

Tailoring the first law of thermodynamics for convective flows

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Equilibrium thermodynamics is grounded in the law of energy conservation, with a specific focus on how systems exchange energy with their environment during transitions between equilibrium states. These transitions are typically characterized by quantities such as heat absorption and the work needed to alter the system's volume. This study is inspired by the potential to develop an analogous, straightforward thermodynamic description for systems that are out of equilibrium. Here, we explore the global energy exchanges that occur during transitions between these nonequilibrium states. We study a system with heat flow and an external (gravity) field that exhibits macroscopic motion, such as Rayleigh-Bénard convection. We show that the formula for system's energy exchange has the same form as in equilibrium. It opens the possibility of describing out-of-equilibrium systems using a few simple laws similar to equilibrium thermodynamics.

I. INTRODUCTION

Consider the phenomenon where water, despite being cooled below its freezing point, remains in a liquid state - an unstable condition known as supercooling. A minor disturbance, such as a simple shake, can trigger a rapid transition to solid ice. Equilibrium thermodynamics provides a comprehensive framework to understand such behaviors, predicting the stability of equilibrium states by analyzing energy flow and exchanges with the surrounding environment [2]. But what about systems that are out of equilibrium? Can their stability also be inferred from energy considerations?

Motivated by this question, this paper explores the possibility of a thermodynamic-like theory for nonequilibrium systems. Specifically, we examine systems like a gas undergoing macroscopic heat-driven convection (illustrated in Fig. 1), which can exhibit abrupt state changes in response to minor temperature variations [10, 14]. Developing a predictive theory for these nonequilibrium transitions, akin to equilibrium thermodynamics, could profoundly enhance our understanding of atmospheric phenomena and improve designs in areas like steady state chemical reactors [13].

To develop a thermodynamic-like theory beyond equilibrium, we concentrated on a basic aspect of equilibrium thermodynamics: energy balance. This concept is represented in thermodynamics by the first law. Energy is a fundamental physical quantity, and the energy balance beyond equilibrium has been studied in many different contexts. The local (in infinitesimally small volume) energy balance is the foundation of linear irreversible thermodynamics [6]. There is a vibrant research field of stochastic thermodynamics related to energy balance for small systems [7, 23, 28, 29, 31].

However, examining the total energy balance in macroscopic nonequilibrium systems has received limited attention. Even for equilibrium systems, hydrodynamic-based examination of the total energy balance in transitions between macroscopic equilibrium states has been performed recently [30]. Beyond equilibrium, a similar approach has

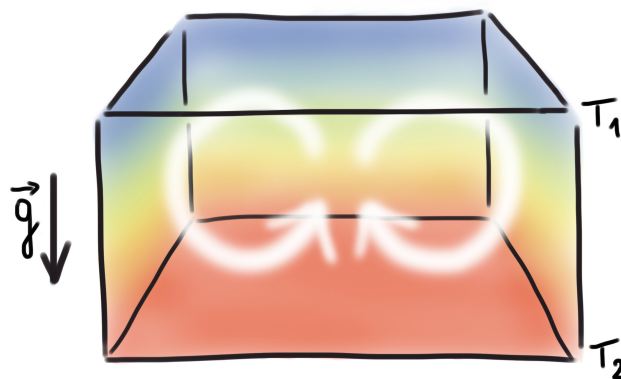


Figure 1. Rayleigh-Bénard convection in a fluid. The figure illustrates the temperature distribution and the resulting convective flow pattern in a fluid subjected to a temperature gradient. The bottom boundary, denoted by T_2 , is at a higher temperature, while the top boundary, denoted by T_1 , is at a lower temperature. The temperature gradient, combined with the gravitational field \mathbf{g} acting downward, induces buoyancy-driven convection. Colors schematically show temperature profile (red - hotter, blue - colder).

been used to study of the total energy balance for a quiescent fluid in a heat flow [15–17, 20]. These studies show that in a mixture of gases in the presence of heat flow or a gravity field, the total energy balance has a simple form, $dE = dQ + dW$, with dQ being the heat, and dW is the volumetric work. The total energy balance in these nonequilibrium systems has the same form as in equilibrium thermodynamics. For more complicated systems that contain macroscopic flow, such as ideal gas between parallel plates in a shearing motion that exhibits nonequilibrium phase transition [22], the energy balance, $dE = dQ + dW + dW_w$, contains another term dW_w which does not appear in equilibrium. It represents the excess shear work of the plate that induces the shearing motion of the gas.

