I. INTRODUCTION

Equilibrium phase transitions are important in almost all areas of science, and it is the understanding, quantitative prediction, and control of them that underpin many areas of modern industry and technology. Equilibrium phases are characterized by their free energy, with the stable phase being the one with lower free energy and phase coexistence being determined by equality of their free energies. This is the same as maximizing the total (first) entropy, as demanded by the second law of equilibrium thermodynamics.1

The present paper continues a series based on a new law for nonequilibrium systems, namely, that the second entropy is maximal (for a recent review of the entire theory, see Ref. 2). Whereas the first or ordinary entropy is the entropy of structure or macrostates, the second entropy is the entropy of fluxes or transitions between macrostates. The claim is that the theory is completely general and encompasses all nonequilibrium systems, and a deal of quantitative evidence in support of the claim has been presented.2–5 The theory to date has been tested for nonequilibrium phenomena for which the answer is already known from existing thermodynamic or statistical mechanical approaches.

This paper addresses a class of nonequilibrium problems for which there is no accepted general theory, namely, the problem of nonequilibrium phases and the transitions between them. These are just as important as their equilibrium counterparts, possibly more so in view of the ubiquity of time-dependent phenomena. The phenomena associated with nonequilibrium phase transitions provide an opportunity to demonstrate that the author’s nonequilibrium theory can quantitatively describe an important nonequilibrium phenomenon that cannot be described with any other nonequilibrium thermodynamic theory.

To date most claims for a nonequilibrium theory have been based on the optimization of the rate of first entropy production, also known as the dissipation. It is claimed that this is an extreme in a stable nonequilibrium phase. Some assert that it should be minimal, others assert it that should be maximal, and still others assert both.6–8 Such disagreement among the protagonists themselves undermines the credibility of such approaches. Several detailed criticisms of these approaches have been made,9–12 including the fact that since the rate of first entropy production is a bilinear function of the forces and fluxes, its extreme values must lie at ±∞.2,13,14

The second entropy in fluctuation approximation turns out to be a quadratic function that is maximized in the optimum nonequilibrium state, and consequently it is larger in the stable phase than in the unstable phase. Its maximum value in any one phase is shown below to be numerically equal to one quarter of the rate of first entropy production, which implies that the rate of first entropy production is greater in the stable phase than in the unstable phase. Obviously, however, this rate of first entropy production is not the maximum rate of first entropy production that is possible in the phase (for the reasons given in the final clause of the preceding paragraph). While it is physically plausible and intuitively appealing that the rate of first entropy production should be larger in the stable nonequilibrium phase than in the unstable nonequilibrium phase, it ought to be clearly understood that this result is a direct consequence of the second law of nonequilibrium thermodynamics and the maximization of the second entropy. It does not arise from any variational principle for the rate of first entropy production or from any variant of the second law of equilibrium thermodynamics.

The particular nonequilibrium phase transition that is analyzed in detail in this paper is the Rayleigh–Bénard problem, which is the transition from heat conduction to convection. To date the main treatment of this problem is hydrodynamic either by stability analysis or by computational fluid dynamics.15,16 There have also been treatments based on the analysis of bifurcations in dynamical equations.17–19 Velarde et al.20 reviewed previous thermodynamic approaches to hydrodynamics and treated the conduction-convection transition with conventional hydrodynamic stability analysis. Velarde et al. defined a thermodynamic function Φ “based on the macroscopic excess work necessary to displace a
system...from a stationary state [p. 550] and used it to study qualitatively fluctuations in Rayleigh–Bénard convection with a Lorenz model.

The present approach provides a thermodynamic alternative to the hydrodynamic solution to the Rayleigh–Bénard problem. The location of the transition predicted by the present theory for a simple model of convection is compared with the conventional Rayleigh stability estimate, and quite good agreement is found. It is concluded that the second law of nonequilibrium thermodynamics, namely, that the second entropy is maximal, is indeed the general thermodynamic principle that determines the stability of nonequilibrium phases.

The paper is organized as follows. In Sec. II the law for nonequilibrium stability is given. In Sec. III the second entropy is written in integral form. It is shown that functional maximization yields the equations of nonlinear hydrodynamics. In Sec. IV a simple model for the Bénard cell is presented. An approximate but analytic formula for the second entropy is compared with Rayleigh’s. The Appendix summarizes relevant properties of the second entropy and treats multicomponent systems and chemical reactions.

II. NONEQUILIBRIUM PHASE STABILITY

The law governing nonequilibrium systems is

\[ \frac{\partial \sigma(\varepsilon, \rho)}{\partial \varepsilon} = \frac{1}{T}, \]  

\[ \frac{\partial \sigma(\varepsilon, \rho)}{\partial \rho} = -\frac{\mu}{T}, \]  

and

\[ \frac{p(\varepsilon, \rho)}{T(\varepsilon, \rho)} = \left( \frac{\partial V(\sigma(\varepsilon, \rho))}{\partial V} \right)_{E, N} = \sigma(\varepsilon, \rho) - \frac{\varepsilon}{T(\varepsilon, \rho)} + \frac{\rho \mu(\varepsilon, \rho)}{T(\varepsilon, \rho)}. \]  

These are for an isolated system at rest with no external potential. The right hand sides of these are all dependent on \( \varepsilon \) and \( \rho \). Such densities will be used at each point in the system, and these equilibrium thermodynamic relationships will be invoked locally.

