Entropie : thermodynamique – énergie – environnement – économie
2026, vol. 7, n° Spécial LILA 3, 1-96 pages, DOI: 10.21494/ISTE.OP.2026.1433 ISTE OpenScience

Operational Extension of the Carnot-Clausius Construct to Nonequilibrium Entropy and the Second Law for Positive and Negative Temperatures

Extension Opérationnelle de l'Approche de Carnot-Clausius à des Entropies de Non Equilibres et Seconde loi de la Thermodynamique pour des Températures Positives et Négatives

P.D. Gujrati

Department of Physics and School of Polymer Science and Polymer Engineering,
The University of Akron, Akron, OH 44325
pdg@uakron.edu

ABSTRACT. The review introduces a recently developed generalized nonequilibrium (NEQ) statistical thermodynamics, called Gen-Th and Gen-GSL-Th, having a *mechanical foundation* in which stochasticity is introduced but not the second law (SL) by following the Boltzmann-(Carnot-Clausius)-Gibbs-Maxwell (BCGM) proposal. Gen-Th is applicable to any system of any size in any arbitrary state, isolated or not, requires new techniques, clarifies various confusing points such as about generalized and exchange macroworks, and yielding many new results. Distinction between uniform and nonuniform deterministic Hamiltonians and their microstates, operationally defined internal variables and NEQ entropy S in an extended state space, and their temporal evolution are the new tools to formulate Gen-Th. By imposing *mechanical equilibrium* (stable or unstable) *principle* (Mec-EQ-P) of analytical mechanics, we formulate a generalized second law (GSL), whose form (but not of SL) remains invariant for both positive and negative temperatures T. The entropy S provides an extension of the Carnot-Clausius approach to equilibrium (EQ) entropy. We clarify the concept of spontaneous processes for both positive and negative NEQ temperatures so that $dS \geq 0$ for $T > 0$ and $dS < 0$ for $T < 0$ without violating GSL/SL. We prove a no-go theorem for the impossibility of a violation of GSL/SL for spontaneous processes. Any violation of GSL/SL is due to nonspontaneous processes such as a creation of internal constraints that are not covered by GSL/SL. Some examples are given including metastable macrostates during vitrification for positive T. We end with some open problems, some of which are also relevant for glasses.

KEYWORDS. Uniform Hamiltonian, Nonuniform Hamiltonian, Mechanical Equilibrium Principle, Irreversibility, Dissipation, Carnot-Clausius Entropy, Positive and Negative Temperatures

1. Introduction

1.1. *Concepts of Stochasticity and Entropy in Thermodynamics*

What distinguishes a thermodynamic system Σ, shown in Fig. 1, from a purely *deterministic* (D) mechanical system Σ^{D} are the *stochastic* concepts of (generalized macro)heat dQ, temperature T, and entropy S[1]. They play central roles in thermodynamics of Σ. In contrast, (generalized macro)work dW is purely *mechanical* and can be introduced even for Σ^{D}, which is traditionally taken to be described by a purely *conservative* Hamiltonian $\mathcal{H}$. Because of this, energy E also plays a prominent role in thermodynamics of Σ for the simple reason that the Hamiltonian dynamics of *microstates*[2] $\mathfrak{m}_k$ of $\mathcal{H}$ for Σ^{D} are governed by their microstate energies E_k. The dynamics is independent of the microstate probability p_k so it is deterministic.

---

[1] We take S to be a pure number without the Boltzmann constant k_{B}; the latter is absorbed in the definition of T, which then has the dimension of energy. This convention is adopted in this review.

[2] We take microstates to be nondegenerate for simplicity in this review.

Definition 1. *Any general, i.e., arbitrary macrostate* $\mathfrak{M}_{arb}$ *of* Σ *is always specified by the collection* $\{\mathfrak{m}_k, p_k\}$*; index* k *is used to specify* E_k *so it does not have to listed in the collection.*

Definition 2. *All quantities pertaining to* $\mathfrak{M}_{arb}$ *are identified as* macroquantities *using the prefix macro, while those pertaining to* $\mathfrak{m}_k$ *are identified as* microquantities *and always carry the index* k *of* $\mathfrak{m}_k$ *using the prefix micro.*

Definition 3. *We will simply use "quantity" to collectively denote both micro- and macro-quantity for short. This should not cause any confusion.*

As microstate energies vary over microstates, the dynamics of the corresponding *macrostate* $\mathfrak{M}_{\mathrm{arb}}$ becomes complex and stochastic as it is governed by the macroscopic energy E that is determined by $\{p_k\}$. It is, therefore, necessary to make a careful and clear distinction between the mechanical evolution of a microstate $\mathfrak{m}_k$ and the stochastic evolution of the macrostate $\mathfrak{M}_{\mathrm{arb}}$. The corresponding processes resulting from these evolutions are identified as mechanical and thermodynamic processes and indicated by $\mathcal{P}^{\mathrm{D}}$ and $\mathcal{P}$, respectively; for simplicity, we use $\bar{\mathcal{P}}$ to indicate both; similarly, we use $\overline{\Sigma}$ to denote Σ and Σ^{D}; the content will clearly specify which one is being discussed.

While the notions of heat and temperature have been well known from daily experience, though not well understood conceptually, much before the formulation of classical thermodynamics (Cl-Th) [2, 3], it is the concept of entropy that has proved not only exotic, but also not easy to comprehend. It has also been mysterious to unravel the theoretical foundations of why the irreversible process quantity $\Delta_{\mathrm{i}}S$[3], the net irreversible change in S in a thermodynamic process $\mathcal{P}$, must always satisfy the *second law* (SL):

$$\Delta_{\mathrm{i}}S \geq 0, \text{ (SL)} \tag{1}$$

which says nothing about the value of S itself over $\mathcal{P}$. Even the role of temperature for SL is not often discussed in the literature, the most prominent exception being [4, for example]. Surprising, the concept of entropy has propagated into various fields since its inception by Clausius [5, 6], and is still highly debated for as argued by Leff [7] that thermodynamics is still far from complete. I am reminded of the following quote by Arnold Sommerfeld [8, p. 215]:

> “Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don’t understand it, but by that time you are so used to the subject, it doesn’t bother you anymore.”

We hope to convince the reader of Lîla-Entropie that the situation is not so dire, see also Sects. 1.3 and 1.4, with the following guiding

Main Motivation 4. *By operationally defining a unique nonequilibrium (NEQ) entropy* S *as an extension of the Carnot-Clausius entropy*[4] *in an appropriately chosen state space* augmented *by internal variables, we are able to formulate a generalized statistical thermodynamics (Gen-Th) that is not encumbered by*

---

[3] All irreversible quantities such as $\Delta_{\mathrm{i}}S$ carry a suffix "i" for irreversibility. All exchange quantities such as $\Delta_{\mathrm{e}}S$ carry a suffix "e" for exchange.

[4] An important goal of the review is to popularize our thesis that Carnot should share some credit for the discovery of S by Clausius; see Sect. 8.

SL for any arbitrary macrostate $\mathfrak{M}_{arb}$ of the system. Thus, it satisfies not only SL but its violation so that we are in a position to reveal the root cause of SL, which has remained an outstanding unsolved problem. Surprisingly, S satisfies the fundamental Clausius identity[5] *for any NEQ $\mathfrak{M}$ and not just $\mathfrak{M}_{eq}$. Imposing* mechanical equilibrium *(stable or unstable)* principle *(Mec-EQ-P) of analytical mechanics on Gen-Th provides a mechanical foundation of a* generalized second law *(GSL) that not only supersedes SL but also operates at all temperatures, positive and negative, without changing its form, and a No-Go Theorem for its violation. Surprisingly, GSL shows that the inequality in Eq. (1) is satisfied only at positive temperatures, but is reversed at negative temperatures and contrary to current wisdom. The latter is commonly taken as a violation of SL, but this conclusion is not correct. We also clear some confusion in the field including a common misconception about the generalized macrowork dW and the exchange macrowork d_eW in modern literature. A distinction between uniform and nonuniform deterministic Hamiltonians allows us to generalize the concept of irreversibility and to demonstrate that GSL is valid for spontaneous processes and not for nonspontaneous processes such as creating internal constraints.*

for this review. The review is comprehensive and ambitious in scope so it is long and requires patience on the part of the reader to go through it.

While it is not usually the case, one can also associate entropy S to any deterministic macrostate $\mathfrak{M}^{\mathrm{D}}$ of Σ^{D} [9] that, however, always remains a *constant of motion* ($dS \equiv d_{\mathrm{i}}S \equiv 0$) as it evolves in time in an infinitesimal mechanical process $\delta\mathcal{P}^{\mathrm{D}}$. On the other hand, S usually but not always *changes* ($dS \neq 0$) in a thermodynamic process $\delta\mathcal{P}$, which explains that the importance of S in thermodynamics is due to its ability to *change* during most processes[6]. As said above and discussed later, dW is a mechanical quantity so the work process is always *isentropic* ($dS \equiv 0$) and reversible ($d_{\mathrm{i}}S \equiv 0$). This thus justifies dQ for Σ to be stochastic ($dS \neq 0$) so it has no relevance for Σ^{D}[7].

The existence of $\mathcal{P}^{\mathrm{D}}$ suggests that introducing an isentropic mechanical process $\delta\mathcal{P}^{\mathrm{D}}$ ($dS = 0$) and a stochastic infinitesimal process $\delta\mathcal{P}^{\mathrm{S}}$ ($dS \neq 0$) in thermodynamics might be extremely useful in that any $\delta\mathcal{P}$ can be treated as a combination of these two independent processes $\delta\mathcal{P}^{\mathrm{D}}$ and $\delta\mathcal{P}^{\mathrm{S}}$. These independent processes are used to identify the generalized macrowork dW and generalized macroheat dQ, respectively, in the first law of thermodynamics; see footnote 7. In an equilibrium process, this process is known as an adiabatic process over which $d_{\mathrm{e}}Q = 0$, which is also true of an isolated system[8]. Indeed, adiabatic processes have been effectively and successfully used in an axiomatic formulation of SL by Giles [10] and by Lieb and Yngvason [11, 12]. Our approach, which is fully introduced in this article, differs from their approach in that we demonstrate that NEQ entropy S can be *uniquely* and *operationally* defined, see Theorem 72 in Sect. 13.1 and Sect. 12, in an appropriately defined extended state space, regardless of the *signature* (positive or negative) of the temperature. The dimension of the state space keeps

---

5. defined in Eq. (103)

6. As constant p_k refer to a purely mechanical system, stochasticity for us will always mean changing p_k so that it will always refer to nonvanishing $\{dp_k\}$ and nonvanishing dS and dQ. We use dissipation in Eq. (10) and irreversibility that follow from irreversibility principle to imply any signature in Gen-Th. In Gen-GSL-Th that is based on the generalized second law, the measure D of dissipation from the principle of dissipation is nonnegative.

7. Indeed, the generalized macroheat dQ is defined in such a way that it is directly proportional to dS in all cases, with the constant of proportinality being the thermodynamic temperature T of the system. This fundamental Clausius identity holds even in nonequilibrium so that dQ should not be confused with the exchange macroheat $d_{\mathrm{e}}Q \doteq \text{đ}Q$ that is normally used in classical thermodynamics (Cl-Th) as $dQ - d_{\mathrm{e}}Q \doteq d_{\mathrm{i}}Q$ is usually nonzero. In this chapter, we will not use symbols like $\text{đ}Q$ as they are not convenient; instead, we use the modern notations like $d_{\mathrm{e}}Q$.

8. The formulations of SL by Clausius and by Kelvin-Planck are not applicable to isolated systems as they cannot perform any cyclic operation of an engine.

on increasing with how far the nonequilibrium macrostate $\mathfrak{M}$ is from the equilibrium (EQ) macrostate $\mathfrak{M}_{\rm eq}$ as described later.

Definition 5. *We use $\mathfrak{M}_{arb}$ to collectively denote NEQ macrostate $\mathfrak{M}$ and EQ macrostate $\mathfrak{M}_{eq}$. However, $\mathfrak{M}$ can be uniquely identified by its argument in a given enlarged state space or has an explicit time dependence in any state space.*

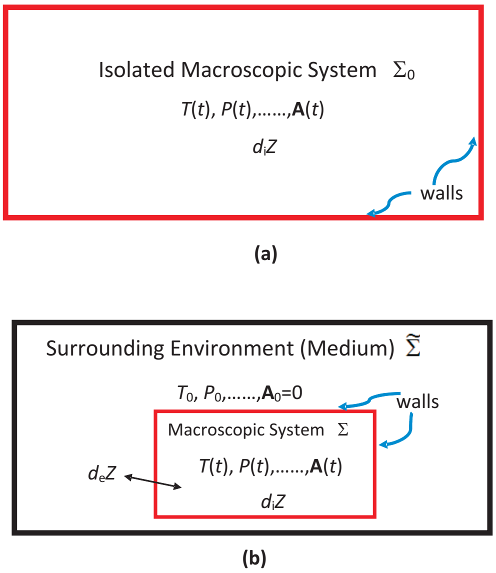

Figure 1. (a) An isolated nonequilibrium system Σ_0 with internally generated $d_{\rm i}Z$ driving it towards equilibrium, during which its SI-fields $T(t), P(t), \cdots, \mathbf{A}(t)$ continue to change to their equilibrium values; $d_{\rm i}Z_k$ denote the microanalog of $d_{\rm i}Z$. The sign of $d_{\rm i}Z$ is determined by the second law. (b) A nonequilibrium systen Σ in a surrounding medium $\widetilde{\Sigma}$, both forming an isolated system Σ_0. The macrostates of the medium and the system are characterized by their fields $T_0, P_0, ..., \mathbf{A}_0 = 0$ and $T(t), P(t), ..., \mathbf{A}(t)$, respectively, which are different when the two are out of equilibrium. Exchange quantities ($d_{\rm e}Z$) carry a suffix "e" and irreversibly generated quantities ($d_{\rm i}Z$) within the system by a suffix "i" by extending the Prigogine notation. Their sum $d_{\rm e}Z + d_{\rm i}Z$ is denoted by dZ, which is a system-intrinsic quantity (see text).

The way to relate Σ and $\Sigma^{\rm D}$ is to allow *stochasticity* in the former by appending to $\Sigma^{\rm D}$ probability as was first proposed by Carnot, Clausius, Maxwell, Boltzmann, and Gibbs (the *BCGM proposal* with standing for Carnot and Clausius for brevity) [5, 13–20]. This is in keeping with a long tradition of treating a thermodynamic process as a stochastic version of a mechanical process by invoking macroheat dQ in the discussion; see for example, [15,17], and is reviewed recently by Gujrati [21,22, unfortunately, it was called the BCM proposal so it did not give full credit to the contribution of Gibbs] and which we follow in this study. The EQ state of $\Sigma^{\rm D}$ is stationary in time so its Hamiltonian must also be stationary with no explicit time dependence. We write it as $\mathcal{H}(\mathbf{x}|\,\mathbf{w})$ [1] with

$$\mathbf{w} = (N, V, \cdots)$$

(N, the number of particles, V, the volume, $\cdots$) appearing as the work parameter in it; here, $\mathbf{x} \doteq \{(\mathbf{r}_i, \mathbf{p}_i)\}, i = 1, 2, \cdots, N$ denotes the set of positions and momenta of N particles in the phase space.

Condition 6. *We will usually consider $N \in \mathbf{w}$ fixed in this study so that it can be used to* fix *the size of the system. In the rest of the review, N is not considered as part of* $\mathbf{X}$ *and* $\mathbf{w}$.

When necessary, time t can also be a parameter in $\mathcal{H}$; we will always show it explicitly and separately by not including in $\mathbf{w}$. The microstates $\mathfrak{m}_{k\text{eq}}(\mathbf{w})$ of microenergy $E_k(\mathbf{w})$ of $\mathcal{H}(\mathbf{x}_k|\,\mathbf{w})$ for Σ^{D} identify the EQ macrostate $\mathfrak{M}_{\text{eq}}(\mathbf{X})$ of Σ with probabilities p_k^{eq} in the state space $\mathfrak{S}_{\mathbf{X}}$ spanned by

$$\mathbf{X} \doteq (E, \mathbf{w}) = (E, V, \cdots),$$

which is the most important state space where all processes $\mathcal{P}$ are executed by varying $\mathbf{w}(t)$. The EQ macrostate $\mathfrak{M}_{\text{eq}}$ is uniquely specified by the collection $\left\{\mathfrak{m}_{k\text{eq}}, p_k^{\text{eq}}\right\}$:

$$\mathfrak{M}_{\text{eq}} \doteq \mathfrak{M}(\mathbf{X}) : \left\{\mathfrak{m}_{k\text{eq}}, p_k^{\text{eq}}\right\}, \tag{2}$$

with $E_{k\text{eq}}$ being specified by $\mathfrak{m}_{k\text{eq}}$. We observe that $\mathfrak{M}_{\text{eq}}$ and the elements of the collection may have an implicit time dependence due to implicit time dependence of $\mathbf{X}(t)$, but do not have an explicit time dependence[9].

It is a fact that Σ in an EQ macrostate $\mathfrak{M}_{\text{eq}}$ is *uniform* and stationary in that it only requires specifying $\mathbf{X}$ for the *entire* system and not of its various parts due to uniformity; we denote the number of observables in $\mathbf{X}$ by n_{eq}. As these quantities are controlled from outside the system, they qualify as (possibly time-dependent) observables of the system; n_{eq} is fixed for a *particular* specification of the system in an investigation and may change in another specification.

In this state space $\mathfrak{S}_{\mathbf{X}}$, E is determined by the Hamiltonian $\mathcal{H}(\mathbf{w})$ of Σ, which is explicitly determined by the work parameter $\mathbf{w} = \mathbf{X} \backslash E$; we have suppressed the phase space variables $\{\mathbf{x}_i \doteq (\mathbf{r}_i, \mathbf{p}_i)\}$ in $\mathcal{H}(\mathbf{w})$ as we explain in Sect. 4.2. We say that $\mathcal{H}(\mathbf{w})$ represents a *uniform Hamiltonian* and the corresponding system is a *uniform* system as discussed properly in Sect. 4.1, where we also introduce a *nonuniform* Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w}, t)$ of a nonuniform system that is built up by various subsystems that are dissimilar in various densities so that it contains the informations of various subsystems.

Definition 7. *Borrowing the concept of equilibrium from analytical mechanics, a microstate $\mathfrak{m}_{keq} \doteq \mathfrak{m}_k(\mathbf{w})$ of a uniform Hamiltonian $\mathcal{H}(\mathbf{w})$ is called an EQ-microstate and also labeled as uniform; see Uniformity Theorem 47 later for proper justification. Their collection $\{\mathfrak{m}_{keq}, p_k^{eq}\}$ in Eq. (2) with special microstate probabilities p_k^{eq} specifies the EQ macrostate $\mathfrak{M}_{eq} \doteq \mathfrak{M}(\mathbf{X})$, which is uniform and* uniquely *specified in the EQ state space $\mathfrak{S}_{\mathbf{X}}$.*

As we will see from the discussion of Eq. (36), this concept of uniformity has nothing to do with the actual distribution of N particles in the phase space $\Gamma_N(\mathbf{x})$. Rather, it refers to the uniform distribution of E_k and $\mathbf{w}$ over Σ in the following sense; if we divide Σ into equal halves, each having half the number of particles, they have the same values in each half [10]. If not, the system is identified as *nonuniform* and out of mechanical equilibrium (NEQ). Such a situation will require a non-stationary Hamiltonian with an explicit time dependence. In other words, a nonuniform Σ^{D} in $\mathfrak{S}_{\mathbf{X}}$, its Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w}, t)$, $\{\mathfrak{m}_k(\mathbf{w}, t)\}$, and $\{E_k(\mathbf{w}, t)\}$ have an explicit time dependence as exhibited here. For a time-dependent

---

[9] The EQ macrostate $\mathfrak{M}_{\text{eq}}$ of Σ is identified by its entropy having the maximum value for fixed observable $\mathbf{X}$ in the state space $\mathfrak{S}_{\mathbf{X}}$.

