GENERAL CHARACTERISTICS OF ENTROPY PRODUCTION IN NONLINEAR DYNAMIC SYSTEMS

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ABSTRACT

A basic expression for entropy production due to irreversible flux of heat or momentum is formulated together with balance equations for energy and momentum in a fluid system. It is shown that entropy production always decreases with time when the system is of a pure diffusion type without advection of heat or momentum. The minimum entropy production (MinEP) property is thus intrinsic to a pure diffusion-type system. However, this MinEP property disappears when the system is subject to advection of heat or momentum. When the rate of advection exceeds the rate of diffusion, entropy production tends to increase over time. A simple stability analysis shows that the rate of change of entropy production is proportional to the growth rate of an arbitrary external perturbation. The entropy production increases when the perturbation grows in the system under a dynamically unstable state, whereas it decreases when the perturbation is damped in the system in a stable state. The maximum entropy production (MaxEP) can therefore be understood as a characteristic feature of systems with dynamic instability. Implications of the result for time evolution of nonlinear dynamic phenomena under different external conditions are discussed from this thermodynamic viewpoint.

INTRODUCTION

Since an early investigation by Ziegler [1], maximum entropy production (MaxEP) has been suggested as a general thermodynamic property of nonlinear non-equilibrium phenomena, with later studies showing that the MaxEP state is consistent with steady states of a variety of nonlinear phenomena. These include the general circulation of the atmosphere and oceans [2–4], thermal convection [5], turbulent shear flow [6], climates of other planets [7], oceanic general circulation [8, 9], crystal growth morphology [10] and granular flows [11]. While the underlying physical mechanism is still debated, the MaxEP state is shown to be identical to a state of maximum generation of available energy [12, 13]. Moreover, recent theoretical studies suggest that the MaxEP state is the most probable state that is realized by non-equilibrium systems [14, 15].

It is known, however, that entropy production in a linear process tends to decrease with time and reach a minimum in a final steady state when a thermodynamic intensive variable (such as temperature) is fixed at the system boundary. This tendency was first suggested for a linear chemical process in a discontinuous system by Prigogine [16], and then extended to the case of a linear diffusion process in a continuous system [17]. Since then, this minimum entropy production (MinEP) principle has become widely known in the field of non-equilibrium thermodynamics. Although a number of attempts have been made to extend this MinEP principle to a general one including nonlinear processes, the results remain controversial and inconclusive (e.g. [18, 19]). In fact, Prigogine [20] noted that “it came as a great surprise when it was shown that in systems far from equilibrium the thermodynamic behavior could be quite different — in fact, even *directly opposite* that predicted by the theorem of minimum entropy production”.

Sawada [21] pointed out the limitations of the MinEP principle, and instead proposed the MaxEP principle as a general variational principle for nonlinear systems that are far from equilibrium. Dewar and Maritan [22] showed using Jaynes’s maximum entropy method that a state of minimum dissipation (MinEP) is selected for a system without dynamic instability, whereas that of maximum dissipation (MaxEP) is selected for a system with dynamic instability. It seems therefore that the existence of dynamic instability plays a key role in determining the behavior of entropy production in nonlinear non-equilibrium systems. However, the nature of the dynamic instability as well as its relation to nonlinearity remains unclear. Moreover, until now, we do not have a reasonable specification of the dynamic conditions under which the MinEP or MaxEP state is realized.

In order to clarify the issues in the phenomena mentioned above, we have investigated the behavior of time evolution of entropy production in a fluid system. Based on a general expression of entropy production and balance equations of energy and momentum, we present a condition under which the MinEP state is realized in the course of time in a system of linear diffusion. We then add nonlinear advection terms in the balance equations, and examine the condition under which the MinEP state becomes unstable and the MaxEP state is realized in the system. We show that the rate of advection of heat or momentum plays an important role in the enhancement of entropy production in a fluid system that possesses dynamic instability. Results obtained from this study are summarized, and a few remarks are presented concerning time evolution of nonlinear dynamic phenomena under different external conditions. This study is an extention of our previous work on thermodynamic properties of dynamic fluid systems by Ozawa and Shimokawa [23].

LINEAR DIFFUSION

Let us consider a fluid system in which several irreversible processes take place. These processes can be molecular diffusion of heat under a temperature gradient, molecular diffusion of momentum under a velocity gradient, or diffusion of a chemical component under a gradient of density of the chemical component. All these diffusion processes contribute to an increase in entropy of the total system consisting of the fluid system and its surroundings. A general expression for the rate of entropy production per unit time by these irreversible processes is given by

$$\dot{\sigma} = \int_V \sum_i \mathbf{J}_i \cdot \mathbf{X}_i \, \mathrm{d}V, \tag{1}$$

where $\dot{\sigma}$ is the rate of entropy production, $\mathbf{J}_i$ is the i-th diffusive flux density, $\mathbf{X}_i$ is the gradient in the corresponding intensive variable that drives the flux, and the integration is taken over the whole volume of the system (e.g. [18]). If the flux density is heat, momentum, or a chemical component, the corresponding intensive variable is temperature ($1/T$), velocity ($-\mathbf{v}/T$), or chemical potential ($-\mu/T$) respectively. It should be noted that the diffusive flux $\mathbf{J}_i$ does not, in principle, include a flux due to advection (i.e. coherent motion of fluid), which is intrinsically a reversible process [1]. However, advection significantly enhances the local gradient of the intensive variable at the moving front, and hence entropy production is also enhanced. We will see how entropy production can change with and without advection.