The total linear momentum of the isolated system may be written \( \mathbf{p} = M \mathbf{v} \), where \( M \) is the total mass and \( \mathbf{v} \) is the center of mass velocity. The entropy may be written \( S(E, N, V, \mathbf{p}) = S(E - P^2/2M, N, V) \), where the right hand side is the entropy of a system at rest. Hence the momentum derivative is

\[ \frac{\partial S(E, N, V, \mathbf{p})}{\partial \mathbf{p}} = \left( \frac{\partial S(E - P^2/2M, N, V)}{\partial \mathbf{p}} \right)_{E, N, V} = -\frac{p}{MT} = -\frac{\mathbf{v}}{T}. \]  

Because of the trivial relationship between momentum and velocity, this shows that momentum is essentially a self-conjugate thermodynamic variable. In terms of the momentum density, \( \mathbf{p} = \mathbf{P}/V \), this is

\[ \frac{\partial \sigma(\varepsilon, \rho, \mathbf{p})}{\partial \mathbf{p}} = -\frac{\mathbf{v}}{T}. \]  

B. Conservation laws

The conservation law for number is

\[ \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J}_N(\mathbf{r}, t). \]  

The number flux is directly related to the local velocity,

\[ \mathbf{J}_N(\mathbf{r}, t) = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t). \]  

Energy is a conserved variable and so it obeys a conservation law,

\[ \frac{\partial s(\mathbf{r}, t)}{\partial t} = \rho(\mathbf{r}, t) \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} - \nabla \cdot \mathbf{J}_E(\mathbf{r}, t). \]  

The energy density \( \varepsilon \) comprises the kinetic energy, the intermolecular potential energy, and the external potential energy \( \varphi^i \), if present. In the event that the latter is explicitly time dependent, its partial temporal derivative is a source of energy, the first term on the right hand side.
There are three types of energy flux into a volume: the heat energy conducted across the boundaries, the molecular energy convected across the boundaries, and the work performed on the volume,

$$\mathbf{J}_E(r,t) = \mathbf{J}_E^0(r,t) + \mathbf{e}(r,t) \mathbf{v}(r,t) + \mathbf{p}_m(r,t) \cdot \mathbf{v}(r,t).$$

(11)

The thermodynamic contribution is due to conduction and occurs in the absence of molecular flow, $\mathbf{v}=0$. Although one can interpret the superscript 0 as signifying this fact, strictly speaking it denotes the adiabatic evolution of an isolated subsystem, with adiabatic referring to the microscopic Hamiltonian dynamics and its macroscopic consequences.\(^1\)

In the steady state, heat flow is denoted $\mathbf{J}_E^0$ and is proportional to the temperature gradient, as will be seen. Only the heat flux should be treated as a fluctuating quantity. The pressure tensor is symmetric\(^2\) and may be written as

$$\mathbf{p}_m = \rho \mathbf{v} \cdot \mathbf{v} \quad \text{for} \quad \text{linear momentum reads}$$

$$\mathbf{p}(r,t) = m_w \rho(r,t) \mathbf{v}(r,t),$$

where $m_w$ is the molecular weight. The conservation law for linear momentum reads

$$\frac{\partial \mathbf{p}(r,t)}{\partial t} = -\rho(r,t) \nabla \mathbf{v}^\text{ext}(r,t) - \nabla \cdot \mathbf{J}_p(r,t).$$

(12)

The first term is the external force per unit volume, and the second term contains the momentum flux tensor, which is\(^2\)

$$\mathbf{J}_p(r,t) = \mathbf{P}(r,t) + m_w \rho(r,t) \mathbf{v}(r,t) \mathbf{v}(r,t).$$

(13)

Only the viscous pressure tensor, $\mathbf{P} = \mathbf{P}(r,t)$, should be treated as a thermodynamic fluctuating quantity; the convective part of this, $m_w \rho \mathbf{v} \mathbf{v}$, and the equilibrium pressure part, $\mathbf{P}_m$, should be treated as mechanical terms.

**C. First entropy production**

The rate of total first entropy production, which may be simply called the entropy production or the dissipation, comprises that due to the subsystem and that due to the reservoir. The rate of change of the first entropy density of the subsystem, $\dot{\sigma}(\mathbf{r}, t)$, is

$$\frac{\partial \sigma(\mathbf{r}, t)}{\partial t} = \left[ \frac{\partial \mathbf{e}}{\partial \mathbf{e}} - \rho \frac{\partial \mathbf{v}^\text{ext}}{\partial \mathbf{e}} \right] \frac{\partial \sigma}{\partial \mathbf{e}} + \frac{\partial \mathbf{p}}{\partial \mathbf{p}} \frac{\partial \sigma}{\partial \mathbf{p}} + \frac{\partial \rho}{\partial \rho} \frac{\partial \sigma}{\partial \rho}$$

$$= \frac{1}{T} \nabla \cdot \mathbf{J}_E + \left[ \nabla \cdot \mathbf{J}_p + \rho \nabla \mathbf{v}^\text{ext} \right] \cdot \frac{\mathbf{v}}{T}$$

$$+ \nabla \cdot \mathbf{J}_0 \left( \frac{\mu}{T} + \frac{\psi}{T^2} - \frac{m_w \rho^2}{2T} \right).$$

(14)

Everything on the right hand side is a function of $(\mathbf{r}, t)$. Notice how the source term that is the external potential has been excluded from the energy contribution to the change in first entropy density. For example, lifting an egg to the top of a wall does not change its entropy even though its gravitational energy is changing. The above expression for the rate of first entropy production can also be obtained starting from the specific entropy, $s(e^\text{int}, \rho_m) = \sigma/m_w \rho$, where the specific internal energy is $e^\text{int} = e/m_w \rho - \mathbf{v}^\text{ext}/m_w \cdot \mathbf{v}/2$.