[10] Of course, we are assuming quasi-additivity of energy so Σ must be as large as Σ_{E} as defined in Sect. 1.2

Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w},t)$, we obtain a nonequilibrium (NEQ) macrostate $\mathfrak{M}(\mathbf{X},t)$ with an explicit time-dependent $\mathfrak{m}_k, p_k$ and E_k so that $\mathfrak{M}(\mathbf{X},t)$ is specified by

$$\mathfrak{M}(\mathbf{X},t):\{\mathfrak{m}_k(t),p_k(t)\}\,, \tag{3}$$

with $E_k(t)$ being specified by the kth microstate $\mathfrak{m}_k(t)$.

Remark 8. *The explicit time dependence in NEQ macrostates and their properties are due to explicit time dependence in nonuniform microstates* $\mathfrak{m}_k(\mathbf{w},t)$*; probabilities* $p_k(t)$ *may also have explicit time dependence.*

As shown later in Sect. 5, we identify an extended state space $\mathfrak{S}_{\mathbf{Z}}$ formed by an operationally defined set $\boldsymbol{\xi}$ of additional state variables, known as *internal variables* [23–36], with

$$\mathbf{Z}\doteq\mathbf{X}\cup\boldsymbol{\xi},\mathbf{W}\doteq\mathbf{w}\cup\boldsymbol{\xi}, \tag{4}$$

in which $\mathfrak{M}(\mathbf{X},t)$ is uniquely described as a macrostate $\mathfrak{M}(\mathbf{Z})$ without any explicit time dependence. This requires that the corresponding Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w},t)$ be equivalently expressed as $\mathcal{H}(\mathbf{x}|\,\mathbf{W})$ with no explicit time dependence. These macrostates still represent NEQ macrostates in $\mathfrak{S}_{\mathbf{Z}}$ as their entropies are strictly less than $S_{\text{eq}}(\mathbf{X})$. As is well known, all NEQ macrostates are governed by the *second law* (SL) in classical thermodynamics.

Consider uniform microstates $\{\mathfrak{m}_k(\mathbf{w})\}$ of Σ^{D}. We construct different macrostates $\mathfrak{M}$ of Σ in $\mathfrak{S}_{\mathbf{X}}$ by appending different choices of $\{p_k\}$ to $\{\mathfrak{m}_k(\mathbf{w})\}$. Only one choice $\left\{p_k^{\text{eq}}(\mathbf{X})\right\}$ gives the *maximum entropy* $S_{\text{eq}}(\mathbf{X})$ and identifies the EQ macrostate $\mathfrak{M}_{\text{eq}}$ of Σ in $\mathfrak{S}_{\mathbf{X}}$. It is a unique and stationary macrostate. Therefore, all other macrostates must denote NEQ macrostates that must still be identified as *uniform macrostates* because of Σ^{D}; see Definition 36. Assuming time-dependent p_k, see footnote 6, to allow for their temporal evolution, they must be expressed as $\mathfrak{M}(\mathbf{X},t)$ having entropy $S(\mathbf{X},t)$. Besides these "uniform" macrostates, there are other NEQ macrostates that originate from $\{\mathfrak{m}_k(\mathbf{w},t)\}$ and various possible sets $\{p_k\}$, all written as $\mathfrak{M}(\mathbf{X},t)$ with entropy $S(\mathbf{X},t)$. They are identified as *nonuniform macrostates*. Both kinds of macrostates are not uniquely defined in $\mathfrak{S}_{\mathbf{X}}$ because of time dependence. We will discover later in Sect. 14.2, see Remark 79, that uniform NEQ macrostates are thermodynamically *irrelevant* as they violate energy conservation during their temporal evolution for arbitrary $\{p_k(t)\}$ in an isolated Σ. Therefore, from now on, such macrostates are not considered in this investigation. Only nonuniform macrostates associated with nonuniform Σ need to be considered that satisfy energy conservation, *i.e.* the first law. Therefore, such macrostates are simply identified as NEQ macrostates and denoted by $\mathfrak{M}(\mathbf{X},t)$ or simply $\mathfrak{M}$ from now on.

From what is said above, $\mathcal{H}_{\text{eq}}\doteq\mathcal{H}(\mathbf{x}|\,\mathbf{w}),\mathfrak{m}_{k\text{eq}}\doteq\mathfrak{m}_k(\mathbf{w})$ and $E_{k\text{eq}}\doteq E_k(\mathbf{w})$ of Σ^{D} that are *uniform* in $\mathbf{w}$ can also be labeled with the suffix "eq" by borrowing this concept from mechanics. This should not cause any confusion, and is in the spirit of and consistent with the well-known result of equilibrium thermodynamics [17] that an EQ macrostate $\mathfrak{M}_{\text{eq}}$ is uniform in the state variable set $\mathbf{X}\doteq(E,\mathbf{w})$ in $\mathfrak{S}_{\mathbf{X}}$. As a consequence of uniformity, $\mathfrak{M}_{\text{eq}}$ and $\mathfrak{m}_{k\text{eq}}$ can neither perform any mechanical work nor generate any mechanical power. Various EQ functions including $S_{\text{eq}}=S(\mathbf{X})$ of $\mathfrak{M}_{\text{eq}}$ remain time independent. (From now on, we will mostly suppress $\mathbf{w}$ for $\overline{\Sigma}$ unless necessary.) In a NEQ state of $\overline{\Sigma}$ that we are interested in, all quantities acquire an *explicit* time dependence. This time-dependence is a result of nonuniformity among various *disjoined* but mutually *interacting* uniform subsystems $\left\{\overline{\Sigma}_l\right\}$ with Hamiltonians $\{\mathcal{H}_{l\text{eq}}\doteq\mathcal{H}_l(\mathbf{x}_l|\,\mathbf{w}_l)\}$ in terms of work variables $\mathbf{w}_l, l=1,2,\cdots$ as discussed in Sect. 5;

nonuniformity results in internal flows among $\{\overline{\Sigma}_l\}$ that affect $\mathbf{X}_l \doteq (E_l, \mathbf{w}_l)$ so a NEQ $\mathfrak{M}(t)$ and $\mathfrak{m}_k(t)$ are each *nonuniform* in $\{\mathbf{X}_l\}$ and $\{\mathbf{w}_l\}$, respectively. Nonuniformity in $\overline{\Sigma}$ can be described *precisely* in terms of a set $\boldsymbol{\xi}$, if we restrict the minimum size λ_{E} of subsystems to satisfy *quasi-additivity* of their energies, λ_{E} being determined by the range of inter-particle interactions; see the discussion following Eq. (44b). This requires imposing minimum size restriction on $\overline{\Sigma}$, which is denoted by $\overline{\Sigma}_{\mathrm{E}}$, for which $\mathbf{Z}$ determines a NEQ state space $\mathfrak{S}_{\mathbf{Z}}$. Thus, we see that the explicit time dependence of $\mathfrak{M}(t)$ for nonuniform $\overline{\Sigma}$ in $\mathfrak{S}_{\mathbf{X}}$ is fully equivalent to the implicit dependence through $\boldsymbol{\xi}(t)$ in $\mathfrak{S}_{\mathbf{Z}}$, see Theorem (38); $p_k(t)$ is allowed to have explicit time as noted above in Remark 8. To make subsystems' entropies additive, we require S to be a *state function* $S(\mathbf{Z})$ in $\mathfrak{S}_{\mathbf{Z}}$, which requires a further restriction on the minimum size as macroscopic (M) to capture *quasi-independence* of subsystems described by Eq. (79). This macroscopic system is identified as Σ_{M} (we do not include $\Sigma_{\mathrm{M}}^{\mathrm{D}}$ here because of the lack of stochasticity) and require the state space $\mathfrak{S}_{\mathbf{Z}}$ to be uniquely specified; in contrast, $\overline{\Sigma}$ and $\overline{\Sigma}_{\mathrm{E}}$ are not uniquely specified in $\mathfrak{S}_{\mathbf{X}}$ and $\mathfrak{S}_{\mathbf{Z}}$, respectively. For the benefits of readers, we collect various acronyms used in the text in the following table.

Table I for Acronyms

BCGM	: Boltzmann-Carnot-Clausius-Gibbs-Maxwell
Cl-Th	: Classical Thermodynamics for Σ_{M}
EQ	: Equilibrium
Gen-Th	: General Thermodynamics ($dW = dQ \gtreqless 0$) for Σ
Gen-GSL-Th	: Gen-Th satisfying GSL ($dW = dQ \geq 0$) for Σ
GSL	: Generalized second law $dQ \geq 0$ for Σ
IC	: Internal constraint
Irr-P	Irreversible Principle ($dW = dQ$) for Σ
Mech-Eq-P	: Mechanical Equilibrium Principle for Σ^{D}
MicroBCGM	: BCGM applied to microstates of Σ^{D}
NEQ	: Nonequilibrium
NEQT	: Nonequilibrium Thermodynamics
SEQ	: Stable Equilibrium
SI	: System-intrinsic
SL	: Second Law $dS \geq 0$
UEQ	: Unstable Equilibrium
VGSL	: Violation of GSL ($dQ < 0$) for Σ
VSL	: Violation of SL ($dS < 0$) for Σ_{M}

Remark 9. *We will use Σ or Σ^D to denote systems with no size restriction so it includes Σ_E or Σ_E^D of an intermediate minimum size, and Σ_M or Σ_M^D of a minimum macroscopic size. Thus, all results valid for Σ or Σ^D also hold for intermediate and macroscopic systems.*

1.2. *Notations*

We usually specify $\overline{\Sigma}$ by $\mathbf{X} \doteq (E, \mathbf{w})$ consisting of *extensive* observables, also customary known as the *extensive state variable*, to identify the state space $\mathfrak{S}_{\mathbf{X}}$. The extensivity of E means that we are not considering nonextensive systems such as self-gravitating systems; see, for example, Katz [37].

The equilibrium microstates $\mathfrak{m}_{k\text{eq}} \doteq \mathfrak{m}_k(\mathbf{w})$ of $\mathcal{H}(\mathbf{w})$ provide a unique specification of $\Sigma^{\rm D}$, while the equilibrium macrostate $\mathfrak{M}_{\rm eq} \doteq \mathfrak{M}(\mathbf{X})$ and entropy $S_{\rm eq} \doteq S(\mathbf{X})$ uniquely specify Σ in $\mathfrak{S}_{\mathbf{X}}$. We find it convenient in this review to allow $\overline{\Sigma}$ to have no constraint on its size by assuming it to have any number of particles $N = 1, 2, 3, \cdots$. However, the following two requirements, quasi-additivity of energy and statistical quasi-independence (required for entropy additivity) require considering two different sizes noted above as $\overline{\Sigma}_{\rm E}$ and $\Sigma_{\rm E}$.

Remark 10. *We use the discrete versions [29, 38, 39] for our systems for which the separating boundaries between various systems or subsystems are taken to be sharp. Therefore, the thermodynamics we develop is not locally defined, which is what is required for a continuous specification as is, for example, developed in [25–27, 40]. Our thermodynamics is over the entire system so all state variables are defined over the whole system.*

What distinguishes discrete approach from the continuous approach is that we proceed using a statistical mechanical approach for the entire system in which microstates as mechanical systems play the central role so that we can formulate the generalized second law [21, 22] as a consequence of only analytical mechanics and the *principle of mechanical equilibrium*, called Mec-EQ-P [41, p. 99], that is introduced in Sect. 6.

Conjugate to $\mathbf{X}$ is the set $\boldsymbol{x} = (T, P, \cdots)$ of fields (temperature, pressure, chemical potential, $\cdots$)[11] that can also be used to specify Σ whose size is fixed by N per Condition 6; see also Remark 16; conjugate to $\mathbf{w}$ is the set $\boldsymbol{w} = (P, \cdots)$ of *intensive* mechanical fields (pressure, chemical potential, $\cdots$)[12]. The system Σ is usually embedded in an extremely large medium $\widetilde{\Sigma}$ as shown in Fig. 1 that can be used to change $\mathbf{X}$ in a process. All quantities pertaining to $\widetilde{\Sigma}$ carry a tilde $\widetilde{()}$ above them. The combination of Σ and $\widetilde{\Sigma}$ form an isolated system Σ_0; all quantities pertaining to Σ_0 carry a suffix 0. We use no suffix for all quantities pertaining to $\overline{\Sigma}$ even if it is isolated. We will use the term "body" to refer to any of $\overline{\Sigma}, \widetilde{\Sigma}$, and Σ_0 and use $\Sigma_{\rm b}$ to denote it. However, to avoid notational complication, we will use the notation suitable for Σ for $\Sigma_{\rm b}$ if no confusion would arise in the context.

As energy or the Hamiltonian plays a special role in classical thermodynamics [15], it is often desirable to think of $\widetilde{\Sigma}$ as a combination of two noninteracting mediums, a work medium $\widetilde{\Sigma}^{\rm w}$ that changes E by performing work on $\overline{\Sigma}$ and a heat medium $\widetilde{\Sigma}^{\rm h}$ that changes E by adding heat to Σ; note that we have restricted $\overline{\Sigma}$ to Σ for $\widetilde{\Sigma}^{\rm h}$ as heat has no meaning for $\Sigma^{\rm D}$. Intensive field for $\widetilde{\Sigma}^{\rm w}$ is the set $\tilde{\boldsymbol{w}} = (\tilde{P}, \cdots)$ and for $\widetilde{\Sigma}^{\rm h}$ is the set $\tilde{\boldsymbol{x}} = (\tilde{T})$. It should be clear that $\overline{\Sigma}_0$ either represents $\Sigma^{\rm D} \cup \widetilde{\Sigma}^{\rm w}$ or $\Sigma \cup \widetilde{\Sigma}$. The isolated system $\overline{\Sigma}_0$ is always assumed to be stationary.

Definition 11. *A description, denoted by* $\mathfrak{q}$, *of a system can be made either using all* n_{obs} *elements of* $\mathbf{X}$ *or of* $\boldsymbol{x}$ *or a combination of* n_{obs} *unconjugated elements from both, and will collectively be shown simply by* $\mathbf{X}^c$ *and treated as the state variable. A similarly description* $\tilde{\mathfrak{q}}$ *of* $\widetilde{\Sigma}$, *and* $\mathfrak{q}_0$ *of* Σ_0 *can also be made.*

The above description is easily extended to $\mathbf{Z}$, etc. The states for $\overline{\Sigma}_{\rm b}$ are specified by the description $\mathfrak{q}$. As an example, if $\mathbf{X}$ contains E and V, then $\mathfrak{q}$ refers to any of these descriptions: (E, V), (T, P),

---

[11] A mechanical field is by definition a derivative of energy with respect to the work parameter. The temperature is the derivative with respect to the entropy. Thus, a field is intensive. However, there are other intensive quantities given by ratios of two intensive quantities such as entropy per particle. The microstate probability $p_k \doteq \mathcal{N}_k/\mathcal{N}$ in Eq. (68) is intensive in the latter sense but can be treated as an extensive quantity as the number of samples in the Gibbs ensemble is kept fixed; see Sect. 9. We will use this observation in Eq. (33).

[12] We have used the chemical potential as a mechanical field as N is considered a work variable in our approch to thermodynamics.

(T, V), and (E, P) for an EQ Σ. Any of these descriptions specify a fixed size. The field conjugate to $\mathbf{Z}$ is $\boldsymbol{z} \doteq (T, \boldsymbol{w}, \boldsymbol{a})$ and $\mathbf{W}$ is $\boldsymbol{v} \doteq (\boldsymbol{w}, \boldsymbol{a})$, where $\boldsymbol{a}$ is the field, also called *affinity*, conjugate to $\boldsymbol{\xi}$. We similarly introduce $\widetilde{\boldsymbol{z}}, \boldsymbol{z}_0, \widetilde{\boldsymbol{w}}, \boldsymbol{w}_0$, and $\widetilde{\boldsymbol{a}}, \boldsymbol{a}_0$ for $\widetilde{\mathbf{Z}}$ and $\mathbf{Z}_0$, respectively, see Definition 12.

Even if $\overline{\Sigma}$ is macroscopic in size, it is extremely small compared to the medium $\widetilde{\Sigma}$ so it does not affect the field $\tilde{\boldsymbol{x}}$ of $\widetilde{\Sigma}$. Thus,

$$\widetilde{\boldsymbol{x}} \approxeq \boldsymbol{x}_0 \tag{5}$$

of Σ_0 so that we will use $\boldsymbol{x}_0$ to specify any $\tilde{\mathfrak{q}}$ of $\widetilde{\Sigma}$.

Definition 12. *For the sake of simplicity, we will restrict* $\mathfrak{q}$ *in this review to stand for the combination* $\mathbf{X}, \widetilde{\mathbf{X}}$ *or* $\mathbf{X}_0$*, as the case may be.*

Claim 13. $\widetilde{\Sigma}$ *is in EQ so there cannot be any irreversibility in it. Any irreversibility in* $\overline{\Sigma}_0$ *will be associated with* $\overline{\Sigma}$*.*

Let $\Gamma(\mathbf{X})$ be the microstate space containing $W(\mathbf{X})$ distinct microstates for Σ_{b}. While a temporal evolution for Σ_{b} is not our primary interest in this review, we still need to remember the importance of temporal evolution in any thermodynamic study. We will say that two microstates belonging to the microstate subspace $\Gamma(\mathbf{X})$ are "connected" if one evolves from the other after some time $\tau_{\mathrm{c}} < \infty$. Before this time, they will be treated as "disconnected." Let $\tau_{\mathrm{c,max}}$ denote the maximum τ_{c} over all pairs of microstates. The space $\Gamma(\mathbf{X})$ is *simply connected* for all times longer than $\tau_{\mathrm{c,max}}$ in that each microstate can evolve into another microstate $\in \Gamma(\mathbf{X})$ in due time. For $t < \tau_{\mathrm{c,max}}$, the space $\Gamma(\mathbf{X})$ will consist of *disjoint components,* an issue that neither Boltzmann nor Gibbs has considered to the best of our knowledge. But the issue, which we consider later in Sect. 9.2, becomes important in considering nonequilibrium states, especially in glasses [42].

1.3. *Our Goals*

There are several important goals that we have in this review. The most important goal is to introduce our various attempts of the past decade and a half for formulating a new general statistical thermodynamics, valid for any temperature, to the reader of Lîla-Entropie. We draw a parallel between EQ entropy S_{eq} and a unique NEQ entropy S_{ieq} so dealing with the latter entropy is not very different from EQ thermodynamics as both give rise to Gibbs fundamental relations. We believe the formulation of Gen-Th to be almost complete at this stage.

One of our other goals is to use BCGM proposal to introduce the above stochasticity and identify NEQ entropy. There are four steps S1, S2, S3, and S4 in adopting this proposal that are introduced in Sect. 10.1 in full details. We first classify a Hamiltonian as uniform and nonuniform, which is novel and central to our approach so that we can uniquely identify m_{ieq} mechanical internal variables that are required to uniquely specify nonuniformity. The intention behind the classification is to relate them to unique equilibrium and nonequilibrium systems $\overline{\Sigma}$, respectively, and uniquely identify their states. The second goal is to use this uniqueness to operationally identify S_{ieq} with no explicit time dependence in terms of S_{eq}; the former requires n_{ieq} internal variables, see Definition (17). While internal variables have been extensively used in thermodynamics [23–33] by introducing them ad hoc and phenomenologically, we are the first one to provide an operational definition [34–36, for example] of them first mechanically and then thermodynamically in a unique manner as discussed here. The third important goal is to establish that the use of $m < m_{\text{ieq}}$ internal variables gives rise to a NEQ S with explicit time dependence.

The fourth goal is to first study a mechanical system Σ^{D} and use it to study the corresponding thermodynamic system Σ to formulate its Gen-Th *without* any requirement that they satisfy SL, which make them very different from Cl-Th and NEQ statistical mechanics. The No-Go theorem shows that there cannot be any violation of GSL unless analytical mechanics is dethroned. The last goal is to apply the new thermodynamics to glasses that form prime and interesting NEQ macrostates.