It is worth mentioning that the term “first law” already appeared in the context of systems with shearing flow

[11, 12]. However, the term “first law” used in papers [11, 12] refers to the fundamental relation solely for internal energy [4, 5]. The fundamental relation is another vivid topic [24, 27] but is beyond the scope of the current paper.

It has been recognized that in steady state systems, there is a component of the heat exchanged with the environment, in addition to the steady state heat flow, known as excess heat and denoted as $\dot{d}Q$. This excess heat may play a crucial role in developing a thermodynamic-like description of steady states [26]. The excess heat by itself has been recently studied by different researchers experimentally [33] and theoretically [1, 3, 8, 9, 21].

On the one hand, the studies mentioned above offer a promising foundation for achieving a thermodynamic-like description of nonequilibrium states. On the other hand, one might be curious that one of the most common systems has not been approached in a thermodynamic-like manner. Indeed, heat-driven convection, which serves as a window to understanding atmospheric phenomena and turbulent systems, still awaits even basic study. A similar observation has been expressed recently by Yoshimura and Ito [34] who claim “Deterministic hydrodynamic systems described by the Navier-Stokes equation are among the least investigated subjects”. Nakagawa and Sasa also made similar observations discussing the concept of heat in nonequilibrium states [25].

Following this line of reasoning, we derive the global energy balance for the nonequilibrium system depicted in Fig. 1. The presented energy balance describes the transitions of the system due to the change of boundary temperatures, the shape of the system, and the shift in the gravity field. The resulting global energy balance mirrors the first law of equilibrium thermodynamics and simplifies to the equilibrium first law when transitions occur between equilibrium states. Given that the system in Fig. 1 captures key features of atmospheric dynamics, heat-driven convection, and turbulence, this achievement represents a significant step toward formulating a thermodynamic-like description for many out-of-equilibrium systems.

II. BALANCE EQUATIONS OF A SINGLE COMPONENT SYSTEM WITH TIME DEPENDENT POTENTIAL

To understand how a nonequilibrium system exchanges energy with its environment, we assume a hydrodynamic description of the system [6]. The total energy consists of macroscopic kinetic energy (related to the macroscopic motion determined by the average velocity field \mathbf{v} in the system), $e_{kin} = \mathbf{v}^2/2$, internal, u , and gravitational energy φ . The total energy density per unit mass is defined as

$$e = e_{kin} + u + \varphi. \quad (1)$$

The flow of the energy is described by corresponding flux

$$\mathbf{J}_e = \rho e \mathbf{v} + P \cdot \mathbf{v} + \mathbf{J}_q, \quad (2)$$

which includes convection (ρ is the volumetric mass density) and fluxes of the energy due to mechanical work, $P \cdot \mathbf{v}$ (the pressure tensor is denoted by P), and the heat flux, \mathbf{J}_q . The evolution equations in hydrodynamics take the form of a balance equation,

$$\frac{\partial}{\partial t} f(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}(\mathbf{r}, t) + \sigma(\mathbf{r}, t), \quad (3)$$

where f is volumetric density, $\mathbf{J}(\mathbf{r}, t)$ is flux and $\sigma(\mathbf{r}, t)$ is the source term. We decompose \mathbf{J} into a convective term, $f(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)$, and the rest (non-convective),

$$\mathbf{J}(\mathbf{r}, t) = f(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) + \mathbf{J}_{nc}(\mathbf{r}, t), \quad (4)$$

which is the definition of non-convective flux $\mathbf{J}_{nc}(\mathbf{r}, t)$. In particular, with

$$f_e = \rho e, \quad (5)$$

$$\mathbf{J}_{nc,e} = P \cdot \mathbf{v} + \mathbf{J}_q, \quad (6)$$

$$\sigma_e = \rho \partial_t \varphi, \quad (7)$$

we obtain the total energy balance equation

$$\partial_t \rho e = -\nabla \cdot \mathbf{J}_e + \rho \partial_t \varphi. \quad (8)$$

