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Steady state of a dissipative flow-controlled system and the maximum entropy production principle

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A theory to predict the steady-state position of a dissipative flow-controlled system, as defined by a control volume, is developed based on the maximum entropy principle of Jaynes, involving minimization of a generalized free-energy-like potential. The analysis provides a theoretical justification of a local, conditional form of the maximum entropy production principle, which successfully predicts the observable properties of many such systems. The analysis reveals a very different manifestation of the second law of thermodynamics in steady-state flow systems, which provides a driving force for the formation of complex systems, including life.

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I. INTRODUCTION

For over three decades, the maximum entropy production (MEP) principle—more precisely termed the "maximum rate of thermodynamic entropy production" principle—has been found to give successful predictions for the steady-state properties of a variety of dynamic many-degree-of-freedom systems subject to flows of mass, energy, momentum, charge, and/or with chemical reactions. Prominent examples include the global general circulation (atmospheric and oceanic) system of the Earth [1–13] and possibly other planetary bodies [14,15], turbulent convection in a heated fluid (Rayleigh-Bénard [16] convection) [17], mantle convection in the Earth [18–20] and moons of Jupiter and Saturn [19], global Earth-biosphere water and nutrient cycles [9,21,22], vegetation spatial distributions [23], biochemical metabolism [24], and ecosystem operation [25]. The Earth climate models include quite accurate predictions of the mean latitudinal air temperature, fractional cloud cover, meridional heat flux [1], mean vertical air temperature profile, vertical heat flux [4], and historical latitudinal air temperature gradients over decadal and glacial-interglacial time scales [12]. The MEP principle has also been invoked for the explanation of shear turbulence (Couette flow) [17], incompressible and compressible turbulent fluid flows [26], currents in electrical circuits [27–30], plasma formation [31] and structure [32], crystal growth [33], chemical cycle kinetics [34], diffusion in nonuniform solids [35], photosynthesis mechanism [36], biomolecular motors [37], and economic activity [38]; several detailed reviews are available [9,11,39,40]. The MEP principle has even been invoked as a technical basis for the Gaia hypothesis [10,21,41,42]. The apparent successes of the MEP principle—which can exclude most details of the dynamics—contradict the prevailing paradigm of developing ever-more-complicated dynamic models of complex systems, for example, the general circulation models of the Earth climate system. This suggests that, in a large class of steady-state systems, the dynamics adjust themselves to achieve a state of MEP, rather than the entropy production being a consequence of the dynamics. This implies the action of an as-yet unrecognized physical principle applicable to flow systems—beyond the domain of present-day thermodynamics—which provides the driving force in the system and so can be used as a "shortcut" in system modeling.

In recent years, several workers have attempted to justify the MEP principle on theoretical grounds. Dewar [43,44] analyzed a time-variant nonequilibrium system in terms of its available paths in parameter space; the transient and the steady-state positions are inferred by the maximum entropy (MaxEnt) method of Jaynes [45–51], using an entropy defined on the set of paths. The analysis has received some criticisms [52,53], suggesting it might apply only in the near-equilibrium linear (Onsager) regime, in which fluxes are linearly proportional to their driving gradients [54,55]. Attard [56,57] also gave an analysis based on an entropy defined on transition probabilities, but cast in the terminology of traditional statistical mechanics (although he denied the MEP principle in favor of an alternative). Beretta [58–61] examined a steepest entropy ascent principle for transitions between states, based on a quantum thermodynamics formulation. Other arguments for MEP have been given by Županović *et al.* [62], based on the "most probable" increase in entropy during a fluctuation (also criticized [52]), and by Martyushev [63], based on a frame of reference (relative velocity) argument. Of course, this is a well-trodden field, with many historical antecedents to the MEP principle (see the fascinating review by Martyushev and Seleznev [39]). If the above objections can be overcome, the path-based analyses hold the promise of predicting the behavior of time-variant systems (transport phenomena). However, they seem unnecessarily complicated for the task of predicting the steady-state position, when (as will be shown) a more direct method is available.

The aim of this work is to outline a theory to *directly* predict the steady-state position of a flow-controlled system, based on Jaynes' MaxEnt method [45–51]. The analysis provides a theoretical derivation of a local, conditional form of the MEP principle for steady-state thermodynamic systems

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of any type (e.g., heat flow, fluid flow, diffusive flow, electrical flow, chemical and process engineering, and biological and human systems). The approach taken here differs from previous analyses [43,44,56,57,62] in that it considers flux rather than path probabilities, to directly obtain the steady-state position. It also employs the local equilibrium assumption commonly used in engineering control volume analysis, but does not appear to be restricted to the linear transport regime; indeed, the linear regime emerges as a first-order approximation to the analysis.

This work is set out as follows. In Sec. II, the principles of Jaynes' generic theory are outlined, leading in Sec. III to a discussion of different types of physical systems, which influences the manner in which Jaynes' method can be applied. Equilibrium systems are first examined, to demonstrate the universality of Jaynes' method and to highlight the (easily overlooked) equilibrium analog of the MEP principle. In Sec. IV, a theory is developed to predict the steady-state position of a flow-controlled thermodynamic system; by comparison to a traditional control volume analysis, this is found to give a local, conditional form of the MEP principle. The implications of the analysis for the formation of complex systems, including life, are discussed in Sec. V.

II. JAYNES' GENERIC THEORY

We first summarize Jaynes' generic formulation of statistical mechanics [45–51], based on the minimum divergence, the maximum relative entropy, or the minimum cross-entropy (MinXEnt) principle, within which the MaxEnt principle can be considered as a special case. Consider a system of N discrete distinguishable entities distributed among s distinguishable categories or "states" within a system, with constant source ("prior") probabilities q_i for the filling of each state $i=1,\dots,s$ (the states i may be multivariate, e.g., $\{i,j,\dots\}$). From information-theoretical considerations [64,65] and/or by combinatorial arguments [66–71], it can be shown that in the asymptotic limit $N\to\infty$ (the Stirling approximation [72] or Sanov's theorem [73]), the "least informative" or the "most probable" distribution of the system is obtained by minimizing the Kullback-Leibler cross-entropy function [74,75] (the negative of the relative entropy function [47])[1]

$$D=\sum_{i=1}^{s} p_i \ln\frac{p_i}{q_i} \tag{1}$$

subject to the natural and the moment constraints on the system, respectively,

$$\sum_{i=1}^{s} p_i = 1, \tag{2}$$

$$\sum_{i=1}^{s} p_i f_{ri} = \langle f_r\rangle, \qquad r=1,\dots,R, \tag{3}$$

where p_i is the probability of the ith category, f_{ri} is the value of property f_r for the ith category, and $\langle f_r\rangle$ is the mathematical expectation of f_{ri} (generally, each f_r is a "conserved quantity"). Applying Lagrange's method of undetermined multipliers to Eqs. (1)–(3) gives the stationary or the most probable distribution of the system,

$$p_i^* = q_i \exp\left(-\lambda_0^* - \sum_{r=1}^{R}\lambda_r f_{ri}\right) = (Z_q^*)^{-1} q_i \exp\left(-\sum_{r=1}^{R}\lambda_r f_{ri}\right),$$

$$Z_q^* = e^{\lambda_0^*} = \sum_{i=1}^{s} q_i \exp\left(-\sum_{r=1}^{R}\lambda_r f_{ri}\right), \tag{4}$$

where λ_r is the Lagrangian multiplier for the rth constraint, λ_0^* is the "Massieu function" [76], Z_q^* is the generalized partition function, and "$*$" denotes a quantity at the stationary position. Here "stationary" implies a time-invariant distribution (4), with no additional physical interpretation. Subsequent generic analyses pioneered by Jaynes [45–51,70] give the relations

$$D^* = -\lambda_0^* - \sum_{r=1}^{R}\lambda_r\langle f_r\rangle, \tag{5}$$

$$\frac{\partial\lambda_0^*}{\partial\lambda_r} = -\langle f_r\rangle, \tag{6}$$

$$\frac{\partial^2\lambda_0^*}{\partial\lambda_r^2} = \langle f_r^2\rangle - \langle f_r\rangle^2 = -\frac{\partial\langle f_r\rangle}{\partial\lambda_r}, \tag{7}$$

$$\frac{\partial^2\lambda_0^*}{\partial\lambda_m\,\partial\lambda_r} = \langle f_r f_m\rangle - \langle f_r\rangle\langle f_m\rangle = -\frac{\partial\langle f_r\rangle}{\partial\lambda_m} = -\frac{\partial\langle f_m\rangle}{\partial\lambda_r}, \tag{8}$$

$$dD^* = -\sum_{r=1}^{R}\lambda_r(d\langle f_r\rangle - \delta W_r) = -\sum_{r=1}^{R}\lambda_r\delta Q_r, \tag{9}$$

where $\delta W_r=\langle df_r\rangle=\Sigma_{i=1}^{s}p_i^* df_{ri}$ and $\delta Q_r=\Sigma_{i=1}^{s}dp_i^* f_{ri}$ can be identified, respectively, as the increments of "generalized work" on the system and "generalized heat" added to the system during a change in the rth constraint $d\langle f_r\rangle$, in which δx denotes a path-dependent differential. (A *path* is here defined as a specified trajectory in macroscopic coordinates, e.g., constant constraints $\{\langle f_r\rangle\}$, constant multipliers $\{\lambda_r\}$, or some mixed form.) To avoid double counting, the δW_r terms represent generalized work processes *in addition to* those introduced by other constraints.[2]

For equal $q_i=s^{-1}$, the foregoing analysis reduces to that of maximizing the Shannon entropy [64]

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[1] The use of the continuous form of Eq. (1), or the von Neumann entropy based on density matrices, requires different mathematics but gives essentially the same macroscopic results (4)–(9) [46,47].

[2] This point is further explained in Sec. III A and footnote 3, by reference to an example equilibrium system.

$$\mathfrak{H} = -\sum_{i=1}^{s} p_i \ln p_i \tag{10}$$

subject to the same constraints (2) and (3). This gives the same relations (4)–(9), except that D^* is replaced with $-\mathfrak{H}^*$ and the q_i cancel from Eq. (4).