With this result, the rate of total first entropy production is

$$\dot{S}_\text{tot}^{(1)} = \int d\mathbf{r} \frac{\partial \sigma(\mathbf{r}, t)}{\partial t} + \oint d\mathbf{r} \cdot \sum_X J_X \frac{\partial S_r^{(1)}}{\partial X}$$

$$= \int d\mathbf{r} \left\{ \frac{1}{T} \nabla \cdot \mathbf{J}_E^0 - \frac{1}{T_m} \mathbf{P}_m (\nabla \mathbf{v}) - \frac{1}{T} \nabla \cdot (\mathbf{e}^\text{int} \mathbf{v}) \right\}$$

$$+ \frac{\mu}{T} \nabla \cdot (\rho \mathbf{v}) \right\} + \oint d\mathbf{r} \cdot \sum_X J_X \frac{\partial S_r^{(1)}}{\partial X}$$

$$= \int d\mathbf{r} \left\{ \mathbf{J}_E \cdot \nabla T^{-1} - \frac{1}{T_m} \mathbf{P}_m (\nabla \mathbf{v}) - \sigma \nabla \cdot \mathbf{v} \right\}$$

$$- \frac{\mathbf{v}}{T} \left[ \nabla \mathbf{e}^\text{int} - \mu \nabla \rho \right]$$

$$- \oint d\mathbf{r} \cdot \left[ \frac{\mathbf{J}_E^0}{T} - \sum_X J_X \frac{\partial S_r^{(1)}}{\partial X} \right].$$

(15)

This uses the fact that the entropy density may be written $\sigma = [e + e^\text{int} - \rho \mu] / T$. Eq. (5). An integration by parts of $\sigma \nabla \cdot \mathbf{v}$ shows that it cancels with the next two terms in the bulk integral, since $TV \sigma = \nabla e^\text{int} - \mu \nabla \rho$. In the first equality, the first integral, which is over the subsystem volume, represents the dissipation of the subsystem, whereas the second integral is over the boundary with the reservoir and represents the entropy production of the reservoir due to the flow of conserved variables across the boundary since $X$ represents energy, number, momentum, etc., depending on the specific reservoir present. The flow is into the reservoir since $\mathbf{n}$ is the normal pointing out of the subsystem. The above implicitly assumes that the boundary is fixed, although this requirement could be relaxed (if, for example, one was dealing with a pressure reservoir). An integration by parts has been performed to obtain the second equality. Notice the distinction between reservoir quantities, denoted by a subscript “$r$,” and subsystem quantities in the boundary integral. This result for the entropy production is formally exact and holds in general, including in constrained nonoptimum states.

In the steady state, the macroscopic state of the subsystem at each point $r$ is constant in time, and so the subsystem dissipation must vanish, $\partial \sigma(r,t)/\partial t=0$. Hence in the steady state the total dissipation is due to the reservoir alone,

$$\overline{\dot{S}_\text{tot}^{(1)}} = \oint \mathbf{r} \cdot \sum_X J_X \frac{\partial S_r^{(1)}}{\partial X}.$$  

(16)

The overline denotes the most likely dissipation, not the maximum dissipation.

In this work heat conduction and convection is treated in detail, in which case one has only a heat reservoir,

$$\sum_X J_X \frac{\partial S_r^{(1)}}{\partial X} = J_E 1/T.$$  

(17)

Also, energy exchange with the reservoir occurs by conduction alone, $\mathbf{J}_E=\mathbf{J}_E^0$, which means that the reservoir velocity vanishes at the boundary, $\mathbf{v}_r=0$. 

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D. Second entropy

A brief summary of the general properties of the second entropy is given in the Appendix. To recapitulate, the second entropy is the associativity with a transition between two macrostates in a specified time. The fluctuation formulation of the second entropy theory has been shown to encompass Onsager’s regression hypothesis, Onsager’s reciprocal relations, and Green–Kubo theory, as well as the macroscopic linear transport laws of hydrodynamics. Conceptually, at the fluctuations level the theory comprises two competing terms: an unfavorable term that is quadratic in the adiabatic fluxes, and a favorable term linear in the total fluxes that is equal to the rate of first entropy production.

That part of the first entropy production due to the viscous pressure tensor is most conveniently evaluated by decomposing the tensors into a scalar times the identity tensor, \( I \), plus a symmetric traceless tensor, denoted by an asterisk. In general, \( I \cdot A = 0 \), and \( A^{\text{sym}} \cdot B^{\text{sym}} = \tilde{A}^{\text{sym}} \cdot \tilde{B}^{\text{sym}} \). The viscous pressure tensor is written as

\[
\Pi = \Pi^{\text{sym}} + \Pi^{*}, \quad \sigma = \frac{1}{3} \text{Tr} \, \Pi, \quad \text{Tr} \, \Pi^{*} = 0 ,
\]

and the velocity gradient tensor is written as

\[
\nabla \mathbf{v} = \frac{\mathbf{v} \cdot \nabla}{3} + \left[ \nabla \mathbf{v} \right]^{\text{sym}}, \quad \text{Tr} \left[ \nabla \mathbf{v} \right]^{*} = 0 .
\]

The viscous pressure tensor is symmetric. (This follows because the net moment of force on an infinitesimal volume element must vanish in both equilibrium and nonequilibrium systems due to the fact that the force moment scales with a lower power of volume than does the moment of inertia, and so the angular acceleration of the volume element would be infinite unless the net force moment vanished.) With this decomposition the first part of the viscous pressure contribution to the rate of first entropy production may be written as

\[
\Pi^{\text{sym}} \left[ \nabla \mathbf{v} \right] = \Pi^{\text{sym}} \nabla \cdot \mathbf{v} + \Pi^{*} \left[ \nabla \mathbf{v} \right]^{\text{sym}}.
\]

The explicit elements of the symmetric traceless velocity gradient tensor are

\[
\left( \nabla \mathbf{v} \right)^{\text{sym}}_{\alpha} = \frac{1}{2} \left[ \frac{\partial v_{\beta}}{\partial x_{\alpha}} + \frac{\partial v_{\alpha}}{\partial x_{\beta}} \right] - \frac{1}{3} \delta_{\alpha \beta} \nabla \cdot \mathbf{v}.
\]

This decomposition for \( \Pi^{\text{sym}} \left[ \nabla \mathbf{v} \right] \) holds analogously for \( J_{E}^{0} \left( \nabla (v / T) \right) \).