With

$$f_\varphi = \rho \varphi, \quad (9)$$

$$\mathbf{J}_{nc,\varphi} = 0, \quad (10)$$

$$\sigma_\varphi = \rho \mathbf{v} \cdot \nabla \varphi + \rho \partial_t \varphi, \quad (11)$$

we get the external potential balance equation

$$\partial_t \rho \varphi = -\nabla \cdot (\rho \varphi \mathbf{v}) + \rho \mathbf{v} \cdot \nabla \varphi + \rho \partial_t \varphi. \quad (12)$$

With

$$f_{ekin} = \rho e_{kin}, \quad (13)$$

$$\mathbf{J}_{nc,ekin} = P \cdot \mathbf{v}, \quad (14)$$

$$\sigma_{ekin} = P : [\nabla \mathbf{v}] - \rho \mathbf{v} \cdot \nabla \varphi, \quad (15)$$

we get the kinetic energy balance equation

$$\partial_t \frac{1}{2} \rho \mathbf{v}^2 = -\nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + P \cdot \mathbf{v} \right) + P : [\nabla \mathbf{v}] + \rho \mathbf{v} \cdot (-\nabla \varphi). \quad (16)$$

With

$$f_u = \rho u, \quad (17)$$

$$\mathbf{J}_{nc,u} = \mathbf{J}_q, \quad (18)$$

$$\sigma_u = -P : [\nabla \mathbf{v}], \quad (19)$$

we obtain the internal energy balance equation

$$\partial_t \rho u = -\nabla \cdot (\rho u \mathbf{v} + \mathbf{J}_q) - P : [\nabla \mathbf{v}]. \quad (20)$$

Notice that the sum of the last three cases gives the energy balance equation (the first case above), because total energy is the sum of external, kinetic and internal energy. It is worth mentioning that the above balance equations generalize the considerations presented in the monograph of Mazur and de Groot [6] to include the time dependent external potential $\varphi(\mathbf{r}, t)$.

We further assume that the above mentioned hydrodynamic densities, fluxes and sources along with the velocity field are known. To determine the evolution of energies in practice we would have to supplement the above description with additional information (equations of states, constitutive relations, boundary conditions). However, as we will see, for the investigation of the general structure of the system's energy exchange with its environment, the above quantities are sufficient and other parts of hydrodynamic theory are not essential. Energy is a fundamental physical quantity conserved on the most basic level. It will be conserved independently of how the heat flux is related to the temperature field or any other system's properties, such as those that are considered in rational and extended thermodynamics [18].

III. GLOBAL ENERGY BALANCE EQUATIONS

In the previous section we discussed time dependent balance equations defined at each point in space. These equations describe both the system and its environment. By the system we mean a part of the space (a region), confined within the volume $V(t)$, which may move over time. For example, in a steady situation presented in Fig. 1, the gas inside the box has a time independent volume V . However, if we consider the motion of the wall, the region V will change over time according to the motion of its boundary, $\partial V(t)$. The motion of the boundary of the system defines the velocity of the boundary of the volume, $\mathbf{v}_V(\mathbf{r}, t)$. This velocity is defined only for \mathbf{r} on the boundary of $V(t)$.