Heat Diffusion

As the simplest example, let us discuss diffusion of heat under temperature gradient in a fluid system. In this case, Eq. (1) is

$$\dot{\sigma}_\mathrm{h} = \int_V \mathbf{J}_\mathrm{h} \cdot \nabla\left(\frac{1}{T}\right) d\,V = \int_V L_\mathrm{h}\left[\nabla\left(\frac{1}{T}\right)\right]^2 \mathrm{d}V, \tag{2}$$

where $\mathbf{J}_\mathrm{h}$ is the diffusive heat flux density due to heat conduction, T is the temperature and L_h is the kinetic coefficient relating the diffusive heat flux and the temperature gradient: $\mathbf{J}_\mathrm{h} = L_\mathrm{h}\,\nabla(1/T) = -\lambda\,\nabla T$, with $\lambda = L_\mathrm{h}/T^2$ being the thermal conductivity in Fourier's law. In Eq. (2) we have assumed linearity between the diffusive heat flux and the temperature gradient.

We can show that the entropy production due to heat diffusion [Eq. (2)] is a monotonically decreasing function of time when the intensive variable (T) is fixed at the boundary of the system and when there is no advective heat transport in the system. Taking the time derivative of Eq. (2), and assuming a constancy of L_h in the temperature range of the system ($\mathrm{d}L_\mathrm{h}/\mathrm{d}t = 0$), we get

$$\frac{\mathrm{d}\dot{\sigma}_\mathrm{h}}{\mathrm{d}t} = 2\int_V \mathbf{J}_\mathrm{h} \cdot \nabla\left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right]\mathrm{d}V. \tag{3}$$

This expression leads, with integration by parts, to

$$\frac{\mathrm{d}\dot{\sigma}_\mathrm{h}}{\mathrm{d}t} = 2\int_A \left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right]\mathbf{J}_\mathrm{h} \cdot \mathbf{n}\,\mathrm{d}A - 2\int_V \left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right]\nabla \cdot \mathbf{J}_\mathrm{h}\mathrm{d}V, \tag{4}$$

where $\mathbf{n}$ is the unit vector normal to the system boundary and directed to outward, and A is the surface bounding the system. The first surface integral varnishes when the temperature is fixed at the boundary (i.e. $\partial T/\partial t = 0$). Using Fourier's law ($\mathbf{J}_\mathrm{h} = -\lambda\,\nabla T$) and assuming the uniformity of λ in the system ($\nabla\lambda = 0$), the second volume integral leads to

$$\frac{\mathrm{d}\dot{\sigma}_\mathrm{h}}{\mathrm{d}t} = 2\int_V \lambda\,\nabla^2 T\,\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\mathrm{d}V. \tag{5}$$

Equation (5) shows that the rate of change of entropy production is a function of the heat diffusion rate ($\lambda\,\nabla^2 T$) and the rate of change of temperature ($\partial T/\partial t$). The heat diffusion rate is related to the balance equation for internal energy (e.g. [25]) as

$$\rho\frac{\partial}{\partial t}\left(c_\mathrm{v}T\right) = -\rho\mathbf{v}\cdot\nabla\left(c_\mathrm{v}T\right) + \lambda\nabla^2 T - p\nabla\cdot\mathbf{v} + \boldsymbol{\Pi} : \nabla\mathbf{v}, \tag{6}$$

where ρ is the fluid density, c_v is the specific heat at constant volume, $\mathbf{v}$ is the fluid velocity, p is the pressure and $\boldsymbol{\Pi}$ is the viscous stress. This equation shows that the rate of temperature increase is caused by the sum of the rates of heat advection, heat diffusion, cooling by volume expansion and viscous heating. Substituting $\lambda\nabla^2 T$ from Eq. (6) into Eq. (5), and assuming a constancy of c_v in the fluid system ($\mathrm{d}c_\mathrm{v}/\mathrm{d}t = 0$), we get

$$\frac{\mathrm{d}\dot{\sigma}_\mathrm{h}}{\mathrm{d}t} = 2\int_V \left[\rho c_\mathrm{v}\frac{\partial T}{\partial t} + \rho c_\mathrm{v}\mathbf{v}\cdot\nabla T + p\nabla\cdot\mathbf{v} - \boldsymbol{\Pi} : \nabla\mathbf{v}\right]\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\mathrm{d}V. \tag{7}$$

