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Variational formulation of nonequilibrium thermodynamics for hydrodynamic pattern formations

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It is shown that a direct extension of the variational principle of near-equilibrium states due to Onsager leads to the analogous principle in hydrodynamic flows; the entropy production rate of an isolated system is maximized both near and far from equilibrium. It possesses as its extremal paths the solutions to the hydrodynamic equation of motion, and provides a general pattern selection criterion far from equilibrium.

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I. INTRODUCTION

Despite important progresses being made recently [1–7], the task of extending the equilibrium statistical mechanics and thermodynamics to the far-from-equilibrium situations, under which many fascinating phenomena including pattern formations in driven systems and self-organizations in living organisms occur [8], remains incomplete. A prime source of difficulties is the apparent lack of a quantity analogous to free energy, whose minimization condition yields macroscopic observables [1,8]. Specific studies of pattern formations have thus been mainly confined to analyzing solutions of phenomenological evolution equations, such as hydrodynamic or reaction-diffusion equations [8]. When confronted with multiple stationary solutions typically generated by bifurcations, one has little guide other than empirical means on how to select or properly weigh the solutions. On the conceptual level, the difficulty in formulating such a variational approach poses an awkward gap in our description of nature between the physical and biological realms, with the latter characterized by the ubiquitous emergence of order out of disorder, whose ‘‘driving force’’ is nowhere obvious.

Such ‘‘pattern selection’’ problem, or more fundamentally the identification of the proper thermodynamic variational principle, is distinct from the focus of the theory of fluctuations [6,7,9,10], where one considers the probability of observing a spontaneous deviation from a particular solution to the macroscopic equation of motion. Our aim in this paper is to examine how one can properly select the particular solution to the equation of motion among the finite or infinite number of possibilities.

In particular, we consider the following variational principle: in isolated macroscopic systems both near and far from equilibrium, the entropy production rate is maximized. The usefulness of the maximum heat flux criterion in convection as an *ad hoc* hypothesis has been noted before [11–13]. Experimental evidences in a diverse range of turbulent flows have been collected recently in Ref. [14], where it was shown that a simple and unified description becomes possible by introducing the assumption of the maximum entropy increase rate. A well-founded theoretical basis for such empirical observations is provided here by arguing that the variational principle formulated by Onsager [15,16] can, in fact, be extended without modification to hydrodynamics far from equilibrium. The hydrodynamic equation of motion can be regarded as the most probable path that emerges from the variational principle. It thus potentially provides an *a priori* principle of pattern selection valid from equilibrium up to turbulent flows; patterns are formed and selected to maximize the rate of entropy increase of the universe containing the system.

In the following section, the general form of the variational principle is stated and its relationship with the Onsager theory is discussed. Hydrodynamics is considered in the context of the variational principle in Sec. III. Section IV discusses implications to the properties of nonequilibrium stationary states using the Rayleigh-Benárd convection (RBC) [8,13,17] as a model system. The relationships of the variational principle to the ‘‘minimum entropy production theorem’’ [18] are also considered in Sec. IV.

II. VARIATIONAL PRINCIPLE

According to the second law, the equilibrium state a_i^∞ of the set of conserved extensive thermodynamic variables a_i of an isolated system (‘‘universe’’) is determined by

$$S(a_i^\infty)=(\text{maximum}), \tag{1}$$

subject to certain constraints, where $S(a_i)$ is the entropy [19]. The variational principle we consider in this paper is a close analog of Eq. (1): for a system with hydrodynamic flows, the most probable macroscopic path $a_i(\mathbf{r},t)$ approaching a_i^∞ satisfies

$$\dot{S}[a_i(\mathbf{r},t)]=(\text{maximum}), \tag{2}$$

subject to appropriate constraints, where $\dot{S}$ is the total rate of entropy increase. The ‘‘constraints’’ include the intrinsic dynamics of a_i, represented by the phenomenological macroscopic equation of motion. Equation (2) states that the time-dependent nonequilibrium trajectory of a macroscopic system $a_i(\mathbf{r},t)$ is determined by the condition that the overall entropy production rate of the universe containing the system is maximized. The intuitive motivation behind Eq. (2) is the expectation that in its approach to equilibrium, an isolated system would follow the most efficient route to increase its

