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Steepest-entropy-ascent model of mesoscopic quantum systems far from equilibrium along with generalized thermodynamic definitions of measurement and reservoir

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This paper presents a nonequilibrium, first-principles, thermodynamic-ensemble based model for the relaxation process of interacting non-equilibrium systems. This model is formulated using steepest-entropy-ascent quantum thermodynamics (SEAQT) and its equation of motion for a grand canonical ensemble and is applied to a many particle system of classical or indistinguishable particles. Two kinds of interactions are discussed, including pure heat diffusion and heat and mass diffusion together. Since no local equilibrium assumption is made, the conjugate fluxes and forces are intrinsic to the subspaces of the state space of one system and/or of the state space of two interacting systems. They are derived via the concepts of hypoequilibrium state and nonequilibrium intensive properties, which describe the nonmutual equilibrium status between subspaces of the thermodynamic state space of a single system and/or of the state space of two interacting systems. The Onsager relations are shown to be thermodynamic kinematic features of the system and are found without knowledge of the detailed mechanics of the dynamic process. A fundamental thermodynamic explanation for the measurement of each intensive property of a system in a nonequilibrium state is given. The fundamental thermodynamic definition of reservoir is also discussed. In addition, the equation of motion for a system undergoing multiple interactions is provided, which permits the modeling of a network of local systems in nonequilibrium at any spatial and temporal scale. Finally, the physical features of a nonequilibrium measurement is illustrated via a case study, and the general validity of the equal probability condition is discussed.

I. INTRODUCTION

The study of nonequilibrium relaxation processes - including chemical kinetics, mass diffusion, and heat diffusion - is typically accomplished using approaches based on microscopic mechanics [1–4] or thermodynamics [5–9]. In particular, thermodynamic approaches are able to generally capture the features of the relaxation process via, for example, the Onsager relations and as a result are more computationally efficient than microscopic approaches but as a consequence also lack much of the detail that microscopic approaches provide. However, most of these thermodynamic approaches have limited or no applicability in the far-from-equilibrium realm, since, for example, the local or near-equilibrium assumption is needed or only analytical or exact solutions at steady state are available or a limited number of non-general solutions are available in the non-linear transient regime. In addition, the governing equations are either phenomenological (e.g., [5, 6, 9]) or stochastic (e.g., [8]) in nature and, thus, do not have a first-principles basis. To address these issues and generalize the application of thermodynamic principles further into the nonequilibrium realm, the thermodynamic features captured can be regarded as a coarse graining of the microscopic dynamics or as a pattern in ensemble evolution [10–13] to exploit the efficiency advantage of such an approach, provide a more

rigorous microscopic basis, and improve the consistency of the thermodynamic description across scales. This philosophy of model reduction has already been used in studying far-from-equilibrium phenomena such as, for example, chemical kinetics, mass and heat diffusion, and thermal expansion [14–18]. Of course, to achieve a more efficient model reduction, it is of great importance to find a general and simple description of nonequilibrium state corresponding to a thermodynamic pattern of the microscopic description, to fundamentally define the macroscopic properties of any thermodynamic state (i.e., extensive or intensive properties for both equilibrium and nonequilibrium states), and to use a thermodynamic governing equation based on first principles.

Steepest-entropy-ascent quantum thermodynamics (SEAQT), which is a first-principles, thermodynamic-ensemble based approach, addresses all of the issues raised above, providing a governing equation able to describe the nonequilibrium process from an entropy generation viewpoint [12, 19–27]. The macroscopic properties of entropy, energy, and particle number, which are well defined for any state of any system [28], are used to develop the governing equation and describe the time evolution of the state of the system. Recently, the state space required to describe the non-equilibrium time evolution trajectory determined by SEA has been significantly simplified via the concept of hypoequilibrium state [16, 18, 29–35], which captures the global features of the microscopic description for the relaxation process. As noted in [33], similar efforts towards model reduction in this vein have been proposed by Beretta *et al.* [36, 37]. In addition, the concept of nonequilibrium

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intensive properties introduced in [16, 29–31] based on the concept of hypoequilibrium state enables a complete description of the nonequilibrium evolution of state when combined with the set of nonequilibrium extensive properties. Unlike the intensive property definitions of other nonequilibrium thermodynamic approaches (definitions which require the local-equilibrium, near-equilibrium, or steady state assumption or a phenomenological stochastic basis), the definitions in the SEAQT framework are fundamental and available to all nonequilibrium states and are especially suitable for the description of the evolution in state of relaxation processes. Both of these concepts enable the generalization of many equilibrium (or near-equilibrium) thermodynamic relations such as the Gibbs relation, the Clausius inequality, and the Onsager relations into the far-from-equilibrium realm in general and to non-quasi-equilibrium processes in particular.

In this paper, SEAQT is applied to the study of the interaction of systems using the grand canonical ensemble. The system studied can be any distinguishable or indistinguishable set particles with or without long distance intermolecular interactions, and the evolution of state of two systems can be that of a non-quasi-equilibrium process. In Sec. II, the equation of motion and the concepts of hypoequilibrium state and nonequilibrium intensive properties are introduced. In Sec. III, interacting systems with heat diffusion only are studied. The Onsager relations and thermodynamic explanations of a measurement (of a system in equilibrium or nonequilibrium) and a reservoir are given. In Sec. IV, interacting systems with heat and mass diffusion are discussed followed in Sec. V by the study of a system interacting with multiple systems and a discussion of the applicability of the SEAQT framework to a network of nonequilibrium systems. Finally, in Sec. VI, the new features of measurements of state of a nonequilibrium system are contrasted with equilibrium measurements of state via a case study. The general validity of the equal probability principle is also discussed.

II. SEAQT EQUATION OF MOTION

A. General equation of motion

In this section, the system and state description in SEAQT is given, and the equation of motion, is presented. Based on the discussion by Grmela [10, 11, 38] and Beretta [12, 13] the general form of a nonequilibrium framework is a combination of both irreversible relaxation and reversible symplectic dynamics. If written in the generalized form of the Ginzburg-Landau equation [10, 13], the equation of motion takes the following form:

$$\frac{d}{dt}\phi(t) = X_{\phi(t)}^H + Y_{\phi(t)}^H \quad (1)$$

where $\phi(t)$ represents the state evolution trajectory, $X_{\phi(t)}^H$ and $Y_{\phi(t)}^H$ are functions of the system state $\phi(t)$ and represent the reversible symplectic and irreversible relaxation dynamics, respectively. In the SEAQT framework, the system is defined by the Hamiltonian operator \hat{H} , the system state is represented by the density operator $\hat{\rho}$, $X_{\phi(t)}^H$ follows the Schrödinger equation, and $Y_{\phi(t)}^H$ is derived from the SEA principle. To describe the evolutionary process, conservation laws are explicitly required in order to construct the equation of motion, which is given by [26]

$$\frac{d\hat{\rho}}{dt} = \frac{1}{i\hbar}[\hat{\rho}, \hat{H}] + \frac{1}{\tau}\hat{D} \quad (2)$$

where the first term is the Schrödinger term and the second is the dissipation term. If the system is in a pure (zero-entropy) state, $\hat{\rho}\hat{\rho} = \hat{\rho}$, the equation of motion reverts back to the Schrödinger equation of quantum mechanics. If the system is in a so-called mixed (nonzero-entropy) state and $\hat{\rho}$ is diagonal in the energy eigenstate basis, \hat{H} commutes with $\hat{\rho}$ and the Schrödinger term goes to zero even though $\hat{\rho}$ may not be a Maxwellian distribution among the energy eigenlevels. The state evolution of such a mixed-state operator cannot be captured by the Schrödinger term and is instead given by the second term to the right of the equals, the dissipation term, which captures the probability redistribution towards the Maxwellian distribution. The dissipation term is constructed using a set of operators called the ‘generators of the motion’. Each generator corresponds to one of the conservation laws to which the system is subjected. For example, a nonreacting isolated system is subject to two conservation laws, probability normalization and energy conservation, so that the generators of the motion are $\{\hat{I}, \hat{H}\}$.

In the study of two interacting systems, the **state space of the system** is given by

$$\mathcal{H} = \mathcal{H}_a \otimes \mathcal{H}_b \quad (3)$$

where $\mathcal{H}_{a(b)}$ are the Hilbert spaces of two systems $a(b)$ (for a general system with a variable number of indistinguishable particle, $\mathcal{H}_{a(b)}$ is a Fock space) and the initial state of the density operator is chosen to be

$$\hat{\rho} = \hat{\rho}_a \otimes \hat{\rho}_b \quad (4)$$

where no correlation term is included. Then minus an interparticle interaction term, the Hamiltonian operator of the system is given by

$$\hat{H} = \hat{H}_a \otimes \hat{I}_b + \hat{I}_a \otimes \hat{H}_b \quad (5)$$

If we assume both system a and system b to consist of a dilute-Boltzmann gas that gives the diagonal density operators $\hat{\rho}_a$ and $\hat{\rho}_b$, the equation of motion reduces to

$$\frac{dp_i^{a(b)}}{dt} = \frac{1}{\tau}D_i^{a(b)}(\mathbf{p}) \quad (6)$$

where $p_i^a(b)$ is the i th diagonal term of $\hat{\rho}^{a(b)}$ in the energy eigenstates basis and represents the probability of the system $a(b)$ being in the eigenstate associated with the i th energy eigenlevel. \mathbf{p} then represents the distributions $\{p_i^a, i = 1, \dots\}$ and $\{p_j^b, j = 1, \dots\}$ for system a and b , and τ is the relaxation time. Clearly, in this case, the diagonal density operators commute with \hat{H} so that the Schrödinger term vanishes.

B. Nonequilibrium state and state evolution description: Hypoequilibrium

The thermodynamic features of the nonequilibrium relaxation process generated by the SEAQT framework have a number of useful characteristics, which lead to a complete description of each state and a fundamental definition of nonequilibrium intensive properties. This description is based on the key concept of hypoequilibrium state, which along with that of nonequilibrium intensive properties, is briefly discussed below.