It is important to note that relations (4)–(9) only concern the stationary position, i.e., they apply "on the manifold of stationary positions." Transitions between stationary positions are thus assumed to be *quasistatic*, i.e., they are idealized as taking place only between stationary positions, without any intermediate nonstationary positions [77]. Comparing Eq. (9) to the derivative of Eq. (5) gives the differential

$$\begin{aligned} d\phi^* &= -d\lambda_0^* = -d \ln Z_q^* \\ &= \sum_{r=1}^{R} \lambda_r \delta W_r + \sum_{r=1}^{R} d\lambda_r \langle f_r \rangle \\ &= dD^* + \sum_{r=1}^{R} \lambda_r d\langle f_r \rangle + \sum_{r=1}^{R} d\lambda_r \langle f_r \rangle . \end{aligned} \tag{11}$$

$d\phi^*$ therefore encompasses "all possible changes" in the stationary position due to changes in the constraints, multipliers, or cross entropy (generalized heat input). For constant multipliers, $d\phi^*|_{\{\lambda_r\}}$ is equal to the weighted change in generalized work on the system; its integrated form ϕ^* can therefore be regarded as a generalized dimensionless free-energy-like function or a *generalized potential* [45–49,51].

We now come to the central tenet of this analysis, the importance of which will become clear in Secs. III and IV. If a dynamic system described by Eqs. (4)–(9) and (11) contains mechanism(s) by which its generalized potential ϕ^* can be dissipated (converted to an unrecoverable form), by processes not represented in the constraints, then by successive increments $d\phi^* < 0$ it will converge to a stationary position of no further extractable generalized work $d\phi^* = 0$, equivalent to the minimum position $\phi^* = \phi^*_{\text{min}}$. Here we confine the discussion to systems with *reproducible* dissipative phenomena, whereupon ϕ^*_{min} will be predictable (i.e., ϕ^* is a state function). If the incremental changes are restricted in some manner—e.g. the system is confined to a constant-constraint $\{\langle f_r \rangle\}$ or a constant-multiplier $\{\lambda_r\}$ path—then ϕ^*_{min} will be the local (path-dependent) minimum. If there is no such path restriction, ϕ^*_{min} will constitute the global minimum.

It is emphasized that the above analysis (1)–(11) is generic, and applies to *any* probabilistic system which can be analyzed by the Kullback-Leibler cross entropy (1) or the Shannon entropy (10). Although its primary application has been to equilibrium thermodynamics, the analysis has far broader power of application [45–51]. For this reason, the symbols used above are generic, and should not be interpreted in terms of particular thermodynamic quantities except when so stated (e.g., the generic entropy $\mathfrak{H}$ should not be confused with the thermodynamic entropy S).

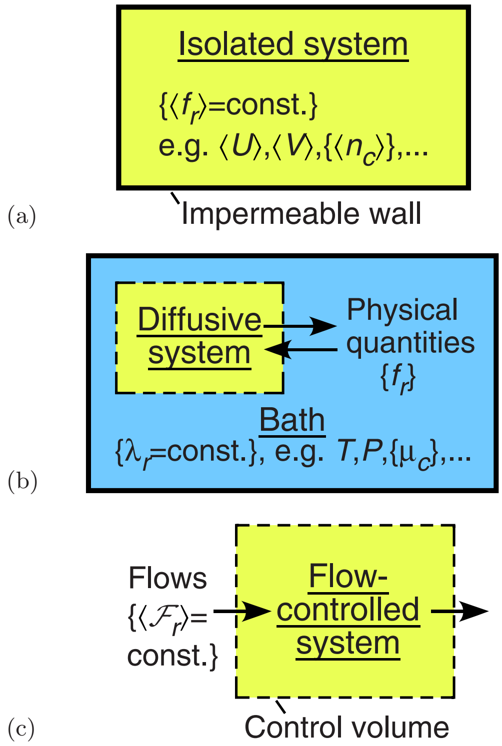

FIG. 1. (Color online) Different types of physical systems: (a) isolated, (b) diffusive, and (c) flow controlled (control volume).

III. TYPES OF SYSTEMS

A. Quantity-constrained (equilibrium) systems

To understand the application of MinXEnt, we now consider several types of probabilistic systems composed of discrete entities, as illustrated in Fig. 1. Historically, Jaynes' method (and its predecessor, traditional statistical mechanics) has been applied to (a) *isolated* (microcanonical) systems [Fig. 1(a)], held in a state of constant mean contents $\langle f_r \rangle$ of various physical quantities f_r by isolation from the rest of the universe, and (b) various types of *open* or *diffusive* (e.g., canonical and grand canonical) systems [Fig. 1(b)], open to the diffusion of various quantities f_r but with no directed flows, and in contact with infinite *generalized baths* of constant corresponding λ_r [45]. Clearly, such representations are convenient models to enable the construction of thermodynamic relationships: no system can really be isolated from the rest of the universe, while the mechanisms used to maintain the generalized baths are not usually explained. Notwithstanding this criticism, in either case the least informative or the most probable position of the system—the *equilibrium position*—can be calculated by the application of MinXEnt (or, for equal q_i, by MaxEnt) subject to the natural and the moment constraints [45]. Jaynes' generic formulation (Sec. II) can then be applied to the analysis of such systems.

As an example, consider an open or "heterogeneous" thermodynamic system for which the "entities" are interpreted either as discrete particles (atoms, ions, molecules, etc.) or, in the Gibbs-Einstein representation, as duplicates of the entire system [78–80]. Each entity has the choice of its (quantized) internal energy U_i ($i = 1, \ldots, s$), volume element V_j (j

$=1,\ldots,t$), and moles of particles n_{N_c} of each chemical species $c=1,\ldots,C$, for which the number of particles N_c can range between zero and (effectively) infinity. The system is constrained by its natural constraint (2), mean internal energy $\langle U\rangle$, mean volume $\langle V\rangle$, and mean moles of particles $\langle n_c\rangle$ of each type c. Assuming, from the principle of insufficient reason [51], that each multivariate state $\{i,j,\{N_c\}\}$ is equiprobable, we maximize the Shannon entropy

$$\mathfrak{H}_{eq} = -\sum_{i=1}^{s}\sum_{j=1}^{t}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\cdots\sum_{N_C=0}^{\infty} p_{i,j,\{N_c\}} \ln p_{i,j,\{N_c\}}, \qquad (12)$$

subject to the constraints, giving the equilibrium position (4),

$$p^*_{i,j,\{N_c\}} = \frac{\alpha^*_{i,j,\{N_c\}}}{\Xi^*},$$

$$\alpha^*_{i,j,\{N_c\}} = \exp\left(-\lambda_U U_i - \lambda_V V_j - \sum_{c=1}^{C}\lambda_c n_{N_c}\right),$$

$$\Xi^* = e^{\lambda_0^*} = \sum_{i=1}^{s}\sum_{j=1}^{t}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\cdots\sum_{N_C=0}^{\infty}\alpha^*_{i,j,\{N_c\}}. \qquad (13)$$

From our existing (historical) knowledge of thermodynamics (e.g., by monotonicity arguments [50] or from the zeroth law of thermodynamics [49,50]), we can identify the Lagrangian multipliers $\lambda_U=1/kT$, $\lambda_V=P/kT$, and $\lambda_c=-\mu_c/kT$, as functions of the Boltzmann constant k, absolute temperature T, absolute pressure P, and molar chemical potential μ_c of each species c, whence

$$\alpha^*_{i,j,\{N_c\}} = \exp\left(-\frac{U_i}{kT} - \frac{PV_j}{kT} + \sum_{c=1}^{C}\frac{\mu_c n_{Nc}}{kT}\right), \qquad (14)$$

and Ξ^* is the grand partition function. Recognizing the thermodynamic entropy as $S=k\mathfrak{H}_{eq}$, Eqs. (5) and (9) give

$$S^* = k\ln\Xi^* + \frac{\langle U\rangle}{T} + \frac{P\langle V\rangle}{T} - \sum_{c=1}^{C}\frac{\mu_c\langle n_c\rangle}{T}, \qquad (15)$$

$$\begin{aligned} dS^* &= \frac{\delta Q_U}{T} + \frac{P\,\delta Q_V}{T} - \sum_{c=1}^{C}\frac{\mu_c\delta Q_{n_c}}{T}\\ &= \frac{1}{T}(d\langle U\rangle - \delta W_U) + \frac{P}{T}(d\langle V\rangle - \delta W_V)\\ &\quad - \sum_{c=1}^{C}\frac{\mu_c}{T}(d\langle n_c\rangle - \delta W_{n_c})\\ &= \frac{d\langle U\rangle}{T} + \frac{Pd\langle V\rangle}{T} - \frac{\Sigma\delta W}{T} - \sum_{c=1}^{C}\frac{\mu_c d\langle n_c\rangle}{T}\\ &\quad - \sum_{c=1}^{C}\frac{\mu_c\delta W_{n_c}}{T}, \end{aligned} \qquad (16)$$

where δQ_U, δQ_V, and δQ_{n_c} are the increments in generalized heats, and δW_U, δW_V, and δW_{n_c} are the increments in generalized work associated, respectively, with constraints $\langle U\rangle$, $\langle V\rangle$, and $\langle n_c\rangle$. In the first line of Eq. (16), the first two terms can be amalgamated into the (actual) heat term $\delta Q/T$ used in thermodynamics; for systems with invariable particle numbers, $\delta Q_{n_c}=0$ and Eq. (16) reduces to the Clausius [81] equality $dS^*=\delta Q/T$. Similarly, in the last line of Eq. (16), the δW_U and the $P\delta W_V$ terms are amalgamated into the combined (actual) work $\Sigma\delta W$; the latter therefore represents the total (actual) work on the system, in addition to the $Pd\langle V\rangle$ and the $\mu_c d\langle n_c\rangle$ works.[3] For this study, we ignore relativistic or other changes in the "mass levels" and set $\Sigma\delta W_{n_c}=0$. It is again emphasized that Eqs. (13)–(16) apply only to quasistatic transitions, in this case "on the manifold of equilibrium positions."