An additional reason for this decomposition is the Curie symmetry principle, which states that scalars, vectors, and traceless second rank tensors do not couple, as proven in Ch. VI in Ref. 21. This means that the transport coefficient is a scalar in each case. The second entropy primarily consists of two quadratic terms for the adiabatic fluxes plus half the rate of total first entropy production, as given above. By writing the viscous pressure tensor as a scalar plus a traceless second rank tensor, one has three independent quadratic terms (a scalar, a vector, and a traceless second rank tensor), each with its own scalar transport coefficient. The term quadratic in the adiabatic energy flux is \( -k_{B} / 4 d_{E} J_{E}^{0} \left( J_{E}^{0} \right) \), the transport coefficient that appears here, \( d_{E} = -\lambda / T^{2} \), is essentially the thermal conductivity, and it is a scalar because in an isotropic medium, different Cartesian components do not couple. The term quadratic in the adiabatic momentum flux is

\[
-\frac{k_{B}}{4} \frac{d_{p}}{d_{p}} J_{E}^{0} \left( J_{E}^{0} \right) = -\frac{k_{B}}{4 d_{p}} \nabla^{2} \Pi^{*}.
\]

In view of the above, the \( \tau \)-dependent part of the second entropy for a single component system for convection is

\[
S^{(2)} (J_{E}^{0}, \Pi^{*}, \Pi^{*}, \rho, \mathbf{v}, |T, \tau| / \tau)
\]

\[
\frac{\dot{S}}{2} \left( J_{E}^{0}, \Pi^{*}, \Pi^{*}, \rho, \mathbf{v}, |T, \tau| / \tau \right)
\]

\[
\frac{1}{2} \left[ \frac{k_{B}}{4 d_{E}} J_{E}^{0} - \frac{k_{B}}{4 d_{p}} \nabla^{2} \Pi^{*} \right]
\]

\[
\frac{1}{2} \left[ \frac{k_{B}}{4 d_{p}} \nabla^{2} \Pi^{*} - \frac{k_{B}}{4 d_{p}} \nabla^{2} \Pi^{*} \right]
\]

A thermal reservoir with only conductive heat flow has been assumed here so that across the boundary \( J_{E}^{0} = J_{E}^{0} (r) \), and there are no other reservoir fluxes. At this stage the sub-system temperature \( T(r) \) is independent of the reservoir temperature \( T_{r}(r) \).

To obtain the steady state, the second entropy should be maximized with respect to the arguments to the left of the vertical bar. The bulk and surface regions can be maximized separately. Functional differentiation with respect to the adiabatic energy flux in the bulk gives

\[
\frac{\delta S^{(2)}(J_{E}^{0})}{\delta J_{E}^{0}(r)} = -\frac{k_{B}}{2 d_{E}} J_{E}^{0} (r) + \frac{1}{2} \nabla \cdot \nabla T^{-1},
\]

which vanishes for the most likely energy flux,

\[
J_{E}^{0}(r) = -\frac{d_{E}}{d_{E}} T^{-1} = -\lambda \nabla T^{-1},
\]

where \( \lambda \) is the thermal conductivity. Functional differentiation with respect to the adiabatic momentum flux, bearing in mind the appearance of the momentum flux in \( J_{E}^{0}(r) \), gives

\[
\frac{\delta S^{(2)}(\Pi^{*})}{\delta \Pi^{*}(r)} = -\frac{k_{B}}{2 d_{p}} d_{p} J_{E}^{0}(r) + \frac{1}{2} \nabla v(r) \nabla \frac{1}{T(r)} - \frac{1}{2} \nabla \cdot \nabla v(r).
\]

Setting this to zero gives the most likely or steady state value of the adiabatic momentum flux,

\[
\Pi^{*}(r) = -\frac{d_{p}}{k_{B} T(r)} \nabla \cdot v(r) = -\eta v \cdot v(r),
\]

and

\[
\tau(r) = -\frac{1}{k_{B} T(r) d_{p}} \nabla \cdot v(r).
\]
\[ \Pi^*(r) = -\frac{dE}{k_B T(r)} - 2\eta [\nabla \mathbf{v}(r)]^{\text{sym}}. \quad (29) \]

Here \( \eta \) is the bulk viscosity and \( \eta \) is the shear viscosity. These are possibly position dependent via their dependence on the local thermodynamic state.

These expressions for the most likely fluxes, together with the conservation laws and the equilibrium equation of state, are formally equivalent to the equations of nonlinear hydrodynamics, as can be readily shown. To take one example, the momentum conservation equation in the most likely state reads

\[ m_0 \rho \frac{d\mathbf{v}}{dt} = -\rho \nabla \psi^{\text{ext}} - \nabla \cdot \mathbf{P} - \mathbf{J} = -\rho \nabla \psi^{\text{ext}} - \nabla p + \eta \nabla \cdot (\nabla \mathbf{v})^{\text{sym}} + 2 \eta \nabla \cdot (\nabla \mathbf{v})^{\text{sym}} = -\rho \nabla \psi^{\text{ext}} - \nabla p + \eta \nabla \mathbf{v} + \left[ \eta_v + \frac{1}{3} \eta \right] \nabla \mathbf{v} \cdot \mathbf{v}. \quad (30) \]

This agrees with de Groot and Mazur.\(^{21}\) This equation determines the most likely velocity \( \mathbf{v} \).