In the attempt to construct global thermodynamics, we focus on how the total energy inside the system, $E(t) \equiv \int_{V(t)} d^3r e(\mathbf{r}, t)$, changes during a process that occurs from an initial time t_i to a final time t_f , $dE \equiv E(t_f) - E(t_i)$. For any energy represented by its volumetric density $f(\mathbf{r}, t)$, the total energy $F(t)$ in the system is given by

$$F(t) \equiv \int_{V(t)} d^3r f(\mathbf{r}, t), \quad (21)$$

and its change after the process by

$$dF \equiv F(t_f) - F(t_i). \quad (22)$$

From the time derivative of Eq. (21) we get the rate of

change,

$$\begin{aligned} \frac{d}{dt} F(t) &= \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{v}_V(\mathbf{r}, t) f(\mathbf{r}, t) \\ &+ \int_{V(t)} d^3r \frac{\partial}{\partial t} f(\mathbf{r}, t), \end{aligned} \quad (23)$$

where $\hat{n}(\mathbf{r}, t)$ is a vector normal to the surface ∂V pointing outside of the volume [30, 32]. The last term can be expressed in terms of the energy balance Eq. (3) with the nonconvective energy flux in Eq. (4) giving

$$\begin{aligned} \frac{dF}{dt} &= \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot [\mathbf{v}_V(\mathbf{r}, t) - \mathbf{v}(\mathbf{r}, t)] f(\mathbf{r}, t) \\ &- \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_{nc}(\mathbf{r}, t) + \int_{V(t)} \sigma(\mathbf{r}, t). \end{aligned} \quad (24)$$

The above formula for the change of energy in the system (understood as a region in space) uses a small number of assumptions. In the above derivation we used Gauss's theorem, $\int_{V(t)} d^3r \nabla \cdot \mathbf{J}_{nc}(\mathbf{r}, t) = \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_{nc}(\mathbf{r}, t)$. Essentially, up to this point, we assumed that the energy densities are given by hydrodynamic balance equations and calculated their changes in a process. From now on, we assume that the system is closed, so there is no flow through the surface ∂V . This means that the flux of the particles through the surface ∂V vanishes in the reference frame where the surface element is at rest,

$$\hat{n}(\mathbf{r}, t) \cdot [\mathbf{v}_V(\mathbf{r}, t) - \mathbf{v}(\mathbf{r}, t)] = 0 \text{ for } \mathbf{r} \in \partial V. \quad (25)$$

As before, $\hat{n}(\mathbf{r})$ is the vector normal to the surface, pointing outside the region V . The above condition simplifies the rate of energy change (24) to

$$\frac{dF}{dt} = - \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_{nc}(\mathbf{r}, t) + \int_{V(t)} d^3r \sigma(\mathbf{r}, t). \quad (26)$$

By integrating the rate of change over time we get the change of energy, $dF \equiv F(t_f) - F(t_i) = \int_{t_i}^{t_f} dF(t)/dt$, in the following form,

$$\begin{aligned} dF &= - \int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_{nc}(\mathbf{r}, t) \\ &+ \int_{t_i}^{t_f} dt \int_{V(t)} d^3r \sigma(\mathbf{r}, t). \end{aligned} \quad (27)$$

The above two equations describe the energy change of a closed hydrodynamic system. We use the former equation to study steady state and the latter equation to study energy exchange during transitions between steady states. In further analysis, we assume slip boundary conditions on the boundaries of a closed system. This means that on the wall, the transverse components of the pressure tensor vanish,

$$\hat{n}(\mathbf{r}) \cdot P(\mathbf{r}) \cdot (\mathbf{1} - \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r})) = 0 \text{ for } \mathbf{r} \in \partial V. \quad (28)$$

The no-slip boundary condition can also be used without changing the main result of the paper.

The above assumptions are sufficient to generalize the first law of thermodynamics to nonequilibrium closed systems including the system shown in Fig. 1. The application of Eq. (26) to the case of external, kinetic, internal and total energy (cf. Eqs. (5-19)) yields the following:

$$\frac{d\Phi}{dt} = \int_{V(t)} d^3r \rho \mathbf{v} \cdot \nabla \varphi + \int_{V(t)} d^3r \rho \partial_t \varphi, \quad (29)$$

$$\begin{aligned} \frac{dE_{kin}}{dt} = & - \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot P \cdot \mathbf{v} + \int_{V(t)} d^3r P : [\nabla \mathbf{v}] \\ & - \int_{V(t)} d^3r \rho \mathbf{v} \cdot \nabla \varphi, \end{aligned} \quad (30)$$

$$\frac{dU}{dt} = - \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_q(\mathbf{r}, t) - \int_{V(t)} d^3r P : [\nabla \mathbf{v}], \quad (31)$$

$$\begin{aligned} \frac{dE}{dt} = & - \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_q(\mathbf{r}, t) \\ & - \int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot P \cdot \mathbf{v} + \int_{V(t)} d^3r \rho \partial_t \varphi. \end{aligned} \quad (32)$$

All of the above rates (left hand side) vanish in a steady state, and the above equations give essential information on the energy balance at a given steady state.