Equations (11), (15), and (16) give the change in the (actual) free-energy function, in energy units,

$$\begin{aligned} dJ^* &= kTd\phi^*_{eq} = -kTd\ln\Xi^*\\ &= -TdS^* + d\langle U\rangle + Pd\langle V\rangle - \sum_{c=1}^{C}\mu_c d\langle n_c\rangle\\ &\quad + T\left\{d\left(\frac{1}{T}\right)\langle U\rangle + d\left(\frac{P}{T}\right)\langle V\rangle - \sum_{c=1}^{C} d\left(\frac{\mu_c}{T}\right)\langle n_c\rangle\right\} \end{aligned} \qquad (17)$$

in which, from Eq. (16), the first four terms on the right correspond to the total work $\Sigma\delta W$. Note that—as per Gibbs [82,83]—we could restrict Eq. (17) to these first four terms, by imposing the Gibbs-Duhem relation $\Sigma_{r=1}^{R} d\lambda_r\langle f_r\rangle=0$. Here we wish, however, to consider all possible changes in J^*, allowing both Gibbs-Duhem paths and non-Gibbs-Duhem paths. Integration of Eq. (17) from a zero reference state then yields[4]

$$J^* = kT\phi^*_{eq} = -kT\ln\Xi^* = -TS^* + \langle U\rangle + P\langle V\rangle - \sum_{c=1}^{C}\mu_c\langle n_c\rangle. \qquad (18)$$

Although less well known, J^* was reported by Gibbs [83]; in modified form, it forms the basis of the available energy, essergy and exergy concepts [83–89]. For constant composition, J^* reduces to the Gibbs free energy $G^*=-TS^*+\langle U\rangle+P\langle V\rangle$ plus a constant, while for constant composition and

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[3] As mentioned in Sec. II, δW_r refers to work terms in addition to those introduced by the other constraints. Thus in the above equilibrium system, the $Pd\langle V\rangle$ work cannot be introduced within the work term δW_U associated with $\langle U\rangle$, since it is already included by virtue of the $\langle V\rangle$ constraint. Similarly, δW_U cannot include the chemical-potential work terms $\mu_c d\langle n_c\rangle$, since these are included by the $\langle n_c\rangle$ constraints. This consideration is quite general: the constraints $\langle f_r\rangle$ must be linearly independent, but need not be orthogonal; the weighted generalized work terms $\lambda_r\delta W_r$ therefore cannot include processes represented by $\lambda_m d\langle f_m\rangle$, $m\neq r$.

[4] Strictly speaking, we must integrate $kd\phi^*_{eq}$ and multiply by T, an awkwardness produced by the conversion of $\ln\Xi^*$ to energy rather than entropy units (see Appendix A). Alternatively, integration of $dJ^*|_{T,P,\{\mu_c\}}$ directly yields Eq. (18) [83].

volume, it gives the Helmholtz free energy $F^*=-TS^*+\langle U\rangle$ plus a constant.

We first examine Eqs. (17) and (18) from the original perspective of Gibbs [82,83] (see also [77,90,91]). Following the standard treatment, we consider an open system surrounded by an intensive variable bath [Fig. 1(b)], with the double system-bath isolated from the rest of the universe; a single isolated system [Fig. 1(a)] can then be considered as a special case. From Eqs. (16) and (17), $dJ^*|_{T,P,\{\mu_c\}}=\Sigma\,\delta W$ gives the total change in work on the system along a Gibbs-Duhem path due to processes not represented in the constraints. Thus $dJ^*|_{T,P,\{\mu_c\}}<0$ indicates spontaneous change (work extraction) and $dJ^*|_{T,P,\{\mu_c\}}>0$ a forced change (work input). If the system contains some reproducible dissipative process(es) by which work can be expended (e.g., friction [48,49] or chemical reactions [92,93]), it will move toward the equilibrium defined by $dJ^*|_{T,P,\{\mu_c\}}=0$ or, in other words, to the minimum free-energy position $J^*=J^*_{\min}$. This was implicitly understood by Gibbs [82], who referred to the equilibrium surface (the "fundamental relation" or Euler surface) as the "surface of dissipated energy." If no work is extracted in useful form, each increment of lost work is given by [94–96]

$$dJ^*|_{T,P,\{\mu_c\}} = -T\,dS^*|_{T,P,\{\mu_c\}} - T\,\delta\sigma|_{T,P,\{\mu_c\}} \le 0, \qquad (19)$$

where $dS^*|_{T,P,\{\mu_c\}}$ and $\delta\sigma|_{T,P,\{\mu_c\}}$, respectively, give the change in entropy within and outside the system. Equation (19) represents the net irreversible increase in entropy in the double system-bath (converted to energy units and with change in sign), reflecting the interplay between irreversible change within the system and the exporting of irreversible change to the bath by the transfer of generalized heats [c.f. [94–98]]. The second term $\delta\sigma|_{T,P,\{\mu_c\}}$ can be labeled the *entropy produced*[5] by the system, since it materializes outside rather inside the system. If the incremental losses are unrecoverable (i.e., $dS^*|_{T,P,\{\mu_c\}}\ge 0$ and $\delta\sigma|_{T,P,\{\mu_c\}}\ge 0$), the equilibrium position $J^*=J^*_{\min}$ will correspond to the position of maximum entropy produced, $\sigma=\sigma_{\max}$ (c.f. [93]).

We now go a step farther than Gibbs, to consider systems which can deviate from a Gibbs-Duhem path during dissipation. We again only consider systems with reproducible processes. Here it is preferable to use the potential $d\psi^*=k\,d\phi^*_{eq}=dJ^*/T$ (the grand potential form of the negative Massieu function [76] or negative Planck potential [94,95,97–100]; see Appendix A) rather than dJ^*, to more effectively handle changes in temperature. From Eq. (17), each increment $d\psi^*<0$ can be divided into two parts: (i) the part $d\psi^*|_{S^*,\langle U\rangle,\langle V\rangle,\{\langle n_c\rangle\}}<0$ which is expended against changes in the intensive variables, causing an irreversible loss of "ability to do generalized work," manifested as an increase in entropy within or outside the system, and (ii) the part $d\psi^*|_{T,P,\{\mu_c\}}<0$, which—as in Eq. (19)—is lost by dissipation within or outside the system. The net loss can thus be written as

$$\begin{aligned} d\psi^* &= -dS^*|_{T,P,\{\mu_c\}} - \delta\sigma|_{T,P,\{\mu_c\}} - dS^*|_{S^*,\langle U\rangle,\langle V\rangle,\{\langle n_c\rangle\}} \\ &\quad - \delta\sigma|_{S^*,\langle U\rangle,\langle V\rangle,\{\langle n_c\rangle\}} \\ &= -dS^* - \delta\sigma \le 0 \end{aligned} \qquad (20)$$

The terms $dS^*|_{S^*,\langle U\rangle,\langle V\rangle,\{\langle n_c\rangle\}}$ and $\delta\sigma|_{S^*,\langle U\rangle,\langle V\rangle,\{\langle n_c\rangle\}}$ constitute "uncompensated transformations" of Clausius [81]—respectively, within and outside the system—since they involve irreversible change(s) in one or more intensive variables. For convenience, the four terms are unified in the second line of Eq. (20), into overall entropy changes within and outside the system.

From Eq. (20), the system will approach the equilibrium position defined by $\psi^*=\psi^*_{\min}$, equivalent to the maximum net irreversible increase in entropy within and outside the system. If $dS^*\ge 0$ and $\delta\sigma\ge 0$, this will again correspond to the state at which maximum thermodynamic entropy is produced, $\sigma=\sigma_{\max}$. If the path of possible transitions is prescribed (e.g., constant $\{\langle f_r\rangle\}$, constant $\{\lambda_r\}$, or a mixed choice), the system will approach the local minimum $\psi^*_{\min}=-\int(dS^*+\delta\sigma)$ along that path; if not, it will converge to the global minimum.

Thus in a dissipative equilibrium system, the final equilibrium will occur at the position of minimum generalized potential ϕ^*_{eq} (maximum Massieu function λ^*_0). If the incremental increases $dS^*\ge 0$ and $\delta\sigma\ge 0$ are unrecoverable, this will be equivalent to the position at which maximum thermodynamic entropy is produced. This provides an *equilibrium analog* of the MEP principle, which is easily overlooked since it involves a connection between equilibrium states and irreversible changes.

We can also consider the multiplier relations (6), the variances (7), and the covariances (8), which yield a highly important set of relations for equilibrium systems, as listed in Table I. These include the "Maxwell relations" [77,101], which express the connections between various material properties or susceptibilities of the system (e.g., heat capacity, compressibility, coefficient of thermal expansion, activity coefficients, etc.). The relations in Table I are valid only at equilibrium, i.e., they apply on the manifold of equilibrium positions. Although discovered long before Jaynes' generic analysis, such relations demonstrate the power of Jaynes' method, particularly when applied to new situations.

B. Flow-controlled (steady-state) systems

We now examine a third kind of probabilistic system, which much more closely matches our experience of real systems and of life on Earth: the *flow-controlled system* [Fig. 1(c)], constrained by flows of various physical quantities f_r through the system. Flow-controlled systems are familiar to fluid mechanics and engineers, as defined by the *control volume*, a geometric region through which fluid(s) can flow (the Eulerian description), bounded by its *control surface*. In the

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[5] It is misleading to call σ the *entropy production*. In English, "production" implies an ongoing phenomenon, hence a rate process (e.g., a nation's steel production). This can only apply to a flow system. Confusingly, the symbol σ is used interchangeably for the amount of thermodynamic entropy produced by a system, its rate of production by a system, or the rate per unit volume; these are labeled σ, $\dot{\sigma}$, and $\hat{\dot{\sigma}}$, respectively here.

TABLE I. Multiplier relations (6), variances (7), and covariances (8) for the example equilibrium thermodynamic system (Sec. III A) at equilibrium [note $\mathrm{var}(a)=\langle a^2\rangle-\langle a\rangle^2$, $\mathrm{cov}(a,b)=\langle ab\rangle-\langle a\rangle\langle b\rangle$, and μ_b implies $b\neq c$].