Note that there is a deep conceptual difference between the present approach and that found in conventional books such as de Groot and Mazur.\(^{21}\) The present approach takes the viscous pressure tensor and the velocity gradient tensor to be independent variables. (It also takes the adiabatic heat flux vector and the temperature gradient to be independent variables.) They can be independently varied in the constrained nonoptimum state. In the most likely state, which in this work is the steady state, they are essentially equal to each other (apart from the transport coefficients), as shown in Eqs. (28) and (29). Most books regard the velocity gradient tensor as the definition of the viscous pressure tensor and freely interchange the two. Such an identification is numerically correct only in the steady state but not more generally. It is a common but unfortunate approach that discards the physical meaning of the two conceptually distinct objects. The present author has previously made similar comments in the context of equilibrium thermodynamics.\(^{1}\)

Now complete the maximization of the second entropy. Setting the derivative with respect to \( \mathbf{J}_E^0 \) to zero in the surface region shows that in the steady state, the subsystem temperature must equal the reservoir temperature around the boundary,

\[ \bar{T}(r) = T_s(r) \quad (\text{bdry}) \quad (31) \]

These steady state results give the maximum value of the second entropy,

\[ \frac{S^{(2)}}{T} = \int dr \left\{ -\frac{k_B}{4d_E} \mathbf{J}_E^0 \cdot \mathbf{J}_E^0 - \frac{k_B}{4d_p} \pi^2 - \frac{k_B}{4d^*_p} \Pi^* \cdot \Pi^* \right\} + \frac{1}{2} S^{(1)} + \frac{1}{4} \int dr \left[ -\frac{1}{T} \mathbf{J}_E^0 \cdot \nabla \mathbf{v} + \frac{1}{4T} \pi \mathbf{v} \cdot \mathbf{v} \right] = \int dr \left[ -\frac{1}{4} \mathbf{J}_E^0 \cdot \nabla \frac{1}{T} + \frac{1}{4T} \pi \mathbf{v} \cdot \mathbf{v} \right] + \frac{1}{4} \int dr \mathbf{r} \cdot \mathbf{v} . \quad (32) \]

The penultimate equality comes from an integration by parts of the energy flux; the remainder, which is the rate of first entropy production of the sub-system, Eq. (15), vanishes in the steady state. The final result has the interpretation of one quarter of the rate of first entropy production of the reservoirs. This is a physically reasonable result, since in the steady state the reservoirs produce entropy, the sub-system does not.

The conclusion is that the maximum value of the second entropy is equal to one quarter of the rate of first entropy production of the reservoirs. However, it is emphasized that the first and second entropy are conceptually distinct, and this numerical equality that occurs in the most likely state does not imply that maximizing the second entropy is the same as or is in any way related to maximizing the rate of first entropy production. As remarked in the fourth and fifth paragraphs of the introduction, although the second entropy maximization shows that the rate of first entropy production is greater in the stable phase than in the unstable phase, the value obtained is not the maximum possible value of the rate of first entropy production in the phase, nor does the value arise from any variational principle based on the rate of first entropy production itself.

The present analysis is rigorously applicable only to the case that the reservoir temperature is not a function of time. This is the same restriction that rigorously ought be applied to hydrodynamics. Of course in practice hydrodynamics is applied to non-steady problems until the time-variation becomes too fast and corrections are required in the form of time-dependent transport coefficients and memory functions. No doubt the regime of application of the present results will be similarly stretched, although in the case of the second entropy there is a formally exact path for treating transient phenomena and including memory effects.\(^{2,22}\)

This section shows that the integral form of the second entropy, Eq. (23), provides the variational principle for single component nonequilibrium systems. Multicomponent systems will be treated elsewhere. The present second entropy theory is more general than nonlinear hydrodynamics since it is identical to the latter in the steady state, but it also applies more generally to constrained nonoptimum states.

**IV. RAYLEIGH–BÉNARD CONVECTION**

Now the second entropy is used to describe the conduction-convection transition in a Rayleigh–Bénard cell. One way to do this would be to maximize numerically the integral representation, Eq. (23), bearing in mind the conservation laws and the equilibrium equation of state. Such an approach would be exact and equivalent to solving the hydrodynamic equations for the flow. In the future, the numerical implementation of Eq. (23) may provide an alternative to...
computational fluid dynamics that with optimization might come to rival it in efficiency, but this not the point of the present paper.

Here an approximate solution is sought. The chief virtue of variational approaches is that they provide a robust approximation scheme: first order errors in the trial function lead to second order errors in the estimated quantity. Of course, the outstanding example of a variational scheme is the second law of equilibrium thermodynamics, which has been much exploited to characterize equilibrium phase transitions. For the present problem of nonequilibrium phase stability, where one wants to compare the value of the second entropy in different phases, one anticipates that a variational scheme with approximate fluxes will be provide an acceptable compromise between simplicity and accuracy.

In the convection calculation below, the maximum value of the second entropy will be estimated from one quarter the rate of first entropy production. As mentioned above at the end of Sec. III D, the two are equal in the full solution of the problem. For an approximate solution such as that obtained below, the estimate need not be a lower bound on the exact second entropy. This point is worth emphasizing: the second entropy obtained for approximate fields of $\epsilon$, $\rho$, and $\mathbf{v}$ is not necessarily less than the exact second entropy. One can only say that in so far as the specified fields and fluxes approximate those that occur in reality, then the calculated second entropy will approximate the actual second entropy to second order in the error in the trial fields and fluxes.

### A. Conduction

For the case of conduction, the total cross-sectional area for heat flux is $L_x L_y$. The temperature profile is

$$ T(y,z) = T_0 + \Delta_T z / L_y, \quad (33) $$

This holds for $|z| \leq L_y / 2$, with the temperature difference being $\Delta_T = T_u - T_d < 0$ and the midplane temperature being $T_0 = [T_u + T_d] / 2$. The density profile is

$$ \rho(y,z) = \rho_0 - \alpha \rho_0 \Delta_T z / L_y, \quad (34) $$

where the coefficient of thermal expansion is $\alpha = -\rho^{-1} \partial \rho / \partial T$ and $\rho_0$ is the midpoint density, $\rho_0 = [\rho_u + \rho_d] / 2$. Since in the equilibrium case one must have $dp(z) / dz = -m_w g \rho(z)$, integration gives the pressure profile

$$ p(y,z) = \rho_0 - m_w g \rho_0 \left[ z - \alpha \Delta_T z^2 / 2 L_y \right]. \quad (35) $$

This assumes that the fluid is incompressible.