For a given system, such as system a , represented by an energy eigenlevel set $\Omega^a = \{(n_i^a, \epsilon_i^a, N_i^a)\}$, where each energy eigenlevel is represented by a triplet of energy (ϵ_i^a) and particle number (N_i^a) eigenvalues and by its degeneracy (n_i^a), the system can be divided into M_a subsystems $\Omega_K^a = \{(n_i^{a,K}, \epsilon_i^{a,K}, N_i^{a,K})\}$, $K = 1, \dots, M_a$, so that the state space of system a (Hilbert space) \mathcal{H}^a can be represented by the **direct sum** of M_a subspaces \mathcal{H}_K^a with $K = 1, 2, \dots, M_a$ [39].

$$\mathcal{H}^a = \bigoplus_{K=1}^{M_a} \mathcal{H}_K^a \quad (7)$$

To be complete, M_a can be infinite. Any state of system a can then be represented by the energy eigenlevel distributions of M_a subspaces given by $\{p_i^{a,K}, K = 1, \dots, M_a\}$.

If the probability distribution in each subsystem yields to a grand canonical distribution, the system is designated as being in an M_a th-order hypoequilibrium state. **Such a state is consistent with original work done by Beretta using a state representation that falls within the exponential family [40].** Based on this definition, it can be shown that any state of the system a is a hypoequilibrium state with order M_a , where M_a is less than or equal to the number of system eigenlevels [16, 29]. A hypoequilibrium state of order 1 corresponds to a state in stable equilibrium. The probability distribution of the K th subspace of the M_a th-order hypoequilibrium state takes the form

$$p_i^{a,K} = \frac{p^{a,K}}{\Xi^{a,K}(\beta^{a,K}, \gamma^{a,K})} e^{-\beta^{a,K} \epsilon_i^{a,K} - \gamma^{a,K} N_i^{a,K}} \quad (8)$$

where $\beta^{a,K}$ and $\gamma^{a,K}$ are parameters, $p^{a,K}$ is the total probability in subspace K of system a , and $\Xi^{a,K}(\beta^{a,K}, \gamma^{a,K})$ is the grand partition function of the subspace with parameters $\beta^{a,K}$ and $\gamma^{a,K}$. To be complete, $\beta^{a,K} = 0$ and $\gamma^{a,K} = 0$ if $\#(\mathcal{H}_a^K) = 1$, $\gamma^{a,K} = 0$

if $\#(\mathcal{H}_a^K) = 2$ and $\#(\mathcal{H}_a^K)$ can be infinite. The grand partition function is written as

$$\Xi^{a,K}(\beta^{a,K}, \gamma^{a,K}) = \sum_{K=1}^{\#(\mathcal{H}_a^K)} n_i^{a,K} e^{-\beta^{a,K} \epsilon_i^{a,K} - \gamma^{a,K} N_i^{a,K}} \quad (9)$$

Then, defining

$$\alpha^{a,K} = \ln \Xi^{a,K}(\beta^{a,K}, \gamma^{a,K}) - \ln p^{a,K} \quad (10)$$

so that the probability distribution of the K th subspace can be represented using $\{(\alpha^{a,K}, \beta^{a,K}, \gamma^{a,K}), K = 1, \dots, M_a\}$, i.e.,

$$p_i^{a,K} = n_i^{a,K} e^{-\alpha^{a,K}} e^{-\beta^{a,K} \epsilon_i^{a,K}} e^{-\gamma^{a,K} N_i^{a,K}} \quad (11)$$

For a given M_a th-order hypoequilibrium state, the intensive properties of the subspaces can be represented by $\beta^{a,K}$ and $\gamma^{a,K}$ or equivalently using temperature and chemical potential defined by

$$T^{a,K} = \frac{1}{k_b \beta^{a,K}}, \quad \mu^{a,K} = \gamma^{a,K} T^{a,K} \quad (12)$$

A M_a th-order hypoequilibrium state can then be represented by a division $\{\Omega_K = (n_i^{a,K}, \epsilon_i^{a,K}, N_i^{a,K}), K = 1, \dots, M_a\}$ of the system and a corresponding triplet set $\{(\alpha^{a,K}, \beta^{a,K}, \gamma^{a,K}), k = 1, \dots, M_a\}$. The intensive property set $\{(T^{a,K}, \mu^{a,K}), K = 1, \dots, M_a\}$ is a generalization of the definition of intensive property at stable equilibrium (T^{eq}, μ^{eq}), which itself is a first-order hypoequilibrium state. Appendix A proves that for the equation of motions used in this paper, if a system begins in a M_a th-order hypoequilibrium state, it remains in a M_a th-order hypoequilibrium state throughout the state evolution as long as the same subsystem division is maintained. Thus, the time evolution of the distribution is given by

$$p_i^{a,K}(t) = n_i^{a,K} e^{-\alpha^{a,K}(t) - \beta^{a,K}(t) \epsilon_i^{a,K} - \gamma^{a,K}(t) N_i^{a,K}} \quad (13)$$

The intensive property set $\{(T^{a,K}(t), \mu^{a,K}(t)), i = 1, \dots, M\}$ is well defined throughout the entire state evolution. This **time evolution of the state of the system** can also be represented by the evolution of the triplet set $\{(\alpha^{a,K}(t), \beta^{a,K}(t), \gamma^{a,K}(t)), K = 1, \dots, M_a\}$, representing just $3M_a$ variables in total. In the discussions below, the triplet $(\alpha^{a,K}, \beta^{a,K}, \gamma^{a,K})$ are also called intensive properties, since it is their gradients that act as conjugate forces and drive the fluxes as in conventional nonequilibrium thermodynamics [5, 6]. The latter two are proportional to the temperature and chemical potential, while the former depends only on the log of a ratio of probabilities. **In addition, it is shown later that the weighted average of $\beta^{a,K}$ and $\gamma^{a,K}$ give the thermodynamic measurements of the intensive properties of a system in nonequilibrium (i.e., hypoequilibrium) states.**

III. INTERACTING SYSTEMS WITH HEAT DIFFUSION ONLY

In this section, system a and system b form a composite system, and only heat diffusion is allowed between them. Both system a and system b can be in nonequilibrium states and are represented by the probability distributions among the energy eigenlevels of systems a and b , i.e., by $\{p_i^a\}$ and $\{p_i^b\}$.

A. Equation of motion

For the case when only heat diffusion is present, five conservation laws hold: probability and particle number conservation for system a and for system b and total energy conservation of the composite system. Thus, the generators of the motion are $\{\hat{I}_a, \hat{I}_b, \hat{N}_a, \hat{N}_b, \hat{H}\}$ constrained by

$$I^a = \sum_i p_i^a = 1 \quad (14)$$

$$I^b = \sum_i p_i^b = 1 \quad (15)$$

$$N^a = \sum_i N_i^a p_i^a = \text{constant} \quad (16)$$

$$N^b = \sum_i N_i^b p_i^b = \text{constant} \quad (17)$$

$$E = \sum_i \epsilon_i^a p_i^a + \sum_i \epsilon_i^b p_i^b = \text{constant} \quad (18)$$

Based on the derivation in Appendix B, the equation of motion for system a takes the form

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} \begin{vmatrix} -p_j^a \ln \frac{p_j^a}{n_j^a} & p_j^a & N_j^a p_j^a & 0 & 0 & \epsilon_j^a p_j^a \\ \langle s \rangle^a & 1 & \langle N \rangle^a & 0 & 0 & \langle e \rangle^a \\ \langle Ns \rangle^a & \langle N \rangle^a & \langle N^2 \rangle^a & 0 & 0 & \langle eN \rangle^a \\ \langle s \rangle^b & 0 & 0 & 1 & \langle N \rangle^b & \langle e \rangle^b \\ \langle Ns \rangle^b & 0 & 0 & \langle N \rangle^b & \langle N^2 \rangle^b & \langle eN \rangle^b \\ \langle es \rangle & \langle e \rangle^a & \langle eN \rangle^a & \langle e \rangle^b & \langle eN \rangle^b & \langle e^2 \rangle \end{vmatrix} \quad (19)$$

The numerator of the ratio of determinants on the right can be expanded to yield

$$\det = -p_j \ln \frac{p_j^a}{n_j^a} |C_1| - p_j^a |C_2^a| + N_j^a p_j^a |C_3^a| - \epsilon_j^a p_j^a |C_4| \quad (20)$$

where $|C_1|$, $|C_2^a|$, $|C_3^a|$, and $|C_4|$ are the minors of the first line of the denominator of the given determinant. By defining

$$\frac{|C_2^a|}{|C_1|} = \alpha_a^0, \quad \frac{|C_3^a|}{|C_1|} = -\gamma_a^0, \quad \frac{|C_4|}{|C_1|} = \beta^0, \quad (21)$$

the equation of motion transforms to

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} (-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \alpha_a^0 - N_j^a p_j^a \gamma_a^0 - \epsilon_j^a p_j^a \beta^0) \quad (22)$$

Now, defining a row vector of extensive properties

$$\vec{l}_j^a = [1 \quad \epsilon_j^a \quad N_j^a] \quad (23)$$

where the subscript j refers to the j th energy eigenlevel and defining a column vector of intensive properties

$$\vec{\eta}_a^0 = \begin{bmatrix} \alpha_a^0 \\ \beta^0 \\ \gamma_a^0 \end{bmatrix} \quad (24)$$

the equation of motion can be written as

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} (-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \vec{l}_j^a \cdot \vec{\eta}_a^0) \quad (25)$$

At stable equilibrium, each element of $\vec{\eta}_a^0$ turns out to be an intensive property of the composite system.