Multiplier relations

$$\langle U\rangle = kT^2\left(\frac{\partial \ln \Xi^*}{\partial T}\right)_{P,\{\mu_c\}}$$

$$\langle V\rangle = -kT\left(\frac{\partial \ln \Xi^*}{\partial P}\right)_{T,\{\mu_c\}}$$

$$\langle n_c\rangle = kT\left(\frac{\partial \ln \Xi^*}{\partial \mu_c}\right)_{T,P,\{\mu_b\}}$$

Variances

$$\mathrm{var}(U) = kT^2\left(\frac{\partial \langle U\rangle}{\partial T}\right)_{P,\{\mu_c\}}$$

$$\mathrm{var}(V) = -kT\left(\frac{\partial \langle V\rangle}{\partial P}\right)_{T,\{\mu_c\}}$$

$$\mathrm{var}(n_c) = kT\left(\frac{\partial \langle n_c\rangle}{\partial \mu_c}\right)_{T,P,\{\mu_b\}}$$

Covariances (Maxwell relations)

$$\mathrm{cov}(U,V) = -\left(\frac{\partial \langle U\rangle}{\partial P}\right)_{T,\{\mu_c\}} = T\left(\frac{\partial \langle V\rangle}{\partial T}\right)_{P,\{\mu_c\}}$$

$$\mathrm{cov}(U,n_c) = \left(\frac{\partial \langle U\rangle}{\partial \mu_c}\right)_{T,P,\{\mu_b\}} = T\left(\frac{\partial \langle n_c\rangle}{\partial T}\right)_{P,\{\mu_c\}}$$

$$\mathrm{cov}(V,n_c) = -\left(\frac{\partial \langle n_c\rangle}{\partial P}\right)_{T,\{\mu_c\}} = \left(\frac{\partial \langle V\rangle}{\partial \mu_c}\right)_{T,P,\{\mu_b\}}$$

$$\mathrm{cov}(n_c,n_b) = \left(\frac{\partial \langle n_c\rangle}{\partial \mu_b}\right)_{T,P,\{\mu_{c\neq b}\}} = \left(\frac{\partial \langle n_b\rangle}{\partial \mu_c}\right)_{T,P,\{\mu_b\}}$$

language of statistical mechanics, flow-controlled systems constitute a separate "ensemble," very different to those examined in equilibrium thermodynamics. For the simplified flow system shown in Fig. 1(c), the mean rate of change in each conserved quantity f_r with respect to time t within the system is

$$\frac{d\langle f_r\rangle}{dt} = \langle \mathcal{F}_r\rangle_{in} - \langle \mathcal{F}_r\rangle_{out} + \langle \dot{f}_r\rangle_{prod}, \tag{21}$$

where $\langle \mathcal{F}_r\rangle_{in}$, $\langle \mathcal{F}_r\rangle_{out}$, and $\langle \dot{f}_r\rangle_{prod}$ represent, respectively, the mean flow rates of f_r into and out of the control volume and the rate of production within the control volume. At steady state, $d\langle f_r\rangle/dt=0$, and so for a system with no production terms, Eq. (21) reduces to

$$\langle \mathcal{F}_r\rangle_{in} = \langle \mathcal{F}_r\rangle_{out} = \langle \mathcal{F}_r\rangle. \tag{22}$$

The mean flow rates $\langle \mathcal{F}_r\rangle$ can then be interpreted as constraints on the distribution of instantaneous flow rates $\mathcal{F}_{ri}$ through the system. By information-theoretical reasoning [64,65] and/or the combinatorial basis of entropy [66–71], the MinXEnt principle can then be used to calculate the stationary or the most probable distribution of flow rates within the system—its *steady-state position*—subject to the constraints on the system. Moment constraints are just moment constraints, regardless of their physical manifestation. In consequence, the entirety of Jaynes' generic approach (Sec. II) can be applied to the analysis of steady state, as well as equilibrium systems. Of course, flow-controlled systems may be subject to variable or cyclic flow rates, causing deviations from the steady-state position; such effects are not considered further here.

Notwithstanding the broad applicability of Jaynes' method to both equilibrium and steady-state systems, it is important to understand their differences. In equilibrium systems, the physical entities represent individual particles (e.g., molecules, ions, oscillators, etc.) or entire systems of such particles, which can choose different values f_{ri} of various physical parameters f_r. In contrast, in the Eulerian description of a steady-state system, the entities represent individual fluid elements (in the limit, points), which may adopt particular instantaneous flow rates $\mathcal{F}_{ri}$ through the system. The latter analysis therefore examines the bulk behavior of many individual particles passing through a control volume, which cannot readily be ascribed to particular particles. A further distinction is that equilibrium systems require no effort to maintain equilibrium, and can undergo reversible or irreversible changes; in contrast, maintenance or alteration of steady-state systems inherently requires an irreversible change in the universe. Aside from these differences, both systems have many features in common:

(i) In keeping with any method of inference, there is no guarantee that a predicted stationary position will occur, in that there may be (unknown) dynamic inhibitions ("nonergodities") which prevent its occurrence. Indeed, in equilibrium thermodynamics the existence of "metastable" states is well known, and is dealt with by kinetic theory (rate processes) and the activation energy concept. However, if the analysis incorporates everything that is known about the system, Jaynes' method will provide the "best representation" and the "expected position" of the system [45]. In this vein, while it may be desirable to seek "mechanistic" or "dynamic" explanations for the observed steady state in particular flow-controlled systems—analogous to justifications of equilibrium using the equations of motion [102] or Boltzmann's H theorem [103]—the general principle must necessarily be inferential (statistical or probabilistic), just as it is in equilibrium thermodynamics.

(ii) For a given constraint set, the stationary position D^* or $\mathfrak{H}^*$ is usually considered unique within its parameter (state function) space [45–51]. However, this depends on the type of constraints, e.g., power-law constraints are known to give multiple stationary positions [104]. The uniqueness of the stationary position, in general, is therefore not claimed here, but is correct in the case of linear moment constraints [50].

(iii) A unique stationary position D^* or $\mathfrak{H}^*$ in parameter space does not imply uniqueness of the dynamic structure(s) which can produce it; indeed, many such structures may be possible. The occurrence of any given structure will depend

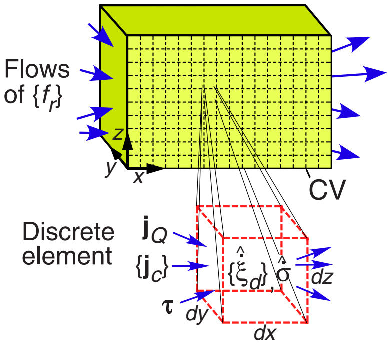

FIG. 2. (Color online) Discretized control volume model of a flow-controlled thermodynamic system.

on the interplay between the system history (hysteresis phenomena) and the dynamics (the extent of fluctuations, or "jitter," in the system), both of which lie outside the domain of Jaynes' method *per se*. This feature is also well known in equilibrium systems, e.g., the equilibrium position of a supersaturated solution does not provide any information about the particle size distribution or geometric form of the precipitant, which instead will depend on localized (history-dependent) nucleation, crystallization, and diffusion phenomena.

(iv) The MEP principle has been criticized for appearing to be a means of selection between a few isolated optima, rather than a true variational principle [40,52]. However, many equilibrium systems also exhibit a discontinuous approach to equilibrium for dynamic reasons, especially those with a phase change, e.g., the rapid solidification of a saturated solution of sodium acetete trihydrate—which can dissolve in its own water of crystallization—when tapped. The equilibrium between nitroglycerine and oxygen also illustrates this point. In flow-controlled systems, we might expect any locally optimal steady states $\{\phi_{opt}^*\}$ to be similarly narrowly defined, since they may require special coordination of flows in different domains. Thus although derived by variational means, there is nothing wrong with the minimization of ϕ^* as a selection principle.

The rationale for the analysis of a steady-state system by Jaynes' method is therefore identical—with many of the same caveats—to that for equilibrium systems.

IV. ANALYSIS OF FLOW-CONTROLLED SYSTEMS

A. Control volume analysis

Calculation of the steady-state position of a flow-controlled system can now proceed, first involving a traditional engineering thermodynamic analysis. Consider the control volume shown in Fig. 2, divided into infinitesimal volume elements, each of which is assumed to satisfy the "local equilibrium assumption." This allows the definition of local specific (per unit mass) quantities including specific internal energy u, specific volume ρ^{-1}, specific moles m_c of each species c, and specific entropy s of each element, where ρ is the fluid density, as well as intensive variables such as temperature T, pressure P, and molar chemical potentials μ_c of each species c on its boundary. The elements are thus sufficiently small for local equilibrium to hold, but obviously represent averages over regions large enough to be considered a thermodynamic continuum. In general, for an element subject to the total entropy flux[6] $\boldsymbol{j}_{s,tot}$, the volumetric rate of entropy production within the element (SI units: J K^{-1} m^{-3} s^{-1}) and overall rate of production (J K^{-1} s^{-1}) are [92,105–107]

$$\hat{\dot{\sigma}} = \frac{\partial \rho s}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_{s,tot} \geq 0, \tag{23}$$

$$\dot{\sigma} = \iiint_{CV} \hat{\dot{\sigma}} dV \geq 0, \tag{24}$$

where $\boldsymbol{\nabla}=[\partial/\partial x, \partial/\partial y, \partial/\partial z]^\top$ is the Cartesian gradient operator, $\boldsymbol{a}\cdot\boldsymbol{b}$ is the vector scalar product (dot product), and $\boldsymbol{a}^\top$ is the transpose of $\boldsymbol{a}$. For an element with mean local heat flux $\boldsymbol{j}_Q$, diffusive mass fluxes $\boldsymbol{j}_c$ of each species c (relative to the mass-average velocity $\boldsymbol{v}$ through the element), viscous stress tensor[7] $\boldsymbol{\tau}$, and molar rate per unit volume $\hat{\dot{\xi}}_d$ of each chemical reaction $d=1,\ldots,D$, from the conservation of energy, mass, momentum, and chemical species, the total entropy flux and the rate of entropy production per volume reduce to [92,105–107]

$$\boldsymbol{j}_{s,tot} = \rho s \boldsymbol{v} + \boldsymbol{j}_Q\left(\frac{1}{T}\right) - \sum_{c=1}^{C} \boldsymbol{j}_c \left(\frac{\mu_c}{M_c T}\right), \tag{25}$$

$$\hat{\dot{\sigma}} = \boldsymbol{j}_Q \cdot \boldsymbol{\nabla}\left(\frac{1}{T}\right) - \sum_{c=1}^{C} \boldsymbol{j}_c \cdot \left[\boldsymbol{\nabla}\left(\frac{\mu_c}{M_c T}\right) - \frac{\boldsymbol{g}_c}{T}\right] - \boldsymbol{\tau} : \boldsymbol{\nabla}\left(\frac{\boldsymbol{v}}{T}\right)^\top - \sum_{d=1}^{D} \hat{\dot{\xi}}_d \frac{A_d}{T} \geq 0, \tag{26}$$

where $\mathbf{A}:\mathbf{B}$ is the tensor scalar product, $\boldsymbol{a}\boldsymbol{b}^\top$ is the vector dyadic product (often simply written as $\boldsymbol{a}\boldsymbol{b}$), M_c is the molecular mass of species c, $\boldsymbol{g}_c$ is the specific body force on each species c, and $A_d = \sum_{c=1}^{C} \nu_{cd}\mu_c$ is the molar chemical affinity of reaction d, wherein ν_{cd} is the stoichiometric coefficient of species c in the dth reaction ($\nu_{cd}>0$ for a product and $A_d<0$ denotes spontaneous forward reaction). Alternative formulations of Eq. (26) are available for different situations [105–107]; the present formulation is sufficiently broad for the present discussion.