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Equation (2) is closely related to Onsager's variational principle [15,16], which states that near equilibrium,

$$\dot{S}-\Phi=(\text{maximum}). \tag{3}$$

In Eq. (3), $\dot{S}$ is the total entropy production rate of a macroscopic system. The ''dissipation function'' Φ is defined as

$$\Phi=\frac{1}{2}\int d\mathbf{r}(L^{-1})_{ij}\mathbf{J}_i\cdot\mathbf{J}_j \tag{4}$$

in terms of the set of fluxes $\mathbf{J}_i$ associated with a_i, and the kinetic coefficient L_{ij} that satisfies the reciprocal relation $L_{ij}=L_{ji}$. Summations over repeated indices are implied. The total entropy production rate is given in terms of the local values $\dot{s}$ by

$$\dot{S}=\int d\mathbf{r}\ \ \dot{s}=\int d\mathbf{r}\ \ \nabla X_i\cdot\mathbf{J}_i, \tag{5}$$

where $X_i=\partial S/\partial a_i$ is the intensive variable conjugate to a_i. The variations refer to those of $\mathbf{J}_i$, or the rate of change of the state, given the state $a_i(\mathbf{r},t)$ at a particular instant. The Euler-Lagrange equation corresponding to Eq. (3) is

$$\mathbf{J}_i=L_{ij}\nabla X_j, \tag{6}$$

the linear phenomenological constitutive equation, which we refer to as the ''equation of motion.'' It is a natural generalization of the typical procedure one performs in equilibrium thermodynamics, where an application of Eq. (1) gives the equation of state.

It is important to recognize Eq. (6) as the *consequence* of the variational principle, the most probable path that maximizes $\dot{S}-\Phi$. Near equilibrium, there typically exists a unique solution to Eq. (6) under the given conditions, and the practical utility of Eq. (3) is rather limited. However, if we were to imagine a situation where there are multiple solutions to the equation of motion, one would have to compare the values of $\dot{S}-\Phi$ corresponding to each extrema and ''choose'' the one with the maximum value. For the subset of trajectories satisfying Eq. (6), we have $\Phi=\dot{S}/2$ from Eqs. (4)–(6). Therefore, when we project the full trajectory space into a subset in which the equation of motion is satisfied, Eq. (3) would reduce to Eq. (2) [25].

Strictly speaking, such an extension would involve the assumption, which goes beyond the original context considered by Onsager, that Eq. (3) continues to be valid when the equation of motion leads to multiple solutions, with the ''maximum'' referring to the *global* maximum. It is the basic assumption we take in this paper. Its intuitive plausibility appears obvious, and is strengthened by the consistency with Eq. (2).

III. HYDRODYNAMICS

Bifurcations producing instabilities and multiple stationary solutions arise from the intrinsic nonlinearity of the underlying equation. However, the nonlinearity in hydrodynamics is due to the conservation laws, and not to a departure from the linear constitutive relations (6). It is worthwhile in this sense to contrast Eq. (6) with the equation that governs the total time evolution of a_i,

$$\frac{\partial}{\partial t}a_i=-(\mathbf{v}\cdot\nabla)a_i-\nabla\cdot\mathbf{J}_i, \tag{7}$$

where $\mathbf{v}$ is the velocity. A traditional approach of formulating thermodynamic descriptions of hydrodynamics has been to start with Eq. (7), and cast it into the ''Onsager form,'' $\partial a_i/\partial t=\mathcal{L}_{ij}X_j$ [20,21], which defines the generalized kinetic coefficient $\mathcal{L}_{ij}$ and is inevitably nonlinear. Such an explicit equation for $a_i(\mathbf{r},t)$ is necessary in considering fluctuations. Since our aim is to formulate a purely thermodynamic variational principle, we instead regard the dynamics of a_i as an implicit consequence of Eq. (6) and the conservation laws.

The Onsager's variational principle can thus be adapted straightforwardly to hydrodynamics. Specifically, we assume local equilibrium in the following sense: although each local volume elements are in equilibrium and their thermodynamic variables are smoothly varying, globally, the system can be far from equilibrium [$a_i(\mathbf{r},t)-a_i^\infty$ is arbitrarily large]. The entropy production rate can be written [22] as

$$\dot{s}=\frac{\pi_{\alpha\beta}}{2T}\left(\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\delta_{\alpha\beta}\frac{\partial v_\gamma}{\partial x_\gamma}\right)+\frac{\lambda}{T}\frac{\partial v_\alpha}{\partial x_\alpha}+\mathbf{J}_q\cdot\nabla\frac{1}{T}, \tag{8}$$

where $\pi_{\alpha\beta}$ and λ are the traceless and bulk parts of the viscous stress tensor, v_α and x_α are the Cartesian components of the velocity and position vectors, $\mathbf{J}_q$ is the heat flux, and T is temperature. The dissipation function can be defined as