B. Hypoequilibrium state and nonequilibrium intensive properties

The initial state of system a is assumed to be a M_a th-order hypoequilibrium state, and the probability for the i th energy eigenlevel represented by the triplet $(n_i^{a,K}, \epsilon_i^{a,K}, N_i^{a,K})$, where $i = 1, 2, \dots, K = 1, 2, \dots, M_a$, is given by

$$p_i^{a,K} = n_i^{a,K} e^{-\alpha^{a,K}} e^{-\epsilon_i^{a,K} \beta^{a,K}} e^{-N_i^{a,K} \gamma^{a,K}} \quad (26)$$

Here the triplet $\{(\alpha^{a,K}, \beta^{a,K}, \gamma^{a,K}), K = 1, \dots, M_a\}$ has been used in the representation. This can be rewritten in terms of a row vector of extensive properties and a column vector of intensive properties such that

$$\ln \frac{p_i^{a,K}}{n_i^{a,K}} = -\alpha^{a,K} - \epsilon_i^{a,K} \beta^{a,K} - N_i^{a,K} \gamma^{a,K} = -\vec{l}_j^{a,K} \cdot \vec{\eta}^{a,K} \quad (27)$$

where the superscripts refer to system a and the K th subspace of system a and the subscript refers to the i th energy eigenlevel in the K th subspace. The row and column vectors are defined as

$$\vec{l}_i^{a,K} = [1 \quad \epsilon_i^{a,K} \quad N_i^{a,K}] \quad (28)$$

$$\vec{\eta}^{a,K} = \begin{bmatrix} \alpha^{a,K} \\ \beta^{a,K} \\ \gamma^{a,K} \end{bmatrix} \quad (29)$$

In Appendix A, it is proven that if the initial state is a hypoequilibrium state, the system with the same subsystem division remains in a hypoequilibrium state throughout

the state evolution, which means that the time evolution of the state distribution of system a takes the form

$$\begin{aligned} p_i^{a,K}(t) &= n_i^{a,K} e^{-\alpha^{a,K}(t)} e^{-\epsilon_i^{a,K} \beta^{a,K}(t)} e^{-N_i^{a,K} \gamma^{a,K}(t)} \\ &= n_i^{a,K} e^{-\bar{l}_i^{a,K} \cdot \bar{\eta}^{a,K}(t)} \end{aligned} \quad (30)$$

where the evolution of the intensive properties $\alpha^{a,K}(t)$, $\beta^{a,K}(t)$, $\gamma^{a,K}(t)$ are the solutions to (see Appendix A)

$$\frac{d\bar{\eta}^{a,K}(t)}{dt} = -\frac{1}{\tau} (\bar{\eta}^{a,K}(t) - \bar{\eta}_a^0(t)) \quad (31)$$

and the equation of motion, Eq. (25), is expressed as

$$\frac{dp_i^{a,K}}{dt} = \frac{1}{\tau} p_i^{a,K} \bar{l}_i^{a,K} \cdot (\bar{\eta}^{a,K} - \bar{\eta}_a^0) \quad (32)$$

Thus, if the initial state of system a is a M_a th-order hypoequilibrium state and that of system b is a M_b th-order hypoequilibrium state, only $3(M_a + M_b)$ ODEs must be solved in order to determine the nonequilibrium evolution.

C. Time evolution of subsystem extensive properties and the Onsager relations

The hypoequilibrium concept can provide additional physical insight [29] to the Onsager reciprocity and dispersion-dissipation relations [40] in the SEA framework. Based on the row vector for extensive properties of one energy eigenlevel, the vector of the extensive properties in the K th subsystem of system a can be defined as a row vector as well such that

$$\bar{L}^{a,K} = \sum_i p_i^{a,K} \bar{l}_i^{a,K} = [p^{a,K} \quad E^{a,K} \quad N^{a,K}] \quad (33)$$

where $p^{a,K}$, $E^{a,K}$, and $N^{a,K}$ are the contributions of the K th subsystem to the total extensive properties of system a and are defined by

$$p^{a,K} = \sum_i p_i^{a,K} \quad (34)$$

$$E^{a,K} = \langle e \rangle^{a,K} = \sum_i \epsilon_i^{a,K} p_i^{a,K} \quad (35)$$

$$N^{a,K} = \langle N \rangle^{a,K} = \sum_i N_i^{a,K} p_i^{a,K} \quad (36)$$

The evolutions of these extensive properties and others are governed by

$$\frac{d\bar{L}^{a,K}(t)}{dt} = -\frac{1}{\tau} (\bar{\eta}^{a,K}(t) - \bar{\eta}_a^0(t))^T [C_1]^{a,K} \quad (37)$$

where

$$[C_1]^{a,K} = \begin{bmatrix} p^{a,K} & \langle e \rangle^{a,K} & \langle N \rangle^{a,K} \\ \langle e \rangle^{a,K} & \langle e^2 \rangle^{a,K} & \langle eN \rangle^{a,K} \\ \langle N \rangle^{a,K} & \langle eN \rangle^{a,K} & \langle N^2 \rangle^{a,K} \end{bmatrix} \quad (38)$$

Here $\langle \dots \rangle^{a,K}$ is the contribution of the K th subspace to the total extensive property $\langle \dots \rangle^a$ of system a .

The rate of entropy change of the K th subsystem is then

$$\begin{aligned} \frac{dS^{a,K}}{dt} &= \frac{d\langle s \rangle^{a,K}}{dt} = \sum_i \frac{d}{dt} (-p_i^{a,K} \ln \frac{p_i^{a,K}}{n_i^{a,K}}) \\ &= \sum_j (-\ln \frac{p_j^{a,K}}{n_j^{a,K}} - 1) \frac{dp_j^{a,K}}{dt} = \sum_j (\bar{l}_j^{a,K} \cdot \bar{\eta}^{a,K} - 1) \frac{dp_j^{a,K}}{dt} \\ &= \frac{d\bar{L}^{a,K}}{dt} \cdot \bar{\eta}^{a,K} - \frac{dp^{a,K}}{dt} \end{aligned} \quad (39)$$

and for system a

$$\frac{dS^a}{dt} = \sum_K \frac{dS^{a,K}}{dt} = \sum_K \frac{d\bar{L}^{a,K}}{dt} \cdot \eta^{a,K} \quad (40)$$

where probability conservation for system a has been used. The rate of change of the entropy for the composite system is then

$$\begin{aligned} \frac{dS}{dt} &= \sum_{m=a,b} \frac{dS^m}{dt} = \sum_{m=a,b} \sum_K \frac{d\bar{L}^{m,K}}{dt} \cdot \bar{\eta}^{m,K} \\ &= \sum_{m=a,b} \sum_K \frac{d\bar{L}^{m,K}}{dt} \cdot (\bar{\eta}^{m,K} - \bar{\eta}_m^0) \end{aligned} \quad (41)$$

The last equal sign is written using the conservation of probability and mass for each subsystem and the conservation of energy for the composite system, i.e., in compact form this is written as

$$\sum_K \bar{\eta}_a^0 \frac{d\bar{L}^{a,K}}{dt} + \sum_K \bar{\eta}_b^0 \frac{d\bar{L}^{b,K}}{dt} = 0 \quad (42)$$

where it is noted that $\alpha_{a(b)}^0$ and $\gamma_{a(b)}^0$ are constant for all K subspaces of system $a(b)$ and β^0 is constant for the composite system. Defining conjugate fluxes and conjugate forces for system a , respectively, as

$$\vec{J}^{a,K} = \frac{d\bar{L}^{a,K}}{dt}, \quad \vec{X}^{a,K} = \bar{\eta}^{a,K} - \bar{\eta}_a^0 \quad (43)$$

the evolutions of the extensive properties for system a can be written from Eqs. (37) and (41) as

$$\vec{J}^{a,K} = \vec{X}^{a,K} \cdot [C_1]^{a,K} \quad (44)$$

and similarly for system b . The rate of change of the entropy for the composite system is then expressed in terms of the conjugate fluxes and forces as

$$\frac{dS}{dt} = \sum_{m=a,b} \sum_K \vec{J}^{m,K} \cdot \vec{X}^{m,K} \quad (45)$$

Since $[C_1]^{a,K}$ is positive definite and symmetric, the Onsager relations are acquired. Specifically, due to the conservation laws, probability and particle number fluxes occur within a given system a or b , while the energy fluxes cross from one system to the next. Thus, the Onsager relations hold here for the relaxation process of system a and for the non-quasi-equilibrium process between systems a and b .

D. Linkage between two systems: Measurement and reservoir

The conservation of probability and particle number for system a leads to

$$\frac{dp^a}{dt} = \sum_K \frac{dp^{a,K}}{dt} = 0 \quad (46)$$

$$\frac{d\langle N \rangle^a}{dt} = \sum_K \frac{d\langle N \rangle^{a,K}}{dt} = 0 \quad (47)$$

which using Eqs. (37) and (38) can be written as

$$\begin{aligned} & \sum_K (\alpha^{a,K} - \alpha_a^0) p^{a,K} + \sum_K \langle e \rangle^{a,K} (\beta^{a,K} - \beta^0) \\ & + \sum_K \langle N \rangle^{a,K} (\gamma^{a,K} - \gamma_a^0) = 0 \end{aligned} \quad (48)$$

$$\begin{aligned} & \sum_K (\alpha^{a,K} - \alpha_a^0) \langle N \rangle^{a,K} + \sum_K \langle eN \rangle^{a,K} (\beta^{a,K} - \beta^0) \\ & + \sum_K \langle N^2 \rangle^{a,K} (\gamma^{a,K} - \gamma_a^0) = 0 \end{aligned} \quad (49)$$