In engineering modeling, the local mass, momentum, and energy conservation equations and local entropy production (26) are usually nonanalytical and so are calculated on a two- or three-dimensional grid of finite rather than infinitesimal

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[6] We adhere *strictly* to engineering convention: a flow is measured in SI units of quantities s^{-1}, while a flux is expressed in quantities m^{-2} s^{-1}.

[7] The viscous stress tensor $\boldsymbol{\tau}$ is equal to the net or the molecular stress tensor $\boldsymbol{\Pi}$ less the uniform pressure component P, whence $\boldsymbol{\tau} = \boldsymbol{\Pi} - P\boldsymbol{\delta}$, where $\boldsymbol{\delta}$ is the Kronecker delta tensor [105–107]. The stress notation of Bird *et al.* [107] is adopted here, in which $P>0$ and $\tau_{ij}>0$ denote compression.

domains (e.g., by the finite element method) such that the local solutions are self-consistent and match the boundary conditions and source-sink terms of the overall control volume [89,105–108]. This approach assumes that the calculated solution is unique. However, for many flow systems, the entropy production (26) is indeterminate since one or more of the fluxes ($\boldsymbol{j}_Q, \boldsymbol{j}_c$, $\boldsymbol{\tau}$, and $\hat{\dot{\xi}}_d$) and/or gradients [$\boldsymbol{\nabla}(T^{-1})$, $\boldsymbol{\nabla}(\mu_c/T)$, $\boldsymbol{g}_c/T$, $\boldsymbol{\nabla}(\boldsymbol{v}/T)^{\top}$, and A_d/T] across the overall control volume are unknown, there being no principle within equilibrium thermodynamics by which they can be determined. In such cases, Eq. (26) has been solved by assuming the near-equilibrium linear (Onsager) regime, for which closure of the equations can be attained by the use of the equilibrium Gibbs-Duhem relation, Curie postulate, tensor symmetry, and specification of the (linear) mass, momentum, and energy diffusion coefficients [105–107]. Outside the linear regime, such as in turbulent fluid flow, these assumptions can produce serious computational difficulties (e.g., the need for extremely small elements) and are commonly handled by broad simplifications or empirical rules. Indeed, for many flow systems, the entropy production is completely disregarded. Equations (23)–(26) therefore apply to a flow-controlled thermodynamic system at steady state, but in many systems they may not uniquely define the steady state.

B. Jaynes' analysis

We now examine a flow-controlled system from Jaynes' perspective (Sec. II). In general, for an infinitesimal fluid element of a control volume, Jaynes' relations for the steady-state position are exactly those given in Eqs. (4)–(11), but this time with mean flux constraints $\boldsymbol{j}_r$ instead of quantity constraints $\langle f_r \rangle$ (for convenience the $\langle \cdot \rangle$ notation is dropped) and increments in generalized heat fluxes $\delta \boldsymbol{q}_r$ instead of in the generalized heats δQ_r. The Lagrangian multipliers, say ζ_r, will of course be different from those of equilibrium thermodynamics λ_r, conjugate to the flux constraints considered. We should also denote the cross entropy or the entropy by some special symbol, e.g., D_{st} or $\mathfrak{H}_{st}$, to emphasize that it applies to a steady-state system and is quite different to that for an equilibrium system, D_{eq} or $\mathfrak{H}_{eq}$. Our generic analysis of the steady-state position of a flow-controlled system is now complete, requiring only the substitution of relevant parameters for the system under consideration.

Returning to the example of Sec. IV A, we consider that each element can experience instantaneous values of the heat flux $\boldsymbol{j}_{Q,\mathcal{I}}$, the mass fluxes $\boldsymbol{j}_{\mathcal{N}_c}$ of each species c, the stress tensor $\boldsymbol{\tau}_{\mathcal{J}}$, and the reaction rates $\hat{\dot{\xi}}_{\mathcal{L}_d}$, where the indices $\mathcal{I}, \mathcal{J}, \mathcal{L}_d, \mathcal{N}_c$, can (in principle) take any value. The system is constrained by mean values of the heat flux $\boldsymbol{j}_Q$, the mass fluxes $\boldsymbol{j}_c$, the stress tensor $\boldsymbol{\tau}$, and the reaction rates $\hat{\dot{\xi}}_d$ through or within the element and by the natural constraint (2), where expectations are taken with respect to the joint probability $\pi_{\boldsymbol{I}} = \pi_{\mathcal{I},\mathcal{J},\{\mathcal{L}_d\},\{\mathcal{N}_c\}}$ of instantaneous fluxes. As for the equilibrium analysis (Sec. III A) we assume equiprobable states, and thus maximize the Shannon entropy,

$$\mathfrak{H}_{st} = -\sum_{\mathcal{I}=-\infty}^{\infty} \sum_{\mathcal{J}=-\infty}^{\infty} \sum_{\mathcal{L}_1=-\infty}^{\infty} \cdots \sum_{\mathcal{L}_D=-\infty}^{\infty} \sum_{\mathcal{N}_1=-\infty}^{\infty} \cdots \sum_{\mathcal{N}_C=-\infty}^{\infty} \pi_{\boldsymbol{I}} \ln \pi_{\boldsymbol{I}}, \qquad (27)$$

subject to its constraints. From Eqs. (4), (5), and (9),

$$\pi_{\boldsymbol{I}}^{*} = \frac{\beta_{\boldsymbol{I}}^{*}}{\mathcal{Z}^{*}},$$

$$\beta_{\boldsymbol{I}}^{*} = \exp\left(-\boldsymbol{\zeta}_Q \cdot \boldsymbol{j}_{Q,\mathcal{I}} - \sum_{c=0}^{C} \boldsymbol{\zeta}_c \cdot \boldsymbol{j}_{\mathcal{N}_c} - \boldsymbol{\zeta}_{\boldsymbol{\tau}} \colon \boldsymbol{\tau}_{\mathcal{J}} - \sum_{d=1}^{D} \zeta_d \hat{\dot{\xi}}_{\mathcal{L}_d} \right), \qquad (28)$$

$$\mathcal{Z}^{*} = e^{\zeta_0^{*}} = \sum_{\mathcal{I}=-\infty}^{\infty} \sum_{\mathcal{J}=-\infty}^{\infty} \sum_{\mathcal{L}_1=-\infty}^{\infty} \cdots \sum_{\mathcal{L}_D=-\infty}^{\infty} \sum_{\mathcal{N}_1=-\infty}^{\infty} \cdots \sum_{\mathcal{N}_C=-\infty}^{\infty} \beta_{\boldsymbol{I}}^{*},$$

$$\mathfrak{H}_{st}^{*} = \ln \mathcal{Z}^{*} + \boldsymbol{\zeta}_Q \cdot \boldsymbol{j}_Q + \sum_{c=1}^{C} \boldsymbol{\zeta}_c \cdot \boldsymbol{j}_c + \boldsymbol{\zeta}_{\boldsymbol{\tau}} : \boldsymbol{\tau} + \sum_{d=1}^{D} \zeta_d \hat{\dot{\xi}}_d, \qquad (29)$$

$$d\mathfrak{H}_{st}^{*} = \boldsymbol{\zeta}_Q \cdot \delta \boldsymbol{q}_Q + \sum_{c=1}^{C} \boldsymbol{\zeta}_c \cdot \delta \boldsymbol{q}_c + \boldsymbol{\zeta}_{\boldsymbol{\tau}} : \delta \mathbf{q}_{\boldsymbol{\tau}} + \sum_{d=1}^{D} \zeta_d \delta q_d, \qquad (30)$$

where the multipliers $\boldsymbol{\zeta}_Q$, $\boldsymbol{\zeta}_c$, $\boldsymbol{\zeta}_{\boldsymbol{\tau}}$, and ζ_d are associated with the heat, the species, the stress tensor, and the reaction constraints ($\boldsymbol{\zeta}_Q$ and $\boldsymbol{\zeta}_c$ are vectors and $\boldsymbol{\zeta}_{\boldsymbol{\tau}}$ is a second-order tensor); $\delta \boldsymbol{q}_Q$, $\delta \boldsymbol{q}_c$, $\delta \mathbf{q}_{\boldsymbol{\tau}}$, and δq_d are the corresponding changes in generalized heat fluxes; ζ_0^{*} is the Massieu function; and $\mathcal{Z}^{*} = e^{\zeta_0^{*}}$ the partition function. We see that $\mathfrak{H}_{st}^{*}$ is a dimensionless flux entropy. Equations (11), (29), and (30) then give the change in a generalized potential function for steady-state systems as follows:

$$\begin{aligned} d\phi_{st}^{*} &= -d\zeta_0^{*} = -d \ln \mathcal{Z}^{*} \\ &= -d\mathfrak{H}_{st}^{*} + \boldsymbol{\zeta}_Q \cdot d\boldsymbol{j}_Q + \sum_{c=1}^{C} \boldsymbol{\zeta}_c \cdot d\boldsymbol{j}_c + \boldsymbol{\zeta}_{\boldsymbol{\tau}} : d\boldsymbol{\tau} + \sum_{d=1}^{D} \zeta_d d\hat{\dot{\xi}}_d \\ &\quad + d\boldsymbol{\zeta}_Q \cdot \boldsymbol{j}_Q + \sum_{c=1}^{C} d\boldsymbol{\zeta}_c \cdot \boldsymbol{j}_c + d\boldsymbol{\zeta}_{\boldsymbol{\tau}} : \boldsymbol{\tau} + \sum_{d=1}^{D} d\zeta_d \hat{\dot{\xi}}_d. \end{aligned} \qquad (31)$$

Again—with Gibbs—we could exclude a net change in the multipliers ζ_r, giving $d\phi_{st}^{*}|_{\{\zeta_r\}} = \Sigma_{r=1}^{R} \zeta_r \delta \boldsymbol{w}_r$, where $\delta \boldsymbol{w}_r$ are changes in generalized work fluxes, in addition to those incorporated by other constraints. However, as with equilibrium systems (Sec. III A), we wish to consider all possible variations of ϕ_{st}^{*}. Integration of Eq. (31), from the zero-flux zero-multiplier (equilibrium) position $\phi_{st0}^{*} = -\mathfrak{H}_{st0}^{*}$ yields

$$\phi_{st}^{*} = -\mathfrak{H}_{st}^{*} + \boldsymbol{\zeta}_Q \cdot \boldsymbol{j}_Q + \sum_{c=1}^{C} \boldsymbol{\zeta}_c \cdot \boldsymbol{j}_c + \boldsymbol{\zeta}_{\boldsymbol{\tau}} : \boldsymbol{\tau} + \sum_{d=1}^{D} \zeta_d \hat{\dot{\xi}}_d. \qquad (32)$$

This is the steady-state analog of the equilibrium generalized potential ϕ_{eq}^{*}. Relations (28)–(32) apply only to quasistatic transitions "on the manifold of steady-state positions." However, in this case—since this is a flow system—they always involve irreversible processes.