If we consider a situation with no convective motion ($\mathbf{v} = 0$), Eq. (7) reduces to

$$\frac{\mathrm{d}\dot{\sigma}_\mathrm{h,stat}}{\mathrm{d}t} = -2\int_V \frac{\rho c_\mathrm{v}}{T^2}\left(\frac{\partial T}{\partial t}\right)^2 \mathrm{d}V \le 0, \tag{8}$$

where the suffix stat denotes the static state with no motion. The rate of change of entropy production is negative in this static case, because ρ and c_v are positive definite. Equation (8) shows that entropy production due to pure heat conduction tends to decrease with time, and reaches a minimum in the final steady state ($\partial T/\partial t = 0$) provided there is no convective motion in the fluid. This tendency was first suggested by Prigogine [16], and is called the minimum entropy production (MinEP) principle. While several attempts have been made to extend this principle to a general one including dynamic motion, the results remain controversial and inconclusive [17, 18]. As we shall see in a later section, when advection due to dynamic motion is nonzero, the local rate of entropy production can either increase or decrease, depending on the rate of heat advection ($\mathbf{v}\cdot\nabla T$); the sign of $\mathrm{d}\dot{\sigma}_\mathrm{h}/\mathrm{d}t$ becomes indefinite and even positive in some cases.

[1] One can include a reversible flux due to advection in the balance equation of entropy, but it results in no contribution to entropy production after the integration over the whole volume of a fluid system (see, e.g., [24], Sec. 49; [13], Sec. 2.4).

Momentum Diffusion

A similar result can be obtained for the diffusion of momentum due to viscosity under a velocity gradient. Suppose that a viscous fluid with a uniform viscosity is flowing in a system with a constant temperature T. In this case, entropy production due to momentum diffusion is given by

$$\dot{\sigma}_{\mathrm{m}} = \int_V \frac{\boldsymbol{\Pi} : \nabla \mathbf{v}}{T} \mathrm{d}V. \tag{9}$$

Here, the numerator represents the scalar product of the viscous stress tensor and the velocity gradient, and is identical to the heating rate due to viscosity per unit volume per unit time in the fluid. Assuming a linear relation between the viscous stress and the velocity gradient, we can drive the time derivative of the rate of entropy production after a few manipulations[2]:

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{m}}}{\mathrm{d}t} = \int_V \frac{\partial}{\partial t}\left(\frac{\boldsymbol{\Pi} : \nabla \mathbf{v}}{T}\right)\mathrm{d}V = 2\int_V \frac{1}{T}\left[\boldsymbol{\Pi} : \nabla\left(\frac{\partial \mathbf{v}}{\partial t}\right)\right]\mathrm{d}V. \tag{10}$$

By a sequence of transformations similar to those from Eq. (3) to Eq. (5), we get

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{m}}}{\mathrm{d}t} = -2\int_V \frac{1}{T}\left[\mu\nabla^2\mathbf{v} + \frac{\mu}{3}\nabla\left(\nabla\cdot\mathbf{v}\right)\right]\cdot\left(\frac{\partial \mathbf{v}}{\partial t}\right)\mathrm{d}V, \tag{11}$$

where μ is the viscosity of the fluid. Here we have assumed that velocity is fixed at the boundary ($\partial\mathbf{v}/\partial t = 0$). The diffusion rate of momentum [$\mu\nabla^2\mathbf{v} + \mu\nabla(\nabla\cdot\mathbf{v})/3$] is related to the balance equation of momentum — the Navier–Stokes equation — as

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\rho(\mathbf{v}\cdot\nabla)\mathbf{v} - \nabla p + \mu\nabla^2\mathbf{v} + \frac{\mu}{3}\nabla(\nabla\cdot\mathbf{v}). \tag{12}$$

Substituting Eq. (12) into Eq. (11) and eliminating the momentum diffusion rate, we get after a few transformations

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{m}}}{\mathrm{d}t} = -2\int_V \frac{1}{T}\left[\left(\rho\frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v}\cdot\nabla)\mathbf{v}\right)\cdot\left(\frac{\partial \mathbf{v}}{\partial t}\right) - p\frac{\partial}{\partial t}(\nabla\cdot\mathbf{v})\right]\mathrm{d}V$$

$$\approx -2\int_V \frac{1}{T}\left(\rho\frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v}\cdot\nabla)\mathbf{v}\right)\cdot\left(\frac{\partial \mathbf{v}}{\partial t}\right)\mathrm{d}V. \tag{13}$$

Here we have assumed incompressibility ($\nabla\cdot\mathbf{v} = 0$) in Eq. (13). If we further assume a situation with no advection of momentum, then $(\mathbf{v}\cdot\nabla)\mathbf{v} = 0$; that is, there is no velocity gradient along the flow direction, corresponding to a laminar flow in the Stokes approximation. In this specific laminar flow case, we get