For conduction, the velocity and the viscous pressure tensors vanish. Also, the reservoir contribution vanishes since $\mathbf{f}(\mathbf{r},t) = T(\mathbf{r},t)$ at the boundary. The most likely value of the energy flux is $\mathbf{J}^0 = k_B^\mathbf{L} dE / dL_y$. Hence the maximum value of the $\tau$-dependent part of the second entropy is

$$ \mathbf{S}^{(2)}_{\text{cond}} = \int dr \left[ dE / 4dE \right] \mathbf{J}^0 + \frac{\tau_0}{2} \nabla \mathbf{T}^{-1} $$

$$ = \frac{\tau_0}{4} \int dr \mathbf{J}^0 \cdot \nabla \mathbf{T}^{-1} $$

$$ = \frac{\tau_0 L_x L_y \Delta_T}{4k_B} \int dz \left( \frac{d\mathbf{T}(z)}{dz} \right)^2 $$

$$ = \frac{\tau_0 L_x L_y \Delta_T^2}{4L_y^2} + O\Delta_T^3. \quad (36) $$

### B. Convection

For the model of a convective roll sketched in Fig. 1, one can imagine the four sided flow as shear flow induced by four rectangular channels. This picture is most appropriate near the midplanes. Doubtless more sophisticated models are possible, but this one yields analytic results and is sufficiently transparent to follow the various contributions to the phenomenon.

The fields of temperature, energy, density, pressure, and velocity need to be specified. Obviously one chooses these in such a way that they approximate the expected fields and that a convective roll results. The focus is on two-dimensional flow in the $x=0$ plane, with the central convecting cell being $|z| \leq L_y / 2$ and $|y| \leq L_x / 2$. The direction of rotation alternates in adjacent cells. Assume that the rotation is counterclockwise in the central cell (Fig. 1).

For convection, the conduction temperature profile, Eq. (33), is perturbed by a term that must be an odd function of $y$ and that reaches its extremes at $y = \pm L_x / 2$. It must also be an even function of $z$ that vanishes at $z = \pm L_y / 2$. Hence to leading order it must be of the form

$$ T(y,z) = T_0 + \frac{\Delta_T z}{L_y} + \alpha \left[ y - \frac{4y^3}{3L_x^2} \left( 1 - \frac{4z^2}{L_y^2} \right) \right]. \quad (37) $$

The constant $\alpha$ is determined from the fact that the temperature field must reach its extreme values at the lower right and upper left corners of the central convection cell (for an anticlockwise roll), where it must equal the temperature of the adjacent reservoirs. Setting the derivative with respect to $z$ to zero in these two corners, it is straightforward to show that $\alpha = -3 \Delta_T / 4 L_y$, so that one has
T(y,z) = T_0 + \frac{\Delta \zeta}{L_z} 3 \frac{\Delta T}{4 L_y} y - 4 \frac{y^3}{3 L_y^2} \left[ 1 - \frac{4 z^2}{L_z^2} \right]. \tag{38}

Using this, the density profile is \( \rho(y,z) = \rho_0 = \alpha \rho \frac{T(y,z) - T_0}{L_z} \) and the internal energy density profile is \( e^{im}(y,z) = \epsilon_0 + c_p \left[ T(y,z) - T_0 \right], \) where \( c_p \) is the heat capacity at constant pressure per unit volume.

In convection, the perturbation of the conduction pressure profile must be odd in \( y, \) must reach its extremes at \( y = \pm L_y/2, \) and must be odd in \( z. \) Hence to leading order it must be of the form

\[
\rho(y,z) = \rho_0 - m_w \rho \left[ z - \frac{\alpha \Delta \zeta}{2 L_z} \right] + b \left[ y - \frac{4 y^3}{3 L_y^2} \right] z, \tag{39}
\]

with \( b \) to be determined.

Now the horizontal and vertical velocity fields are obtained near the midplane planes of their respective channels. The fluid is assumed incompressible, \( \nabla \cdot \mathbf{v} = 0, \) which means that the scalar part of the most likely viscous pressure tensor vanishes, \( \overline{\pi} = 0. \) Setting the rate of change in (most likely) momentum to zero, Eqs. (12) and (29), and using the incompressibility assumption give the differential equation for the vertical velocity. For the horizontal flux near \( y = 0, \) one has

\[
\eta \frac{\partial^2 v_y(y,z)}{\partial z^2} = \frac{\partial p(y,z)}{\partial y} = b \left[ 1 - \frac{4 y^2}{L_y^2} \right] z. \tag{40}
\]

Since the velocity vanishes at the wall and at the center, \( v_y(y,0) = v_y(y, \pm L_y/2) = 0, \) this has solution

\[
v_y(y,z) = \frac{b}{6 \eta} \left[ 1 - \frac{4 y^2}{L_y^2} \right] \left[ z^3 - \frac{L_y^2}{4} z \right]. \tag{41}
\]

The number flux in the upper channel across the plane at \( y = 0 \) is

\[
\dot{N}_y = L_y \int_{-L_y/2}^{L_y/2} dz \rho(0,z) v_y(0,z) = - \rho_b b L_y L_z^4 \frac{3 L_y^2}{2 \eta}. \tag{42}
\]

where only \( \rho_b, \) the leading order contribution to the density, is retained.

Now for the vertical velocity near the midplane \( z = 0. \) The differential equation is

\[
\eta \frac{\partial^2 v_z(y,z)}{\partial y^2} = \frac{\partial p(y,z)}{\partial z} + m_w \rho \frac{\partial p(y,z)}{\partial y} = \left[ b + m_w \rho \frac{3 \alpha \Delta T}{4 L_y} \left[ 1 - \frac{4 z^2}{L_z^2} \right] \right] \left[ y - \frac{4 y^3}{3 L_y^2} \right] = B(z) \left[ y - \frac{4 y^3}{3 L_y^2} \right]. \tag{43}
\]

With the velocity vanishing at \( y = 0 \) and reaching its maximum magnitude at \( |y| = L_y/2, \) this has solution

\[
v_z(y,z) = \frac{B(z)}{\eta} \left[ - 5 y L_y^2 + \frac{y^3}{4} + \frac{y^5}{6} - \frac{y^5}{15 L_y^2} \right]. \tag{44}
\]

Using this, the number flux in the right hand vertical channel across the plane at \( z = 0 \) is

\[
\dot{N}_z = L_z \int_0^{L_z/2} dy \rho(0,z) v_z(0,z) = - \frac{61 \rho_b L_y L_z^4}{45 \times 2^7 \eta} B(0). \tag{45}
\]

Again only the leading order contribution to the density has been retained.