C. Synthesis

We can now combine the control volume (Sec. IV A) and the Jaynesian (Sec. IV B) analyses of the example problem (Fig. 2). Since the fluxes in Eqs. (26) and (32) are linearly independent (not necessarily orthogonal), it is possible to equate similar terms, giving the following identities:

$$\phi^*_{st} = -\mathfrak{H}^*_{st} - \frac{\theta\mathcal{V}}{k}\hat{\dot{\sigma}}, \tag{33}$$

$$\boldsymbol{\zeta}_Q = -\frac{\theta\mathcal{V}}{k}\nabla\left(\frac{1}{T}\right), \tag{34}$$

$$\boldsymbol{\zeta}_c = \frac{\theta\mathcal{V}}{k}\left[\nabla\left(\frac{\mu_c}{M_c T}\right) - \frac{\mathbf{g}_c}{T}\right], \tag{35}$$

$$\boldsymbol{\zeta}_{\boldsymbol{\tau}} = \frac{\theta\mathcal{V}}{k}\nabla\left(\frac{\boldsymbol{v}}{T}\right)^{\top}, \tag{36}$$

$$\zeta_d = \frac{\theta\mathcal{V}}{k}\frac{A_d}{T}, \tag{37}$$

where θ and $\mathcal{V}$, respectively, are characteristic time and volume scales for the system considered, which emerge from the fact that ϕ^*_{st}, $\mathfrak{H}^*_{st}$, and each product in Eq. (32) must be dimensionless.[8,9]

From Eq. (33) and the foregoing analysis (Secs. II and III A), if the flow-controlled system contains some process(es) which dissipate its generalized potential ϕ^*_{st}, it will move by increments,

$$d\phi^*_{st} = -d\mathfrak{H}^*_{st} - \frac{\theta\mathcal{V}}{k}\delta\hat{\dot{\sigma}} \leq 0 \tag{38}$$

until it converges to a final steady-state position given by $d\phi^*_{st}=0$, hence at minimum ϕ^*_{st}. Equation (38) is analogous to Eq. (20) for equilibrium systems, accounting for the loss of generalized potential within and outside the system. If $d\mathfrak{H}^*_{st} \geq 0$ and $\delta\hat{\dot{\sigma}} \geq 0$, the steady-state position $\phi^*_{st} = \phi^*_{st,\min}$ will correspond to the position of maximum entropy production $\hat{\dot{\sigma}} = \hat{\dot{\sigma}}_{\max}$. The analysis therefore provides a theoretical justification for a local form of the MEP principle, conditional on the assumption that incremental increases in $\mathfrak{H}^*_{st}$ and $\hat{\dot{\sigma}}$ are unrecoverable. As with equilibrium systems (Sec. III A), the dissipation may be confined to a constant-multiplier $\{\zeta_r\}$, constant-constraint $\{\boldsymbol{j}_r\}$, or mixed constraint path, leading to a local (path-dependent) minimum $\phi^*_{st,\min}$ or may be free to choose its own path, whereupon it will attain a global minimum.

Processes for which $\delta\hat{\dot{\sigma}} > 0$ (to which the MEP principle applies) are here termed *exoentropogenic*,[10] since they result in the production of entropy and its export to the rest of the universe. Exoentropogenic processes are one class of processes leading to the formation of steady-state flow systems, in the same way that *exothermic* reactions—in which the heat $\delta Q < 0$—are one class of processes which generate equilibrium systems. It is left as an open question here whether exoentropogenic processes (and hence the MEP principle) are universal in application, or are merely an important class of processes applicable to flow systems at steady state.

D. Implications

The analysis has several important implications. First, under conditions in which the MEP principle applies, from Eqs. (26) and (33):

(i) If the fluxes or rates $\boldsymbol{j}_Q$, $\boldsymbol{j}_c$, $\boldsymbol{\tau}$, and $\hat{\dot{\xi}}_d$ in Eq. (26) are indeed constant, the system will achieve MEP by maximizing the magnitudes of the gradients or forces $|\nabla(T^{-1})|$, $|\nabla(\mu_c/T)|$, $|\boldsymbol{g}_c/T|$, $|\nabla(\boldsymbol{v}/T)^{\top}|$, and $|A_d/T|$ across or within each element, each weighted by its conjugate flux term. Since the gradients can be interpreted as measures of disequilibrium of the system, we see that a flow-controlled system is driven to a steady-state position of *maximum disequilibrium*.

(ii) If, on the other hand, the gradients or forces $\nabla(T^{-1})$, $\nabla(\mu_c/T)$, $\boldsymbol{g}_c/T$, $\nabla(\boldsymbol{v}/T)^{\top}$, and A_d/T in Eq. (26) are fixed, the system will be driven to maximize the fluxes or rates $\boldsymbol{j}_Q$, $\boldsymbol{j}_c$, $\boldsymbol{\tau}$, and $\hat{\dot{\xi}}_d$, again in the form of a weighted sum. In other words, the most probable response of a system to gradients or forces in one or more intensive variables λ_r is *the occurrence of flow* of the corresponding physical quantities f_r, at their maximum mean flow rates. This is also consistent with maximum disequilibrium of the system.

The distinction between fixed flux $\boldsymbol{j}_r$ (Neumann) and intensive variable gradient $\nabla\lambda_r$ (Dirichlet) boundary conditions is well known in the solution of differential equations. In the MaxEnt analysis of a steady-state system, the choice between such boundary conditions plays exactly the same role as the choice between fixed content $\langle f_r \rangle$ and intensive variable λ_r constraints in an equilibrium system or, in other words, between corresponding microcanonical and canonical representations. Although the two representations within each pair are different, the mathematical apparatus used to examine either set of constraints is the same (c.f. [45]). Flow-controlled systems can also be subject to composite flux-gradient (Robin) boundary conditions, or a mixed set of conditions, giving rise to steady states which have no equi-

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[8] An alternative view, not considered further here, is to interpret $(\theta\mathcal{V}/k)(\boldsymbol{g}_c/T)\cdot\boldsymbol{j}_c$ as a generalized work flux, which must be subtracted from a redefined generalized heat flux $\delta\boldsymbol{q}'_{j_c} = (\theta\mathcal{V}/k)\nabla(\mu_c/M_c T)\cdot\boldsymbol{j}_c$.

[9] Note that $\theta\mathcal{V}$ has SI units of m^3 s, equivalent to a four-dimensional space-time element, or action divided by pressure.

[10] From ancient Greek: *exo-*, outer or external (obverse *endo-*, within or internal); *tropos*, transformation (used by Clausius [81]); and *-genic*, generating or producing.

librium analog in quantity-constrained systems.

To achieve maximum $\hat{\sigma}$ in Eq. (26), the conjugate vectorial fluxes and gradients should be collinear. A consequence of the MEP principle is that the free fluxes or gradients will try to orient themselves to attain collinearity, to the maximum extent allowable by competition between different flows and/or by anisotropy within the system (e.g., due to the velocity gradient). Similarly, the system will endeavor to align its principal stresses with the principal directions of the velocity gradient. This may provide an explanation for the many simplifications used in control volume analysis, such as tensor symmetry.

While Eq. (26) is in differential form, in systems with simple boundary conditions it may be possible to apply its finite difference approximation to much larger domains. This appears to be the case for the Earth climate system, which has been analyzed (on a whole-Earth scale) using simple two-box or ten-box models [1–13]. The analysis also indicates MEP to be a local principle, which need not apply to the universe as a whole. Only the entropy production of a system—not the entire universe—is maximized, since it is only within a system that there exist mechanisms by which the MEP state can be attained. This is a characteristic feature of previous applications of the MEP principle, which has incited much debate [1–4,9,11,40].

Tidying up the analysis, Eqs. (33)–(37) can be substituted into Eqs. (28)–(32). Steady-state analogs of the four laws of equilibrium thermodynamics can also be obtained from Jaynes' approach [49,50], as set out in Appendix B. We can also consider the set of multiplier relations (6), variances (7), and covariances (8) for steady-state systems, examined further in Appendix C. The analysis therefore provides a set of *testable* laws and transport relations for the behavior of steady-state thermodynamic systems. Furthermore, as shown in Appendix C, the Onsager linear regime emerges as a first-order approximation to the analysis, in the vicinity of equilibrium. The analysis therefore provides a general mathematical formalism for the analysis of flow systems—including nonequilibrium thermodynamic systems—both near and far from equilibrium.