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{m,lam}}}{\mathrm{d}t} = -2\int_V \frac{\rho}{T}\left|\frac{\partial \mathbf{v}}{\partial t}\right|^2 \mathrm{d}V \le 0, \tag{14}$$

where the suffix lam denotes the laminar flow with no momentum advection. The rate of entropy production in an incompressible laminar flow tends to decrease with time and reach a minimum in the final steady state ($\partial\mathbf{v}/\partial t = 0$). This result shows another aspect of MinEP for a laminar flow. In an isothermal condition, this tendency is akin to that of minimum dissipation of kinetic energy in a slow incompressible steady flow suggested by Helmholtz [26] and Rayleigh [27]. However, as we shall see in the next section, when advection of momentum is nonzero (i.e. turbulent flow), the sign of $\mathrm{d}\dot{\sigma}_{\mathrm{m}}/\mathrm{d}t$ becomes indefinite, and the entropy production can either decrease or increase depending on the rate of advection determined by the flow pattern produced in the fluid system.

NONLINEAR ADVECTION

We now discuss the effect of advection of heat or momentum on entropy production in a fluid system. The advection process is a typical nonlinear process since it is described as the product of the velocity and gradient of an intensive variable, which is also a function of the velocity. A fundamental difficulty arises from the presence of this nonlinear term in solving the balance equation of energy or momentum [Eq. (6) or (12)]. Exactly the same difficulty arises from this advection term in solving the equation of entropy production. We do not know, in a deterministic sense, how the rate of entropy production will change once advection becomes a dominant process in the transport of heat or momentum. However, advection of heat or momentum generally increases the local gradient of temperature or velocity at the moving front, which results in an enhancement of entropy production. Here we discuss the conditions under which advection enhances entropy production, using the general equations of entropy production [Eqs. (5) and (11)] as follows.

Heat Advection

Let us go back to the example of entropy production due to heat diffusion. With the presence of convective motion, the MinEP condition [Eq. (8)] cannot be justified since it requires $\mathbf{v} = 0$. Even in this case, Eq. (5) for the rate of change of entropy production remains valid. Assuming a constancy of c_{v} ($\mathrm{d}c_{\mathrm{v}}/\mathrm{d}t = 0$) in Eq. (6), and substituting the rate of change of temperature ($\partial T/\partial t$) into Eq. (5), we get

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{h,adv}}}{\mathrm{d}t} = -2\int_V \frac{\rho c_{\mathrm{v}}}{T^2}\kappa\nabla^2 T\left(\kappa\nabla^2 T - \mathbf{v}\cdot\nabla T - \frac{p\,\nabla\cdot\mathbf{v}}{\rho c_{\mathrm{v}}} + \frac{\boldsymbol{\Pi} : \nabla\mathbf{v}}{\rho c_{\mathrm{v}}}\right)\mathrm{d}V$$

$$\approx -2\int_V \frac{\rho c_{\mathrm{v}}}{T^2}\kappa\nabla^2 T\,(\kappa\nabla^2 T - \mathbf{v}\cdot\nabla T)\,\mathrm{d}V, \tag{15}$$

where the suffix adv denotes the presence of heat advection and $\kappa = \lambda/\rho c_{\mathrm{v}}$ is the thermal diffusivity. The approximation in Eq. (15) corresponds to an assumption that the cooling rate by volume expansion ($\nabla\cdot\mathbf{v}$) and the heating rate by viscous dissipation ($\boldsymbol{\Pi}:\nabla\mathbf{v}$) are negligibly small compared with diffusive heating ($\kappa\nabla^2 T$) and advective cooling ($\mathbf{v}\cdot\nabla T$). Under this assumption, we can get a sufficient condition for the increase of entropy production ($\mathrm{d}\dot{\sigma}_{\mathrm{h,adv}}/\mathrm{d}t \ge 0$) as

[2] Assuming linearity, $\boldsymbol{\Pi}:\nabla\mathbf{v} = [2\mu\,(\nabla\mathbf{v})^{\mathrm{s}} - (2/3)\mu(\nabla\cdot\mathbf{v})\boldsymbol{\delta}]:[(\nabla\mathbf{v})^{\mathrm{s}} + (\nabla\mathbf{v})^{\mathrm{a}}] = 2\mu\,(\nabla\mathbf{v})^{\mathrm{s}}:(\nabla\mathbf{v})^{\mathrm{s}} - (2/3)\mu(\nabla\cdot\mathbf{v})^2$, with $\boldsymbol{\delta}$ denoting the unit tensor, and $\mathbf{T}^{\mathrm{s}}$ and $\mathbf{T}^{\mathrm{a}}$ denoting symmetric and asymmetric parts of a tensor $\mathbf{T}$. Then, $\partial(\boldsymbol{\Pi}:\nabla\mathbf{v})/\partial t = 2[2\mu\,(\nabla\mathbf{v})^{\mathrm{s}} - (2/3)\mu(\nabla\cdot\mathbf{v})\boldsymbol{\delta}]:[\nabla(\partial\mathbf{v}/\partial t)]^{\mathrm{s}} = 2\,\boldsymbol{\Pi}:\nabla(\partial\mathbf{v}/\partial t)$.