α_a^0 and γ_a^0 can then be determined from Eqs. (48) and (49) such that

$$\begin{aligned} \alpha_a^0 &= \sum_K \alpha^{a,K} p^{a,K} + \sum_K \langle e \rangle^{a,K} \beta^{a,K} \\ & + \sum_K \langle N \rangle^{a,K} \gamma^{a,K} - \beta^0 \langle e \rangle^a - \gamma_a^0 \langle N \rangle^a \end{aligned} \quad (50)$$

$$\begin{aligned} A_{NN}^a \gamma_a^0 &= \sum_K \alpha^{a,K} \langle N \rangle^{a,K} + \sum_K \langle eN \rangle^{a,K} \beta^{a,K} \\ & + \sum_K \langle N^2 \rangle^{a,K} \gamma^{a,K} - A_{eN}^a \beta^0 \end{aligned} \quad (51)$$

where $A_{NN}^a = \langle N^2 \rangle^a - \langle N \rangle^a \langle N \rangle^a$ and $A_{eN}^a = \langle eN \rangle^a - \langle e \rangle^a \langle N \rangle^a$. Thus, γ_a^0 and α_a^0 are only a function of β^0 and system a properties. Furthermore, the evolutions of sub-system properties can be calculated via

$$\frac{d\alpha^{a,K}}{dt} = -\frac{1}{\tau} (\alpha^{a,K} - \alpha_a^0) \quad (52)$$

$$\frac{d\gamma^{a,K}}{dt} = -\frac{1}{\tau} (\gamma^{a,K} - \gamma_a^0) \quad (53)$$

$$\frac{d\beta^{a,K}}{dt} = -\frac{1}{\tau} (\beta^{a,K} - \beta^0) \quad (54)$$

where the time evolutions of $\alpha^{a,K}$, $\gamma^{a,K}$ and $\beta^{a,K}$ are as well determined using only properties of system a and β^0 . The influence of system b only occurs via β^0 so that if a different system b were to provide the same β^0 , the time evolution of system a would be the same.

To study the linkage between systems a and b , the explicit form of $\beta^0 = |C_4|/|C_1|$ is given using fluctuations of the extensive properties of energy and particle number,

i.e.,

$$|C_1| = \begin{vmatrix} A_{NN}^a & 0 & A_{eN}^a \\ 0 & A_{NN}^b & A_{eN}^b \\ A_{eN}^a & A_{eN}^b & A_{ee} \end{vmatrix} \quad (55)$$

$$|C_4| = \begin{vmatrix} A_{Ns}^a & A_{NN}^a & 0 \\ A_{Ns}^b & 0 & A_{NN}^b \\ A_{es} & A_{eN}^a & A_{eN}^b \end{vmatrix} \quad (56)$$

where

$$A_{UV}^{a(b)} = \langle UV \rangle^{a(b)} - \langle U \rangle^{a(b)} \langle V \rangle^{a(b)}, \quad A_{UV} = A_{UV}^a + A_{UV}^b \quad (57)$$

and $A_{UV}^{a(b)}$ is the fluctuation of extensive properties U and V in system $a(b)$, while A_{UV} is the sum of the fluctuations of systems a and b .

Now, if system b is much smaller than system a , i.e., if $A_{UV}^a \gg A_{UV}^b$ for any set of extensive properties, $\beta^0 \rightarrow \tilde{\beta}^a$ where

$$\tilde{\beta}^a \equiv \lim_{\frac{A_{UV}^b}{A_{UV}^a} \rightarrow 0} \frac{|C_4|}{|C_1|} = \left| \frac{A_{es}^a}{A_{Ns}^a} \frac{A_{eN}^a}{A_{NN}^a} \right| / \left| \frac{A_{ee}^a}{A_{eN}^a} \frac{A_{eN}^a}{A_{NN}^a} \right| \quad (58)$$

then the stable equilibrium temperature of system b is $\tilde{\beta}^a$ provided the state of system a remains in a nonequilibrium state (for example, if system a relaxes much slower than system b or is controlled by some external interaction). Thus, $\tilde{\beta}^a$ is a temperature measurement of system a and can be used as an expression for the experimental measurement of system a in nonequilibrium. In addition, $\tilde{\beta}^a$ also turns out to be the β^0 in the equation of motion for a single system relaxation, i.e., when system b is not present.

Now, if system b is much larger than system a , i.e., $A_{UV}^a \ll A_{UV}^b$ for any set of extensive properties, $\beta^0 \rightarrow \tilde{\beta}^b = 1/k_b T^b$; and T^b is the temperature measurement of system b . In this case, system b is not necessarily in stable equilibrium but can still act as a heat reservoir at temperature T^b .

IV. INTERACTING SYSTEMS WITH HEAT AND MASS DIFFUSION

For the case when both heat and mass diffusion are present, four conservation laws hold: probability conservation for both system a and system b , and total energy and total particle number conservation for the composite system. Thus, the generators of the motion are $\{\hat{J}_a, \hat{I}_b, \hat{N}, \hat{H}\}$ constrained by

$$I^a = \sum_i p_i^a = 1 \quad (59)$$

$$I^b = \sum_i p_i^b = 1 \quad (60)$$

$$N = \sum_i N_i^a p_i^a + \sum_i N_i^b p_i^b = \text{const} \quad (61)$$

$$E = \sum_i \epsilon_i^a p_i^a + \sum_i \epsilon_i^b p_i^b = \text{const} \quad (62)$$

Similar to the derivation in Appendix B, the equation of motion for this case is

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} \begin{vmatrix} -p_j^a \ln \frac{p_j^a}{n_j^a} & p_j^a & 0 & \epsilon_j^a p_j^a & N_j^a p_j^a \\ \langle s \rangle^a & 1 & 0 & \langle e \rangle^a & \langle N \rangle^a \\ \langle s \rangle^b & 0 & 1 & \langle e \rangle^b & \langle N \rangle^b \\ \langle es \rangle & \langle e \rangle^a & \langle e \rangle^b & \langle e^2 \rangle & \langle eN \rangle \\ \langle Ns \rangle & \langle N \rangle^a & \langle N \rangle^b & \langle eN \rangle & \langle N^2 \rangle \end{vmatrix} \quad (63)$$

The numerator of the ratio of determinants on the right can be expanded to yield

$$\det = -p_j^a \ln \frac{p_j^a}{n_j^a} |C_1| - p_j^a |C_2^a| - \epsilon_j^a p_j^a |C_3| + N_j^a p_j^a |C_4| \quad (64)$$

where $|C_1|$, $|C_2^a|$, $|C_3|$, and $|C_4|$ are the minors of the first line of a given determinant. By defining

$$\frac{|C_2^a|}{|C_1|} = \alpha_a, \quad \frac{|C_3|}{|C_1|} = \beta, \quad \frac{|C_4|}{|C_1|} = -\gamma \quad (65)$$

the equation of motion transforms into

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} (-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \alpha_a - \epsilon_j^a p_j^a \beta - N_j^a p_j^a \gamma) \quad (66)$$

Using the row vector \vec{l}_j^a of Eq. (23) and defining a new column vector $\vec{\eta}_a^0$ of intensive properties, the equation of motion is rewritten as

$$\frac{dp_j^a}{dt} = \frac{1}{\tau} (-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \vec{l}_j^a \cdot \vec{\eta}_a^0) \quad (67)$$

where the column vector is defined as

$$\vec{\eta}_a^0 = \begin{bmatrix} \alpha_a \\ \beta^0 \\ \gamma^0 \end{bmatrix} \quad (68)$$

Thus, the discussion using the concept of hypoequilibrium state given in Secs. III.B and III.C can be repeated here with the only difference being the definition of $\vec{\eta}_a^0$. Furthermore, the discussion in Sec. III.D is simplified here since only probability conservation holds for system a with the consequence that

$$\frac{dp^a}{dt} = \sum_K \frac{dp^{a,K}}{dt} = 0 \quad (69)$$

from which, α_a can be calculated, i.e.,

$$\alpha_a = \sum_K \alpha^{a,K} p^{a,K} + \sum_K \langle e \rangle^{a,K} \beta^{a,K} + \sum_K \langle N \rangle^{a,K} \gamma^{a,K} - \beta^0 \langle e \rangle^a - \gamma^0 \langle N \rangle^a \quad (70)$$

Here, α_a is a function of β^0 , γ^0 , and system a properties. Furthermore, the evolutions of subsystem (i.e., subspace) properties can be determined from

$$\frac{d\alpha^{a,K}}{dt} = -\frac{1}{\tau} (\alpha^{a,K} - \alpha_a) \quad (71)$$

$$\frac{d\gamma^{a,K}}{dt} = -\frac{1}{\tau} (\gamma^{a,K} - \gamma^0) \quad (72)$$

$$\frac{d\beta^{a,K}}{dt} = -\frac{1}{\tau} (\beta^{a,K} - \beta^0) \quad (73)$$

For this case, the time evolution of $\alpha^{a,K}$, $\gamma^{a,K}$ and $\beta^{a,K}$ are as well determined using properties of system a and β^0 and γ^0 only. The influence of system b is via β^0 and γ^0 , which relates to the energy and particle number fluxes between the two systems.

To study the linkage between systems a and b , the explicit form of $\beta^0 = |C_3|/|C_1|$ is given using fluctuations of the extensive properties, i.e.,

$$|C_1| = \begin{vmatrix} A_{ee} & A_{eN} \\ A_{eN} & A_{NN} \end{vmatrix}, \quad |C_3| = \begin{vmatrix} A_{es} & A_{eN} \\ A_{Ns} & A_{NN} \end{vmatrix}, \quad (74)$$

$$|C_4| = \begin{vmatrix} A_{es} & A_{ee} \\ A_{Ns} & A_{eN} \end{vmatrix} \quad (74)$$

The measurements of the intensive properties $\tilde{\beta}^a$ and $\tilde{\gamma}^a$ of system a are given as

$$\tilde{\beta}^a \equiv \lim_{\frac{A_{bUV}^b}{A_{bUV}^a} \rightarrow 0} \frac{|C_3|}{|C_1|} = \begin{vmatrix} A_{es} & A_{eN} \\ A_{Ns} & A_{NN} \end{vmatrix} / \begin{vmatrix} A_{ee} & A_{eN} \\ A_{eN} & A_{NN} \end{vmatrix} \quad (75)$$

$$\tilde{\gamma}^a \equiv \lim_{\frac{A_{bUV}^b}{A_{bUV}^a} \rightarrow 0} \frac{|C_4|}{|C_1|} = \begin{vmatrix} A_{es} & A_{ee} \\ A_{Ns} & A_{eN} \end{vmatrix} / \begin{vmatrix} A_{ee} & A_{eN} \\ A_{eN} & A_{NN} \end{vmatrix} \quad (76)$$

When system b is in stable equilibrium and much larger than system a , system b acts as a heat and mass reservoir.