1.4. *Significant Results*

We now list some significant results that will be justified in the review. They relate to any system $\overline{\Sigma}$, which can be of any size, and play an important role in achieving our goals in 1.3 and fulfilling our goals in Main Motivation 4. We enforce the BCGM proposal on Σ^{D} that follows analytical mechanics [41,43] to develop Gen-Th.

R1 The Hamiltonian $\mathcal{H}$, microstates $\mathfrak{m}_k$ and microenergy E_k of a nonuniform system Σ^{D} in $\mathfrak{S}_{\mathbf{X}}$ have explicit time dependence as shown in Sec. 5; the time dependency is absent for a uniform system, which is described by a stationary $\mathcal{H}$.

R2 The Hamiltonian $\mathcal{H}$, microstates $\mathfrak{m}_k$ and microenergy E_k of a nonuniform system Σ^{D} does not carry explicit time dependence if it is expressed in a suitably chosen $\mathfrak{S}_{\mathbf{Z}} \supset \mathfrak{S}_{\mathbf{X}}$ despite being nonuniform as shown in Sec. 5 by introducing m_{ieq} mechanical internal variables.

R3 A nonuniform macrostate $\mathfrak{M}$, its macroenergy E and entropy S of Σ in $\mathfrak{S}_{\mathbf{X}}$ have explicit time dependence; the time dependence disappears for $\mathfrak{M}_{\text{eq}}$ in $\mathfrak{S}_{\mathbf{X}}$ and $\mathfrak{M}_{\text{ieq}}$ in $\mathfrak{S}_{\mathbf{Z}}$.

R4 We support the proposal that Clausius entropy of Cl-Th be called Carnot-Clausius entropy to give Carnot proper credit for his important contribution in its discovery, see Sect. 8.

R5 $S_{\text{ieq}} = S(\mathbf{Z})$ and $S(\mathbf{Z}', t)$ are the operational extensions of the Carnot-Clausius entropy of Cl-Th to any NEQ macrostate $\mathfrak{M}_{\text{ieq}}$ and $\mathfrak{M}$, but without the imposition of SL.

R6 The SI-first law

$$dE = dQ - dW \tag{6}$$

in terms of generalized macroheat and macrowork applies to any arbitrary macrostate $\mathfrak{M}_{\text{arb}}$ of a thermodynamic system Σ of *any* size, not necessarily macroscopic, as discussed in Sec. 10.3. Conventional formulation of the first law in Cl-Th is in terms of the exchange quantities

$$d_{\text{e}}E = d_{\text{e}}Q - d_{\text{e}}W, \tag{7}$$

which is very different but also applicable to any arbitrary macrostate $\mathfrak{M}_{\text{arb}}$. Considering internal processes, we also have another version of the first law

$$d_{\text{i}}E = d_{\text{i}}Q - d_{\text{i}}W, \tag{8}$$

in which $d_{\text{i}}E \equiv 0$ as no internal process can change the energy of the system.

R7 In Gen-Th, Σ satisfies the *irreversibility principle*

$$d_{\rm i}Q \equiv d_{\rm i}W \lesseqgtr 0, \tag{9}$$

derived in Sect. 10.5, for any $\mathfrak{M}_{\rm arb}$ so that the sign and magnitude of $d_{\rm i}Q$ are determined by those of the irreversible mechanical macrowork $d_{\rm i}W$ during evolution, as discussed in Sec. 10.3. The above principle also follows directly from Eq. (9). The *dissipation* in Gen-Th is measured [44] by

$$D \doteq \Delta_{\rm i}W \lesseqgtr 0, \tag{10}$$

as discussed in Sect. 13.3. It is concluded that dissipation is not proportional to irreversible entropy generation $d_{\rm i}S$, a surprising result, as shown in Eq. (15a).

R8 NEQ thermodynamic temperature for $\mathfrak{M}_{\rm arb}$ of Σ of any size is given by

$$T \doteq dQ/dS \equiv (\partial E/\partial S)_{\mathbf{W}} \equiv \ (\partial E/\partial S)_{\mathbf{W}',t} \tag{11}$$

that follows from Theorem 66 and Definition 63. As a consequence, we obtain the *Fundamental Clausius Identity*

$$dQ = TdS \tag{12}$$

that remains valid in all cases. This temperature is always defined so it covers both positive and negative thermodynamic temperatures.

R9 During evolution of Σ in any $\mathfrak{M}_{\rm arb}$ that must follow analytical mechanics and the *principle of mechanical equilibrium*, called Mec-EQ-P [41], $d_{\rm i}W \geq 0$, which proves the *generalized second law* (GSL)

$$d_{\rm i}Q \equiv d_{\rm i}W \geq 0 \text{ (GSL)} \tag{13}$$

for Σ, which includes $\Sigma_{\rm E}$ and $\Sigma_{\rm M}$. We use Gen-GSL-Th to denote the resulting thermodynamics with GSL, which *cannot* be violated without violating analytical mechanics. This then becomes a *No-Go-Theorem* for GSL-violation with the reverse inequality above. A consequence of GSL is the *principle of dissipation*

$$D = \Delta_{\rm i}W = \Delta_{\rm i}Q \geq 0; \tag{14}$$

see Eq. (131a), it does not require identifying the thermodynamic temperature.

R10 It is found that in Gen-GSL-Th

$$Td_{\rm i}S = d_{\rm i}Q + (1 - T/T_0)d_{\rm e}Q \geq 0, \tag{15a}$$

where T_0 is the temperature of the medium $\tilde{\Sigma}$. Introducing $d_{\rm i}S^{\rm (w)}$ by $d_{\rm i}W = Td_{\rm i}S^{\rm (w)}$, see Eq. (124),

$$d_{\rm i}S^{\rm (w)} \geq 0 \text{ for } T \geq 0, d_{\rm i}S^{\rm (w)} \leq 0 \text{ for } T \leq 0 \tag{15b}$$

for any system Σ of *any size*, including $\Sigma_{\rm M}$, interacting or not. Introducing $d_{\rm i}S^{\rm (h)}$ by $d_{\rm i}S - d_{\rm i}S^{\rm (w)}$, see Eq. (125) so that

$$Td_{\rm i}S^{\rm (h)} = (1 - T/T_0)d_{\rm e}Q \gtreqless 0, \tag{15c}$$

which identifies the *irreversible entropy generation due to exchange macroheat*. The consequences for $d_{\rm i}S^{\rm (h)}$ for both positive and negative temperatures are carefully discussed in Sect. 13.4 under the condition of zero $d_{\rm i}S^{\rm (w)}$ in Gen-Th. All the above conclusions should be compared with that in Eq. (27) describing the conventional statement of SL, and the discussion following it.

R11 From Sect. 13.4, we find that under the condition of zero $d_{\mathrm{i}}S^{(\mathrm{w})}$ so that $dS = d_{\mathrm{i}}S^{(\mathrm{h})}$, macroheat flows from hot to cold for positive temperatures and cold to hot body at negative temperatures in Gen-GSL-Th, without violating GSL ($\Delta_{\mathrm{i}}Q \geq 0$) :

$$d_{\mathrm{i}}S^{(\mathrm{h})} \geq 0, T \geq 0, d_{\mathrm{i}}S^{(\mathrm{h})} \leq 0, T \leq 0. \tag{16}$$

R12 Combining Eqs (15b) and (16), we obtain

$$d_{\mathrm{i}}S \geq 0 \text{ for } T > 0, d_{\mathrm{i}}S < 0 \text{ for } T < 0; \tag{17}$$

see also Remark 30. Thus, $d_{\mathrm{i}}S < 0$ is not a violation of GSL and, therefore, SL for Σ_{M} as $dQ \geq 0$ for $T < 0$. We now have the precise and correct extension of SL for Σ in terms of T. We express this extension of SL by GSL/SL.

1.5. *Layout*

The table of contents clearly outlines the layout of the paper. The next section briefly discusses basic thermodynamic concepts, while Sect. 3 deals with some important concepts, many of which are later covered in detail in the rest of the paper. We generalize the concepts of *irreversibility* and *spontaneity* to fit the new thermodynamics, Gen-Th, we want to develop. Sects. 4, 5, and 6 deal with mechanical concepts applicable to microstates. It is here that we introduce the new concepts of *uniform and nonuniform Hamiltonians* and of microworks, and the importance of the *mechanical equilibrium principle*; the latter forms the backbone of our novel approach that is the *reverse* of what is taken in Cl-Th. We argue that *unstable* systems are as important as *stable* systems to consider for a complete formulation of Gen-Th. Stochasticity as part of the BCGM proposal is covered in Sects. 7.1, 8, 9, and 10.1. Sect. 8 is an important one, where we promote our thesis that Carnot must share partial credit with Clausius for inventing the thermodynamic entropy S, and suggest it be called the *Carnot-Clausius* (C-C) *entropy*. We present a *statistical definition of entropy* $\mathcal{S}$ in Sect. 9 and establish that it is not different from the operational definition of the C-C entropy so we make no distinction between them in the review unless necessary. Hierarchical nature of the *equilibration* of internal variables in time are covered in Sect. 11. Identification of *NEQ thermodynamic temperature* is covered in Sect. 12. Gen-Th is formulated in Sect. 13, which is insured to be blind to SL so it supersedes Cl-Th; the latter includes SL as part of it. We also identify the measure D of *dissipation*. The formulation of *generalized second law* (GSL) and the *principle of dissipation* is covered in Sect. 14 by implementing (S4-GSL). Vitrification is studied in Sect. 15 by applying Gen-GSL-Th. Sect. 16 provides a summary and some clarifying discussion of some of the important results. The last section lists some of the unanswered problems in this review that should, hopefully, be investigated for a better understanding of the new thermodynamics.

2. Basic Concepts

2.1. *Entropy Formulations*

There are two distinct approaches to understand the physics of the entropy.

A. One is the original thermodynamic approach of Carnot [13] and Clausius [5] in classical thermodynamics, where it appears as a primitive stochastic concept, and determines the Gibbs fundamental relation from which follows the entire EQ thermodynamics (EQT). It has been expressed by S above for which we have the famous EQ Clausius equality to determine the EQ entropy change $dS_{\text{eq}} \doteq dS$ in terms of the EQ macroheat $dQ_{\text{eq}} \doteq dQ$

$$dS_{\text{eq}} = dQ_{\text{eq}}/T \tag{18}$$

in any reversible process with SI-temperature T equal to the MI-temperature T_0.

B. In time, the concept of EQ thermodynamic entropy S_{eq} went through various incarnations that resulted in the other approach. Boltzmann's formulation

$$S_{\text{B}} \doteq \ln W_{\text{m}} \tag{19a}$$

is in terms of the number W_{m} of distinct microstates $\{\mathfrak{m}_k\}, k = 1, 2, 3, \cdots$. Gibbs' formulation

$$S_{\text{G}} \doteq -\textstyle\sum_k p_k^{\text{eq}} \ln p_k^{\text{eq}} \tag{19b}$$

is in terms of microstate probabilities $\{p_k^{\text{eq}}\}$. Both formulations are *statistical* in nature for $\mathfrak{M}_{\text{eq}}$, and are different in spirit as we have discussed extensively [9, 35, 36, 45, 46] with the Gibbs formulation S_{G} more general than the Boltzmann formulation S_{B}, which is a special case of the former for equiprobable probabilities $p_k = 1/W_{\text{m}}$; see, however, Lavis for an alternative view [47]. The last incarnation in the form of S_{G} gave birth to EQ statistical mechanics [15, 17, for example] that justifies the equilibrium version of classical thermodynamics (Cl-Th) for an interacting system in Fig. 1(b), and raised S to be the primitive stochastic concept of state variables specifying $\mathfrak{M}_{\text{eq}}$. By using the third law, one can also show the equivalence of S_{B} and S_{G}.

A deterministic system Σ^{D} can always be associated with *constant* microstate probabilities p_k, not necessarily equal to $1/W_{\text{m}}$ for $\forall k$, in time [9] during any mechanical process $\mathcal{P}_{\text{mech}}$. This makes $\mathcal{P}_{\text{mech}}$ *isentropic* with its constant $\mathcal{S}$ determined by Eq. (24). As $dp_k \equiv 0, \forall k$, such a process will not result in any generalized macroheat as demonstrated by Eq. (85b), which is consistent with the mechanical nature of $\mathcal{P}_{\text{mech}}$ as discussed above. Therefore, stochasticity in thermodynamics is not just associating any probability to $\mathfrak{m}_k$. It must *change* in time in any thermodynamic process $\mathcal{P}$ involving macroheat; see footnote 6. In our view, therefore,

Definition 14. *Stochasticity always means ability to* change $\{p_k\}$ *during any thermodynamic process involving macroheat so as to distinguish a mechanical system from a thermodynamic system Σ in a general discussion. Isentropic $\mathcal{P}$ is no different from a mechanical process $\mathcal{P}_{mech}$.*

2.2. *Gibbs Ensemble*

Intuitively, a microstate $\mathfrak{m}$ is nothing but an instantaneous state of Σ in classical thermodynamics or an eigenstate of its Hamiltonian in quantum thermodynamics. If we consider an instantaneous *ensemble* [14] of Σ by making a large number of its *replicas* at any instant t, all prepared under identical conditions, then $\{\mathfrak{m}_k\}$ is the set formed from distinct microstates at that time. We use this approach to identify the statistical formulation of entropy in Sect. 9. Each microstate is specified by the instantaneous values of the state variables in the corresponding replica. How often a particular microstate $\mathfrak{m}_k$ appears among the replicas determines its probability p_k. The connection with classical thermodynamics is through the *ensemble averages* $\langle\bullet\rangle$ for any macrostate

$$\langle\bullet\rangle \doteq \textstyle\sum_k p_k (\bullet)_k, \tag{20}$$

where $(\bullet)_k$ refers to the microstate value.

Remark 15. *It should be emphasized that the ensemble average is defined for any* Σ*, regardless of its size. For example, it is as valid for the toss of a single coin that is repeated many number of times; the many attempts form the ensemble. This observation will prove useful when we discuss the first law in Sect. 10.3.*

Remark 16. *Thermodynamic limit in statistical mechanics corresponds to the limit in which the size of the system becomes infinitely large. Thus, to specify the size of the system, we need to use one of the extensive components in* $\mathbf{X}$ *to specify it. As we are going to be mainly dealing with a single-component system, it is convenient to reserve* N *for this purpose; see also Condition 6. If we are dealing with a multi-component system, we can either use the number of particles of one of the chemical components or use some other component of* $\mathbf{X}$*, such as the volume* V *to fix the size.*

The ensemble average $\langle Z\rangle$ of some quantity Z, which is also written simply as Z, is

$$Z \doteq \langle Z\rangle = \textstyle\sum_k p_k Z_k, \tag{21a}$$

where Z_k is the value Z takes on $\mathfrak{m}_k$. Thus, statistical thermodynamics requires a probabilistic approach for $\mathfrak{M}$. In contrast, the classical thermodynamics has no association with microstates and/or their probabilities. In this review, we use the statistical approach in which we treat each microstate as a mechanical object, whose average properties not only determine thermodynamics but also provide a *mechanical explanation* of why SL emerges in thermodynamics [21, 22, 48]; the latter has eluded a mechanical understanding until now.

We will take the work set $\mathbf{w}$ to be the same for all microstates so it does not carry the index k of $\mathfrak{m}_k$. We will not consider here the case when $\mathbf{w}$ is fluctuating (over $\mathfrak{m}_k$), to which the present method is easily extended [48, 49]. Thus, $\{\mathfrak{m}_k\}$ only differ in microenergies $\{E_k\}$ but not in $\mathbf{w}$. Because of this, we only need to introduce the thermodynamic energy as the ensemble average in the Gibbs ensemble[13]

$$E \doteq \langle E\rangle = \textstyle\sum_k p_k E_k. \tag{21b}$$

Thermodynamic concept of internal macroenergy E of $\mathfrak{M}$ as an (ensemble) average quantity is probably the most important mechanical macroquantity of a thermodynamic system Σ, which requires a mechanical specification in terms of its conservative Hamiltonian $\mathcal{H}$ that describes the conservative or deterministic evolution of the corresponding mechanical analog system Σ^{D}. Averaging brings about stochasticity mentioned above in a thermodynamic specification of Σ provided heat is involved as discussed later.

It happens that for $\mathfrak{M}_{\mathrm{eq}}$, p_k takes a special value[14] p_k^{eq} for equilibrium microstate $\mathfrak{m}_{k\mathrm{eq}}$, see Eq. (2), to determine the EQ macroenergy

$$E_{\mathrm{eq}} \doteq \textstyle\sum_k p_k^{\mathrm{eq}} E_{k\mathrm{eq}}. \tag{21c}$$

---

[13] p_k^{eq} and p_k^{ieq} are determined by using the Lagrange multiplier technique under appropriate constraints, and have been determined is several of publications such as [35, see Sect. 8.2] to which we refer the reader for more detail. It should be stressed that the technique can be applied to a system of any size so the forms of p_k^{eq} and p_k^{ieq} are not limited to only macroscopically large system Σ_{M}. which can be applied to.

[14] p_k^{eq} and p_k^{ieq} are determined by using the Lagrange multiplier technique under appropriate constraints, and have been determined is several of publications such as [35, see Sect. 8.2] to which we refer the reader for more detail. It should be stressed that the technique can be applied to a system of any size so the forms of p_k^{eq} and p_k^{ieq} are not limited to only macroscopically large system Σ_{M}. which can be applied to

What we observe is that E_k is oblivious to the value of p_k so it does not change as we replace the latter by p_k^{eq}. In other words, the same set $\{\mathfrak{m}_{k\text{eq}}, E_{k\text{eq}}\}$ specify different macrostates $\mathfrak{M}$ for different choice of p_k, one of which is $\mathfrak{M}_{\text{eq}}$ given in Eq. (2). However, it can be shown [82] that any other choice than p_k^{eq} will not satisfy the first law. The most transparent way to think about it is to think of an isolated system, whose macrostate is identified by $\{\mathfrak{m}_{k\text{eq}}, p_k\}$ having fixed $\{E_{k\text{eq}}\}$. This macrostate must be treated as a NEQ macrostate as the EQ macrostate is given by Eq. (2). These probabilities must change in time to comply with SL, so the generalized macroheat in Eq. (85b) must be nonzero. However, there is no generalized macrowork so the first law is violated.

2.3. *NEQ Entropy*

As is well known, S plays important roles in various fields that range from classical thermodynamics of Carnot-Clausius [2,3,5,13–17,25–28,50–61], quantum mechanics and uncertainty [62–64], black holes [65,66] and gravitating systems [37], coding and computation [67–69], to information technology [70–73], it appears to not have a standard definition in all cases, despite being well defined under *equilibrium* (EQ) conditions; see, for example [12,14,16,45,46,74], where S_{eq} is a unique *state* function of n_{eq} *observables* specified by $\mathbf{X}$. It is known that S_{eq} is stationary for fixed $\mathbf{X}$ so that it has no *explicit* time dependence. When observables in $\mathbf{X}$ are allowed to have *implicit* time dependence, they can be used to define a reversible process $\mathcal{P}_{\text{rev}}$ so that S_{eq} will have an implicit time dependence during $\mathcal{P}_{\text{rev}}$. Whether S has any physical significance for a NEQ macrostate $\mathfrak{M}$ of Σ has been a topic of extensive debate; see for example [11,12,45,46,74,75, and references therin]. What is undisputable is that such an entropy must have an *explicit time dependence*. Therefore, in this review, we are primarily interested in understanding this concept in nonequilibrium (NEQ) statistical thermodynamics of irreversible processes (we will use NEQT to denote NEQ thermodynamics in this review) based on our own ongoing research in this direction. This review aims not only at developing our new approach, but also at removing certain deficiencies and misunderstandings about NEQ processes as currently employed in modern NEQ studies related to fluctuation theorems.