This is as far as our comparative analysis of steady-state thermodynamics can take us, using the parameters of equilibrium thermodynamics, and it is important that it not be taken too far. For example, in many systems the local equilibrium assumption—which forces the MEP principle to adopt a local formulation—may be too restrictive; such considerations lead into the domain of more complicated approaches, such as extended irreversible thermodynamics [109,110]. For more comprehensive treatments, it may be necessary to abandon the connection with equilibrium parameters and conduct the steady-state analysis using the "raw" Lagrangian multipliers ζ_r—or some functions thereof—obtained directly by MinXEnt. The raw multipliers (the "ideal" gradients) could then be correlated with the actual gradients by *gradient coefficients*, analogous to the activity and the fugacity coefficients of equilibrium thermodynamics. In some systems, it may even be necessary to adopt process- and direction-specific time and volume scales $\theta_{r\imath\mathrm{J}}$ and $\mathcal{V}_{r\imath\mathrm{J}}$ (possibly also varying with position), leading to weighted scales θ_{sys} and $\mathcal{V}_{sys}$ for the system as a whole. The analysis extends naturally to further developments, for example, the use of a "local steady-state assumption" in the analysis of transient phenomena. This leads into a higher-order theory of acceleration phenomena, in which a maximum is sought in the sum of products of accelerative transport terms $\partial \boldsymbol{j}_r/\partial t$ and gradients of the gradients $\boldsymbol{\nabla}\boldsymbol{\zeta}_r^{\top}$ (a conditional maximum $\hat{\sigma}$ principle) [111], an idea best examined elsewhere.

V. DISCUSSION

The foregoing analysis would be incomplete without a brief account of its implications. From Sec. IV, MEP emerges as a local, conditional principle, in which each local control volume behaves as an *actor* or *agent* which seeks to minimize its generalized potential ϕ_{st}^{*} and hence (conditionally) to maximize its local entropy production. This provides a driving force for the formation and the reinforcement of "emergent" self-organization of the system as a whole, since by such "cooperative federalism," each local "selfish" control volume can achieve much higher entropy production than it could of its own volition. We therefore see that the MEP principle drives the formation of *structure* and *function*. Of course, this does not in any way preclude the development of *competition* between control volumes—or even between associations of control volumes or entire systems—for a greater share of generalized potential; such competitive forces are certainly well known to us. These twin effects, a predominant higher level cooperation and a lower level (but occasionally overwhelming) competition, are the hallmark of the "dynamic steady state" of a dissipative flow-controlled system.

The analysis therefore confirms a number of aspects of the philosophy of Prigogine and co-workers on nonequilibrium dissipative systems [92,93,112,113], even though his "minimum entropy production principle" (valid only in the linear regime) is quite different [11,39]. It also provides an explanation for the "constructal law" of Bejan [114]: "for a finite size flow system to persist in time (to survive) its configuration must evolve… [to] provide easier and easier access to the currents that flow through it." Furthermore, it confirms the essence of the (nonmathematical) gradient theory of Schneider and Sagan [115], who argued that "nature abhors a gradient," i.e., the occurrence of flow is a natural response to a physical gradient.

Finally, the analysis goes to the heart of the "riddle of life" posed by many scientists (e.g., [116,117]), concerning the perceived contradiction between the second law of thermodynamics and the existence of life. To recap, it is one thing to suggest that life *can* form, in that its ability to increase the thermodynamic entropy of the universe exceeds the reduction in entropy associated with its structure. But if life were merely an accident—a fluctuation—why should it not just die out? Why should it be so resilient to extreme events, as evidenced by its regrowth after the many mass-extinction episodes in the history of the Earth? As shown, the existence and the evolution of life are driven by a deeper, purely probabilistic form of the second law [71]:

"A system tends toward its most probable form."

This "MaxProb" principle [66–71], applied to an isolated or an open dissipative equilibrium system, drives the system toward the equilibrium position $\mathfrak{H}_{eq}^*$ or S^* of minimum generalized potential ϕ_{eq}^* (e.g., minimum free energy F^*, G^*, or J^*) since this is more probable than other forms of the system. In contrast, in a flow system it provides a driving force for the formation of complex dissipative structures, including life, to attain the local steady-state position $\mathfrak{H}_{st}^*$ of minimum generalized potential ϕ_{st}^*, hence (conditionally) of maximum $\hat{\sigma}$, since this position—not the equilibrium position—is more probable than other realizations of the system. The above probabilistic statement of the second law therefore contains within it both a "force of death" and a "force of life," associated, respectively, with constraints on the mean contents $\langle f_r \rangle$ or fluxes $\langle \boldsymbol{j}_r \rangle$ (or their corresponding multipliers). It also implies a surprising inevitability to the evolution of life in a flow-controlled system, whenever the conditions are suitable, and indeed, of other complex systems such as fluid turbulence, biological and ecological structures, transport and communications networks, economic systems, and human (or sentient) civilization.

VI. CONCLUSIONS

In this study, a clear distinction is made between (i) *quantity-controlled systems*, constrained by a set of mean physical quantities $\langle f_r \rangle$ and/or their corresponding multipliers λ_r, which converge toward an *equilibrium* position, and (ii) *flow-controlled systems*, as defined by a control volume (the Eulerian description), constrained by a set of mean fluxes $\langle \boldsymbol{j}_r \rangle$ and/or their corresponding multipliers ζ_r, which converge toward a *steady-state position*. A theory to determine the steady-state position of a flow-controlled thermodynamic system is derived using the generic MaxEnt principle of Jaynes [45–51,65]. The analysis is shown to yield a local, conditional form of the MEP principle. It also yields steady-state analogs of the four laws of equilibrium thermodynamics, and sets of multiplier, variance, and covariance (Maxwell-like) relations applicable to flow-controlled systems at steady state. The derivation is limited to reproducible flow-controlled systems, but does not appear to be restricted to the near-equilibrium linear regime; indeed, the latter can be recovered as a special case (see Appendix C). The analysis reveals a very different manifestation of the second law of thermodynamics in steady-state systems, which provides a driving force for the formation of complex dissipative systems, including life.

Further work is required on the scope of the present analysis, and the relationship between concepts developed here and those of others, e.g., between the steady-state generic entropy $\mathfrak{H}_{st}^*$, the path-based entropies of Dewar [43,44] and Attard [56,57], and the quantum formulation of Beretta [58–61]. Greater attention should also be paid to the tremendous power of the MinXEnt/MaxEnt method pioneered by Jaynes [45–51] and its combinatorial (probabilistic) basis [66–71].

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APPENDIX A: TERMINOLOGY

From the foregoing discussion (especially Secs. II–IV), it is evident that there are difficulties in terminology concerning the negative Massieu function $\phi^* = -\lambda_0^* = -\ln Z_q^*$. Although described herein as a free-energy-like concept or generalized potential, from Eq. (5) it has more in keeping with an entropy-related quantity. In equilibrium systems, ϕ_{eq}^* is usually multiplied by kT to give the free energy; but as shown in Sec. III A, it is more appropriate to multiply it by k to avoid complications with changes in the intensive variables. The free-energy concept of Gibbs [83], designed purely for changes in the extensive variables, is thus less versatile than the slightly older concept of Massieu [76], adopted by many well-known thermodynamicists (c.f. [77,95,97–100]) for this reason. Concepts related to the free energy, such as essergy and exergy [84–89], suffer from the same disadvantage (a further disadvantage is their need for an unchanging reference system). In steady-state systems, we could multiply ϕ_{st}^* by $kT/\theta\mathcal{V}$ to give the "free power" or by $k/\boldsymbol{\nabla}(T^{-1})\theta\mathcal{V}$ to give a flux analog, but neither choice makes much sense and would involve the same awkwardness in the handling of intensive variables as does the free energy. If ϕ_{st}^* must have units, it is preferable to multiply it by $k/\theta\mathcal{V}$ to give it the same units as $\hat{\sigma}$; being of opposite sign, we could call this (as would Gibbs [82]) the "available capacity for entropy production" or (as would Brillouin [118]) the "free negentropy production." Provided that the dissipative processes are macroscopically reproducible, the fact that this quantity has entropy units (a nonconserved quantity) instead of energy units (a conserved quantity) will not affect its application.

APPENDIX B: STEADY-STATE "LAWS"

Steady-state analogs of the laws of equilibrium thermodynamics are readily obtainable from Jaynes' generic approach [49,50].[11] Although unsurprising, they are included here for completeness. First, two control volumes which are joined (side by side) such that their fluxes are combined (i.e., $\langle \boldsymbol{j}_m \rangle_{tot} = \langle \boldsymbol{j}_m \rangle_1 + \langle \boldsymbol{j}_m \rangle_2$ for $\langle \boldsymbol{j}_m \rangle \in \{\langle \boldsymbol{j}_r \rangle\}$) will attain a steady-state

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[11] Tribus [49] would distinguish them as "laws of thermostatics" and "laws of thermodynamics."

position of identical multipliers $\{\zeta_m\}$ and so will share common mth gradients; this is the zeroth law. The first law is simply a definition of generalized heat and work for the flux of a conserved quantity, which at steady state is given by $d\langle \boldsymbol{j}_r\rangle = \delta \boldsymbol{q}_r + \delta \boldsymbol{w}_r$; thus, $\delta \boldsymbol{q}_r$ gives a (spontaneous) change in the distribution of instantaneous fluxes, while $\delta \boldsymbol{w}_r$ represents a (recoverable) change in the instantaneous fluxes themselves. The second law can be stated in many ways (see Sec. V); in a state function sense, it is given by the generalized Clausius equality (30). The third law—arguably more of a definition of a convenient reference state—can be stated as "the steady-state entropy $\mathfrak{H}_{st}^*$ approaches zero at the position of zero gradients," i.e., when it relaxes to an equilibrium position.

APPENDIX C: JAYNES' RELATIONS

In linear transport theory, it is common to employ the so-called "Curie postulate," in which the scalar, the vector, or the tensor fluxes j_r, $\boldsymbol{j}_r$, or $\mathbf{j}_r$ are assumed to depend on forces or gradients of the same type $\Delta\lambda_r$, $\boldsymbol{\nabla}\lambda_r$ or $\boldsymbol{\nabla}\boldsymbol{\lambda}_r^{\top}$, but not on those of other types [105–107,119]. This postulate cannot be assumed to apply in general. In consequence, Jaynes' relations (6)–(8) and higher derivatives for scalar and each com-

TABLE II. Multiplier relations (C1), variances (C2), and covariances (C3) for the steady-state thermodynamic system of Fig. 2, at steady state (here $K=\theta\mathcal{V}/k$, while subscripts b and e, respectively, imply $b\neq c$ and $e\neq d$). The parameters held constant in each partial derivative can be judged by context.