V. SYSTEM INTERACTING WITH MULTIPLE SYSTEMS

If there are R different kinds of interactions that system a experiences, the equation of motion (25) or (67) changes to

$$\frac{dp_j^a}{dt} = \sum_{r=1}^R \left[\frac{1}{\tau^r} \left(-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \vec{l}_j^a \cdot \vec{\eta}_a^r \right) \right] \quad (77)$$

Defining

$$\frac{1}{\tilde{\tau}} = \sum_{r=1}^R \frac{1}{\tau^r}, \quad \frac{\tilde{\eta}_a^0}{\tilde{\tau}} = \sum_{r=1}^R \frac{\vec{\eta}_a^r}{\tau^r} \quad (78)$$

where the first equation is *Matthiessen's rule*, the equation of motion is rewritten as

$$\frac{dp_j^a}{dt} = \frac{1}{\tilde{\tau}} (-p_j^a \ln \frac{p_j^a}{n_j^a} - p_j^a \vec{l}_j^a \cdot \vec{\eta}_a^0) \quad (79)$$

which recovers the form of Eq. (25). Thus, the discussion in Secs. III.B and III.C and in Appendix A still hold, and the evolution of hypoequilibrium state and the definition of nonequilibrium intensive properties can be applied to the study of a network of nonequilibrium systems with non-quasi-equilibrium interactions.

VI. MODEL: INDISTINGUISHABLE PARTICLE SYSTEM

This section presents a case study of the application of the SEAQT framework based on a grand canonical ensemble and illustrates the special feature of measurements of state on a system in nonequilibrium. As shown in Sec. III.D, the state measurement of a nonequilibrium system (**system a**) is given by a small equilibrium system (**system b**) attached to it. When there is no flux between the two systems, the intensive properties of the small equilibrium system provide the nonequilibrium measurements of properties of the large system. Temperature or chemical potential differences between the small system and the subsystems of the large system are always present. However, a unique equilibrium state of the small system can be found that allows the conjugate forces from different intensive property gradients to balance. Thus, in contrast to the state measurement of an equilibrium system, the state measurement of a nonequilibrium system is determined by the coupling of conjugate forces.

A. System definition

An indistinguishable particle system [32] is studied below using an occupation number representation. The state space of the system is a Fock space, which is the sum of N -particle state spaces [41]. The N -particle basis state is $|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \dots\rangle$, $\sum_k n_{\nu_k} = N$. The space spanned by the occupation number basis, which is also that of the energy eigenlevels of the Hamiltonian, is the Fock space $\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{F}_N$, where $\mathcal{F}_N = \text{span}\{|n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \dots\rangle | \sum_k n_{\nu_k} = N\}$. The occupation number n_{ν_k} is the particle number distributed in single-particle energy eigenlevels ν_k . In order to determine the system properties, the grand partition function is used, which is defined as

$$\Xi(\beta, \gamma) = \sum_N e^{-\gamma N} \sum_{S_N} e^{-\beta E_{S_N}} \quad (80)$$

The sum over S_N is a summation over N -particle energy eigenlevels.

The partition function Ξ is now determined for a three-dimensional, infinite-potential-well model in the continuous limit. Its natural logarithm takes the form [32]

$$\ln \Xi(\beta, \gamma) = \mp \frac{V}{\lambda_T^3} (2s + 1) Li_{5/2}(\mp e^{-\gamma}) \quad (81)$$

where fermions take the minus sign and bosons the plus. s is the spin of a particle, V is the volume, $Li_s(z)$ is the polylogarithm function, and λ_T , a function of β , is the de Broglie wavelength of the thermal energy defined by

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_b T}} = \frac{h}{\sqrt{2\pi m / \beta}} \quad (82)$$

In the present example, a continuous-limit form is intentionally used even for microscale systems so that the focus is on the thermodynamic features of the evolution without the quantum effect present. To include the quantum effect, a partition function based on discrete energy eigenlevels would be needed to generate the result in which case the discussion on the thermodynamic features given below would still nonetheless be valid.

B. Initial nonequilibrium state

The study here uses fermions as an example. A second-order hypoequilibrium state is defined as the initial state of **system a**. The system eigenstates $\phi_i = |n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, \dots\rangle$ are randomly separated into two subsystems (1 and 2) with equal probability, namely, $\Omega_1 = \{\phi_i^1, i = 1, \dots\}$ and $\Omega_2 = \{\phi_i^2, i = 1, \dots\}$. The energy and particle number of each eigenstate $\phi_i^{1(2)}$ in subsystem 1 (or 2) are represented by $\epsilon_i^{1(2)}$ and $N_i^{1(2)}$, respectively. The partition functions are then defined as

$$\Xi^1 = \sum_{\Omega_1} e^{-\beta \epsilon_i^1 - \gamma N_i^1} \simeq \Xi^2 = \sum_{\Omega_2} e^{-\beta \epsilon_i^2 - \gamma N_i^2} \simeq \frac{1}{2} \Xi \quad (83)$$

where $\Xi = \Xi(\beta, \gamma)$ is the system partition function given by Eq. (81). A second-order hypoequilibrium initial state is chosen using a generalized Maxwellian distribution

$$p_i^1 \propto e^{-\beta^1 \epsilon_i^1 - \gamma^1 N_i^1}, \quad p_i^2 \propto e^{-\beta^2 \epsilon_i^2 - \gamma^2 N_i^2} \quad (84)$$

which results in a second-order hypoequilibrium initial state in the form of Eq. (8). The superscript a , which stands for the nonequilibrium system to be measured, has been omitted for convenience. Thus,

$$p_i^1 = \frac{e^{-\beta^1 \epsilon_i^1 - \gamma^1 N_i^1}}{\Xi^1(\beta^1, \gamma^1) + \Xi^2(\beta^2, \gamma^2)}, \quad p_i^2 = \frac{e^{-\beta^2 \epsilon_i^2 - \gamma^2 N_i^2}}{\Xi^1 + \Xi^2} \quad (85)$$

A generalized equal-probability condition for the nonequilibrium initial states is then assumed so that

$$\frac{p^1}{p^2} = \frac{\Xi^1(\beta^1, \gamma^1)}{\Xi^2(\beta^2, \gamma^2)} \quad (86)$$

This condition leads to the same intensive property “ α ” of two systems and no net probability driving force. Equation (86) reduces to the equal-probability condition of the microstates of the grand canonical ensemble in statistical mechanics at stable equilibrium, i.e.,

$$\frac{p^1}{p^2} = \frac{\Xi^1(\beta^{eq}, \gamma^{eq})}{\Xi^2(\beta^{eq}, \gamma^{eq})} = \frac{1}{2} \Xi : \frac{1}{2} \Xi \quad (87)$$

The generalized equal-probability condition is relaxed later to illustrate that the probability driving force is extremely strong (Fig. 3) and would, thus, be hard to maintain so that the generalized equal-probability condition is very likely to hold in a wide range of nonequilibrium systems.

For a macroscopic volume, Eqs. (81) and (86) indicate that p^1/p^2 increases dramatically since $\ln \Xi \propto V$ so that one of the subsystems (or subspaces) has a very small probability during the evolution. For such a case, both the equilibrium temperature and chemical potential are determined by the other subsystem only, for example, subsystem 1. The β, γ of subsystem 2 then decay exponentially towards those of subsystem 1 according to the intensive property evolutions (Eqs. (52)-(54) or (71)-(71)) in which case subsystem 1 acts as a reservoir. Thus, from a practical standpoint, the grand canonical ensemble formulation of the SEAQT framework is primarily suited to the study of microscopic systems. For macroscopic systems, use of the canonical ensemble [16, 29] or single particle ensemble is more suitable [35]. Furthermore, a nonequilibrium macroscopic system is less likely to violate Eq. (86) (i.e., the equal-probability principle), since an extremely large driving force would be required to produce such a nonequilibrium state. For these reasons, a volume $\sim \lambda_T$ is used for system a in the case study presented here to illustrate the details of nonequilibrium evolution as well as the impact of a violation of Eq. (86). Such a selection ensures that the driving forces from α, β, γ are comparable and the intermediate p^1/p^2 ratio is never too large during the relaxation process.

The initial temperatures and e^γ s of subsystems (or subspaces) 1 and 2 are chosen to be (500 K, 5) and (300 K, 10^3), respectively. With these values for γ^1 and γ^2 , subsystem 1 has a considerable indistinguishability effect, while subsystem 2 is almost a classical ideal gas. The two subsystems have different specific property values initially, and the equilibrium temperature is not just simply a mass averaged value.