There have been serious thoughts and concerns, see for example a beautiful exposition by Lieb and Yngvason [12], about the notion of nonequilibrium (NEQ) entropy S, while no such concern and dispute exist about equilibrium (EQ) entropy $S_{\text{eq}} \doteq S(\mathbf{X})$ for a given n_{eq} for $\mathfrak{M}_{\text{eq}}$. It is evident that S, if it exists, must be time dependent and expressed as $S(\mathbf{X}, t)$ as the corresponding macrostate $\mathfrak{M}(\mathbf{X}, t)$ must be time dependent. Therefore, our primary goal is to introduce the readers of the project Lîla-Entropie of our excursion of the last decade and a half or so to uniquely identify NEQ entropy $S(\mathbf{X}, t)$, which we simply denote by $S(t)$ as a function of time, a topic that has been quite controversial over the years. The time dependence distinguishes it from the time-independent equilibrium entropy S_{eq} when the system is in equilibrium. We have succeeded in this endeavor by identifying a particular class of NEQ macrostate $\mathfrak{M}_{\text{ieq}}$ that we have labeled as a macrostate in *internal equilibrium* (IEQ) at each instant of time. This requires a certain number $n_{\text{ieq}}(t) \doteq n_{\text{eq}} + m_{\text{ieq}}(t)$ of extensive state variables in $\mathbf{Z}_{\text{ieq}}(t \doteq \mathbf{X}(t) \cup \boldsymbol{\xi}_{\text{ieq}}(t))$ in accordance with Eq. (4), which includes *internal variables* [24,27–29,35] in $\boldsymbol{\xi}_{\text{ieq}}(t)$ having $m_{\text{ieq}}(t)$ components along with observables in $\mathbf{X}(t)$ so that $\mathbf{Z}_{\text{ieq}}(t)$ uniquely identifies $\mathfrak{M}_{\text{ieq}} \doteq \mathfrak{M}(\mathbf{Z}_{\text{ieq}}(t))$ and its entropy $S_{\text{ieq}} \doteq S(\mathbf{Z}_{\text{ieq}}(t))$ without any explicit time dependence.

Definition 17. *A particular NEQ macrostate $\mathfrak{M}_{ieq}$ is* uniquely *described in an appropriately chosen state space $\mathfrak{S}_{\mathbf{Z}}^{ieq}$ with $n_{ieq} \doteq n_{eq} + m_{ieq}$ state variables just as $\mathfrak{M}_{eq}$ is uniquely described in $\mathfrak{S}_{\mathbf{X}}$ with n_{eq}, and* *possesses many but not all properties of* $\mathfrak{M}_{eq}$*, the most important being the entropy* $S_{ieq} = S(\mathbf{Z}_{ieq})$ *that is a unique function of* $\mathbf{Z}_{ieq}$ *with no explicit time dependence, making* S_{ieq} *a* state function *in* $\mathfrak{S}_{\mathbf{Z}}^{ieq}$*. For this reason, these NEQ macrostates* $\mathfrak{M}_{ieq}$ *are identified as being in internal equilibrium (IEQ) and properly introduced below in Sect. 5.*

In Sect. 9, we justify that the following generalization of S_{G} as

$$\mathcal{S} \doteq -\textstyle\sum_k p_k \ln p_k =< (-\eta_k) > \tag{22}$$

uniquely and operationally defines the additive entropy of any arbitrary macrostate $\mathfrak{M}$ with any arbitrary microstate probabilities of a countable set of microstate, including the one given in Eq. (3); here, η_k is what Gibbs [14] calls the *index of probability*

$$\eta_k \equiv \ln p_k. \tag{23}$$

We identify $\mathcal{S}$ as the *general statistical entropy* that subsumes S_{B} and S_{G}.

2.4. *Equivalence of Statistical and Thermodynamic Entropies*

Relationship between statistical and thermodynamic entropies ($\mathcal{S}$, S_{B},S_{G} and S) has been investigated earlier by us [45,46]. For $\mathfrak{M}_{\mathrm{eq}}$, $\mathcal{S}$ obviously reduces to S_{B} and S_{G}. As there is close similarity between $\mathfrak{M}_{\mathrm{eq}}$ and $\mathfrak{M}_{\mathrm{ieq}}$, we have shown that $\mathcal{S}$ and S are identical for both macrostates. The equivalence becomes questionable when the thermodynamic entropy is not a state function. In that case, S cannot be measured or computed analytically by using state variables alone. Thus, while $\mathcal{S}$ can be computed in principle in all cases, there is no way to compare its value with S in all cases and no comment can be made about their relationship in general, and our previous investigation required the following

Conjecture 18. *We merely conjecture [45, 46] with respect to the equivalence of* $\mathcal{S}$ *and* S *for all macrostates of* Σ_M *by extending our demonstration of their equivalence [46] for* $\mathfrak{M}_{ieq}$*.*

The way to justify the conjecture is as follows. We consider a nonstate function entropy $S(\mathbf{Z}', t)$ of $\mathfrak{M}(\mathbf{Z}', t)$ in $\mathfrak{S}_{\mathbf{Z}}$. We will establish that the same entropy becomes a state function $S(\mathbf{Z})$ in an enlarged state space $\mathfrak{S}_{\mathbf{Z}}$ with $\mathbf{Z}'$ a proper subset of $\mathbf{Z}$ so that $\mathfrak{M}(\mathbf{Z}', t)$ becomes a unique macrostate $\mathfrak{M}_{\mathrm{ieq}} \doteq \mathfrak{M}(\mathbf{Z})$ in $\mathfrak{S}_{\mathbf{Z}}$. Thus, $S(\mathbf{Z}')$ is no different than S_{G} using $\left\{p_k^{\mathrm{ieq}}\right\}$ in $\mathfrak{S}_{\mathbf{Z}}$. This justifies the above Conjecture. This allows us to identify S_{G} as the *statistical entropy* formulation of the thermodynamic entropy S in all cases. Indeed, we use S_{G} to also stand for the thermodynamic entropy S in all cases for any arbitrary macrostate. As a consequence, we

Remark 19. *Because of this equivalence between* $\mathcal{S}$, S_G*, and* S*, we will no longer make any distinction between the statistical entropy and the thermodynamic entropy and will use the standard notation* S *for all three of them, unless clarity is needed.*

Thus, S is always given by its general formalism [14,34,71] in Eq. (24), which we rewrite for S as the average of $S_k \doteq -\ln \eta_k$:

$$S = \langle S \rangle \doteq -\textstyle\sum_k p_k \ln p_k, \tag{24}$$

for any arbitrary collection $\{p_k\}$. The validity of the above S is based on the use of Stirling's approximation in Sect. 9. We will not be concerned about the error involved in this approximation, and accept the formula to be the definition of S. Different choices for $\{p_k\}$ result in different macrostates and averages for the same microstates. A constant $p_k, \forall k$, describes a pure mechanical system, see footnote 6, with constant E and S.

2.5. *Thermodynamic Processes*

A reversible process $\mathcal{P}_{\text{rev}}$, also called an equilibrium process and also expressed as $\mathcal{P}_{\text{eq}}$, resides entirely in the EQ state space $\mathfrak{S}_{\mathbf{X}}$ as shown by γ_{12} in Fig. 2 between two EQ macrostates shown symbolically as 1 and 2 in the state space formed by two observables X_1 and X_2. A process such as $\mathcal{P}_{12}$ between the same two EQ macrostates but leaves the EQ state space along ξ is identified as an irreversible or a nonequilibrium (NEQ) process. Thus,

Definition 20. *By* irreversibility *of a process $\mathcal{P}$ is meant the* fixed signature *of any nonzero process quantities $d_i\mathfrak{Q}$ that include $d_i\mathbf{W}, d_iS, d_iW$, and d_iQ during any elemental process $\delta\mathcal{P}$ of $\mathcal{P}$.*

Definition 21. *Irreversibility requires a state space larger than the EQ state space $\mathfrak{S}_{\mathbf{X}}$. The additional state variables such as ξ in Fig. 2 are commonly called* internal variables *[24, 27–29, 35]. The extended state space is denoted in this review by $\mathfrak{S}_{\mathbf{Z}}$ with $\mathbf{Z}$ in Eq. (4) having n state variables with $\boldsymbol{\xi}$ denoting the set of m_{int} internal variables that are operationally constructed in Sect. 5. The dimension of $\mathfrak{S}_{\mathbf{Z}}$ given by*

$$n = n_{eq} + m_{int}. \tag{25}$$

Two such macrostates $1'$ and $2'$ are shown in Fig. 2 that are connected by a process γ'_{12} that lies entirely in the state space $\mathfrak{S}_{\mathbf{Z}}, n = 3$, so it identifies an internal equilibrium process $\mathcal{P}_{\text{ieq}}$. However, processes $\mathcal{P}'_{12}$ and $\mathcal{P}''_{21}$ may lie outside. In that case, they describe non-IEQ processes in $\mathfrak{S}_{\mathbf{Z}}$ so that the entropy along these processes is not a state function. These processes can become IEQ processes with state function entropies S'_{ieq} in a larger state space $\mathfrak{S}_{\mathbf{Z}'} \supset \mathfrak{S}_{\mathbf{Z}}$.

2.6. *Irreversibility and SL*

Carnot [13] was the first one to introduce the concept of *irreversibility* in thermodynamics of real physical systems such as heat engines, see for example [76, and references therin], and to argue on general grounds that the efficiency ϵ^{IrC} of an irreversible Carnot (IrC) engine $\mathbb{E}^{\text{IrC}}$ *cannot* exceed the efficiency ϵ^{RC} of a reversible Carnot (RC) engine $\mathbb{E}^{\text{RC}}$:

$$\epsilon^{\text{IrC}} \leq \epsilon^{\text{RC}}. \tag{26a}$$

It is easy to demonstrate (see later) that the non-negative difference $\Delta\epsilon \doteq \epsilon^{\text{RC}} - \epsilon^{\text{IrC}}$ is related to the irreversible entropy generation $\Delta_{\text{i}}S|_{\text{C-cyc}}$ over the Carnot cycle (C-cyc) underlying the Carnot engine [35, Eq. (137)] as follows

$$\epsilon^{\text{IrC}} = \epsilon^{\text{RC}} - T_{0C}\, \Delta_{\text{i}}S|_{\text{C-cyc}} / \Delta_{\text{e}}Q_{\text{H}}, \tag{26b}$$

where $T_{0C} \geq 0$ is the temperature of the colder heat medium to which the macroheat is rejected and $\Delta_{\text{e}}Q_{\text{H}} > 0$ is the macroheat accepted from the hotter heat medium, ensuring that

$$\Delta\epsilon \geq 0.$$

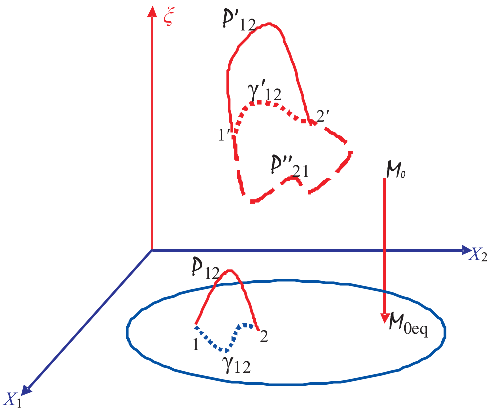

Figure 2. The equilibrium macrostates of an isolated system Σ_0 or an interacting system Σ in $\mathfrak{S}_{\mathbf{X}}$, shown here by the $X_1 - X_2$ plane, lie inside the enclosed region bounded by the solid blue curve. The plane $\mathfrak{S}_{\mathbf{X}}$ corresponds to the internal variable $\xi = 0$. Two equilibrium macrostates $\mathfrak{M}_{1\text{eq}}$ and $\mathfrak{M}_{2\text{eq}}$ for an interacting system are indicated by 1 and 2 and are connected by one of many reversible processes $\mathcal{P}_{\text{rev}}$ shown by the dashed blue curve γ_{12} lying entirely in $\mathfrak{S}_{\mathbf{X}}$. A possible irreversible process $\mathcal{P}_{\text{irr}} = \mathcal{P}_{12}$ is shown by the solid red curve; the latter leaves $\mathfrak{S}_{\mathbf{X}}$ and comes back to 2 in it. The NEQ macrostate $\mathfrak{M}_0$ of an isolated system Σ_0 approaches equilibrium along the solid red arrow at fixed $\mathbf{X} = \mathbf{X}_0$ and turns into $\mathfrak{M}_{0\text{eq}}$ lying in $\mathfrak{S}_{\mathbf{X}}$. This evolution process *cannot* be reversed. Macrostates $1'$ and $2'$ represent two NEQ macrostates with $\xi \neq 0$ with two possible NEQ processes $\mathcal{P}'_{12}$ and $\mathcal{P}'_{21}$ between them. All the states with $\xi \neq 0$ along the process γ'_{12} but not necessarily along $\mathcal{P}'_{12}$ and $\mathcal{P}'_{21}$ between $1'$ and $2'$ represent macrostates in internal equilibrium.

Remark 22. *It is important to emphasize the fact that* $\Delta_i S|_{cyc}$ *in Eq. (26b) appears along with a prefactor* T_{0C} *so that* $T_{0C}\ \Delta_i S|_{cyc}$ *has the same dimension as that of the exchange macroheat* $\Delta_e Q_H$*; see footnote 1. It is natural to identify a* cycle irreversible macroheat

$$\Delta_i Q|_{C\text{-}cyc} \doteq T_{0C}\ \Delta_i S|_{C\text{-}cyc} \geq 0$$

for the Carnot cycle, which is directly proportional to the irreversible entropy generation $\Delta_i S|_{C\text{-}cyc}$*, with the constant of proportionality given by the colder temperature. As a consequence,* $\Delta\epsilon$ *is expressed as a function of two macroheats,* $\Delta_i Q|_{C\text{-}cyc}$ *and* $\Delta_e Q_H$*, so that it is dimensionless as defined. It then follows that the Carnot efficiency can be defined in terms of macroheats without bringing in the concept of entropy. As engine thermodynamics is the foundation of thermodynamics, the latter can be developed in terms of macroheats and macroworks; the concept of temperature is not required. We establish that entropy can be identified in terms of macroheat by bringing in the central concept of (NEQ) temperature, see Sect. 12, in thermodynamics. Both quantities are stochastic macroquantities, which makes temperature also a stochastic macroconcept; the latter has no meaning for a microstate.*

The mechanical (classical or quantum) view of the universe, when treated as a deterministic system Σ^{D}, cannot be reconciled with the above irreversible aspect of reality, which invariably requires spontaneous processes for its emergence as discussed below. These internal processes requires the suffix i to be described by $\Delta_{\text{i}}Q$, $\Delta_{\text{i}}S$ or other macroquantities and are always found to be controlled by the celebrated second law (SL) first recognized by Carnot [13] as shown in Eq. (26a), but clearly proposed by Clausius [6], according to which the irreversible entropy generation

$$d_{\mathrm{i}}S \geq 0, \quad \text{(SL)} \tag{27}$$

in an infinitesimal process $\delta\mathcal{P}$ in Σ as follows from Eq. (1). As T does not appear here, the inequality should not be affected by whether T is positive or negative. This creates a logical problem at $T = 0$ for the existence of NEQ macrostates $\mathfrak{M}$ as we will discuss later. It also creates some confusion for $T < 0$. It is the conventional wisdom [4] that Eq. (27) holds even for negative T. We quote Ramsey:

> "Of the alternative conventional statements of the second law of thermodynamics, some are applicable without modification for negative temperatures while others must be modified. The entropy formulation remains unaltered: (a) The entropy of a system is a variable of its state and the entropy of an isolated system can never decrease."

Therefore, to validate this claim, it is desirable to have a formulation of SL that remains valid, regardless of the signature of T, *i.e.*, that is valid for any temperature, positive or negative.

To clarify the physics behind an irreversible process, we first consider the sudden expansion of a gas, which is initially confined in a given volume V_1 in a cylinder with a removable partition, to a larger volume $V_2 > V_1$ by abruptly removing the partition from inside the cylinder, is such a process. Once the partition is removed, there is no way to internally control or *reverse* expansion unless the partition is moved back by an external agent such as by hand to a volume between V_1 and V_2. Another version undergoing a similar process is a system Σ_{ic} consisting of two subsystems Σ_1 and Σ_2 that share a common inert wall shown by the red partition in Fig. 3(a) so that Σ_1 and Σ_2 remain noninteracting. If initially they are not in equilibrium with each other, they will remain so permanently due to the inert partition that creates an internal constraint (IC) as carefully discussed by Callen [3] and below in Sect. 3.4. We denote this particular nonuniform Σ by Σ_{ic}, whose macrostate $\mathfrak{M}_{\mathrm{ic}}$ is a special NEQ macrostate $\mathfrak{M}$ in that it remains stationary unless the partition (IC) is removed by an outside agent. As soon as that happens, there will be irreversible internal flow of matter and energy to make Σ more and more uniform until finally, it asymptotically becomes fully uniform and time independent. The latter is an example of an equilibrium macrostate $\mathfrak{M}_{\mathrm{eq}}$. Once Σ arrives in this macrostate, it will remain there *forever* so that $\mathfrak{M}_{\mathrm{eq}}$ is also stationary just as $\mathfrak{M}_{\mathrm{ic}}$ is. Despite this, their entropies are different. Indeed, $S_{\mathrm{ic}} < S_{\mathrm{eq}}$. Once the partition is removed, the corresponding NEQ entropy S of $\mathfrak{M}$ approaches S_{eq} from below due to irreversible flow that cannot stop unless by some outside agent. It is this behavior of S that is controlled by SL as shown in Eq. (1).

Another very common example of irreversibility is the dissipation of macrowork to macroheat by friction [28].

It is fair to say that almost all real processes are irreversible to some extend. Reversible processes are idealization for which the concept of EQ entropy S_{eq} and temperature T_{eq} are well established [17, 28]. However, the situation with extending these concepts to NEQ $\mathfrak{M}$ remained in controversy. However, we believe that some incontrovertible progress has been made recently in this direction by extending the dimension of the state space by operationally introducing internal variables to form $\mathfrak{S}_{\mathbf{Z}}$. Introduction of this extended state space is the most novel approach by us to introduce unique entropy S_{ieq} and thermodynamic temperature T_{ieq} for a special class NEQ macrostate $\mathfrak{M}_{\text{ieq}}$ that is uniquely specified in $\mathfrak{S}_{\mathbf{Z}}^{\text{ieq}}$ with n_{ieq} components. One can then construct a generalized thermodynamics in this space. Both positive and negative T_{ieq} are allowed. Once $\mathfrak{S}_{\mathbf{Z}}^{\text{ieq}}$ is identified, one can also investigate a NEQ macrostate $\mathfrak{M}$, which is not in IEQ in this space, by identifying its nonunique entropy and temperature that have explicit time dependence. This procedure can be used to identify NEQ entropy S and T (again both signs are allowed) for any arbitrary NEQ macrostate $\mathfrak{M}$.

3. Some Important Concepts

This section introduces some important concepts of interest and some new terminology that are used extensively in the review. The concepts are examined later in detail.

3.1. *SI and MI Quantities*

As our interest is in describing a NEQ process $\mathcal{P}$ undertaken by some macrostate, we need to characterize it by thermodynamic quantities. Because of the possible presence of the medium in Fig. 1(b), we have introduced two different specifications for $\overline{\Sigma}$, which are normally not used in NEQ thermodynamics (NEQT) but we find their usage very useful.

1. *System-intrinsic* (SI) *quantities*. These quantities[15] $\mathfrak{q} \doteq \mathfrak{q}(\mathbf{Z}^{\text{c}})$ and their changes $d\mathfrak{q}$ are functions of the state variable $\mathbf{Z}^{\text{c}}$, recall Definition 12, associated with the system Σ. Mostly, $\mathfrak{q}$ will simply represent $\mathbf{Z}^{\text{c}}$. Process quantities (dW, dW_k), (dQ, dQ_k) and dp_k are also SI-quantities. For example, P, which represents the pressure of the system, is the SI-pressure and is a field variable associated with V. As this pressure refers to the system, it may be different from the pressure $\widetilde{P}$ of the medium so it also describes it even when Σ is isolated as shown in Fig. 1(a). In the presence of the medium, it is this pressure that is exerted on the medium $\widetilde{\Sigma}$.