$$\mathbf{v}\cdot\nabla T \geq \kappa\nabla^2 T \geq 0 \text{ or } \mathbf{v}\cdot\nabla T \leq \kappa\nabla^2 T \leq 0 \;\Rightarrow\; \frac{\mathrm{d}\dot{\sigma}_{\mathrm{h,adv}}}{\mathrm{d}t} \geq 0. \quad (16)$$

Condition (16) means that, when advective cooling ($\mathbf{v}\cdot\nabla T$) is greater than diffusive heating ($\kappa\nabla^2 T$), the local temperature decreases further ($\partial T/\partial t \leq 0$) because of Eq. (6), and thus entropy production increases because of Eq. (5). Alternatively, when advective heating ($-\mathbf{v}\cdot\nabla T > 0$) is greater than diffusive cooling ($-\kappa\nabla^2 T > 0$), the local temperature increases further ($\partial T/\partial t \geq 0$) because of Eq. (6), and thus entropy production increases because of Eq. (5). These conditions generally hold true during the development of convective motion ($\partial\mathbf{v}/\partial t > 0$) in a fluid system whose Rayleigh number is larger than the critical value for the onset of convection. The rate of entropy production thus tends to increase with time and reaches a maximum value through the development of convective motion, as suggested from previous studies [5, 6]. Moreover, it is known from numerical simulations that a state of convection tends to move to a state with higher rate of entropy production when the system has multiple steady states and the system is subject to external perturbations [8, 9, 28]. These results are consistent with condition (16) under which entropy production increases with time through the development of convective motion in a system with dynamic instability.

One can see from condition (16) that entropy production can decrease with time when the heat advection rate is smaller than the heat diffusion rate, i.e., $|\mathbf{v}\cdot\nabla T| \leq |\kappa\nabla^2 T|$. Such a situation can be realized in the relaxation period of a convection system towards a steady state, or in a convection system whose boundary temperature is unbounded so that the mean temperature gradient becomes smaller through the development of convective motion. One such example is thermal convection of a fluid system under fixed heat flux at the boundary. Entropy production as well as the overall temperature contrast at the boundary decreases with the onset of convection in this case (e.g. [29]). A quantitative analysis on the reduction of entropy production using Eq. (16) would therefore be attractive. Here it should be noted that the decrease of entropy production in this case is not in direct contradiction to the stability criterion of MaxEP, because relative stability of each steady state should be compared under the same boundary forcing condition, i.e., the same temperature contrast at the boundary characterized by the same Rayleigh number.

Momentum Advection

We can obtain a similar result for entropy production due to momentum diffusion. With the presence of advection of momentum [$(\mathbf{v}\cdot\nabla)\mathbf{v} \neq 0$], the MinEP condition [Eq. (14)] cannot be justified. Even in this case, Eq. (11) for the rate of change of entropy production remains valid. Assuming incompressibility of fluid and substituting the rate of change of velocity from Eq. (12) into Eq. (11), we get

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{m,adv}}}{\mathrm{d}t} = -2\int_V \frac{\rho}{T}\left(\nu\nabla^2\mathbf{v}\right)\cdot\left(\nu\nabla^2\mathbf{v} - (\mathbf{v}\cdot\nabla)\mathbf{v} - \frac{\nabla p}{\rho}\right)\mathrm{d}V, \quad (17)$$

where the suffix adv denotes the presence of momentum advection and $\nu = \mu/\rho$ is the kinematic viscosity. We can then find a sufficient condition for the increase of entropy production ($\mathrm{d}\dot{\sigma}_{\mathrm{h,adv}}/\mathrm{d}t \geq 0$) as

$$\left[(\mathbf{v}\cdot\nabla)\mathbf{v} + \frac{\nabla p}{\rho}\right]\cdot\mathbf{e} \geq \left|\nu\nabla^2\mathbf{v}\right| \;\Rightarrow\; \frac{\mathrm{d}\dot{\sigma}_{\mathrm{m,adv}}}{\mathrm{d}t} \geq 0, \quad (18)$$

