\eta}(\mathbf{n})) = G(\mathbf{n}) = \sum_i \mu^{i}(\mathbf{n}) n_i =: \mathcal{G}(\mathbf{n}). \]

This function is called the transformed Gibbs free energy, introduced by Yoshimura and S. I. [10] for ideal dilute solutions. While they introduced it ad hoc, we reproduce it via the affine transformation that sets the origin of the \( \theta \)-coordinates to the steady state, providing an underlying structure and motivation of the transformed Gibbs free energy.

Since affine transformations do not change the induced geometric structures, we still obtain the Bregman divergence in (63) and the line element in (64) from the affine-transformed quadruplet. In particular, using the definition of the Bregman divergence in (6) and \( \bar{\theta}(\mathbf{n}^{\ast}) = 0 \), we obtain
\[ \mathcal{D}(\mathbf{n}||\mathbf{n}^{\ast}) = \bar{\varphi}(\mathbf{n}) - \bar{\varphi}(\mathbf{n}^{\ast}) = \mathcal{G}(\mathbf{n}) - \mathcal{G}(\mathbf{n}^{\ast}), \]
which reproduces the relation obtained for ideal dilute solutions in Ref. [10] and generalizes it for non-ideal cases. This expression is similar to the expression of the Hatano–Sasa excess entropy production [47] or a boundary part of the nonadiabatic entropy [48] in stochastic thermodynamics, and therefore implies that the transformed Gibbs free energy is its chemical-thermodynamic counterpart.

VI. CONCLUSION

In this paper, we construct dually flat geometry for chemical thermodynamics, which is applicable for open, non-ideal systems. Since dually flat geometry captures mathematical structures of stochastic thermodynamics, our results would enable us to import those stochastic-thermodynamic structures into the study of chemical thermodynamics. Such applications would highlight the similarities and differences in the structures of stochastic and chemical thermodynamics, and provide new insights into chemical thermodynamics.

Note added: Recently, the preprint about a Hessian geometric structure of chemical thermodynamic systems [49] has been submitted on arXiv. Our study had been independently conducted, and an oral presentation of our result had been previously done in the Physical Society of Japan 2021 Autumn Meeting [50].

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