2. *Medium-intrinsic* (MI) *quantities*. These quantities $\tilde{\mathfrak{q}} \doteq \tilde{\mathfrak{q}}(\widetilde{\mathbf{Z}}^{\text{c}})$ and their changes $d\mathfrak{q}$ are functions of the state variable $\widetilde{\mathbf{Z}}^{\text{c}}$ associated with the system $\widetilde{\Sigma}$, and are defined only when the latter is interacting with the system as in Fig. 1(b). Process quantities $(d_{\text{e}}W, d_{\text{e}}W_k)$, $(d_{\text{e}}Q, d_{\text{e}}Q_k)$ and $d_{\text{e}}p_k$ are also MI-quantities. For example, $\tilde{P} \approxeq P_0$ represents the pressure of the medium, which it exerts on Σ.

As seen from Fig. 1(b), the specification of $\overline{\Sigma}$ can be accomplished by using quantities referring to $\overline{\Sigma}$ or to $\widetilde{\Sigma}$. For the dual specification to be valid, it is important that any mutual interaction between Σ and $\widetilde{\Sigma}$ can be neglected. This is the weakest requirement for their energies to be *quasi-additive* as introduced later in Sect. 5. so that the macroenergy E_0 of Σ_0 is approximately additive

$$E_0 \approxeq E + \tilde{E} \tag{28}$$

in terms of the macroenergies E and $\tilde{E}$ of Σ and $\widetilde{\Sigma}$, respectively. We have used this fact above in Eq. (5). It is well known that for a EQ process $\mathcal{P}_{\text{eq}}$ it makes no difference whether we use Σ or $\widetilde{\Sigma}$ for the specification. However, for a NEQ $\mathcal{P}$, the choice makes a very big difference.

---

[15] SI-quantities are also called generalized quantities in this review.

The negative pressure $(-\tilde{P})$ can be identified as the *reaction* pressure by Σ on $\tilde{\Sigma}$ and is a function of $\tilde{\mathbf{Z}}$, which makes it different from the SI-pressure P introduced above. To make this distinction obvious, we identify it as MI-pressure of Σ. Their difference is the pressure imbalance

$$P_{\mathrm{imb}} \doteq P - \tilde{P}, \tag{29a}$$

which represents the net pressure exerted by Σ on the boundary separating it from $\tilde{\Sigma}$, and increases or decreases its volume V depending on the sign of P_{imb}. The net macrowork done by P_{imb} is always found to be nonnegative in Cl-Th so that

$$dW_{\mathrm{imb}} \doteq (P - \tilde{P})dV \geq 0. \tag{29b}$$

As this is a consequence of the second law [28], this macrowork is also known as the $irreversible$ macrowork and will be written as dW_{irr} or simply $d_{\mathrm{i}}W$ using the modern notation introduced below. In EQ, V does not change, which requires P_{imb} to vanish, *i.e.*, P and $\tilde{P}$ to have the same magnitude so that $d_{\mathrm{i}}W \equiv 0$. As P_{imb} causes *irreversibility* in any NEQ process, there is a need to make a clear distinction between the two, and to introduce the concept of $d_{\mathrm{i}}W$.

We now use Eq. (28) to determine the pressure P_0 of Σ_0 that is given by $P_0 \approxeq P(\partial V/\partial V_0) + \tilde{P}(\partial \tilde{V}/\partial V_0) \approxeq Px + \tilde{P}(1-x)$, where we have introduced $x \doteq \partial V/\partial V_0$. For a macroscopically large medium compared to the system, $V_0 \approxeq \tilde{V}$ so that $x \approxeq 0$. Consequently, $P_0 \approxeq \tilde{P}$, which explains why all the fields for $\tilde{\Sigma}$ are shown with the suffix 0 used for Σ_0 in Fig. 1(b). This approximate equality is always assumed in this review, see Eq. (5), whenever we speak of a medium.

Definition 23. *There are two kinds of EQ microstates that we will consider in this review by borrowing terminology from analytical mechanics: stable EQ (SEQ) microstate* $\mathfrak{m}_{kseq}$ *and Unstable EQ (UEQ) microstate* $\mathfrak{m}_{kueq}$*. The corresponding systems are denoted by* $\overline{\Sigma}^{s}$ *and* $\overline{\Sigma}^{u}$*, respectively. Their respective macrostates are: stable EQ (SEQ) macrostate* $\mathfrak{M}_{seq}$ *with probabilities* $\{p_k^{seq}\}$ *and Unstable EQ (UEQ) macrostates* $\mathfrak{M}_{ueq}$ *with probabilities* $\{p_k^{ueq}\}$*, respectively.*

We will not consider neutral EQ (micro/macro)states here.

Remark 24. *We use compact notation* Q *for* $(\mathsf{Q}^s,\mathsf{Q}^u)$*, and* Q_{eq} *for* $(\mathsf{Q}_{seq},\mathsf{Q}_{ueq})$*. Thus, we say that* $\mathfrak{M}_{eq}$ *controls* $\mathfrak{M}$ *:*$(\mathfrak{M}^s,\mathfrak{M}^u)$*-evolution along continuous curves, and* $\mathfrak{m}_{keq}$ *controls* $\mathfrak{m}_k$ *:*$(\mathfrak{m}_k^s,\mathfrak{m}_k^u)$*-evolution along dashed-dot trajectories. We also let* Q *denote* E_k*,* E_{keq}*, and* $\mathbf{F}_{wk}$*, the latter defined later.*

3.2. *Spontaneous Processes*

Spontaneous processes are usually defined as a process that controls irreversibility. However, we generalize it because of our emphasis on a mechanical approach so we generalize it.

Definition 25. *A* spontaneous process $\bar{\mathcal{P}}_{spon}$ *in* $\bar{\Sigma}$ *occurs naturally (on its own) without any assistance from the outside of* Σ *so it is an internal process. In this case,* $\bar{\Sigma}$ *is said to possess* spontaneity *and can be treated as an isolated system.*

Remark 26. *We have given a definition of a spontaneous process that is general in that it can also occur in a mechanical system* Σ^D*. We have used this extension to unravel the root cause of SL as we will see later by looking for a mechanical root of SL.*

Example 27. $\mathcal{P}_{spon}^{D}$: *The simplest realization of a spontaneous process* $\mathcal{P}_{spon}^{D}$ *is a process that goes on within an isolated system* Σ^{D} *in Fig. 1(a) without any medium so there is nothing outside. Consider two massless springs* 1 *and* 2 *of spring constants* k_1 *and* k_2 *that are connected by a mass* M*; other ends of the springs are fixed at the two opposite walls of an enclosed container. Initially,* M *is at rest and held by a latch at a distance* $x \neq x_{eq} = 0$ *(see below) from the equilibrium point of the combined potential energy of the spring given by*

$$U(x) \doteq (k_1 + k_2)x^2/2. \tag{30}$$

The equilibrium point, where the force on M *vanishes, is at* $x_{eq} = 0$*. The latch is connected by a timer that releases the latch at some pre-fixed time so that* M *is free to move. The container, springs,* M*, latch and the timer form the isolated system* Σ^{D}*. For* $k = k_1 + k_2 > 0$*, springs form a stable effective spring, and we have a stable system* Σ^{sD} *so that* M *begins to move due to the force exerted by the springs. This force is internal to* Σ^{sD}*, which makes this motion spontaneous. The motion is a repeated oscillation about the stable EQ point* $x_{seq} = 0$ *that lasts forever. For* $k = k_1 + k_2 < 0$*, springs form an unstable effective spring, and we have an unstable system* Σ^{uD} *with its unstable EQ point at* $x_{ueq} = 0$*. The nonzero spring force on* M *at* $x \neq x_{ueq}$ *takes it away from* x_{ueq} *forever so that* M *never returns back to* x *or* x_{ueq}*. This is what is expected of an UEQ point.*

Example 28. $\mathcal{P}_{spon}$: *We now consider the spontaneous process* $\mathcal{P}_{spon}$ *in* Σ *associated with* Σ^{D} *in Example 27. The initial position of* M *at* $x \neq x_{eq}$ *identifies the NEQ macrostate* $\mathfrak{M}$*. For a stable system* Σ^{s}*, the oscillations of* M *and, therefore of the associated stable NEQ macrostate* $\mathfrak{M}^{s}$*, eventually stop so that* M *arrives and stays at* $x_{\mathrm{seq}} = 0$ *and* $\mathfrak{M}^{s}$ *converges to* $\mathfrak{M}_{seq}$*. On the other hand, for an unstable system* Σ^{u}*, its unstable NEQ macrostate* $\mathfrak{M}^{u}$ *runs away from* $\mathfrak{M}_{ueq}$*.*

The discussion of irreversible processes in Sect. 2.6 helps further clarify the meaning of spontaneous processes as those that naturally occur within an isolated system. Their behavior in Σ^{s} is customarily believed to be controlled by SL, see Eq. (27), which *drives* any NEQ $\mathfrak{M}$ to converge to $\mathfrak{M}_{\mathrm{seq}}$ so that it becomes uniform and stationary and ensures that S achieves its maximum possible value S_{eq}. If Σ^{s} is in the macrostate $\mathfrak{M}_{\mathrm{seq}}$ initially, it will stay there forever unless a thermodynamic fluctuation in or a temporary mechanical disturbance to $\mathfrak{M}_{\mathrm{seq}}$ occurs. Any such disturbance will bring the perturbed macrostate $\mathfrak{M}^{\mathrm{s}}$ back to $\mathfrak{M}_{\mathrm{seq}}$ due its stability by spontaneous forces, which are intrinsic to Σ, and is driven by SL. This suggests a strong *correlation between stability and SL* for Σ^{s}. The situation is the same even for a stable system Σ^{s} in a medium $\tilde{\Sigma}$ so stability and SL seem to be strongly correlated. The actual form of U is not relevant as long as it is stable.

But the behavior of Σ^{u} is so different to have any faith in the application of SL in this case as the NEQ macrostate runs farther and farther away from the UEQ macrostate. As this is counter to the convergence discussed above, it suggests that the behavior of the unstable system will be not satisfying SL; however, compare with Remark 67. We call such a scenario as the *violation of SL* (VSL). In order to understand this perplexing result, we have extended the definition of a spontaneous process to Σ^{D} as noted above.

All microscopic processes $\mathcal{P}^{\mathrm{D}}$ in the isolated system Σ are *system-intrinsic* (SI) and generated *internally* to change E_k and are governed by Hamiltonian dynamics of $\mathfrak{m}_k$. The resulting macroscopic processes $\mathcal{P}$ are *spontaneous*[16] and are governed by SL in Cl-Th, which is only satisfied by a macroscopic system $\Sigma_{\rm M}$ [3,12,15,17].

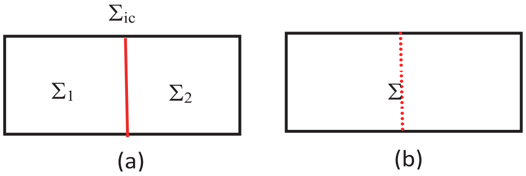

Figure 3. A system Σ is shown in two different forms. In (a), it appears as composed of two distinct subsystems Σ_1 and Σ_2 with a red partition separating them so that they are not in equilibrium with each other, to ensure that Σ is not in equilibrium. We say that Σ has an internal constraint (IC) due to the red partition. This form is denoted by $\Sigma_{\rm ic}$. In (b), IC is removed as denoted by broken red partition. The removal initiates an internal process of mixing, which cannot be controlled by any external agent. This is a spontaneous process.

3.3. *Nonspontaneous Processes*

Any SL-violation, being uncommon and controversial, will most probably result in puzzling outcomes, not all of which are recognized or discussed so far in the current literature until recently by us [21,22,44]. Also, there is no serious inquiry into thermodynamics supporting VSL because the root cause of SL and any special stochasticity for its validity are not understood; however, see [4].

Claim 29. *A* nonspontaneous *process $\bar{\mathcal{P}}_{nonspon}$ is not internally generated and requires an external medium $\tilde{\Sigma}$ to counteract an spontaneous process.*

The counteraction results in VSL. A nonspontaneous process such as the intervention carried out by Maxwell's demon [19] that is external to $\bar{\Sigma}$ only creates an *internal constraint* as carefully discussed by Callen [3] and below in Sect. 3.4, whose removal, however, is controlled by SL. Evidently, a nonspontaneous process is not controlled by SL as it violates SL (VSL) so that $d_{\rm i}S < 0$.

The investigation of VSL has become an important activity recently. Such violations will dethrone SL from being a universal law of Nature for macroscopically large $\Sigma_{\rm M}$. In order to carefully understand dethroning, we need to determine conditions necessary for $dS > 0$ and $dS < 0$, respectively. Thus, we will need to construct a new thermodynamics, to be called *general thermodynamics* (Gen-Th) in which the second law is not enshrined. In contrast, it is enshrined in Cl-Th by making it an axiom [3] or by assuming it by "proving" under some assumptions. Thermodynamics in which SL is violated is subsumed in Gen-Th. An important consequence of Gen-Th is the *irreversibility principle* [34,46] given in Eq. (9) and derived in Sect. 10.5, which establishes the equality of $d_{\rm i}Q$ and $d_{\rm i}W$ that are distinct (stochastic and mechanical) irreversible macroquantities, respectively, but their signs are not fixed. We use the latter and the *Mechanical Equilibrium Principle* (Mec-EQ-P) of Energy [41] discussed in Sect. 6 to establish a generalized second law (GSL) in Eq. (13). which does not require identifying any NEQ temperature in conformity with Remark 22. However, once such a T is defined, GSL retains its form for all temperatures, positive and negative. This makes GSL not only supersede SL but also clarifies for the first time that the inequality for SL changes its form depending on the sign of the temperature.

---

[16] All processes in Σ are synonymously identified as spontanious, internal, or SI processes in that none of them is affected by anything exterior to it. Thus, we use these terms interchangeably.

3.4. *Internal Constraint (IC)*

We now discuss the relevance of internal constraints (IC's) [3] for GSL/SL by focusing on Fig. 3, which describes the creation of an internal constraint in an *isolated* system Σ that is initially in a stable EQ macrostate. It is shown by Σ_{seq} in Fig. 3(a). The system is in contact with a work medium $\tilde{\Sigma} = \widetilde{\Sigma}^{\text{w}}$ that works on the red partition to move it in to and out of Σ_{seq} that divides Σ into two parts of equal volume. The partition is completely noninteracting (inert), see Sect. 2.6, in that it does not allow for the flow of any kind (matter and energy) across it. The blue partition between Σ_{seq} and $\tilde{\Sigma}$ provides thermal insulation between them so $\tilde{\Sigma}$ manipulates the macrostate $\mathfrak{M}_{\text{seq}}$ of Σ_{seq} by inserting the noninteracting partition instantly into Σ_{seq}. The insertion, being instantaneous, picks out a particular microstate $\mathfrak{m}_{k\text{seq}}$ in each member of the Gibbs ensemble by giving rise to two microstates of the two parts of Σ, which we denote by $\mathfrak{m}_{k_{\text{L}}}$ and $\mathfrak{m}_{k_{\text{R}}}$. Just as in the Szilard problem [72], in which the insertion leaves the number of particles in the two parts different, there is no guarantee that the insertion divides $\mathbf{X}$ evenly so the density $\mathbf{X}/N$ remains the same in the two parts. Thus, insertion will not divide $\mathbf{X}$ into equal halves for the two parts. This means that the two parts will not be in equilibrium or reach equilibrium with each other because of the noninteracting partition, even though each will come to its own SEQ macrostate in time. This situation is an example of IC discussed by Callen. We denote this state of Σ by Σ_{iceq} as shown in Fig. 3(b). It differs from Σ_{ieq} in that the latter continues to evolve in time while the former is unchanging unless the constraint is removed or altered.

The insertion results in reducing the entropy of Σ and has been discussed recently in [77]. This reduction is not a violation of SL as the insertion is done by an outside agent so the process is not spontaneous. The same is also true of Maxwell's demon who reduces the entropy by acting as an outside agent. In contrast, the process (b)$\longrightarrow$(c) in which IC is removed results in spontaneous mixing in the two parts. It is this part that is controlled by SL.

We now $\mathfrak{M}_{\text{ueq}}$ of an isolated system Σ_{ueq} in unstable equilibrium. Instability results in the energy of Σ_{ueq} continuously falling "downhill" during its spontaneous evolution as shown in Fig. 4 and fully discussed in Sect. 6. It is discovered that this evolution forces T to be negative, system gets more and more nonuniform so the entropy continuously decreases. As Callen's IC is some form of constraint to partition the system into pars, each part still continue to evolve spontaneously by its energy going downhill. It does not run "uphill" towards $\mathfrak{M}_{\text{ueq}}$. Such an "uphill" climb will correspond to a nonspontaneous reaction to the creation of IC in $\mathfrak{M}^{\text{u}}$. During (a)$\longrightarrow$(b), $dQ > 0$ as discussed in Sect. 14 so $dS = d_{\text{i}}S < 0$ as seen from Eq. (15b) with the result that $T < 0$. Thus, there is no violation of GSL/SL by IC for Σ_{ueq}; creating IC is of no consequence for any $\mathfrak{M}^{\text{u}}$, a fact that has not been noted before.

3.5. *Justifying The Second Law*

Several proofs [9, 15, 51, 78–83, see for example] for the validity of SL in Eq. (27) are empirical or use some assumptions. Because of them, it is common to think that SL cannot be justified based purely on the use of analytical mechanics. For example, Keizer [84] notes:

> ". . . the second law has never been justified on the basis of mechanical laws."

We have overcome this shortcoming by focusing on dynamical evolution during $\mathcal{P}^{\text{D}}$ in this study. We believe to have made the first ever successful attempt [21, 22] not only to justify SL but also its generalization to GSL (generalized SL) using analytical mechanics and to alleviate the concern expressed by Keizer. As discussed above and in [21,22], the irreversibility requires *stochasticity* that is appended in Σ^{D} by introducing probability following the BCGM proposal to capture thermodynamic irreversibility. Einstein [85] was convinced that classical thermodynamics as

> " ... the only physical theory of universal content ... will never be overthrown,"

and Eddington [86] considered the fundamental axiom of the second law (SL) in terms of entropy S for an isolated system Σ as its cornerstone holds

> " ... the supreme position among the laws of Nature."

It is customary to claim SL to be a consequence of our "ignorance" of the intricate dynamics of constituent particles of the system that are too numerous for our gross senses to observe [87, for example]. However, this idea is in some sense defeated by Maxwell's demon [19], who overcomes this "ignorance" by a precise control of these particles and hopefully restores reversibility by decreasing entropy by violating SL and dethroning the latter as a supreme law of Nature.

3.6. *Generalized Second Law (GSL)*

We have two approaches to include SL in the BCGM proposal: (1) To "prove" it following Boltzmann through the H-theorem [20,88,89] that requires using the molecular chaos assumption (*Stosszahlansatz*) or master equations [15,90], both of which are probabilistic in nature but have limitations [48]. (2) To adopt SL in the axiomatic formulation of classical thermodynamics (Cl-Th) as an axiom, see Callen [3, for example], so it does not require any proof, but it does not unravel the mystery behind SL if the latter ever fails.

We show that GSL is the appropriate generalization of SL that fulfils the requirement of bringing T in the discussion of SL.