where $\mathbf{e} = \nabla^2\mathbf{v}/|\nabla^2\mathbf{v}|$ is the unit vector in the direction of $\nabla^2\mathbf{v}$. Condition (18) means that, when advective export of momentum [$(\mathbf{v}\cdot\nabla)\mathbf{v}$] plus pressure deceleration [$\nabla p/\rho$] in the $\mathbf{e}$ direction is greater than diffusive import of momentum $|\nu\nabla^2\mathbf{v}|$, the local velocity in that direction decreases further because of Eq. (12), and thus entropy production increases because of Eq. (11). Alternatively, when advective import of momentum [$-(\mathbf{v}\cdot\nabla)\mathbf{v}$] plus pressure acceleration [$-\nabla p/\rho$] in the $-\mathbf{e}$ direction is larger than diffusive export of momentum $|\nu\nabla^2\mathbf{v}|$, the local velocity increases further because of Eq. (12), and thus entropy production increases because of Eq. (11). It is known that advection of momentum is negligibly small in laminar flows whereas it is considerably large in turbulent flows. Thus, this condition generally holds true during the development of turbulent motion in a fluid system whose Reynolds number is larger than the critical value for the onset of turbulence. The rate of entropy production thus tends to increase to a maximum value through the development of turbulent motion [5]. Malkus [30] and Busse [31] suggested that the observed mean state of turbulent shear flow corresponds to the state with the maximum rate of momentum transport by turbulent motion. Malkus [32] also showed that velocity profiles estimated from maximum dissipation of kinetic energy due to the mean velocity field and a smallest scale of motion at the system boundary resemble those of observations. Since the dissipation rate is proportional to the entropy production rate, these results are consistent with condition (18) under which entropy production increases with time towards a maximum value when the system is in a state of dynamic instability.

One can also see from this condition (18) that entropy production can decrease with time when the momentum advection is less than the rates of diffusion and acceleration by the pressure gradient: $[(\mathbf{v}\cdot\nabla)\mathbf{v} + \nabla p/\rho]\cdot\mathbf{e} \leq |\nu\nabla^2\mathbf{v}|$. Such a condition can be realized in the relaxation period of a turbulent fluid system, or in a fluid system whose boundary velocity is unbounded so that the momentum advection becomes less significant than the sum of momentum diffusion and pressure acceleration. Examples include turbulent shear flow under a fixed shear stress and turbulent pipe flow under a fixed pressure gradient. Entropy production as well as the overall velocity gradient is known to decrease with the onset of turbulence in these cases [33, 34]. Again, the decrease of entropy production in these cases is not in direct contradiction to the stability criterion of MaxEP, because relative stability of each steady state should be compared under the same boundary forcing condition, i.e., the same velocity contrast applied to the entire system characterized by the same Reynolds number.

It should be noted that the condition [(16) or (18)] is a *sufficient* condition rather than a *necessary and sufficient* condition for $\mathrm{d}\dot{\sigma}_{\mathrm{adv}}/\mathrm{d}t \geq 0$ — entropy production for the total system can increase even if local entropy production decreases in some places. In order to get the exact condition for $\mathrm{d}\dot{\sigma}_{\mathrm{adv}}/\mathrm{d}t \geq 0$, we need to treat the integral equation [(5) or (11)]. In what follows we shall deal with the integral equation based on the concept of linear stability analysis.

Stability Analysis

Suppose that a fluid system is subjected to a small disturbance. The disturbance is considered to be so small that its decomposition into spatial and temporal contributions may be possible. In this case, arbitrary small disturbances of temperature and velocity can be expanded into infinite Fourier series, whose components take the general forms:

$$\delta T = \delta T_0 \exp\left[i(k_x x + k_y y + k_z z) + p_k t\right], \tag{19}$$

$$\delta \mathbf{v} = \delta \mathbf{v}_0 \exp\left[i(k_x x + k_y y + k_z z) + p_k t\right], \tag{20}$$

where δT and $\delta \mathbf{v}$ are the disturbances of temperature and velocity, δT_0 and $\delta \mathbf{v}_0$ are their amplitudes, $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$ is the wave number, and p_k is the complex growth rate of the disturbance of the wave number k. When the real part of p_k is negative for all k, the fluid system is stable with respect to the perturbation. The onset of instability is characterized by a critical condition beyond which the real part of p_k becomes larger than zero ($p_k^{(r)} > 0$) at a particular wave number (k_c). The critical condition must be determined by solving the governing equations [(6) and (12)] with appropriate boundary conditions. For a fluid layer heated from below, the critical condition is expressed by the Rayleigh number: Ra > Ra*, where Ra* is the critical value beyond which instability is manifested [35]. In the case of a fluid layer (thickness d) between two rigid boundary surfaces, it is known that Ra* ≈ 1708 and $k_c \approx 3.12/d$ (cf. [24, 25]), as illustrated in Fig. 1.