Multiplier relations

$$-\langle j_{Q\iota}\rangle = -\frac{\partial \zeta_0^*}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$-\langle j_{c\iota}\rangle = \frac{\partial \zeta_0^*}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$-\langle \tau_{\iota\jmath}\rangle = \frac{\partial \zeta_0^*}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{v_\jmath}{T}\right)\right]}$$

$$-\langle \hat{\dot{\xi}}_d\rangle = \frac{\partial \zeta_0^*}{\partial\left(K\dfrac{A_d}{T}\right)}$$

Variances

$$\mathrm{var}(j_{Q\iota}) = \frac{\partial\langle j_{Q\iota}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$\mathrm{var}(j_{c\iota}) = -\frac{\partial\langle j_{c\iota}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$\mathrm{var}(\tau_{\iota\jmath}) = -\frac{\partial\langle \tau_{\iota\jmath}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{v_\jmath}{T}\right)\right]}$$

$$\mathrm{var}(\hat{\dot{\xi}}_d) = -\frac{\partial\langle \hat{\dot{\xi}}_d\rangle}{\partial\left(K\dfrac{A_d}{T}\right)}$$

Covariances (Maxwell-like relations)

$$\mathrm{cov}(j_{Q\iota},j_{Q\jmath}) = \frac{\partial\langle j_{Q\iota}\rangle}{\partial\left[K\dfrac{\partial}{\partial\jmath}\left(\dfrac{1}{T}\right)\right]} = \frac{\partial\langle j_{Q\jmath}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$\mathrm{cov}(j_{Q\iota},j_{c\kappa}) = \frac{\partial\langle j_{Q\iota}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\kappa}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\kappa}}{T}\right]\right]} = -\frac{\partial\langle j_{c\kappa}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$\mathrm{cov}(j_{Q\iota},\tau_{\kappa\ell}) = \frac{\partial\langle j_{Q\iota}\rangle}{\partial\left[K\dfrac{\partial}{\partial\kappa}\left(\dfrac{v_\ell}{T}\right)\right]} = -\frac{\partial\langle \tau_{\kappa\ell}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$\mathrm{cov}(j_{Q\iota},\hat{\dot{\xi}}_d) = \frac{\partial\langle j_{Q\iota}\rangle}{\partial\left(K\dfrac{A_d}{T}\right)} = -\frac{\partial\langle \hat{\dot{\xi}}_d\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{1}{T}\right)\right]}$$

$$\mathrm{cov}(j_{c\iota},j_{c\jmath}) = -\frac{\partial\langle j_{c\iota}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\jmath}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\jmath}}{T}\right]\right]} = -\frac{\partial\langle j_{c\jmath}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$\mathrm{cov}(j_{c\iota},j_{b\kappa}) = -\frac{\partial\langle j_{c\iota}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\kappa}\left(\dfrac{\mu_b}{M_bT}\right)-\dfrac{g_{b\kappa}}{T}\right]\right]} = -\frac{\partial\langle j_{b\kappa}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$\mathrm{cov}(j_{c\iota},\tau_{\kappa\ell}) = -\frac{\partial\langle j_{c\iota}\rangle}{\partial\left[K\dfrac{\partial}{\partial\kappa}\left(\dfrac{v_\ell}{T}\right)\right]} = -\frac{\partial\langle \tau_{\kappa\ell}\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$\mathrm{cov}(j_{c\iota},\hat{\dot{\xi}}_d) = -\frac{\partial\langle j_{c\iota}\rangle}{\partial\left(K\dfrac{A_d}{T}\right)} = -\frac{\partial\langle \hat{\dot{\xi}}_d\rangle}{\partial\left[K\left[\dfrac{\partial}{\partial\iota}\left(\dfrac{\mu_c}{M_cT}\right)-\dfrac{g_{c\iota}}{T}\right]\right]}$$

$$\mathrm{cov}(\tau_{\iota\jmath},\tau_{\kappa\ell}) = -\frac{\partial\langle \tau_{\iota\jmath}\rangle}{\partial\left[K\dfrac{\partial}{\partial\kappa}\left(\dfrac{v_\ell}{T}\right)\right]} = -\frac{\partial\langle \tau_{\kappa\ell}\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{v_\jmath}{T}\right)\right]}$$

$$\mathrm{cov}(\tau_{\iota\jmath},\hat{\dot{\xi}}_d) = -\frac{\partial\langle \tau_{\iota\jmath}\rangle}{\partial\left(K\dfrac{A_d}{T}\right)} = -\frac{\partial\langle \hat{\dot{\xi}}_d\rangle}{\partial\left[K\dfrac{\partial}{\partial\iota}\left(\dfrac{v_\jmath}{T}\right)\right]}$$

$$\mathrm{cov}(\hat{\dot{\xi}}_d,\hat{\dot{\xi}}_e) = -\frac{\partial\langle \hat{\dot{\xi}}_d\rangle}{\partial\left(K\dfrac{A_e}{T}\right)} = -\frac{\partial\langle \hat{\dot{\xi}}_e\rangle}{\partial\left(K\dfrac{A_d}{T}\right)}$$

ponent of vector and tensor multipliers in a steady-state system will be of generalized form

$$\frac{\partial \zeta_0^*}{\partial \zeta_{r\imath\jmath}} = -\langle j_{r\imath\jmath}\rangle, \tag{C1}$$

$$\frac{\partial^2 \zeta_0^*}{\partial \zeta_{r\imath\jmath}^2} = \langle j_{r\imath\jmath}^2\rangle - \langle j_{r\imath\jmath}\rangle^2 = -\frac{\partial\langle j_{r\imath\jmath}\rangle}{\partial \zeta_{r\imath\jmath}}, \tag{C2}$$

$$\frac{\partial^2 \zeta_0^*}{\partial \zeta_{m\kappa\ell}\,\partial\,\zeta_{r\imath\jmath}} = \langle j_{r\imath\jmath} j_{m\kappa\ell}\rangle - \langle j_{r\imath\jmath}\rangle\langle j_{m\kappa\ell}\rangle = -\frac{\partial\langle j_{r\imath\jmath}\rangle}{\partial \zeta_{m\kappa\ell}} = -\frac{\partial\langle j_{m\kappa\ell}\rangle}{\partial \zeta_{r\imath\jmath}}, \tag{C3}$$

$$\begin{aligned}\frac{\partial^2 \zeta_0^*}{\partial \zeta_{n\varphi\vartheta}\,\partial\,\zeta_{m\kappa\ell}\,\partial\,\zeta_{r\imath\jmath}} &= -\frac{\partial\langle j_{r\imath\jmath}\rangle}{\partial \zeta_{n\varphi\vartheta}\,\partial\,\zeta_{m\kappa\ell}} = -\frac{\partial\langle j_{m\kappa\ell}\rangle}{\partial \zeta_{n\varphi\vartheta}\,\partial\,\zeta_{r\imath\jmath}}\\ &= -\frac{\partial\langle j_{n\varphi\vartheta}\rangle}{\partial \zeta_{r\imath\jmath}\,\partial\,\zeta_{m\kappa\ell}},\end{aligned} \tag{C4}$$

$$\vdots$$

where the expectation notation $\langle\cdot\rangle$ is reinstated; $\imath,\jmath,\kappa,\ell,\varphi,\vartheta\in\{x,y,z\}$ (with $\jmath,\ell,\vartheta$ redundant for vectors and all directions redundant for scalars). Each partial derivative is taken at constant other Lagrangian multipliers.

Relations (C1)–(C3) for the example system (Fig. 2) are listed in Table II. Analogous to those in Table I, the identities in Table II apply only at steady state, i.e., they describe quasistatic transitions on the manifold of steady-state positions. Note that these relations do not impose tensor symmetry, e.g., $\partial\langle\tau_{\imath\jmath}\rangle/\partial\zeta_{\tau_{\jmath\imath}}=\partial\langle\tau_{\jmath\imath}\rangle/\partial\zeta_{\tau_{\imath\jmath}}$ does not imply $\langle\tau_{\imath\jmath}\rangle=\langle\tau_{\jmath\imath}\rangle$ unless $\zeta_{\tau_{\imath\jmath}}=\zeta_{\tau_{\jmath\imath}}$.

Furthermore, each flux can be expanded in a Taylor series about the zero-multiplier (equilibrium) position $\langle j_{r\imath\jmath}\rangle|_{\{\zeta_r=0\}}=0$ (see Appendix B), yielding [77]

$$\langle j_{r\imath\jmath}\rangle = \sum_{m\kappa\ell} L^0_{r\imath\jmath,m\kappa\ell}\zeta_{m\kappa\ell} + \frac{1}{2!}\sum_{m\kappa\ell}\sum_{n\varphi\vartheta} L^0_{r\imath\jmath,m\kappa\ell,n\varphi\vartheta}\zeta_{m\kappa\ell}\zeta_{n\varphi\vartheta} + \cdots \tag{C5}$$

with the equilibrium-limit derivatives

$$L^0_{r\imath\jmath,m\kappa\ell} = \left.\frac{\partial\langle j_{r\imath\jmath}\rangle}{\partial\zeta_{m\kappa\ell}}\right|_{\{\zeta_r=0\}},$$

$$L^0_{r\imath\jmath,m\kappa\ell,n\varphi\vartheta} = \left.\frac{\partial^2\langle j_{r\imath\jmath}\rangle}{\partial\zeta_{m\kappa\ell}\,\partial\,\zeta_{n\varphi\vartheta}}\right|_{\{\zeta_r=0\}}.$$

Close to equilibrium, this can be approximated by discarding all but the first-order terms

$$\langle j_{r\imath\jmath}\rangle \approx \sum_{m\kappa\ell} L^0_{r\imath\jmath,m\kappa\ell}\zeta_{m\kappa\ell}. \tag{C6}$$

By the use of Jaynes' method, we therefore recover the near-equilibrium linear regime (C6) with, from Eq. (C3), the Onsager reciprocal relations $L^0_{r\imath\jmath,m\kappa\ell}=L^0_{m\kappa\ell,r\imath\jmath}$ [54,55]. For simple boundary conditions, these relations may apply to the overall system as well as at local scales. However, the analysis goes well beyond Onsager's, indicating that the reciprocal relations (C3) and higher derivatives [Eq. (C4) and onward] also apply well away from equilibrium, at least when expressed in terms of the raw multipliers (see Sec. IV D) at local scales, although they will not then enter into expansions (C5) and (C6). Of course, expansion (C5) [hence Eq. (C6)] will become more and more inaccurate with increasing distance from equilibrium, even if successively higher-order terms are included. From Eq. (C4) and onward, each set of higher-order derivatives will also obey a symmetry relation, both near and far from equilibrium.

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