From number conservation, one must have \( \dot{N}_y = - \dot{N}_z. \) Using the above expressions and solving for \( b \) yields

\[
b = - \frac{3 m_w \rho \alpha \Delta T}{4 L_y} \frac{61 L_z^4}{15 L_y^4 + 61 L_y^4}, \tag{46}
\]

and hence

\[
B(0) = \frac{3 m_w \rho \alpha \Delta T}{4 L_y} \frac{15 L_y^4}{15 L_y^4 + 61 L_y^4}. \tag{47}
\]

It ought to be mentioned that these are approximations for the field variables. In particular, the velocity field does not satisfy the condition for an incompressible fluid in the steady state in a small temperature gradient, which is \( \nabla \cdot \mathbf{v} = 0. \) Using the above expressions and solving for \( b \) yields

\[
B(0) = \frac{3 m_w \rho \alpha \Delta T}{4 L_y} \frac{15 L_y^4}{15 L_y^4 + 61 L_y^4}. \tag{48}
\]

Because \( v_z \) is odd in \( y, \) only the internal part of the energy density contributes to this because it is also odd. Taking this convective energy transport to be the dominant form of energy transport, this net flux across the midplane represents the flow of energy from the hot reservoir to the cold reservoir. Hence the rate of first entropy production of the reservoirs is

\[
S^{(1)} = E_{\text{conv}} \left[ \frac{1}{T_+} - \frac{1}{T_-} \right] = - \frac{m_w \rho \alpha \Delta T L_y^3}{4 \eta} \frac{31 L_y^4}{21 \times 2^7 \eta T_0^5} \frac{15 L_y^4 + 61 L_y^4}, \tag{49}
\]

which is positive, as it must be.

As noted at the end of Sec. III, the maximum value of the second entropy divided by \( \tau \) is one quarter of the rate of first entropy production of the reservoirs. Hence for convection,

\[
S^{(2)}_{\text{conv}} = \frac{\tau}{4} S^{(1)} = - \frac{m_w \rho \alpha \Delta T L_y^3}{4 \eta} \frac{31 L_y^4}{21 \times 2^7 \eta T_0^5} \frac{15 L_y^4 + 61 L_y^4}. \tag{50}
\]

C. Phase coexistence

The stable nonequilibrium phase is the one with the greatest second entropy. The ratio of the second entropy for convection to that for conduction is
The present analysis uses approximate values of the field variables, \( \tilde{\eta} \). This indicates that the present approximations overestimate the exact second entropy for the specified boundary conditions. In any case, given the simplicity of the model and the crudity of the approximations, the present estimate is surprisingly good. It supports the notion that in general, variational results with very little work.

### V. CONCLUSION

In this paper an integral formulation of the second entropy was given. It was shown that the functional maximization of the integral with respect to the fluxes, together with the conservation laws and the equilibrium equation of state applied locally, was equivalent to the equations of nonlinear hydrodynamics. Hence the integral form of the second entropy represents a variational formulation of nonlinear hydrodynamics. The merits of such a variational approach were illustrated by a relatively simple calculation of convection that yielded an estimate of the Rayleigh–Bénard transition which it is enabled to produce disorder.

More generally, the second entropy provides a way to understand in physical terms how order can arise in nonequilibrium systems. The second entropy basically consists of two terms: a quadratic term that is negative and that represents the entropic cost of ordering the fluxes and a linear term, which is positive and is the first entropy that is produced by the flow down the thermodynamic gradient. Both terms are on-going and are linear in time. These two competing terms determine the stable state: small fluxes grow since that is the regime in which the linear term dominates and large fluxes are naturally damped when the quadratic term becomes dominant. The second entropy shows that the ordered state is the most probable state, provided that it facilitates the production of first entropy at a sufficiently great rate.

An interesting consequence of the second entropy theory is the way in which it accounts for the spontaneous induction of both dynamic and structural orders in nonequilibrium systems. For the present case of heat flow, the dynamic order is obvious whether it is the net flux of energy in the case of conduction or the macroscopic motion of matter and energy in the case of convection. Less obvious but still present is the induced structural order as a nonzero energy moment and temperature gradient in the subsystem in the case of conduction or these plus spontaneous pressure gradients that occur in convection. This induced structural order facilitates the production of first entropy.

The significance of thermodynamics is its universality, and the present second entropy theory for nonequilibrium thermodynamics is no exception. It applies to living as well as to nonliving systems. Of course it is something of a leap to go from heat convection to life itself, and doubtlessly a few devils lurk among the details; nevertheless life must also be subject to the general principle of nonequilibrium thermodynamics, namely, the maximization of second entropy. In this regard one can see that life represents a form of order, with perhaps the structural aspects being more obvious than the dynamic aspects. However, common with the type of nonequilibrium transitions treated here, the structures of the living biosphere and of individual bio-organisms enable entropy to be produced at a greater rate than it otherwise would be, (i.e., on a dead planet or by inanimate matter). This notion is similar to Prigogine’s interpretation of dissipative structures. What is added in the present perspective is the competition between the two effects: life can be regarded as an organization that produces change in time, with the complexity of the organism determined by the balance between the improbability of maintaining its order and the rate at which it is enabled to produce disorder.