Let's start with Eq. (29) for external potential energy. At a steady state the external potential does not change, $\partial_t \varphi = 0$. Therefore, Eq. (29) yields,

$$\int_{V(t)} d^3r \rho \mathbf{v}^{st} \cdot \nabla \varphi = 0. \quad (33)$$

It follows that the gravitational field globally does not perform work in a steady state because for a homogeneous gravity field pointing downward in the vertical z -coordinate, $\nabla \varphi = \hat{e}_z g$ holds, and Eq. (33) results in the vanishing of the center of mass velocity, $\int_{V(t)} d^3r \rho \mathbf{v}^{st} = 0$. Therefore, in the reference frame where the boundaries of the system are immobile, the center of mass velocity vanishes, the position of the center of mass is constant and gravity does not perform work. This conclusion also holds for any potential field, like the gravity field around the earth, in a system with the mass continuity equation $\partial_t \rho = -\nabla \cdot (\rho \mathbf{v})$.

Eq. (33) simplifies the steady state form of Eq. (30). Moreover, the system is closed, so on the surface we have $\hat{n}(\mathbf{r}, t) \cdot \mathbf{v}^{st} = 0$, and the application of the slip boundary conditions given by Eq. (28) yields,

$$\int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot P^{st} \cdot \mathbf{v}^{st} = 0. \quad (34)$$

The last two equations applied to Eq. (30) at steady state, where $dE_{kin}/dt = 0$, yield

$$\int_{V(t)} d^3r P^{st} : [\nabla \mathbf{v}^{st}] = 0. \quad (35)$$

The above term appears locally in hydrodynamic equations for kinetic and internal energy balance (16), (20). It describes the work of mechanical forces inside the fluid, typically appearing during expansion and viscous dissipation. Eq. (35) indicates that although the expansion-dissipation exists locally in a steady state, it globally disappears.

Finally, the vanishing of the global mechanical work inside the fluid given by Eq. (35) simplifies the steady state form of Eq. (31), which in steady state becomes

$$\int_{\partial V(t)} d^2r \hat{n}(\mathbf{r}, t) \cdot \mathbf{J}_q^{st}(\mathbf{r}, t) = 0. \quad (36)$$

This implies that although heat may locally enter or leave the system in a steady state, the total heat does not flow into the system. Consequently, there is no need to introduce the notion of 'excess heat' [26], which is the heat in addition to the constant steady state heat flux.

It is worth noting that Eqs. (33-36) also hold for quasi-steady states, i.e. when there exists a time scale for which the system can be effectively treated as being in a steady state. In this case we would consider time averages of Eqs. (29-32). With a similar reasoning we obtain Eqs. (33), (34) and (36) with the symbol ' st ' denoting the average over a sufficiently long time scale. Eq. (35) would change to $\int_{V(t)} d^3r \{P : [\nabla \mathbf{v}]\}^{st} = 0$, with $\{P : [\nabla \mathbf{v}]\}^{st}$ denoting the time average of $P : [\nabla \mathbf{v}]$ in a given quasi-steady state.

The above equations apply to a steady state with convection that is schematically shown in Fig. 1 and also to other steady states including e.g. those with much more complicated patterns of temperature and velocity fields [19]. These steady state equations give important insight into the rate of the global energy exchange of such systems with their surroundings. From the perspective of the global energy of the system, gravity does not perform work, there is no global compression-dissipation, and there is no heat. Thus, from the perspective of global energy, the system appears to be in equilibrium (no global flux of heat, no global work).