$$\Phi=\frac{1}{2}\int d\mathbf{r}\left(\frac{\pi_{\alpha\beta}\pi_{\beta\alpha}}{2T\eta}+\frac{\lambda^2}{T\zeta}+\kappa^{-1}\mathbf{J}_q\cdot\mathbf{J}_q\right), \tag{9}$$

where η, ζ are the shear and bulk viscosities, and κ is the heat conductivity. Application of Eq. (3) gives the equation of motion,

$$\pi_{\alpha\beta}=\eta\left(\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\delta_{\alpha\beta}\frac{\partial v_\gamma}{\partial x_\gamma}\right), \tag{10a}$$

$$\lambda=\zeta\frac{\partial v_\alpha}{\partial x_\alpha}, \tag{10b}$$

$$\mathbf{J}_q=\kappa\nabla\frac{1}{T}. \tag{10c}$$

The rest of the ingredients necessary to obtain the full set of hydrodynamic equations of motion in the schematic form of Eq. (7) are simply the conservation laws of mass, momentum, and energy, which should be regarded as *constraints*

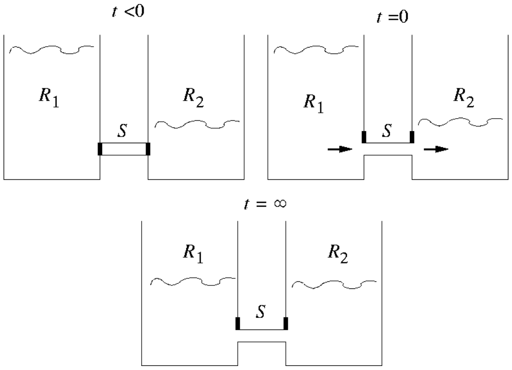

FIG. 1. An example of a time-dependent nonequilibrium trajectory between two equilibrium states generating quasistationary states. The total isolated system is partitioned into three subsystems, $\mathcal{S}$, $\mathcal{R}_1$, and $\mathcal{R}_2$, where $\mathcal{R}_1$ and $\mathcal{R}_2$ serve as reservoirs to $\mathcal{S}$. The subsystems are initially segregated, each with different X_i. At $t=0$, the gates are opened, inducing flows $\mathbf{J}_i$. By taking the volume ratio of the reservoirs to $\mathcal{S}$ and the transport coefficient of $\mathcal{R}_1$ and $\mathcal{R}_2$ large enough [23], the time dependence of the nonequilibrium relaxations can be made to approximate the stationary state flows.

present even for microscopic dynamics. In theories [7,10] considering the generalization of the Onsager-Machlup theory [9], the dissipation function has usually been defined as a quadratic form of Eq. (7). When we consider the conservation laws as part of the constraints, Eq. (9) is the more natural form.

Therefore, the extremal paths of the variational principle (3), extended to far from equilibrium, coincide with the macroscopic trajectories one normally obtains by solving the full Navier-Stokes and energy equations. Equation (2) applies if we restrict ourselves to the subset of trajectories satisfying the equation of motion. It corresponds to the situation where we ignore the vastly improbable fluctuations away from the trajectories satisfying Eq. (6).

IV. STATIONARY STATES

We now consider the consequences of the variational principle to the stationary states. In reality, realizations of stationary states can, in fact, only be quasistationary since the reservoirs cannot be infinite in size (Fig. 1). Any nonequilibrium process occurring within the system of interest, $\mathcal{S}$, is being *driven* by the imbalance of X_i between the two reservoirs, and $\mathcal{S}$ is *forced* to utilize the best possible route to relieve the imbalance, allowing the universe to reach the global equilibrium most efficiently. Equation (2) quantifies such an intuitive statement; since the dissipation occurring in the reservoirs is negligible by definition, the rate of entropy increase of the universe equals the entropy production within $\mathcal{S}$, which would be maximized [Eq. (6.4) of Ref. [15]].

The often-used term for Eq. (3), "the principle of least dissipation," refers to a rather different special case as follows: the flux on the boundaries of $\mathcal{S}$ is prescribed, which *fixes* the entropy production rate for stationary states. Equation (3) then implies that Φ is minimized [15]. This special case is also the most relevant one if we are considering the probability of a *spontaneous* fluctuation of a part of the system which is either in equilibrium [9] or in a stationary state [7,10]. Since the particular part of the system where the improbable fluctuation is occurring is not *driven* by the surrounding region (the average net flux around the subsystem boundary is fixed), the most probable path creating the particular fluctuation is the one that minimizes the dissipation.