We shall then examine the behavior of entropy production at the onset of convective instability. Substituting the temperature disturbance Eq. (19) into Eq. (5), we get

$$\frac{\mathrm{d}\dot{\sigma}_{\mathrm{h,dis(k)}}}{\mathrm{d}t} \approx 2k^2 p_k \int_V \lambda \left(\frac{\delta T}{T}\right)^2 \mathrm{d}V, \tag{21}$$

where the suffix dis(k) denotes the presence of a disturbance with the wave number k. One can see from Eq. (21) that the rate of change of entropy production by the disturbance is proportional to the growth rate p_k because all other factors [k^2, λ, $(\delta T/T)^2$] are positive definite. If $p_k^{(r)}$ is negative, then the disturbance is damped and entropy production thereby decreases[3]. This condition corresponds to the stable state with Ra < Ra* (Fig. 1). By contrast, when Ra exceeds the critical value Ra*, $p_k^{(r)}$ becomes larger than zero at the certain wave number k_c, and entropy production starts to increase at the onset of convective instability. A similar result can be obtained for entropy production due to momentum diffusion under velocity gradient. By substituting Eq. (20) into Eq. (11), the rate of change of entropy production is shown to be proportional to p_k. It is generally known that the onset of instability of such a system is determined by the Reynolds number: Re [36]. When Re becomes larger than a critical value (Re > Re*), $p_k^{(r)}$ of a certain wave number becomes positive and entropy production starts to increase. These results are consistent with the findings in the preceding sections that entropy production tends to increase when the system is in a state of dynamic instability.

[3] The imaginary part of p_k is zero when Ra > 0 in this case (cf. [24, 25]).

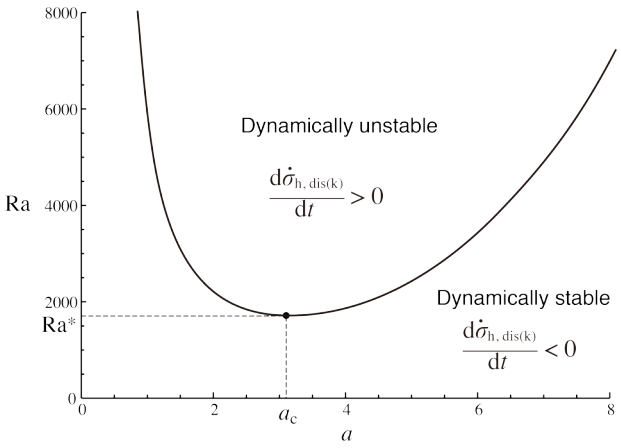

Fig. 1. Relation between the Rayleigh number Ra and the dimensionless wave number $a \equiv k\,d$. The sold line corresponds to the marginal state for the onset of instability (cf. [24, 25]). Entropy production tends to decrease with time when Ra is less than the critical value: Ra < Ra*. Entropy production starts to increase at the onset of instability when Ra > Ra*.

SUMMARY

In this paper, we have discussed some general characteristics of entropy production in a fluid system. We have shown that entropy production always decreases with time when the system is of a pure diffusion type without advection of heat or momentum. Thus, the minimum entropy production (MinEP) property is intrinsic to a system of a pure diffusion type; e.g., heat conduction in a static fluid or momentum diffusion in laminar flow. However, this MinEP property is no longer guaranteed when the system is in a dynamically unstable state. In this state, entropy production tends to increase by the growth of the advection rate over the diffusion rate of the corresponding extensive quantity. The hypothesis of maximum entropy production (MaxEP) suggested as a selection principle for multiple steady states of nonlinear non-equilibrium systems [1, 6, 13–15, 21–23] can therefore be seen to be a characteristic feature of systems with nonlinear dynamic instability.

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REFERENCES

[1] H. Ziegler, Zwei Extremalprinzipien der irreversiblen Thermodynamik, *Ing. Arch.* 30, 410–416, 1961.

[2] G.W. Paltridge, Global dynamics and climate—A system of minimum entropy exchange, *Q. J. Roy. Meteorol. Soc.* 101, 475–484, 1975.

[3] G.W. Paltridge, The steady-state format of global climate, *Q. J. Roy. Meteorol. Soc.* 104, 927–945, 1978.

[4] H. Ozawa, A. Ohmura, Thermodynamics of a global-mean state of the atmosphere—A state of maximum entropy increase, *J. Clim.* 10, 441–445, 1997.