C. Results: Measurements

Fig. 1 shows the evolutions of the nonequilibrium temperatures and Fermi levels (or proportionally the chemical potentials) of two subsystems and the nonequilibrium measurements of temperature and Fermi level of the whole system. Fig. 2 shows the entropy evolution for the system as a whole. The coupling of temperature and Fermi level (chemical potential) evolutions has a strong influence on the thermodynamic measurements of a nonequilibrium system. During a nonequilibrium relaxation, the conjugate flux of energy and mass are determined by the the coupled temperature and chemical potential driving forces. It is possible that the temperature measurement (black curve in Fig. 1a) is higher than both of the individual subsystem temperatures of system a, since the chemical potential conjugate force

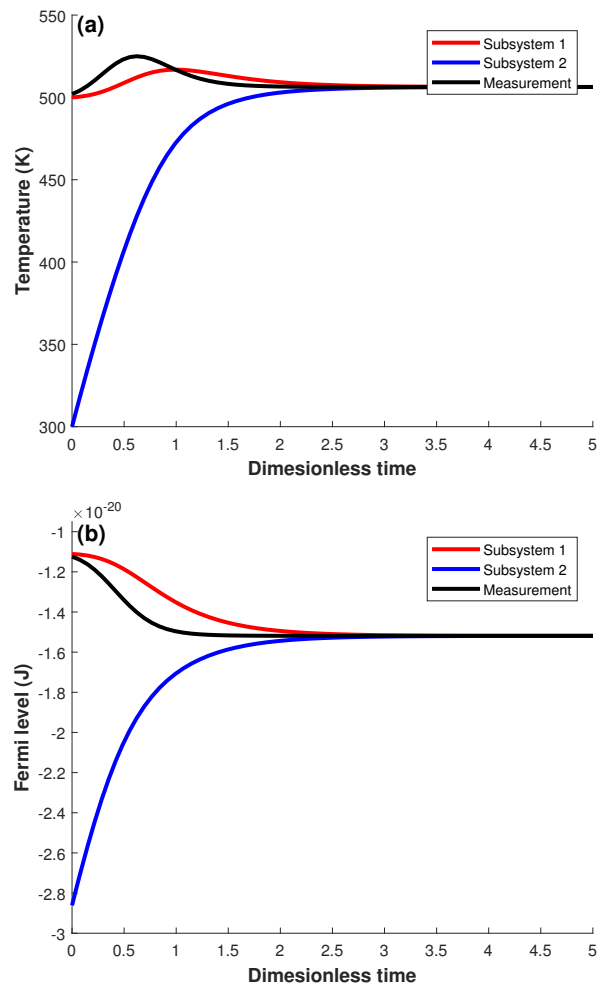


FIG. 1. The nonequilibrium (a:top figure) temperature and (b:bottom figure) Fermi level evolutions of two subsystems (red and blue curves) are compared with the nonequilibrium measurement of temperature and Fermi level of the whole system (black curve). The coupling of energy and mass flows has a strong influence on the thermodynamic measurement of the temperature and chemical potential (and Fermi level) of a nonequilibrium system.

can also drive the energy flow. This result shows that the small equilibrium system b (i.e., the measurement system) needs an even higher temperature than any of the subsystem temperatures in order to balance the additional driving forces from the chemical potential when a nonequilibrium measurement is made.

In Fig. 3, the impact of another intensive property α , which is the Lagrange multiplier of the probability conservation, is studied to show the effect resulting from a violation of the equal-probability condition [Eq. (86)]. The α and probability evolutions of two different initial conditions are compared. The solid line (initial condition 1) takes the same initial condition as Fig. 1 and satisfied Eq. (86). For the dashed line (initial condition 2), the initial temperature and chemical potential

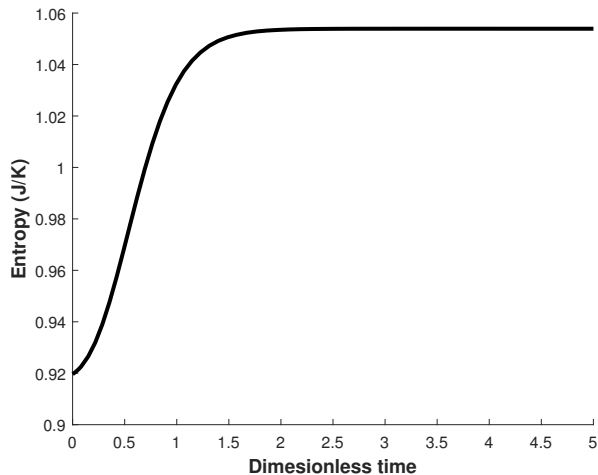


FIG. 2. The evolution of entropy of the nonequilibrium system.

are the same as for the solid line, but the initial p^1 is reduced by 5% so that the equal probability condition no longer holds. In the evolution of α for subsystems 1 and 2 (Fig. 3a), mutual equilibrium of α is maintained throughout the evolution for the solid red and blue curves (the red lies underneath the blue). However, the α measurement is different from the two subsystem α 's due to the coupling of all three conjugate forces. For the case of the dashed curves, the small deviation of 5% from the initial probability of the solid curve results in a very large α difference for the two subsystems and, as a consequence, a probability driving force. In Fig. 3b, the two subsystems increase their probability difference for the case of initial condition 2 (dashed curves), approaching the solid lines (case of initial condition 1) in the initial phase of the relaxation in order to recapture the equal probability condition. This implies that at the beginning of the relaxation, the α conjugate force is stronger than the energy and chemical potential conjugate forces that cause the two subsystem probabilities to merge. Moreover, when a macroscopic system is studied, the α driving force is significantly even stronger and dominates the initial phase of the relaxation. Thus, the general equal-probability condition (Eq. (86)) is very likely to hold in most nonequilibrium systems except microscopic ones, since a very large thermodynamic driving force is needed to prevent a nonequilibrium state from violating Eq. (86).

VII. CONCLUSIONS

This paper provides a thermodynamic investigation of interacting systems undergoing heat and/or mass interactions. In order to apply the SEAQT framework to all kinds of systems, the grand canonical ensemble and the grand partition function are used. The evolutions of intensive and extensive properties as well as the On-

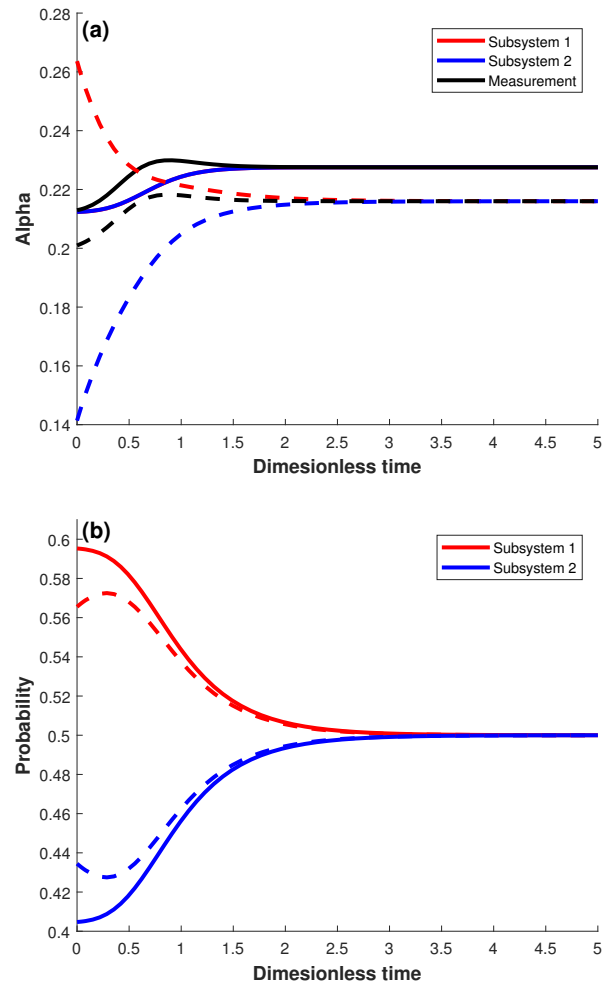


FIG. 3. (a:top figure) α and (b:bottom figure) probability evolutions of systems starting from two different initial conditions. Initial condition 1 (solid line) satisfies the equal-probability condition whereas initial condition 2 (dashed line) does not. Note that in (a), the subsystem 1 evolution is identical to that of subsystem 2 and, thus, the red curve is not seen in the figure since it lies below the blue curve.

sager relations of the relaxation process of non-quasi-equilibrium processes in general are discussed. Both temperature and chemical potential measurements to a system in nonequilibrium are explained from a thermodynamic viewpoint, independent of the microscopic interactions taking place in the measurement. The investigation presented here provides a first-principles explanation for the experimental phenomenological measurement. In addition, both heat and mass reservoirs are defined thermodynamically. A system interacting with multiple systems is discussed showing how the SEAQT framework and the concepts of hypoequilibrium state and nonequilibrium intensive properties can be applied to studying a network of nonequilibrium systems, which in turn permits the study of a macro/mesoscopic system with discrete local systems in nonequilibrium. Finally, results show that the temperature measurement to a nonequilibrium system may

result in a temperature value higher than those of the nonequilibrium temperatures of the subsystems (approximately, the temperature defined phenomenologically by the molecular kinetic energy in the Boltzmann Equation) due to the chemical potential driving force. A strong probability driving force appears when the system is in a nonequilibrium state that departs from the generalized equal-probability condition.