The "minimum entropy production theorem" for stationary states [18] might appear to contradict Eq. (2) near equilibrium. To illustrate its relationship to Eq. (2), we consider a generalized version of the proof in Ref. [18]. One *presupposes* the equation of motion (6), which gives $\dot{S}=\int d\mathbf{r} L_{ij}\boldsymbol{\nabla}X_i\cdot\boldsymbol{\nabla}X_j$. The deterministic time evolution is then followed along a solution. Taking a time derivative and integrating by parts,

$$\frac{\partial\dot{S}}{\partial t}=\oint L_{ij}\frac{\partial X_j}{\partial t}\boldsymbol{\nabla}X_i\cdot d\mathbf{A}-\int d\mathbf{r}\nabla^2 X_i L_{ij}\frac{\partial X_j}{\partial t},\qquad(11)$$

where the first integral is over the boundaries between $\mathcal{S}$ and the reservoirs. For the series of quasistationary states generated as in Fig. 1, the values of X_i in $\mathcal{R}_m$, $X_i^{(m)}$ are independent of $\mathbf{r}$, and change only quasistatically in t. Using Eqs. (6) and (7), we get

$$\frac{\partial\dot{S}}{\partial t}=AJ_i^{(m)}\frac{\partial}{\partial t}X_i^{(m)}+\int d\mathbf{r}\frac{\partial a_i}{\partial t}\frac{\partial a_j}{\partial t}\frac{\partial X_i}{\partial a_j}+\int d\mathbf{r}(\mathbf{v}\cdot\boldsymbol{\nabla})a_i\frac{\partial X_i}{\partial t},\qquad(12)$$

where A is the surface area of the boundaries and $J_i^{(m)}$ is the flux out into $\mathcal{R}_m$. The integrand in the second term can be recognized as a special case of the second-order variation of entropy,

$$\delta^2 S=\frac{\partial^2 S}{\partial a_i\partial a_j}\delta a_i\delta a_j\leqslant 0,\qquad(13)$$

necessarily negative definite from the second law. For a time interval δt small enough such that $\delta X_i^{(m)}\simeq 0$, the first term in Eq. (12) is negligible. If we assume $\mathbf{v}=\mathbf{0}$, the entropy production monotonically decreases to reach the stationary state, which was the origin of the term "minimum entropy production." More appropriately, in the absence of convection, the stationary state is an attractor with minimum dissipation under the deterministic dynamics of trajectories maximizing Eq. (3). The stationary state near equilibrium thus can be thought of as a "saddle point" when we use the variations in trajectory, $\delta\mathbf{J}_i$ and δt, as the two axes (Fig. 2).

For a larger time interval $dt\gg\delta t$, for which $dX_i^{(m)}$ is nonnegligible, it is more convenient to observe that the series of quasistationary states satisfy

$$\dot{S}=\oint d\mathbf{A}\cdot\mathbf{J}_i X_i,\qquad(14)$$

since the overall entropy of $\mathcal{S}$ remains constant in stationary states. The quasistatic rate $d\dot{S}/dt$ is given by

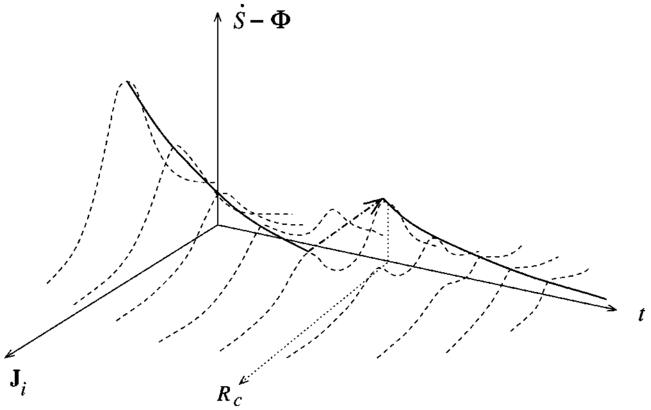

FIG. 2. A schematic rendering of the evolution of entropy production landscape expected for Fig. 1. A RBC system initially with $R>R_c$ at $t=0$ evolves toward the equilibrium where $R=0$ at $t=\infty$. At each t, the system $\mathcal{S}$ is in quasistationary states for the given $R(t)$. The $\mathbf{J}_i$ axis represents the space of macroscopic trajectories satisfying the conservation laws. The dotted lines are the $\dot{S}-\Phi$ profiles at each t. The thick solid lines are the loci of trajectories, given by Eq. (6), maximizing $\dot{S}-\Phi$. The convective roll state is replaced by conduction at the instability threshold where $R(t)=R_c$.

$$\frac{d\dot{S}}{dt}=A\frac{d}{dt}(J_i\Delta X_i)\leq 0, \tag{15}$$

where $J_i=J_i^{(2)}=-J_i^{(1)}$ and $\Delta X_i=X_i^{(2)}-X_i^{(1)}$. The inequality reflects the expectation that the magnitude of J_i, and therefore ΔX_i, would only decrease in time as the equilibrium is approached.