Darwin summed up evolution as the survival of the fittest. To many this is unsatisfying in the sense that it is arguably tautological and frustratingly silent on the nominal contradiction between the evolution of life and the second law of equilibrium thermodynamics. The second entropy theory provides the missing driving force for evolution and the ultimate limitation to evolution. It suggests that organisms, ecosystems, and society evolve toward ever increasing rates of entropy production and that they will cease evolving when their complexity becomes commensurate with their rates of production. In short, fitness survives, but dissipation thrives.

### APPENDIX: THE SECOND ENTROPY

Consider an isolated system. Let \( x \) be a vector of nonconserved phase variables (e.g., energy or density moments, number of reactants, position of solutes, etc.). The first entropy for the macrostate \( x \) is


\[ S^{(1)}(x) = k_B \ln \int d\Gamma \delta(x(\Gamma) - x), \]  

where the integral is confined to the energy and momentum hypersurface and \( \Gamma \) is a point in the subsystem phase space. The exponential of the first entropy gives essentially the probability of the macrostate. The second entropy for the transition \( x \rightarrow x' \) in time \( \tau \) is formally

\[ S^{(2)}(x', x | \tau) = k_B \ln \int d\Gamma \delta(\dot{x}(\Gamma) - x) \delta(x(\Gamma') - x'), \]  

where \( \Gamma' = \Gamma(\tau + \tau, \Gamma, \tau) \) is the adiabatic evolution of \( \Gamma \) in time \( \tau \). The exponential of the second entropy gives the transition probability. Writing \( \dot{x}(x, \tau) \) as the most likely transition value, one has the formally exact reduction condition

\[ S^{(2)}(\dot{x}(x, \tau), x | \tau) = S^{(1)}(x). \]  

To obtain tractable analytic results, one proceeds to the fluctuation level of approximation. For simplicity take \( \dot{x} = (\dot{x}) = 0 \), and write the fluctuation form of the first entropy as

\[ S^{(1)}(x) = \frac{1}{2} x S x, \]  

where the fluctuation matrix \( S \) can be written as the inverse of the matrix of static correlation functions. The quadratic form for the second entropy is

\[ S^{(2)}(x', x | \tau) = \frac{1}{2} x A(\tau) x + x B(\tau) x' + \frac{1}{2} x' A(\tau) x' \]
\[ = \frac{1}{2} [x' - x] A(\tau) [x' - x] + x [B(\tau) + A(\tau)] [x' - x] + x [A(\tau) + B(\tau)] x \]
\[ = \frac{1}{2} [x' + A(\tau)^{-1} B(\tau)] A(\tau) [x' + A(\tau)^{-1} B(\tau)] x \]
\[ + \frac{1}{2} x [A(\tau) - B(\tau)] A(\tau)^{-1} B(\tau) x. \]  

This is the most general quadratic form for the case that the variables are all of the same time parity, in which case time symmetry implies \( A' = A \) and \( B = B^T \). The fluctuation matrices \( A \) and \( B \) can be formally expressed in terms of time correlation functions (see Sec. IC2 of Ref. 2). These equalities, in which no further approximations have been introduced, emphasize various physical aspects of the second entropy. The most likely value is readily obtained by maximization,

\[ \dot{x}(x, \tau) = -A(\tau)^{-1} B(\tau) x, \]  

and so from the third equality for \( S^{(2)} \) and the reduction condition, one deduces the exact result,

\[ A(\tau) - B(\tau) A(\tau)^{-1} B(\tau) = S. \]  

Now to make approximations, write \( A(\tau) = -D(\tau)^{-1} + a(\tau) \) and \( B(\tau) D(\tau)^{-1} + b(\tau) \), where \( a \) and \( b \) are relatively small and \( D(\tau) \sim |\tau| D \). The appearance of the absolute value arises from the time symmetry of the fluctuations. This resembles a small \( \tau \) expansion but not exactly so. Inserting this in the reduction condition yields

\[ A(\tau) + B(\tau) = a(\tau) + b(\tau) = S/2 + \ldots, \]  

where higher order terms here and below are neglected. Using this in the second equality for the second entropy yields

\[ S^{(2)}(x', x | \tau) \approx -\frac{1}{2} \dot{x} D^{-1} \dot{x} + \frac{\tau}{2} \dot{x} S x + \frac{1}{2} \dot{x} S x, \]  

where \( \dot{x} = (x' - x)/\tau \) is the coarse velocity. One can identify the final term as the first entropy of the initial state and the second term as half the rate of first entropy production since \( \dot{x} = \frac{dS(x)}{dx} \) is the thermodynamic force. The approximation breaks the symmetry between \( x' \) and \( x \), and as well the second entropy no longer obeys exactly the reduction condition. The most likely coarse velocity is

\[ \dot{x} = -\frac{\tau}{2} \frac{x}{D S x}. \]

This can be seen to be Onsager’s regression hypothesis. (If a reservoir was applied, this subsystem thermodynamic force would equal the thermodynamic force applied by the reservoir.) Since \( A \) and hence the transport matrix \( D \) are second derivative matrices, they are symmetric, and so this also encompasses Onsager’s reciprocal relations. Multiplying both sides of this result by \( x \) and taking the average yield the Green–Kubo formulae. 2,3

The maximum value of the approximate form for the second entropy, which is its value in the most likely state, is

\[ \overline{S^{(2)}}(x | \tau) = \frac{\tau}{4} \dot{x} S x + \frac{1}{2} \dot{x} S x. \]  

As mentioned above, the approximation no longer obeys the reduction condition. The \( \tau \)-dependent term here is one quarter of the rate of first entropy production.

One of the reasons for using the approximate form for the second entropy is that the physical identification of the two final terms makes it particularly easy to generalize to the case where a reservoir is attached to the subsystem. One simply has to add to the isolated system result one half of the entropy production of the reservoir plus one half of the entropy production of the subsystem that is due to the reservoir plus the subsystem dependent part of the first entropy of the reservoir. One does not add any term that is quadratic in the reservoir fluxes because it is assumed that the conductivity of the reservoir is infinite.