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Appendix A: Hypoequilibrium state evolution

The equation of motion of every energy eigenlevel in the K th subspace of system a takes the form

$$\frac{dp_j^{a,K}}{dt} = \frac{1}{\tau} (-p_j^{a,K} \ln \frac{p_j^{a,K}}{n_j^{a,K}} - p_j^{a,K} \alpha - \epsilon_j^{a,K} p_j^{a,K} \beta - N_j^{a,K} p_j^{a,K} \gamma) \quad (\text{A1})$$

Defining

$$\vec{l}_j^{a,K} = \begin{bmatrix} 1 & \epsilon_j^{a,K} & N_j^{a,K} \end{bmatrix}, \quad \vec{\eta}^{a,K} = \begin{bmatrix} \alpha^{a,K} \\ \beta^{a,K} \\ \gamma^{a,K} \end{bmatrix}, \quad \vec{\eta}_a^0 = \begin{bmatrix} \alpha_a \\ \beta^0 \\ \gamma^0 \end{bmatrix} \quad (\text{A2})$$

the equation of motion is written as

$$\frac{dp_j^{a,K}}{dt} = \frac{1}{\tau} (-p_j^{a,K} \ln \frac{p_j^{a,K}}{n_j^{a,K}} - p_j^{a,K} \vec{l}_j^{a,K} \cdot \vec{\eta}_a^0) \quad (\text{A3})$$

For the K th subspace of system a , the probability distribution, grand partition function, and $\alpha^{a,K}$ are given by

$$p_j^{a,K} = n_j^{a,K} e^{-\alpha^{a,K}} e^{-\epsilon_j^{a,K} \beta^{a,K}} e^{-N_j^{a,K} \gamma^{a,K}} \quad (\text{A4})$$

$$\Xi^{a,K}(\beta^{a,K}, \gamma^{a,K}) = \sum_{i=1}^{\#(\mathcal{H}_a^K)} n_i^{a,K} e^{-\beta^{a,K} \epsilon_i^{a,K} - \gamma^{a,K} N_i^{a,K}} \quad (\text{A5})$$

$$\alpha^{a,K} = \ln \Xi^{a,K}(\beta^{a,K}, \gamma^{a,K}) - \ln p^{a,K} \quad (\text{A6})$$

The equation of motion then simplifies to

$$\frac{dp_j^{a,K}}{dt} = \frac{p_j^{a,K}}{\tau} \vec{l}_j^{a,K} \cdot (\vec{\eta}^{a,K} - \vec{\eta}_a^0) \quad (\text{A7})$$

Using the relation

$$\begin{aligned} \ln \frac{p_j^{a,K}}{n_j^{a,K}} &= -\eta^{a,K} - \epsilon_j^{a,K} \beta^{a,K} - N_j^{a,K} \gamma^{a,K} \\ &= -\vec{l}_j^{a,K} \cdot \vec{\eta}^{a,K} \end{aligned} \quad (\text{A8})$$

and the fact that the degeneracy $n_j^{a,K}$ is a constant, the equation of motion can also be written as

$$-\frac{d}{dt} (\vec{l}_j^{a,K} \cdot \vec{\eta}^{a,K}) = \frac{1}{\tau} (\vec{l}_j^{a,K} \cdot \vec{\eta}^{a,K} - \vec{l}_j^{a,K} \cdot \vec{\eta}_a^0) \quad (\text{A9})$$

$$\vec{l}_j^{a,K} \cdot \left(\frac{d\vec{\eta}^{a,K}}{dt} + \frac{1}{\tau} \vec{\eta}^{a,K} - \frac{1}{\tau} \vec{\eta}_a^0 \right) = 0 \quad (\text{A10})$$

For any equation of motion that can reduce to the form of Eq. (A10) above (e.g., multiple interacting nonequilibrium systems), the system remains in a hypoequilibrium state throughout its evolution provided the system's initial state is a hypoequilibrium state. The solution of this equation is

$$p_j^{a,K}(t) = n_j^{a,K} e^{-\vec{l}_j^{a,K} \cdot \vec{\eta}^{a,K}(t)} \quad (\text{A11})$$

and $\eta^{a,K}(t)$ is found from

$$\frac{d\vec{\eta}^{a,K}(t)}{dt} = -\frac{1}{\tau} (\vec{\eta}^{a,K}(t) - \vec{\eta}_a^0(t)) \quad (\text{A12})$$

which governs the evolutions of the nonequilibrium intensive properties.

For any three eigenstates, p_i , p_j , and p_k , of system a , represented by \vec{l}_i , \vec{l}_j , and \vec{l}_k where for simplicity the superscripts have been omitted, the following relation is found:

$$\ln \frac{p_j}{n_j} = -\vec{l}_j \cdot \vec{K}^{ijk} \quad (\text{A13})$$

provided \vec{l}_i , \vec{l}_j , and \vec{l}_k are linearly independent, i.e.,

$$\begin{vmatrix} 1 & \epsilon_i & N_i \\ 1 & \epsilon_j & N_j \\ 1 & \epsilon_k & N_k \end{vmatrix} \neq 0, \quad \text{or} \quad \begin{vmatrix} \epsilon_j - \epsilon_i & N_j - N_i \\ \epsilon_k - \epsilon_i & N_k - N_i \end{vmatrix} \neq 0 \quad (\text{A14})$$

In Eq. (A13), \vec{K}^{ijk} is defined as

$$\vec{K}^{ijk} \equiv \begin{bmatrix} 1 & \epsilon_i & N_i \\ 1 & \epsilon_j & N_j \\ 1 & \epsilon_k & N_k \end{bmatrix}^{-1} \begin{bmatrix} -\ln \frac{p_i}{n_i} \\ -\ln \frac{p_j}{n_j} \\ -\ln \frac{p_k}{n_k} \end{bmatrix} \quad (\text{A15})$$

The time evolution of these three energy eigenlevels (or eigenstates) obeys the following equations:

$$-\frac{d}{dt} (\vec{l}_j \cdot \vec{K}^{ijk}) = \frac{1}{\tau} (\vec{l}_j \cdot \vec{K}^{ijk} - \vec{l}_j \cdot \vec{\eta}) \quad (\text{A16})$$

$$\vec{l}_j \cdot \left(\frac{d\vec{K}^{ijk}}{dt} + \frac{1}{\tau} \vec{K}^{ijk} - \frac{1}{\tau} \vec{\eta} \right) = 0 \quad (\text{A17})$$

Because \vec{l}_i , \vec{l}_j , and \vec{l}_k are linearly independent,

$$\frac{d\vec{K}^{ijk}}{dt} + \frac{1}{\tau} \vec{K}^{ijk} - \frac{1}{\tau} \vec{\eta} = 0 \quad (\text{A18})$$

If \vec{l}_i , \vec{l}_j , and \vec{l}_k are in the same K th subspace of system a which is in hypoequilibrium with intensive properties

$\vec{\eta}^{a,K}$, the initial condition for the equation of motion of \vec{K}^{ijk} is

$$\vec{K}^{ijk}(t=0) = \vec{\eta}^{a,K} \quad (\text{A19})$$

Thus, the \vec{K}^{ijk} of any three independent energy eigenlevels in the K th subspace of system a follows the same ordinary differential equation, i.e., the same time evolution,

$$\vec{K}^{ijk}(t) = \vec{\eta}^{a,K}(t) \quad (\text{A20})$$

and, therefore, the system always remains in a hypoequilibrium state. If no linearly independent triplet of \vec{l}_i , \vec{l}_j , and \vec{l}_k exists in the subspace, one can set $\gamma = 0$ or $\beta = 0$ for the case when two linearly independent \vec{l}_i and \vec{l}_j exist in the subspace and set both $\gamma = 0$ and $\beta = 0$ for the case of a single eigenlevel in the subspace.

Appendix B: Equation of motion

The energy eigenlevels of system a and b are represented by $\{(n_i^a, \epsilon_i^a, N_i^a)\}$ and $\{(n_j^b, \epsilon_j^b, N_j^b)\}$. The state of the system can be represented by two probability distributions among the energy eigenlevels of systems a and b given by $\{p_i^a, p_j^b, i, j = 1, 2, \dots\}$. The distance between two states is defined here as the Fisher-Rao metric [12, 26]. Equivalently, the square root of the probability distribution $\{x_i^a, x_j^b, i, j = 1, 2, \dots\}$ can be used to represent the system state. One can prove that the Fisher-Rao metric of the probability space becomes the Euclidean metric in the space of $\{x_i^a, x_j^b, i, j = 1, 2, \dots\}$. The distance between states for both representations is given by

$$dl = \frac{1}{2} \sqrt{\sum_i p_i^a \left(\frac{d \ln p_i^a}{d\theta}\right)^2 + \sum_j p_j^b \left(\frac{d \ln p_j^b}{d\theta}\right)^2} d\theta \quad (\text{B1})$$

$$dl = \sqrt{\sum_i \left(\frac{dx_i^a}{d\theta}\right)^2 + \sum_j \left(\frac{dx_j^b}{d\theta}\right)^2} d\theta \quad (\text{B2})$$

where dl is the distance between $p(\theta + d\theta)$ and $p(\theta)$ or $x(\theta + d\theta)$ and $x(\theta)$ and θ is a continuous parameter. **Properties of the system are functions of the state** $\{x_i^a, x_j^b\}$

such that

$$I^a = \sum_i (x_i^a)^2 = 1 \quad (\text{B3})$$

$$I^b = \sum_j (x_j^b)^2 = 1 \quad (\text{B4})$$

$$N^a = \langle N \rangle^a = \sum_i N_i^a (x_i^a)^2 = \text{const} \quad (\text{B5})$$

$$N^b = \langle N \rangle^b = \sum_j N_j^b (x_j^b)^2 = \text{const} \quad (\text{B6})$$

$$E = \langle e \rangle^a + \langle e \rangle^b = \sum_i \epsilon_i^a (x_i^a)^2 + \sum_j \epsilon_j^b (x_j^b)^2 = \text{const} \quad (\text{B7})$$

$$S = \langle s \rangle^a + \langle s \rangle^b = - \sum_i (x_i^a)^2 \ln \frac{(x_i^a)^2}{n_i^a} - \sum_j (x_j^b)^2 \ln \frac{(x_j^b)^2}{n_j^b} \quad (\text{B8})$$

where $\langle \dots \rangle^{a(b)}$ indicates the expectation value in system $a(b)$. **The entropy $\langle s \rangle^{a(b)}$ uses the von Neumann form [42] and includes the eigenlevel degeneracy $n_i^{a(b)}$ [16]. For interacting systems with heat diffusion only, the steepest entropy ascent time evolution is subject to the conservation of only the first five properties (Eqs. (B3)-(B7)). The gradient vectors in state space for the properties defined by Eqs. (B3)-(B7) are given by**