In what follows we study the energy exchange in transitions between steady states. We assume that at the initial time t_i the system is at a steady state, which is then disturbed by a small change of boundary temperatures, external gravitational field or the motion of the surrounding wall. After time t_f the system reaches another steady state. The change in energy is described in this situation by Eq. (27), which applied to the cases of external, kinetic, internal and total energy (cf. Eqs.

(5-19)) yields,

$$d\Phi = -dW_\varphi + dW_{dt\varphi}, \quad (37)$$

$$dE_{kin} = dM_S - dP_V + dW_\varphi, \quad (38)$$

$$dU = dQ + dP_V, \quad (39)$$

$$dE = dQ + dM_S + dW_{dt\varphi}, \quad (40)$$

where we used the following definitions of the heat differential,

$$dQ = - \int_{t_i}^{t_f} dt \int_{\partial V} d^2r \hat{n} \cdot \mathbf{J}_q(t), \quad (41)$$

volumetric mechanical work differential,

$$dP_V = - \int_{t_i}^{t_f} dt \int_{V(t)} d^3r P : [\nabla \mathbf{v}], \quad (42)$$

mechanical surface force differential,

$$dM_S = - \int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r \hat{n} \cdot P \cdot \mathbf{v}, \quad (43)$$

potential work differential,

$$dW_\varphi = - \int_{t_i}^{t_f} dt \int_{V(t)} d^3r \rho \mathbf{v} \cdot \nabla \varphi, \quad (44)$$

and potential source differential,

$$dW_{dt\varphi} = \int_{t_i}^{t_f} dt \int_{V(t)} d^3r \rho \partial_t \varphi. \quad (45)$$

Formula (40) is the main result of the paper. It expresses the balance of total energy and is a generalization of the first law of equilibrium thermodynamics. The total energy changes due to heat, work on the surface of the system, and the work of the external potential field. Without the gravity field ($dW_{dt\varphi} = 0$) and neglecting macroscopic motion ($dE = dU$), the above formula reduces to the equilibrium first law, $dU = dQ - p dV$, where we use the fact that under these conditions we get $dM_S = -p dV$ [16].

IV. SUMMARY

This study is driven by the possibility of extending thermodynamic principles to describe systems that are not in equilibrium. As a preliminary step, we examine total energy exchange in a closed system with macroscopic motion, exemplified by Rayleigh-Bénard convection. Consequently, we extend the first law of equilibrium thermodynamics beyond equilibrium to the form

$dE = dQ + dM_S + dW_{dt\varphi}$. This is valid for transitions between steady states and for turbulent states that exhibit steady-state-like behavior over time. For transitions between equilibrium states, this generalization reduces to the equilibrium first law.

Two aspects are particularly noteworthy. First, the nonequilibrium first law that we derive retains the same form as the equilibrium first law. The heat and work differentials are physically interpretable in a manner akin to equilibrium thermodynamics. Second, in equilibrium states, viscous dissipation, compression, heat, and mechanical work vanish locally by definition. In nonequilibrium steady states, although heat, surface mechanical work, and viscous dissipation-compression may exist locally, they vanish globally.

This similarity enables a global thermodynamic description of steady states, comparable to equilibrium systems, and paves the way for studying heat and surface work differentials. Heat should be measured by monitoring the total heat on the system's surface, and work differentials by measuring the force on the wall and its displacement. This approach opens avenues for numerical and experimental investigations of out-of-equilibrium systems. These include systems relevant to climate dynamics and steady state chemical reactors in industry. For instance, understanding heat-driven convection is fundamental in meteorology, where it plays a critical role in weather patterns and climate dynamics. In industrial applications, heat-driven convection is essential in designing more efficient cooling systems, chemical reactors, and energy generation processes.

Importantly, the heat in transitions between steady states has never been studied for systems with heat-driven convection. This reveals an entirely unexplored field of global thermodynamics, currently in its infancy. From the perspective of a potentially existing thermodynamic description of nonequilibrium states, we might be at a similar juncture to where thermodynamics was when Carnot and Clausius began studying heat differentials.

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