[5] E.D. Schneider, J.J. Kay, Life as a manifestation of the second law of thermodynamics, *Mathematical and Computer Modelling,* 19, 25–48, 1994.
[6] H. Ozawa, H., S. Shimokawa, H. Sakuma, Thermodynamics of fluid turbulence: A unified approach to the maximum transport properties, *Phys. Rev.* E 64, 026303, 2001.
[7] R.D. Lorenz, J.I. Lunine, P.G. Withers, C.P. McKay, Titan, Mars and Earth: Entropy production by latitudinal heat transport, *Geophys. Res. Lett.* 28, 415–418, 2001.
[8] S. Shimokawa, H. Ozawa, On the thermodynamics of the oceanic general circulation: Irreversible transition to a state with higher rate of entropy production, *Q. J. Roy. Meteorol. Soc.* 128, 2115–2128, 2002.
[9] S. Shimokawa, H. Ozawa, Thermodynamics of irreversible transitions in the oceanic general circulation, *Geophys. Res. Lett.* 34, L12606, 2007. [doi: 10.1029/2007 GL030208]
[10] A. Hill, Entropy production as the selection rule between different growth morphologies, *Nature* 348, 426–348, 1990.
[11] Y. Nohguchi, H. Ozawa, On the vortex formation at the moving front of lightweight granular particles, *Physica* D 238, 20–26, 2009.
[12] E.N. Lorenz, Generation of available potential energy and the intensity of the general circulation, in R.L. Pfeffer, (ed.), *Dynamics of Climate,* pp. 86–92. Pergamon, Oxford, 1960.
[13] H. Ozawa, A. Ohmura, R.D. Lorenz, T. Pujol, The second law of thermodynamics and the global climate system: A review of the maximum entropy production principle, *Rev. Geophys.* 41, 1018, 2003. [doi: 10.1029/2002RG000113]
[14] R. Dewar, Information theory explanation of the fluctuation theorem, maximum entropy production and self-organized criticality in non-equilibrium stationary states, *J. Phys.* A 36, 631–641, 2003.
[15] R.K. Niven, Steady state of a dissipative flow-controlled system and the maximum entropy production principle, *Phys. Rev.* E 80, 021113, 2009.
[16] I. Prigogine, Modération et transformations irréversibles des systémes ouverts, *Bulletin de la Classe des Sciences, Academie Royale de Belgique* 31, 600–606, 1945.
[17] P. Glansdorff, I. Prigogine, Sur les propriétés différentielles de la production d'entropie. *Physica* 20, 773–780, 1954.
[18] S.R. de Groot, P. Mazur, Non-equilibrium Thermodynamics, North-Holland Publ., Amsterdam, 1962.
[19] I. Gyarmati, Non-equilibrium Thermodynamics, Field Theory and Variational Principles, Springer, Berlin, 1970. [First published in Hungarian, 1967]
[20] I. Prigogine, From Being to Becoming, Time and Complexity in the Physical Sciences, Freeman, San Fransisco, 1970.
[21] Y. Sawada, A thermodynamic variational principle in nonlinear non-equilibrium phenomena, *Prog. Theor. Phys.* 66, 68–76, 1981.
[22] R.C. Dewar, A. Maritan, A theoretical basis for maximum entropy production, in R.C. Dewar, C.H. Lineweaver, R.K. Niven, K. Regenauer–Lieb (eds.), *Beyond the Second Law: Entropy Production and Non-equilibrium Systems*, Springer, Berlin, 2013 (in press).
[23] H. Ozawa, S. Shimokawa, The time evolution of entropy production in nonlinear dynamic systems, in R.C. Dewar, C.H. Lineweaver, R.K. Niven, K. Regenauer–Lieb (eds.), *Beyond the Second Law: Entropy Production and Non-equilibrium Systems*, Springer, Berlin, 2013 (in press).
[24] L.D. Landau, E.M. Lifshitz, Fluid Mechanics, 2nd ed. Pergamon Press, Oxford, 1987. [First published in Russian, 1944]
[25] S. Chandrasekhar, Hydrodynamic and Hydromagnetic Stability, Oxford Univ. Press, Oxford, 1961.
[26] H. Helmholtz, Zur Theorie der stationären Ströme in reibenden Flüssigkeiten, *Verhandlungen des naturhistorisch-medicinischen Vereins zu Heidelberg* 5, 1–7, 1869.
[27] Lord Rayleigh, On the motion of a viscous fluid, *Phil. Mag.* 26, 776–786, 1913.
[28] M. Suzuki, Y. Sawada, Relative stabilities of metastable states of convecting charged-fluid systems by computer simulation, *Phys. Rev.* A 27, 478–489, 1983.
[29] Y. Kawazura, Z. Yoshida, Entropy production rate in a flux-driven self-organizing system, *Phys. Rev.* E 82, 066403, 2010.
[30] W.V.R. Malkus, Outline of a theory of turbulent shear flow, *J. Fluid Mech.* 1, 521–539, 1956.
[31] F.H. Busse, Bounds for turbulent shear flow, *J. Fluid Mech.* 41, 219–240, 1970.
[32] W.V.R. Malkus, Borders of disorder: in turbulent shear flow, *J. Fluid Mech.* 489, 185–198, 2003.
[33] D.M. Paulus Jr., R.A. Gaggioli, Some observations of entropy extrema in fluid flow, *Energy* 29, 2487–2500, 2004.
[34] R.K. Niven, Simultaneous extrema in the entropy production for steady-state fluid flow in parallel pipes, *J. Non-Equilib. Thermodyn.* 35, 347–378, 2010.
[35] Lord Rayleigh, On convection currents in a horizontal layer of fluid, when the higher temperature is on the under side, *Philos. Mag.* 32, 529–546, 1916.
[36] O. Reynolds, On the dynamical theory of incompressible viscous fluids and the determination of the criterion, *Philos. Trans. Roy. Soc. London* 186, 123–164, 1895.