$$\mathbf{g}_{I^a} = \sum_i \frac{\partial I^a}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial I^a}{\partial x_j^b} \hat{e}_j^b = \sum_i 2x_i^a \hat{e}_i^a \quad (\text{B9})$$

$$\mathbf{g}_{I^b} = \sum_i \frac{\partial I^b}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial I^b}{\partial x_j^b} \hat{e}_j^b = \sum_j 2x_j^b \hat{e}_j^b \quad (\text{B10})$$

$$\mathbf{g}_{N^a} = \sum_i \frac{\partial N^a}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial N^a}{\partial x_j^b} \hat{e}_j^b = \sum_i 2x_i^a N_i^a \hat{e}_i^a \quad (\text{B11})$$

$$\mathbf{g}_{N^b} = \sum_i \frac{\partial N^b}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial N^b}{\partial x_j^b} \hat{e}_j^b = \sum_j 2x_j^b N_j^b \hat{e}_j^b \quad (\text{B12})$$

$$\begin{aligned} \mathbf{g}_E &= \sum_i \frac{\partial E}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial E}{\partial x_j^b} \hat{e}_j^b \\ &= \sum_i 2x_i^a \epsilon_i^a \hat{e}_i^a + \sum_j 2x_j^b \epsilon_j^b \hat{e}_j^b \end{aligned} \quad (\text{B13})$$

$$\begin{aligned} \mathbf{g}_S &= \sum_i \frac{\partial S}{\partial x_i^a} \hat{e}_i^a + \sum_j \frac{\partial S}{\partial x_j^b} \hat{e}_j^b = \sum_i [-2x_i^a \\ &\quad - 2x_i^a \ln \frac{(x_i^a)^2}{n_i^a}] \hat{e}_i^a + \sum_j [-2x_j^b - 2x_j^b \ln \frac{(x_j^b)^2}{n_j^b}] \hat{e}_j^b \end{aligned} \quad (\text{B14})$$

where $\hat{e}_i^a(b)$ is the unit vector for each dimension.

The **SEA principle** upon which the equation of motion is based is defined as the direction at any instant of time along which the system state evolves that has the largest entropy gradient consistent with the conservation constraints. The resulting equation of motion for the case when the symplectic term (or Schrödinger term) is zero

is then expressed as [22–25, 43]

$$\frac{d\mathbf{x}}{dt} = \frac{1}{\tau(\mathbf{x})} \mathbf{g}_{S \perp L(\mathbf{g}_{I^a}, \mathbf{g}_{I^b}, \mathbf{g}_{N^a}, \mathbf{g}_{N^b}, \mathbf{g}_E)} \quad (\text{B15})$$

where τ , which is a function of system state, is the relaxation time that describes the speed at which the state

evolves in state space in the direction of steepest entropy ascent. $L = L(\mathbf{g}_{I^a}, \mathbf{g}_{I^b}, \mathbf{g}_{N^a}, \mathbf{g}_{N^b}, \mathbf{g}_E)$ is the manifold spanned by the first five gradients, and $\mathbf{g}_{S \perp L}$ is the component of the gradient of the entropy perpendicular to this manifold, i.e., the hyper-surface that yields to the five conservation laws. The right hand side of Eq. (B15) takes the form of a ratio of determinants, which is

$$\mathbf{g}_{S \perp L(\mathbf{g}_{I^a}, \mathbf{g}_{I^b}, \mathbf{g}_{N^a}, \mathbf{g}_{N^b}, \mathbf{g}_E)} = \frac{\begin{vmatrix} \mathbf{g}_S & \mathbf{g}_{I^a} & \mathbf{g}_{N^a} & \mathbf{g}_{I^b} & \mathbf{g}_{N^b} & \mathbf{g}_E \\ (\mathbf{g}_S, \mathbf{g}_{I^a}) & (\mathbf{g}_{I^a}, \mathbf{g}_{I^a}) & (\mathbf{g}_{N^a}, \mathbf{g}_{I^a}) & (\mathbf{g}_{I^b}, \mathbf{g}_{I^a}) & (\mathbf{g}_{N^b}, \mathbf{g}_{I^a}) & (\mathbf{g}_E, \mathbf{g}_{I^a}) \\ (\mathbf{g}_S, \mathbf{g}_{N^a}) & (\mathbf{g}_{I^a}, \mathbf{g}_{N^a}) & (\mathbf{g}_{N^a}, \mathbf{g}_{N^a}) & (\mathbf{g}_{I^b}, \mathbf{g}_{N^a}) & (\mathbf{g}_{N^b}, \mathbf{g}_{N^a}) & (\mathbf{g}_E, \mathbf{g}_{N^a}) \\ (\mathbf{g}_S, \mathbf{g}_{I^b}) & (\mathbf{g}_{I^a}, \mathbf{g}_{I^b}) & (\mathbf{g}_{N^a}, \mathbf{g}_{I^b}) & (\mathbf{g}_{I^b}, \mathbf{g}_{I^b}) & (\mathbf{g}_{N^b}, \mathbf{g}_{I^b}) & (\mathbf{g}_E, \mathbf{g}_{I^b}) \\ (\mathbf{g}_S, \mathbf{g}_{N^b}) & (\mathbf{g}_{I^a}, \mathbf{g}_{N^b}) & (\mathbf{g}_{N^a}, \mathbf{g}_{N^b}) & (\mathbf{g}_{I^b}, \mathbf{g}_{N^b}) & (\mathbf{g}_{N^b}, \mathbf{g}_{N^b}) & (\mathbf{g}_E, \mathbf{g}_{N^b}) \\ (\mathbf{g}_S, \mathbf{g}_E) & (\mathbf{g}_{I^a}, \mathbf{g}_E) & (\mathbf{g}_{N^a}, \mathbf{g}_E) & (\mathbf{g}_{I^b}, \mathbf{g}_E) & (\mathbf{g}_{N^b}, \mathbf{g}_E) & (\mathbf{g}_E, \mathbf{g}_E) \end{vmatrix}}{\begin{vmatrix} (\mathbf{g}_{I^a}, \mathbf{g}_{I^a}) & (\mathbf{g}_{N^a}, \mathbf{g}_{I^a}) & (\mathbf{g}_{I^b}, \mathbf{g}_{I^a}) & (\mathbf{g}_{N^b}, \mathbf{g}_{I^a}) & (\mathbf{g}_E, \mathbf{g}_{I^a}) \\ (\mathbf{g}_{I^a}, \mathbf{g}_{N^a}) & (\mathbf{g}_{N^a}, \mathbf{g}_{N^a}) & (\mathbf{g}_{I^b}, \mathbf{g}_{N^a}) & (\mathbf{g}_{N^b}, \mathbf{g}_{N^a}) & (\mathbf{g}_E, \mathbf{g}_{N^a}) \\ (\mathbf{g}_{I^a}, \mathbf{g}_{I^b}) & (\mathbf{g}_{N^a}, \mathbf{g}_{I^b}) & (\mathbf{g}_{I^b}, \mathbf{g}_{I^b}) & (\mathbf{g}_{N^b}, \mathbf{g}_{I^b}) & (\mathbf{g}_E, \mathbf{g}_{I^b}) \\ (\mathbf{g}_{I^a}, \mathbf{g}_{N^b}) & (\mathbf{g}_{N^a}, \mathbf{g}_{N^b}) & (\mathbf{g}_{I^b}, \mathbf{g}_{N^b}) & (\mathbf{g}_{N^b}, \mathbf{g}_{N^b}) & (\mathbf{g}_E, \mathbf{g}_{N^b}) \\ (\mathbf{g}_{I^a}, \mathbf{g}_E) & (\mathbf{g}_{N^a}, \mathbf{g}_E) & (\mathbf{g}_{I^b}, \mathbf{g}_E) & (\mathbf{g}_{N^b}, \mathbf{g}_E) & (\mathbf{g}_E, \mathbf{g}_E) \end{vmatrix}} \quad (\text{B16})$$

where (\dots, \dots) denotes the scalar product of two vectors in state space and the determinant in the denominator is a Gram determinant. The equation of motion of the probability for a given eigenlevel p_i^a is then given by the inner product of $x_i^a \hat{e}_i^a$ and $\frac{d\mathbf{x}}{dt}$ such that

$$\frac{dp_i^a}{dt} = (x_i^a \hat{e}_i^a, \frac{d\mathbf{x}}{dt}) = \frac{1}{\tau} (x_i^a \hat{e}_i^a, \mathbf{g}_{S \perp L(\mathbf{g}_{I^a}, \mathbf{g}_{I^b}, \mathbf{g}_{N^a}, \mathbf{g}_{N^b}, \mathbf{g}_E)}) \quad (\text{B17})$$

The inner products of the gradient vectors and $x_i^a \hat{e}_i^a$ are

expressed as

$$(x_i^a \hat{e}_i^a, \mathbf{x}) = p_i^a \quad (\text{B18})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_{I^a}) = 2p_i^a \quad (\text{B19})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_{I^b}) = 0 \quad (\text{B20})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_{N^a}) = 2N_i^a p_i^a \quad (\text{B21})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_{N^b}) = 0 \quad (\text{B22})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_E) = 2\epsilon_i^a p_i^a \quad (\text{B23})$$

$$(x_i^a \hat{e}_i^a, \mathbf{g}_S) = -2p_i^a - 2p_i^a \ln \frac{p_i^a}{n_i^a} \quad (\text{B24})$$

and every inner product between two gradient vectors can be calculated by the linear combination of the inner products of gradient vectors and $x_i^a \hat{e}_i^a$. For example, $(\mathbf{g}_{N^a}, \mathbf{g}_E) = \sum_i 2N_i^a (x_i^a \hat{e}_i^a, \mathbf{g}_E) = 4 \sum_i N_i^a \epsilon_i^a p_i^a = 4(eN)^a$. The explicit form of Eq. (B15) is then given by Eq. (19).

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