Figure 2 summarizes the expected behavior of the overall nonequilibrium thermodynamics represented by variational principle (3). A RBC system of Fig. 1, initially set up with a Rayleigh number above the threshold, $R>R_c$, at $t=0$, is allowed to relax toward equilibrium. At each time t, $\mathcal{S}$ is in a quasistationary state with $R=R(t)$. For any t, solutions to the equation of motion (6) correspond to the set of extrema of $\dot{S}-\Phi$. The maximum would be selected, which should also be hydrodynamically stable to be physically realizable. Equation (14) implies that for a given R, the overall heat flux, or the Nusselt number $\mathcal{N}$, would be maximized. For $t<t_c$ [where $R(t_c)=R_c$], convective rolls with a band of wave numbers are stable [13,24], and the roll with the maximum $\mathcal{N}$ would be realized. At the threshold, the rolls become unstable, and the conduction becomes the only stable solution for $R<R_c$. When we restrict ourselves to the loci of local maxima of Eq. (3), or equivalently, make a projection of the thick lines in Fig. 2 onto the t versus $\dot{S}$ plane (Fig. 3), the variational principle now takes the form of Eq. (2). Equation (15) dictates that the slope is negative therein.

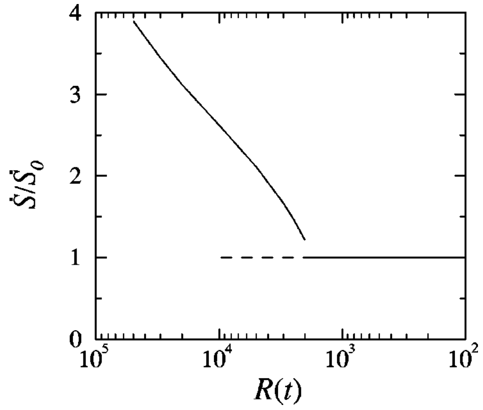

FIG. 3. A projection of the maximal path in Fig. 2 onto the t-$\dot{S}$ plane. The y axis shown is the the entropy production rate normalized by the pure conduction value, equal to the Nusselt number $\mathcal{N}$. The solid line for $R>R_c=1708$ is from Ref. [24] for the rolls with Prandtl number $P=7.0$ and wave number $\alpha=3.117$. The solid and dashed lines at $\mathcal{N}=1$ represent the stable and unstable branches of the conduction mode.

V. DISCUSSIONS

It should be noted that the existence and stability of the stationary solutions are determined not by the variational principle, but via the full nonlinear dynamics of Eq. (7). The entropy production rate is *not* a potential or Lyapunov function to the dynamics. Therefore, it is possible, and in fact has been noted before [13], that a solution might remain unstable and thus physically inaccessible even though it has a larger overall heat flux.

The plot of entropy production rate as a function of control parameter, such as Fig. 3, is a close analog of the equilibrium counterpart, the free energy versus an intensive variable. The threshold in RBC would then be an example of nonequilibrium phase transition. Unlike the full landscape shown in Fig. 2, it can be straightforwardly obtained for cases where one can obtain solutions to the nonlinear hydrodynamic equation. Thus the entropy production rate is seen to play the role of thermodynamic potentials for nonequilibrium stationary states.

Onsager's variational principle, Eq. (3), depends crucially on the validity of the linear phenomenological equation of motion, which justifies *a posteriori* the definition of the dissipation function (4). It remains to be seen whether Eq. (2), which appears general, still holds for systems where the basic dissipative relation is intrinsically nonlinear, as is typical in chemical reactions.

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[25] Equation (2) applies to an isolated system, whereas $\dot{S}$ in Eq. (3) is the entropy production rate of a general system $\mathcal{S}$. We can define $\mathcal{S}$ such that it contains all possible irreversibilities that can occur. In contrast to near-equilibrium cases, such a provision is necessary when patterns can arise, since $\mathcal{S}$ would then be macroscopically inhomogeneous.