Remark 30. *GSL shows that*

$$d_iS \text{ or } \Delta_iS \leq 0 \text{ for } T \leq 0, \tag{31}$$

compare with Eq. (15b) in R11, contradicting the conventional wisdom expressed in Eq. (1). We have established [22] that the irreversibility principle in Eq. (9) along with the principle of mechanical equilibrium *of analytical mechanics [41] requires that Eq. (13) be satisfied; this equation does not require knowing the NEQ temperature of the system as noted above. Therefore, it must remain valid for any NEQ temperature, positive or negative, so it is more general than SL in Eq. (27) in which the nature of the inequality may depend on the sign of the temperature; however, compare with Conjecture 67. As Eq. (13) completely bypasses Problem 68, we have called the inequality in it the* generalized second law *(GSL).*

3.7. *SL Violation*

The violation of SL (VSL) is a topic of current interest and has created an active industry of interesting attempts to demolish SL [91–104] by following the above challenge posed by Maxwell [19]. These attempts in Σ, whose size ranges from mesoscopic to cosmological scales, cast doubt on Cl-Th of a NEQ macrostate $\mathfrak{M}$. These recent attempts span widely different fields from information to biological thermodynamics. If correct, these *violations* suggest a new law, viz. the violation of SL (VSL), separate from SL. As physics is an experimental science, these violations not only pose a challenge to the current understanding of SL but give hope that we might be able to unravel the mystery behind SL as its root cause has never been formally identified so far, making it only an empirical law.

As SL and VSL do not hold in Nature simultaneously within the same process, each must hold under certain conditions that must be *distinct*. They are not known a priori and need to be identified. Their occurrence will make SL not a fundamental law of Nature that is obeyed under *all* conditions so its supremacy becomes questionable. Therefore, to investigate the possibility of VSL, we have introduced a new thermodynamics called *generalized thermodynamics* (Gen-Th) that may or may not support SL. This allows us to identify distinct conditions needed for SL and VSL in different processes as we discuss in this review.

We emphasize that the two approaches noted in Sect. 3.6 deal only with macroscopically *large* systems Σ_{M} [3, 12, 15, 17], as SL is assumed to be valid only for such systems, for which energy and entropy *additivities* hold. However, its violation (VSL) can occur for finite size systems (to be denoted by Σ_{E} and for which only energy but not entropy additivity holds as clarified later) that are much smaller than Σ_{M} . Therefore, we will also be interested in a system of any size, even a system of a single particle, for reasons given later; see also Remark 9.

3.8. *Partitioning*

An SI-quantity of $\overline{\Sigma}$ depends only on the system quantities such as its Hamiltonian, energy, entropy, temperature, pressure, etc., not all of which are extensive; see Definition 11. State variables in $\mathbf{Z}$ and the set $\{p_k\}$ always refer to the system so they represent SI-quantities. However, we focus on extensive quantities among these in this section to exploit a very important partitioning of them, which proves extremely useful in our approach. This partitioning is unique to our approach and goes beyond the scope of the original introduction in [26, 27]. The partitioning is based on the discussion of dW_{imb} in Sect. 3.1; see Eq. (29b). Changes represented by $d\mathbf{Z}$ always refer to the changes in the state of the system, regardless of the process that brings about them so they also represent SI-quantities. Similarly, dW and dQ in Sect. 10.2 are also SI-quantities. Thus, an extensive process quantity $d\mathbf{\Omega}$ such as $d\mathbf{Z}$,dW,dQ, and dS is an SI extensive quantity and is controlled by the response of the system alone during some $\mathcal{P}$.

Remark 31. *We also find it convenient to include dp_k as extensive for the simple reason that p_k by definition is a fraction of extensive quantities with fixed denominator $\mathcal{N}$ as seen from Eq. (68).*

Mechanical and thermodynamic processes are of two kinds:

1. External: They occur due to *external imbalance* of mechanical and thermal forces between a system and its surroundings (the medium) in an interacting system shown in Fig. 1(b). For a macroscopic medium, which we assume in this review, they are specified by the external change $d_{\mathrm{e}}\mathbf{\Omega}$ such as $d_{\mathrm{e}}\mathbf{Z}$ that is controlled by the medium alone as shown in the figure; the system plays no role in it. Therefore, it is customary to call $d_{\mathrm{e}}\mathbf{\Omega}$, which in classical thermodynamics (Cl-Th) is often denoted by $đ$q but which we avoid here in view of the modern notation, an *exchange quantity* as shown by

the double arrow in Fig. 1(b) denoting this exchange between Σ and $\widetilde{\Sigma}$. It denotes a MI-quantity introduced in Sect. 3.1. Its accumulation over the entire process is denoted by the MI-quantity $\Delta_{\mathrm{e}}\mathfrak{Q}$.

2. Internal: They occur due to *internal imbalance* of mechanical and thermal forces as exemplified by P_{imb} in Eq. (29a) in both an isolated system and interacting system shown in Fig. 1. They result, see footnote 3 and Fig. 1, in the internal or irreversible ("i") change shown by $d_{\mathrm{i}}\mathfrak{Q}$ and its accumulation $\Delta_{\mathrm{i}}\mathfrak{Q}$, which together with the exchange counterpart $d_{\mathrm{e}}\mathfrak{Q}$ or $\Delta_{\mathrm{e}}\mathfrak{Q}$ determines the SI-quantity $d\mathfrak{Q}$ or $\Delta\mathfrak{Q}$:

$$d\mathfrak{Q} = d_{\mathrm{e}}\mathfrak{Q} + d_{\mathrm{i}}\mathfrak{Q}, \Delta\mathfrak{Q} = \Delta_{\mathrm{e}}\mathfrak{Q} + \Delta_{\mathrm{i}}\mathfrak{Q}, \tag{32}$$

where $d\mathfrak{Q}$ can either denote a macroquantity such as dW, dS, etc. or a microquantity (associated with $\mathfrak{m}_k$) such as

$$\begin{aligned} dW &= d_{\mathrm{e}}W + d_{\mathrm{i}}W, dW_k = d_{\mathrm{e}}W_k + d_{\mathrm{i}}W_k, \\ dQ &= d_{\mathrm{e}}Q + d_{\mathrm{i}}Q, dQ_k = d_{\mathrm{e}}Q_k + d_{\mathrm{i}}Q_k, \\ dS &= d_{\mathrm{e}}S + d_{\mathrm{i}}S, dp_k = d_{\mathrm{e}}p_k + d_{\mathrm{i}}p_k, \end{aligned} \tag{33}$$

etc. It should be obvious that the internal quantity $d_{\mathrm{i}}\mathfrak{Q}$ or $\Delta_{\mathrm{i}}\mathfrak{Q}$ is a *mixed* quantity; it is neither SI- or MI-quantity in general.

As $d_{\mathrm{i}}\mathrm{q}$ is the additional contribution to $d_{\mathrm{e}}\mathfrak{Q}$ and is determined by process irreversibility, it is most easily understood by focusing only an *isolated* system Σ as all processes associated with it are purely internal so they are not controllable from any outside agent. This extremely simplifies the discussion so we mostly focus in this review on the isolated Σ for which the following Remark holds.

Remark 32. *As all exchanges $\{d_e\mathfrak{Q}\}$ for isolated $\bar{\Sigma}$ vanish identically,*

$$d_e\mathfrak{Q} \equiv 0, d_e\mathfrak{Q} \equiv 0, \tag{34}$$

so we avoid complications introduced by various exchanges. Accordingly, all process quantities in $\bar{\Sigma}$ can be written without the suffix "i"

$$d\mathfrak{Q} \equiv d_i\mathfrak{Q}, \Delta\mathfrak{Q} \equiv \Delta_i\mathfrak{Q}, d\mathbf{Z} \equiv d\boldsymbol{\xi};$$

the last equation follows from the fact that $\mathbf{X}$ remains constant throughout the process for an isolated system. We see that only for an isolated system, the internal change becomes a SI-change.

Remark 33. *One additional benefit of considering isolated systems is that numerical simulations of isolated systems are probably the simplest possible ones, as one is not encumbered by interactions from the outside. It is easy to verify if the microstate energy E_k determined by the Hamiltonian one chooses decreases to its minimum or increases to its maximum as the NEQ system evolves in time; see Fig. 4, which is described in Sect. 13.3.*

While partitions $dS = d_{\mathrm{e}}S + d_{\mathrm{i}}S, (dN = d_{\mathrm{e}}N + d_{\mathrm{i}}N$ if there are chemical reactions in Σ), etc. of changes in observables (they are path-independent process quantities) are well known in Cl-Th [25–28], we are the first one to extend them to other process quantities, path-dependent or not, such as dW, dW_k, dQ, dQ_k, dp_k as shown in Eq. (33). The extension has proved extremely helpful in developing our NEQ thermodynamic and statistical mechanical approach.

As $d_{\rm i}\mathfrak{Q}$ quantifies a NEQ process, also known as irreversible process, we must make a distinction between process quantities that are either controlled by the system alone such as $d\mathfrak{Q}$ or by the medium $\widetilde{\Sigma}$ alone such as $d_{\rm e}\mathfrak{Q}$; the latter include the two extremely important medium-dependent exchange process quantities $d_{\rm e}W$ and $d_{\rm e}Q$ that play central role in the traditional formulation of the first law in Cl-Th. Unfortunately, this distinction, which is well appreciated by pure thermodynamicists, is not appreciated by many physicists and scientists in modern microscopically based NEQ statistical mechanics, and had created too many misunderstandings that are still being perpetrated to date as we will discuss later; see footnote 25 and Sect. 16.8.

The above decomposition of $d\mathfrak{Q}$ is valid whether $d\mathfrak{Q}$ denotes a macroquantity such as dW, dS, etc. or a microquantity (associated with $\mathfrak{m}_k$) such as dW_k, dp_k, etc.

The above partitioning also remains valid for Σ of any size, and not just a macroscopically large system. It is found that $d_{\rm i}\mathsf{q}$ or $\Delta_{\rm i}\mathsf{q}$ is always of a *fixed* sign

$$d_{\rm i}\mathfrak{Q}\text{ or }\Delta_{\rm i}\mathfrak{Q}\begin{cases}\geq 0\\ \leq 0\end{cases}, \tag{35}$$

depending on its definition. Once the definition is accepted, the signature *cannot* change during any real process. It is this fixed signature that is a signal of *irreversibility* of a process $\mathcal{P}$, see Definitions 20 and 21. For a reversible process $\mathcal{P}_{\rm rev}$, inequalities in Eq. (35) turn into an equality [28]. It is clear, therefore, that we need to understand the *rational for this fixed signature* to justify the universality of SL.

In the following, we will mostly discuss $d\mathsf{q}$ and its parts, but the discussion is also applicable to $\Delta\mathsf{q}$ and its parts. We will pay close attention to generalized macrowork dW and macroheat dQ and their parts.

Remark 34. *It should be emphasized that, being universal, SL is supposed to apply to all systems, regardless of their physical and chemical composition. Therefore, we only consider a generic $\overline{\Sigma}$ without paying any attention to its physical or chemical properties. This means that all we require is the* existence *of some deterministic Hamiltonian for Σ^D but without specifying its form.*

4. Mechanical Uniformity and Nonuniformity

4.1. *Uniform (EQ) and Nonuniform (NEQ) Hamiltonians*

It is a well-known fact [17] that a thermodynamic system Σ in EQ is *uniform* in that its entropy $S_{\rm eq}(\mathbf{X})$ is a sate function of the state variable $\mathbf{X}$ that *uniquely* specifies the system. No information about the internal structure of Σ is relevant. This thermodynamic specification also has a purely mechanical interpretation for the Hamiltonian.

Definition 35. *As a consequence of uniformity, the Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w})$ of the mechanical analog system Σ^D depends on the work parameter $\mathbf{w} \doteq \mathbf{X}\backslash E$; no information about its internal structure is needed to uniquely specify Σ^D. We say that $\mathcal{H}(\mathbf{x}|\,\mathbf{w})$ is a* uniform Hamiltonian *that mechanically describes a* uniform system *Σ^D and Σ.*

For reasons that will become clear below, see Uniformity Theorem 47, we use $\mathcal{H}_{\rm eq}$ for the uniform $\mathcal{H}(\mathbf{x}|\,\mathbf{w})$. As $\mathcal{H}_{\rm eq}$ depends on $\mathbf{w}$ for the entire $\Sigma^{\rm D}$, its microstates $\{\mathfrak{m}_k(\mathbf{w})\}$ having microenergies

$\{E_k(\mathbf{w})\}$ represent a uniform Σ^{D} in the state space $\mathfrak{S}_{\mathbf{X}}$. We similarly use $\mathfrak{m}_{k\mathrm{eq}}$ for $\mathfrak{m}_k(\mathbf{w})$. This uniformity of Σ^{D} and $\{\mathfrak{m}_k(\mathbf{w})\}$ results in a uniform macrostate, which is the EQ macrostate $\mathfrak{M}_{\mathrm{eq}} \doteq \mathfrak{M}(\mathbf{X})$ of Σ with a state function entropy $S_{\mathrm{eq}}(\mathbf{X})$; it is uniquely specified in Eq. (2).

Definition 36. *A system $\overline{\Sigma}$ is said to be* uniform *in the state space $\mathfrak{S}_{\mathbf{X}}$, if it is uniquely specified by its Hamiltonian with no* explicit *time dependence in that state space. If not, it is said to be* nonuniform *in $\mathfrak{S}_{\mathbf{X}}$ and requires explicit time dependence. Uniformity in $\mathfrak{S}_{\mathbf{X}}$ should not be confused with homogeneity in the phase space of or the real and momentum spaces occupied by $\overline{\Sigma}$.*

We need to clarify the importance of the identification of $\mathfrak{M}_{\mathrm{eq}}$ in Eq. (2) formed by uniform microstates $\{\mathfrak{m}_k(\mathbf{w})\}$. If we use $p_k(t)$ with explicit time dependence in place of p_k^{eq} to identify a macrostate, then such a macrostate must be identified as a NEQ uniform macrostate $\mathfrak{M}$. But it is easy to see that the evolution of such a macrostate cannot satisfy energy conservation. This point is carefully discussed in [22, see Remark 22 and discussion following it] to which we refer the reader to but we briefly discuss it later; see Remark 79 in Sect. 14.2. Thus, NEQ uniform macrostates are not relevant for a proper thermodynamics.

Definition 37. *As a consequence of nonuniformity, the Hamiltonian $\mathcal{H}_{ieq} \doteq \mathcal{H}(\mathbf{x}|\,\mathbf{W})$ of its mechanical analog system Σ^D depends on the work parameter $\mathbf{W}$, which explicitly and completely includes information about its nonuniformity to uniquely specify Σ^D. We say that $\mathcal{H}_{ieq}$ is a* nonuniform *Hamiltonian with nonuniform microstates $\{\mathfrak{m}_{kieq}\}$ that mechanically describes a nonuniform system Σ^D or Σ uniquely in $\mathfrak{S}_{\mathbf{Z}}$. The same Hamiltonian can be equivalently expressed as nonuniform $\mathcal{H}(\mathbf{x}|\,\mathbf{W}', t)$ with explicit time dependence where $\mathbf{W}'$ is a subset of $\mathbf{W}$.*

Microstate energies $\{E_k\}$ play a prominent role in the mechanical specification of Σ^{D} for the simple reason that the dynamics of individual microstate $\mathfrak{m}_k$ is usually different for different microstates that having different energies; see footnote 2. We refer to E_k as *fluctuating* over the microstates. For the sake of simplicity, we assume components of the work parameter to be *fixed* over microstates, but it is easy to extend the discussion to a fluctuating work parameter [48, see, for example, Section 12.5 there]. This SI-specification of Σ^{D} is entirely in terms of its *system-intrinsic* (SI) Hamiltonian; see Sect. 3.1.

4.2. *Uniform Mechanical Systems* $\overline{\Sigma}$

We first consider the mechanical system $\overline{\Sigma}$ in $\mathfrak{S}_{\mathbf{X}}$ for which $\mathbf{w}$ uniquely specifies the *entire* system and its uniform Hamiltonian $\mathcal{H}_{\mathrm{eq}} \doteq \mathcal{H}(\mathbf{x}|\,\mathbf{w})$. It simply means that no distinction can be made among various parts of the system $\overline{\Sigma}$. Accordingly, we use $\mathfrak{m}_{k\mathrm{eq}} \doteq \mathfrak{m}_k(\mathbf{w})$ to denote one of its microstates with microenergy $E_{k\mathrm{eq}} \doteq E_k(\mathbf{w})$. It is easily seen that with $E_{k\mathrm{eq}}$ replaced by E_k to simplify the notation,

$$dE_k = \frac{\partial E_k}{\partial \mathbf{x}} \cdot d\mathbf{x} + \frac{\partial E_k}{\partial \mathbf{w}} \cdot d\mathbf{w} = \frac{\partial E_k}{\partial \mathbf{w}} \cdot \dot{\mathbf{w}} dt \tag{36}$$

as the first term in the first equation vanishes due to Hamilton's equations of motion, which merely confirms that $E_k(\mathbf{w})$ is not a function of $\mathbf{x}$ as expected. As this dependence and particle positions in the phase space would have included the effects of interparticle potentials, they play no role in determining dE_k. Thus, dE_k is determined solely by the variation $d\mathbf{w}$ of the work parameter $\mathbf{w}$ or its rate of variation $\dot{\mathbf{w}}$ multiplied by dt. The SI-microwork $dW_k(t)$ can be expressed in terms of instantaneous microforce, also known as the *generalized* microforce, in $\mathfrak{m}_k$

$$\mathbf{f}_{\mathrm{w}k} \doteq -\partial E_k / \partial \mathbf{w} \tag{37}$$

by

$$dW_k(\mathbf{w}) = \ \mathbf{f}_{\mathrm{w}k} \cdot d\mathbf{w} = -dE_k, \tag{38}$$

in $\mathfrak{S}_{\mathbf{X}}$. It can also be written in terms of the instantaneous microstate power $\mathsf{P}_k(t)$ in $\mathfrak{S}_{\mathbf{X}}$ as

$$dW_k(t) = -dE_k(t) = \mathsf{P}_k(t)dt, \tag{39}$$

with

$$\mathsf{P}_k(t) \doteq \mathbf{f}_{\mathrm{w}k} \cdot \dot{\mathbf{w}}. \tag{40}$$

4.3. *Nonuniform Mechanical Systems* Σ^D

The mechanical analog system Σ^{D} of a NEQ thermodynamic system Σ cannot be simply represented by $\mathcal{H}(\mathbf{x}|\,\mathbf{w})$. It is clear that more parameters than in $\mathbf{w}$ are now needed to uniquely specify the NEQ nature of Σ^{D}. We find that these additional parameters result form the knowledge of the internal structure such as by taking Σ^{D} to consist of two identical uniform subsystems, with the same number of particles N, but with different work parameters $\mathbf{w}_1 \neq \mathbf{w}_2$. Such a situation arises due to an internal partition that creates an internal constraint that we discussed in Sect. 3.4, and discussed by Callen [3]. This nonuniformity in the work parameter makes Σ^{D} *nonuniform* in densities $\mathbf{w}_1/N \neq \mathbf{w}_2/N$, and appears in the nonuniform Hamiltonian that is written as $\mathcal{H}(\mathbf{x}|\,\mathbf{W})$, with $\mathbf{W}$ including the additional work parameters not included in $\mathbf{w}$. Nonuniformity results in nonuniform microstates $\mathfrak{m}_k(\mathbf{w},t)$ that have explicit time dependence in $\mathfrak{S}_{\mathbf{X}}$. However, by properly identifying the additional work parameters in $\mathbf{W}$ as we will do in Sect. 5, we can identify an *extended state space* $\mathfrak{S}_{\mathbf{Z}}$ in which $\mathfrak{m}_k(\mathbf{W})$ is uniquely specified so that it has no explicit time dependence. We have identified these microstates as in IEQ and expressed as $\mathfrak{m}_{k\mathrm{ieq}} \doteq \mathfrak{m}_k(\mathbf{W})$ in $\mathfrak{S}_{\mathbf{Z}}$.

The Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w},t)$ in $\mathfrak{S}_{\mathbf{X}}$ is equivalently expressed as $\mathcal{H}_{\mathrm{ieq}} \doteq \mathcal{H}(\mathbf{x}|\,\mathbf{W})$ with no explicit time dependence in $\mathfrak{S}_{\mathbf{Z}}$ for which $n = n_{\mathrm{ieq}}$, see Sect. 5 for justification. The equivalence holds because the number of independent variables are the same in the two Hamiltonians. Corresponding microstates $\{\mathfrak{m}_{k\mathrm{ieq}}\}$ with microenergies $\{E_{k\mathrm{ieq}}\}$ are, as said earlier, in internal equilibrium (IEQ) in $\mathfrak{S}_{\mathbf{Z}}$ and determine $\mathfrak{M}_{\mathrm{ieq}}$ in Eq. (3) for $n = n_{\mathrm{ieq}}$. From what is said above, $\mathcal{H}_{\mathrm{eq}} \doteq \mathcal{H}(\mathbf{x}|\,\mathbf{w}), \mathfrak{m}_{k\mathrm{eq}} \doteq \mathfrak{m}_k(\mathbf{w})$ and $E_{k\mathrm{eq}} \doteq E_k(\mathbf{w})$ of Σ^{D} that are *uniform* in $\mathbf{w}$ can also be labeled with the suffix "eq" for simplicity, even though the concept of equilibrium in thermodynamics is usually considered an average one over microstates. However, the concept of equilibrium is also in analytical mechanics so there is no harm in our usage. This should not cause any confusion, and is in the spirit of and consistent with the well-known result of equilibrium thermodynamics [17] that an EQ macrostate $\mathfrak{M}_{\mathrm{eq}}$ is uniform in the state variable set $\mathbf{X} \doteq (E,\mathbf{w})$ that defines the EQ state space $\mathfrak{S}_{\mathbf{X}}$. As a consequence of uniformity, $\mathfrak{m}_{k\mathrm{eq}}$ can neither perform any mechanical work nor generate any mechanical power spontaneously unless disturbed externally; see Sect. 4.2. (From now on, we will mostly suppress $\mathbf{w}$ for Σ^{D} and Σ unless necessary.)

Situation with $\mathcal{H}_{\mathrm{ieq}}$ with no explicit time dependence in $\mathfrak{S}_{\mathbf{Z}}$ is different as we show. Eq. (36), with E_k replacing $E_{k\mathrm{ieq}}$ for notational simplicity, changes to

$$dE_k = \frac{\partial E_k}{\partial \mathbf{W}} \cdot d\mathbf{W} = -\mathbf{F}_{\mathrm{w}k} \cdot d\mathbf{W} = -dW_k, \tag{41a}$$

where the SI-microforce

$$\mathbf{F}_{\mathrm{w}k} \doteq -\partial E_k/\partial \mathbf{W} = (\mathbf{f}_{\mathrm{w}k}, \mathbf{F}_{\xi k}) \tag{41b}$$

with

$$\mathbf{F}_{\xi k} \doteq -\partial E_k/\partial \boldsymbol{\xi}, \tag{41c}$$

represents the instantaneous generalized microforce by $\mathfrak{m}_k$ in $\mathfrak{S}_{\mathbf{Z}}$. We see that $\mathfrak{m}_{k\text{ieq}}$ can perform the SI-microwork done by it, which is given by

$$dW_k(\mathbf{W}) = \mathbf{F}_{\mathrm{w}k} \cdot d\mathbf{W} = -dE_k, \tag{41d}$$

without being disturbed by the medium as the internal variable $\boldsymbol{\xi}$ can change internally so $d\boldsymbol{\xi} \neq 0$ as we will see. This explains the difference between $\mathfrak{m}_{k\text{eq}}$ and $\mathfrak{m}_{k\text{ieq}}$. Furthermore, the presence of $\mathbf{F}_{\xi k}$ clarifies the significance of $\boldsymbol{\xi}$ as the *internal work parameter* for $\Sigma_{\mathrm{E}}^{\mathrm{D}}$. Thus, $E_k(\mathbf{W})$ continues to change with $\mathbf{w}$ and $\boldsymbol{\xi}$ and results in the above microwork. The corresponding instantaneous microstate power in $\mathfrak{S}_{\mathbf{Z}}$ is

$$\mathsf{P}_k(t) \doteq \mathbf{F}_{\mathrm{w}k} \cdot \dot{\mathbf{W}}, \tag{41e}$$

which can be directly used in Eq. (39) to obtain $dW_k(t)$.

As the same system can be described by $\mathcal{H}(\mathbf{w}, t)$ in $\mathfrak{S}_{\mathbf{X}}$, we can express Eq. (41a) as follows:

$$dE_k = \frac{\partial E_k}{\partial \mathbf{w}} \cdot d\mathbf{w} + \frac{\partial E_k}{\partial t} dt = -dW_k. \tag{42a}$$

Comparing it with Eq. (41a), we see that the explicit time derivative is related to the "missing" internal variable $\boldsymbol{\xi}$ in $\mathfrak{S}_{\mathbf{X}}$ and that

$$\frac{\partial E_k}{\partial t} = \frac{\partial E_k}{\partial \boldsymbol{\xi}} \cdot \dot{\boldsymbol{\xi}} \tag{42b}$$

in terms of he time derivative of the missing internal variable $\boldsymbol{\xi}$. This discussion is easily extended to a microstate of $\mathcal{H}(\mathbf{W}', t)$ that is defined in a smaller state space $\mathfrak{S}_{\mathbf{Z}'}$ than $\mathfrak{S}_{\mathbf{Z}}$ with missing internal variable $\boldsymbol{\xi}''$ so that $\boldsymbol{\xi} \equiv \boldsymbol{\xi}' \cup \boldsymbol{\xi}''$; here $\boldsymbol{\xi}'$ is the internal variable in $\mathbf{Z}'$. Thus,

$$dE_k = \frac{\partial E_k}{\partial \mathbf{W}'} \cdot d\mathbf{W}' + \frac{\partial E_k}{\partial t} dt = -dW_k, \tag{43a}$$

in which the time derivative is determined by the missing internal variable $\boldsymbol{\xi}''$:

$$\frac{\partial E_k}{\partial t} = \frac{\partial E_k}{\partial \boldsymbol{\xi}''} \cdot \dot{\boldsymbol{\xi}}'' = -\mathbf{F}_{\xi'' k} \cdot \dot{\boldsymbol{\xi}}''. \tag{43b}$$

We can summarize our conclusion in the following

Theorem 38. *Explicit time dependence in the Hamiltonian, its microstates and microenergies of a nonuniform system* Σ_E^D *is due to missing internal variables in* $\mathfrak{S}_{\mathbf{Z}'}$ *with respect to the state space* $\mathfrak{S}_{\mathbf{Z}}$ *in which* Σ *is uniquely described. By letting* $\mathbf{Z}'$ *to denote* $\mathbf{X}$*, time dependence in* $\mathfrak{S}_{\mathbf{X}}$ *is due to all internal variables in* $\boldsymbol{\xi}$*.*

Proof. The proof follows from comparing Eq. (43a) in $\mathfrak{S}_{\mathbf{Z}'}$ with Eq. (41a) in $\mathfrak{S}_{\mathbf{Z}}$. The last part above follows from setting $\mathbf{Z}' = \mathbf{X}$ so that $\boldsymbol{\xi}'' = \boldsymbol{\xi}$. ■

For an arbitrary nonuniform Hamiltonian of Σ with $n < n_{\text{ieq}}$, all SI-quantities acquire an *explicit* time dependence as in $\mathcal{H}(\mathbf{X}, t)$ or in $\mathcal{H}(\mathbf{W}', t)$. This time-dependence is a result of missing internal variables. As we see in Sect. 5, internal variables emerge due to nonuniformity among various *disjoined* but mutually *interacting* uniform subsystems $\{\Sigma_l\}$ with Hamiltonians $\{\mathcal{H}_{l\mathrm{eq}} \doteq \mathcal{H}_l(\mathbf{x}_l|\,\mathbf{w}_l)\}$ in terms of work variables $\mathbf{w}_l, l = 1, 2, \cdots$; interactions ensure that we are not dealing with internal constraints discussed earlier in Sect. 3.4. Nonuniformity results in internal flows among $\{\Sigma_l\}$ that affect $\mathbf{X}_l \doteq (E_l, \mathbf{w}_l)$ so $\{\mathfrak{m}_k(t)\}$ are individually *nonuniform* in $\{E_l\}$ and $\{\mathbf{w}_l\}$, respectively. We find there that nonuniformity in $\mathfrak{m}_k(t)$ can be described *precisely* in terms of a set $\boldsymbol{\xi}$ of *internal variables* [24, 27–29, 35] if we restrict the minimum size λ_{E} of subsystems to satisfy *quasi-additivity* of their energies, λ_{E} being determined by the range of inter-particle interactions; see the discussion following Eq. (44b). This requires imposing minimum size restriction on Σ or Σ^{D}, which is denoted by Σ_{E} or $\Sigma_{\mathrm{E}}^{\mathrm{D}}$, for which $\mathbf{W} \doteq (\mathbf{w}, \boldsymbol{\xi})$ acts as the work variable and $\mathbf{Z} \doteq (E, \mathbf{W})$ as the state variable that determines a NEQ state space $\mathfrak{S}_{\mathbf{Z}}$ for Σ_{E} or $\Sigma_{\mathrm{E}}^{\mathrm{D}}$. Thus, we see that the explicit time dependence of $\mathfrak{M}(t)$ for nonuniform Σ in $\mathfrak{S}_{\mathbf{X}}$ is fully equivalent to the implicit dependence through missing $\boldsymbol{\xi}''(t)$ in $\mathfrak{S}_{\mathbf{Z}'}$ with $n < n_{\mathrm{ieq}}$. To make subsystems' entropies additive, we require S to be a *state function* $S(\mathbf{Z})$ in $\mathfrak{S}_{\mathbf{Z}}$, which requires a further restriction on the minimum size as macroscopic (M) to capture *quasi-independence* of subsystems. This macroscopic system is identified as Σ_{M} or $\Sigma_{\mathrm{M}}^{\mathrm{D}}$ that require the state space $\mathfrak{S}_{\mathbf{Z}}$ to be uniquely specified; in contrast, Σ (or Σ^{D}) and Σ_{E} (or $\Sigma_{\mathrm{E}}^{\mathrm{D}}$) are not uniquely specified in $\mathfrak{S}_{\mathbf{X}}$ and $\mathfrak{S}_{\mathbf{Z}}$, respectively.

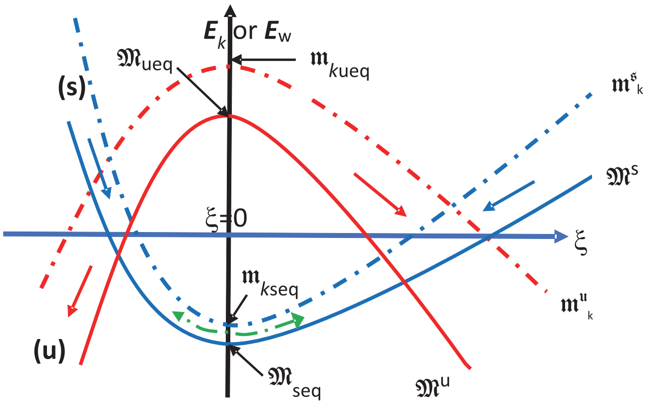

Figure 4. Schematic forms of microenergy E_k (dashed-dot curves) so that $dE_k = -dW_k$ in Eq. (39) and macrowork function E_{w} (solid curves) so that $\Delta E_{\mathrm{w}} = -\Delta W$ as functions of the internal variable $\boldsymbol{\xi}$, with $\xi = 0$ denoting EQ in $\mathfrak{S}_{\mathbf{Z}}$ for an isolated system. Alternatively, these curves can be considered as a function of time t in $\mathfrak{S}_{\mathbf{X}}$, which increases along the directions of the blue and red arrows. We only consider the case when each curve has a single extremum. The discussion is easily extended to more complex forms. The blue color curves and solid blue arrows represent the evolution controlled by the stable (s) case. The red color curves and solid red arrows represent the evolution controlled by the unstable (u) case. In both cases, the arrows lower the energy. The extrema of all curves occur at $\boldsymbol{\xi} = 0$ and represent a uniform body. For the extremum to denote equilibrium, we must also have $\dot{\boldsymbol{\xi}} = 0$ there. The green double-arrow is discussed in the text.

Claim 39. *For Σ or Σ^D that are not as big as Σ_E or Σ_E^D, or are described in the state space $\mathfrak{S}_{\mathbf{X}}$, internal variables as discussed in Sect. 5 cannot be introduced. The explicit time dependence in this case must be taken as a given fact that has no justification in terms of internal variables. Such explicit time dependence in $\mathfrak{S}_{\mathbf{X}}$ is described by Eq. (42a) and applies to all nonuniform Σ or Σ^D of any size. In contrast, the explicit time dependence described by Eq. (43a) in $\mathfrak{S}_{\mathbf{Z}'}$ is applicable to systems at least large as Σ_E or Σ_E^D.*

Claim 40. *If we are interested in making subsystems' entropies of Σ in $\mathfrak{S}_{\mathbf{Z}'}$ or $\mathfrak{S}_{\mathbf{Z}}$ additive, we require a further restriction on the minimum size of Σ and, therefore, of Σ^D as macroscopic (M) to capture* quasi-independence *of subsystems of Σ. This macroscopic system is identified as Σ_M or Σ_M^D that require the state space $\mathfrak{S}_{\mathbf{Z}'}$ or $\mathfrak{S}_{\mathbf{Z}}$ for its specification. We observe that NEQ Σ (or Σ^D) and Σ_E (or Σ_E^D) are not uniquely specified in $\mathfrak{S}_{\mathbf{X}}$ and $\mathfrak{S}_{\mathbf{Z}'}$, respectively.*

We thus see that implicit time-dependence in $\boldsymbol{\xi}$ for $\Sigma_{\mathrm{E}}^{\mathrm{D}}$ in $\mathfrak{S}_{\mathbf{Z}}$ is equivalent to the explicit time dependence in $\mathfrak{S}_{\mathbf{X}}$ without any $\boldsymbol{\xi}$ for Σ^{D}. The main difference is that for Σ^{D} not as big as $\Sigma_{\mathrm{E}}^{\mathrm{D}}$, its nonuniformity cannot be described by $\boldsymbol{\xi}$ and must be captured by time dependence only. The variation of $E_k(\boldsymbol{\xi})$ for an isolated system $\Sigma_{\mathrm{E}}^{\mathrm{D}}$ in $\mathfrak{S}_{\mathbf{Z}}$ as shown in Fig. 1 with $\boldsymbol{\xi}$ can also be treated as time variation of $E_k(t)$ for Σ^{D} in $\mathfrak{S}_{\mathbf{X}}$. This is also consistent with the way a time-dependent Hamiltonian is treated in mechanics [1] by considering t as a parameter in the Hamiltonian so we can use t instead of $\boldsymbol{\xi}$, in which case Eq. (41d) reduces to Eq. (39) obtained in $\mathfrak{S}_{\mathbf{X}}$, where Σ^{D} has no restriction on its size. We will not be concerned with the actual time dependence of $\boldsymbol{\xi}$ in $\mathfrak{S}_{\mathbf{Z}}$ in this investigation; all we need to remember is that it can be accounted for by an explicit time dependence in $\mathsf{P}_k(t)$ and other quantities but only for Σ_{E} or $\Sigma_{\mathrm{E}}^{\mathrm{D}}$ in $\mathfrak{S}_{\mathbf{X}}$. According to the discussion above, we can consider either $\boldsymbol{\xi}$ explicitly (to be specified in Sect. 5) and use the state space $\mathfrak{S}_{\mathbf{Z}}$, or consider t instead in the state space $\mathfrak{S}_{\mathbf{X}}$ without any specification of $\boldsymbol{\xi}$. In the former case, microstates are specified in $\mathfrak{S}_{\mathbf{Z}}$, which restricts Σ^{D} to $\Sigma_{\mathrm{E}}^{\mathrm{D}}$.

5. Mechanical Internal Variables

The situation with a nonuniform Σ^{D} requires careful consideration as we now require internal variables symbolized by $\boldsymbol{\xi}$ above to capture nonuniformity as mentioned in 4.1. Even though the use of internal variables has been very common in the past to successfully describe nonequilibrium macrostates $\mathfrak{M}$ like glasses [27–29, 105–107], they have been introduced phenomenologically but their precise nature has never been theoretically clarified. In contrast to their original usage, our introduction of $\boldsymbol{\xi}$ is mathematically well defined by the nature of nonuniformity that is easily identified even at a mechanical level by focusing on subsytems that are nonuniform. As energy quasi-additivity is required for this, we must restrict the deterministic nonuniform mechanical system to $\Sigma_{\mathrm{E}}^{\mathrm{D}}$, but denote it by Σ^{D} in this section to simplify notation unless clarity is needed. We now turn to this definition [35]. The physical significance of $\boldsymbol{\xi}$ becomes clear when we consider the microwork. done by it; see Eq. (41d).

For simplicity, we consider Σ^{D} to be formed by two different and disjoined but mutually interacting subsystems Σ_1^{D} and Σ_2^{D} that are each uniform in $\mathfrak{S}_{\mathbf{X}}$. We assume that each subsystem contains w components of work parameter set. The internal variables are required to *uniquely* specify $\{\mathfrak{m}_k\}$ in $\mathfrak{S}_{\mathbf{Z}}$; they are not specified uniquely in $\mathfrak{S}_{\mathbf{X}}$. We consider Σ^{D}, Σ_1^{D}, and Σ_2^{D} in microstate $\mathfrak{m}_k, \mathfrak{m}_{k_1}$, and $\mathfrak{m}_{k_2}$ of energy E_k, E_{k_1}, and E_{k_2}, respectively. We also introduce $n_1 = N_1/N$ and $n_2 = N_2/N$. If we *neglect* the energy δE_k due to the interface between Σ_1^{D} and Σ_2^{D} to satisfy quasi-additivity, the Hamiltonians of the three bodies (we do not show their arguments $\mathbf{x}_k, \mathbf{x}_{k_1}$ and $\mathbf{x}_{k_2}$, respectively, but use microstate suffixes) are related by

$$\mathcal{H}_k(\mathbf{w}, \boldsymbol{\xi}) \approxeq \mathcal{H}_{k_1}(\mathbf{w}_1) + \mathcal{H}_{k_2}(\mathbf{w}_2), \tag{44a}$$

which ensures microenergy *quasi-additivity*

$$E_k \approxeq E_{1k_1} + E_{2k_2} = N(n_1 e_{1k_1} + n_1 e_{2k_1}) = N e_k, \tag{44b}$$

where e's denote energy densities per particle in their respective systems. Quasi-additivity can be justified only if we *restrict* the minimum sizes of $\Sigma_1^{\rm D}$ and $\Sigma_2^{\rm D}$ to be some $\lambda_{\rm E}$ that itself is determined by the range of inter-particle interactions. This explains why $\Sigma^{\rm D}, \Sigma_1^{\rm D}$, and $\Sigma_2^{\rm D}$ must be denoted by $\Sigma_{\rm E}^{\rm D}, \Sigma_{\rm 1E}^{\rm D}$, and $\Sigma_{\rm 2E}^{\rm D}$. We also have $\mathfrak{m}_k \approxeq \mathfrak{m}_{k_1} \otimes \mathfrak{m}_{k_2}$. As the right side in Eq. (44a) including $E_{1k_1} + E_{2k_2}$ contains $2(w+1)$ independent variables, $\mathcal{H}_k(\mathbf{w}, \boldsymbol{\xi})$ must depend on $2w+1$ arguments as part of $\mathbf{w}$ and $\boldsymbol{\xi}$ along with the energy E_k, the left side in Eq. (44a) also contains $2w+2$ independent variables so $\mathcal{H}_k(\mathbf{w}, \boldsymbol{\xi})$ *uniquely* describes $\Sigma_{\rm E}^{\rm D}$. The discussion in Sect. 4 applies to any $\Sigma_{\rm E}^{\rm D}$ and $\Sigma_{\rm M}^{\rm D}$. In general, $\Sigma_{\rm E}^{\rm D}$ is much smaller in size than $\Sigma_{\rm M}^{\rm D}$. The additivity of extensive (which t is not) work parameters $\mathbf{w}_1$ and $\mathbf{w}_2$ in Eq. (44c) is not affected by the presence or absence of δE_k so that we can introduce the extensive work parameter set

$$\mathbf{w} \doteq \mathbf{w}_1 + \mathbf{w}_2 \tag{44c}$$

containing w components. We still need $w{+}1$ additional independent extensive work variables in addition to E_k to ensure that the number of variables on both sides in Eq. (44a) are equal as they must be for quasi-equality. We find it convenient introduce the following new extensive *internal variable* set

$$\boldsymbol{\xi}_k^{\rm E} \doteq (\xi_{{\rm E}k}, \boldsymbol{\xi}) \tag{45}$$

containing $w+1$ components[17], where

$$\xi_{{\rm E}k} \doteq E_{1k_1}/n_1 - E_{2k_2}/n_2, \boldsymbol{\xi} \doteq \mathbf{w}_1/n_1 - \mathbf{w}_2/n_2, \tag{46}$$

and the extensive work parameter, see Conclusion 42 below for clarity,

$$\mathbf{W}_k \doteq (\mathbf{w}, \boldsymbol{\xi}_k^{\rm E}) \tag{47}$$

containing $2w+1$ independent components besides E_k that uniquely specify $\Sigma_{\rm E}^{\rm D}$, with $\mathfrak{m}_k$ determined by $\mathbf{W}_k$ in $\mathfrak{S}_{\mathbf{Z}}$. It is easily verified that

$$F_{{\rm E}k} \doteq -\partial E_k/\partial \xi_{{\rm E}k} = 0, \tag{48}$$

making E_k and $\xi_{{\rm E}k}$ independent of each other so the variation of $\xi_{{\rm E}k}$ does not generate any SI-microwork $dW_{{\rm E}k} \doteq F_{{\rm E}k} d\xi_{k{\rm E}}$, see Eq. (41d),

$$dW_{{\rm E}k} \equiv 0 \tag{49}$$

for any $\{\mathbf{w}_l\}_{l=1,2}$, and results in Conclusions 41 and 42:

Conclusion 41. *By construction,* (E_k, ξ_{Ek}) *and* $(w_l \in \mathbf{w}, \xi_l \in \boldsymbol{\xi})$ *form pairs of independent variables. By convention, all components of* $\mathbf{w}$ *are independent, which also means that all components* ξ_{Ek} *and* ξ_l *of* $\boldsymbol{\xi}_k^E$ *are independent.*

Conclusion 42. *Despite Eq. (49),* ξ_{Ek} *is included in* $\mathbf{W}_k$*, in which* $\mathbf{w}$ *remains constant as* Σ^D *evolves in time; however,* $\boldsymbol{\xi}_k^E$ *continues to change due to internal flows including that due to energy flow captured by* ξ_{Ek}*.*

We can easily extend the above discussion to any numbers m of subsystems $\left\{\Sigma_l^{\rm D}\right\}, l = 1, 2, \cdots, m$ forming $\Sigma_{\rm E}^{\rm D}$, each specified by its own E_{lk_l} and observable set $\mathbf{w}_l$ to allow for a complex form of nonuniformity in terms of uniform subsystems; Eq. (47) remains valid for any m. It is easy to verify that all

---

[17] In our previous publications, $\xi_{{\rm E}k}$ has been written as $\xi_{k{\rm E}}$.

internal variables in $\boldsymbol{\xi}$, whose number we denote by ι, can be expressed as a *linearly independent combinations* of $\{\mathbf{w}_l\}$ [35, 48], with m and ι increasing with the degree of nonuniformity of $\mathfrak{m}_k(\boldsymbol{\xi})$. Similarly, we form *linearly independent combinations* of $\{E_{lk_l}\}$ to identify $(m-1)$ independent variables $\{\xi_{\mathrm{E}k}\}$.

Remark 43. *Even though the definition of* $\boldsymbol{\xi}_k^E$ *is not unique, we choose it so that it vanishes when* Σ_E^D *is uniform as defined in Eq. (46).*

Example 44. *As a concrete example, let us focus on two* ($m=2$) *subsystems* Σ_1^D *and* Σ_2^D *of* Σ^D*, for simplicity, each of which is uniform (no internal variables for them) but* Σ^D *is not. We let* $E_{k_l}, \mathbf{w}_l \doteq (N_l, V_l)$ *specify uniform microstates* $\mathfrak{m}_{k_l}$, $l=1,2$ *in* $\mathfrak{S}_{\mathbf{X}}$*. We now focus on the nonuniform microstate* $\mathfrak{m}_k$ *of* Σ^D*, which require internal variables along with* E_k *and* $\mathbf{w} \doteq (N,V)$ *to be specified in* $\mathfrak{S}_{\mathbf{Z}}$*. We keep observables* E_k *and* $\mathbf{w} \doteq (N,V)$ *of* Σ_E^D *fixed along with* N_1 *and* N_2 *of* Σ_{1E}^D *and* Σ_{2E}^D*, respectively. Following Eq. (46), we have*

$$\xi_{Ek} \doteq E_{k_1}/n_1 - E_{k_2}/n_2, \xi_V \doteq V_1/n_1 - V_2/n_2, \tag{50}$$

to identify $\mathbf{Z} = (E_k, \xi_{Ek}, \xi_V)$ *for* Σ_E^D*. Densities in* Σ_{1E}^D *and* Σ_{2E}^D *are equal in a* uniform *microstate* $\mathfrak{m}_k(\boldsymbol{\xi}_k^E)$ *of* Σ_E^D *so* $\boldsymbol{\xi}_k^E = 0$ *and need not be considered. This is consistent with the fact that uniform* $\mathfrak{m}_{keq}$ *is uniquely specified in* $\mathfrak{S}_{\mathbf{X}}$*. In this case, we have a trivial additivity of the Hamiltonians in Eq. (44a) given by*

$$\mathcal{H}_k(\mathbf{w}) \simeq \mathcal{H}_{k_1}(\mathbf{w}_1) + \mathcal{H}_{k_2}(\mathbf{w}_2) \tag{51}$$

with no internal flows between subsystems. In a nonuniform microstate, $\boldsymbol{\xi}_k^E \neq 0$*. We recall that* $\mathbf{w}$ *is* fixed *for* $\mathfrak{m}_k(\boldsymbol{\xi}_k^E)$ *but* $\mathbf{w}_1$ *and* $\mathbf{w}_2$ *can change due to possible transfers (internal flows) between* Σ_{1E}^D *and* Σ_{2E}^D *with* $d\mathbf{w}_1 = -d\mathbf{w}_2$*. The following rates are easily obtained from Eqs. (44b) and (50):*

$$\begin{aligned}
&\dot{E}_{k_1} = n_1(\dot{E}_k + n_2\dot{\xi}_{Ek}),\\
&\dot{E}_{k_2} = n_2(\dot{E}_k - n_1\dot{\xi}_{Ek}),\\
&\dot{\mathbf{w}}_1 = -\dot{\mathbf{w}}_2 = n_1 n_2 \dot{\boldsymbol{\xi}}
\end{aligned} \tag{52}$$

for $\mathfrak{m}_k(\boldsymbol{\xi}_k^E)$*. As* $\mathbf{W}$*, i.e.,* $\boldsymbol{\xi}$ *in Eq. (47) for* Σ^D *is the work variable in* $\mathcal{H}_k(\boldsymbol{\xi}_k^E)$ *(we suppress* $\mathbf{w}$ *as it it constant),* $E_k(\boldsymbol{\xi}_k^E)$ *corresponding to* $\mathfrak{m}_k(\boldsymbol{\xi}_k^E)$ *is only a function of* $\boldsymbol{\xi}$ *due to Eq. (48). This is shown in Fig. 1. As* $\boldsymbol{\xi}_k^E$ *continuously changes due to transfers between* Σ_1^D *and* Σ_2^D*, this causes variations in* $E_k(\boldsymbol{\xi})$*. The variation is similar to the variation in* $E_k(t)$ *for a* Σ^D *in* $\mathfrak{S}_{\mathbf{X}}$ *as discussed in Sect. 4. Different components of* $\boldsymbol{\xi}_k^E$ *take different times when they vanish. They are called relaxation times so the components can be ordered according to them [34] as fast and slow. As* Σ_E *or* Σ_M *evolves in time, they disappear at different times, making* $\mathfrak{m}_k$ *more or less uniform, a point that is discussed in Sect. 6. For a single* ξ *in the Fig. 4,* $\mathfrak{M}^s$ *(*$\mathfrak{M}^u$*) becomes more and more (less and less) uniform as* t *increases so that* $dS > (<)\ 0$ *during any infinitesimal change* dt*. In summary, as long as an internal variable is used, the system is restricted to be at least* Σ_E^D *in size and requires* $\mathfrak{S}_{\mathbf{Z}}$ *for unique specification. There is no explicit time dependence in this state space. If considerations of subsystems are not important in any discussion then quasi-additivity is not an issues as is the case for the the discussion of Eq. (39). In that case,* Σ^D *can be considered as a whole in* $\mathfrak{S}_{\mathbf{X}}$*; there is no need to consider* δE_k *separately, which is included in* $\mathcal{H}_k(\mathbf{w}, t)$*. Thus, the mechanical situation here is that of Sect. 4.*

In view of Conclusion 42, we need not include $\xi_{\mathrm{E}k}$ in the Hamiltonian $\mathcal{H}_k(\boldsymbol{\xi}_k^{\mathrm{E}})$ and its microstate $\mathfrak{m}_k(\boldsymbol{\xi}_k^{\mathrm{E}})$ and express them simply by $\mathcal{H}_k(\boldsymbol{\xi})$ and $\mathfrak{m}_k(\boldsymbol{\xi})$, respectively, as the main interest is in the microwork. dW_k, which is discussed in Eq. (41d).

5.1. *Mechanical State Variables*

The state variables to *uniquely* specify $\mathfrak{m}_k$ of $\Sigma_{\rm E}^{\rm D}$ depends on the number m of uniform subsystems needed to capture nonuniformity. As each subsystem requires $n_{\rm eq}$ state variables to uniquely specify its microstate $\mathfrak{m}_{kl}, l = 1, 2, \cdots, m$ so the number of state variables to uniquely specify $\mathfrak{m}_k$ is exactly $mn_{\rm eq}$, which includes $n_{\rm eq}$ state variables $(E_k, \mathbf{w})$ required to specify $\mathfrak{m}_k$, just as they are needed for each subsystems. Therefore, we now provide an *operational definition* of internal variables.

Definition 45. *The remainder*

$$m_{ieq} \doteq (m-1)n_{eq}$$

is the exact *number of internal variables* $\{\xi_{Ek}\}$ *and in* $\boldsymbol{\xi}$ *that are needed to uniquely specify* $\mathfrak{m}_k$ *mechanically. We identify such a unique specification of* $\mathfrak{m}_k$ *requiring*

$$n_{int} = n_{ieq} \doteq mn_{eq},$$

see Eq. (25), by saying that it describes a microstate in internal equilibrium *(IEQ) in the state space* $\mathfrak{S}_{\mathbf{Z}_n}$ *with* $n = n_{ieq}$ *for reasons that are implied by Definition 17 for the resulting macrostate; see also Sect. 13. A specification of* $\mathfrak{m}_k$ *with* $n_{int} < n_{ieq}$ *does not uniquely describe the microstate. Such a specification is then said to be* nonunique *or* not-in-internal equilibrium *(NIEQ) specification of* $\mathfrak{m}_k$*.*

The IEQ specification requires working in the state space $\mathfrak{S}_{\mathbf{Z}_n}$, while NIEQ specification requires working in the state space $\mathfrak{S}_{\mathbf{Z}_n}$ with with $n < n_{\rm ieq}$. In the following, we will simply use $\mathfrak{S}_{\mathbf{Z}}$ for the state space and clearly state the value of intendant n. Thus, $\mathfrak{S}_{\mathbf{Z}}$ need not result in an IEQ specification in all cases. We will similarly use $\mathbf{W}$ in Eq. (47) to denote the work parameter for any n in the following.

6. Mechanical Equilibrium Principle of Energy (Mec-EQ-P) for m_k

6.1. *Equilibrium Point and Uniformity*

We first enunciate the Mech-EQ-P:

> MEC-EQ-P: The mechanical equilibrium (Mec-EQ) point at $E_k^{\rm eq}$ is the *equilibrium point* [41] in the SI-evolution under the SI-micorforce $\mathbf{F}_{\xi k}$, where not only the SI-internal velocity $\dot{\boldsymbol{\xi}}_k^{\rm eq}$ but also the SI-micorforce $\mathbf{F}_{\xi k}^{\rm eq}$ *vanish*:
>
> $$\dot{\boldsymbol{\xi}}_k^{\rm eq} = 0, \tag{53a}$$
>
> $$\mathbf{F}_{\xi k}^{\rm eq} = -\partial E_k/\partial \boldsymbol{\xi}_k^{\rm eq} = 0. \tag{53b}$$

We consider an isolated system $\Sigma^{\rm D}$ shown in Fig. 1(a) with fixed $\mathbf{w}$. Microstates $\{\mathfrak{m}_{k\rm eq}\}$ of a uniform Hamiltonian system $\Sigma^{\rm D}$ play an important role in our approach as we explain now; see Uniformity Theorem 47 that establishes that uniform microstates of $\mathcal{H}(\mathbf{w})$ are indeed the EQ microstates $\{m_{k\rm eq}\}$, *i.e.*, the mechanical equilibrium microstates. This finally explains why we have used the suffix "eq" on them. Any nonuniformity in $\Sigma^{\rm D}$ endows $\{\mathfrak{m}_k\}$ with explicit time dependence as $\{\mathfrak{m}_k(t)\}$ for $\Sigma^{\rm D}$ or implicit time dependence through $\boldsymbol{\xi}_k^{\rm E}$ as $\mathfrak{m}_k(\boldsymbol{\xi}_k^{\rm E})$ for $\Sigma_{\rm E}^{\rm D}$ or $\Sigma_{\rm M}^{\rm D}$. Corresponding microenergies are either indicated as $\{E_k(t)\}$ in $\mathfrak{S}_{\mathbf{X}}$ or as $\left\{E_k(\boldsymbol{\xi}_k^{\rm E})\right\}$ in $\mathfrak{S}_{\mathbf{Z}}$ as shown in Sect. 5. We wish to establish that $\{\mathfrak{m}_{k\rm eq}\}$

are the *extremum* points of $\{E_k(t)\}$ or of $\left\{E_k(\boldsymbol{\xi}_k^{\rm E})\right\}$. In the following, we will simply denote both energy functions $\{E_k\}$ symbolically as $\{\mathfrak{m}_k\}$.

We follow Ramsey's proposal[18] and assume for simplicity that E_k has only a single extremum at $E_{k\rm eq}$. Depending on the nature of $\Sigma^{\rm D}$, we classify each energy function E_k to possess a *stable* equilibrium (SEQ) or an *unstable* equilibrium (UEQ), and denote these points by $\mathfrak{m}_{k\rm seq}, E_{k\rm seq}$ and $\mathfrak{m}_{k\rm ueq}, E_{k\rm ueq}$, respectively, and the corresponding energy functions symbolically by $\{\mathfrak{m}_k^{\rm s}\}$ and $\{\mathfrak{m}_k^{\rm u}\}$, respectively; see dashed-dotted blue and red curves, respectively, in Fig. 4. A neutral EQ microstate is not considered as it plays no role in thermodynamics as will become clear later.

Claim 46. *The directions of blue and red arrows on them denote increasing t during their temporal SI-evolution controlled by internally generated processes due to SI-microforces so they are mechanically* spontaneous*, see Definition 25, and generate micropower $\mathsf{P}_k(t)$. Processes going in the directions* opposite *to the blue and red arrows can only occur if they are driven by the outside so they are nonspontaneous, see Claim 29.*

We denote the extremum points of the curves $\{\mathfrak{m}_k^{\rm s}\}$ and $\{\mathfrak{m}_k^{\rm u}\}$ by $\{\mathfrak{m}_{k\rm seq}\}$ and $\{\mathfrak{m}_{k\rm ueq}\}$, respectively, as shown in Fig. 4. In analytical mechanics, there is no dissipation in a mechanical evolution but $\mathfrak{m}_k^{\rm s}$ is special in that its evolution will normally undergo oscillations about $\mathfrak{m}_{k\rm seq}$ that will persist forever as manifested by the dashed-dot blue curve; in contrast, the evolution of $\mathfrak{m}_k^{\rm u}$ has no oscillation, see the dashed-dot red curve there, as $\mathfrak{m}_k^{\rm u}$ runs away from $\mathfrak{m}_{k\rm ueq}$ but terminates is a *catastrophe* to be discussed later in which $\mathfrak{m}_k^{\rm u}$ becomes extremely nonuniform, which for $\Sigma_{\rm E}$ or $\Sigma_{\rm M}$ corresponds to an extremely large $\iota = \iota_{\rm cats}$; see (c) in Sect. 13.4. We say that $\mathfrak{m}_{k\rm ueq}$ is the *source* for the SI-evolution of $\mathfrak{m}_k^{\rm u}$.

As we are eventually interested in $\mathfrak{m}_k^{\rm s}$ and $\mathfrak{m}_k^{\rm u}$ in a thermodynamic setting, there will be macroheat that we discuss in Sect. 10.3 to be simultaneously considered. As is well known, its presence is due to dissipation so all thermodynamic processes in stable $\mathfrak{M}^{\rm s}$ terminate asymptotically at $\mathfrak{M}_{\rm seq}$ as shown by the solid blue curve in the figure. Keeping this in hindsight, we intentionally overlook oscillations in $\mathfrak{m}_k^{\rm s}$ as they do not affect the change in $E_k^{\rm s}$ during its SI-evolution to $\mathfrak{m}_{k\rm seq}$ only, making the latter as the *sink* for the SI-evolution of $\mathfrak{m}_k^{\rm s}$.

Time-independent EQ macrostate $\mathfrak{M}_{\rm eq} \doteq (\mathfrak{M}_{\rm seq},\mathfrak{M}_{\rm ueq})$ of the corresponding thermodynamic system Σ requires corresponding time-independent macroenergy $E_{\rm eq} \doteq (E_{\rm seq}, E_{\rm ueq})$; here, we have classified $\mathfrak{M}_{\rm eq} \doteq (\mathfrak{M}_{\rm seq},\mathfrak{M}_{\rm ueq})$ as stable and unstable EQ macrostate, respectively, depending on the nature of $\mathfrak{m}_{k\rm eq} \doteq (\mathfrak{m}_{k\rm seq},\mathfrak{m}_{k\rm ueq})$. Macrostates corresponding to $\{\mathfrak{m}_k^{\rm s}\}$ and $\{\mathfrak{m}_k^{\rm u}\}$ are denoted by $\mathfrak{M}^{\rm s}$ and $\mathfrak{M}^{\rm u}$, respectively.

This is a useful strategy, since oscillations become thermodynamically irrelevant as $\mathfrak{M}^{\rm s}$ asymptotically approaches $\mathfrak{M}_{\rm seq}$; see below. This also clarifies the importance of the uniform microstate $\mathfrak{m}_{k\rm eq}$; see the Uniformity Theorem 47. We first treat $\Sigma_{\rm E}$, whose results pave the way for a clear understanding of what to expect for Σ. In analytical mechanics, the temporal evolution of $\boldsymbol{\xi}_k^{\rm E}$ and $\mathfrak{m}_k(\boldsymbol{\xi}_k^{\rm E})$ in $\mathfrak{S}_{\mathbf{Z}}$ is controlled by $\mathfrak{m}_{k\rm eq}$, and is governed by the emergent SI-microforce $\mathbf{F}_{{\rm w}k}$ in Eq. (41b) by controlling internal flows within $\mathfrak{m}_k(\boldsymbol{\xi}_k^{\rm E})$. The emergent processes in $\Sigma_{\rm E}$ resulting in the SI-microwork in Eq. ((41d)) are commonly identified as *spontaneous* since they are internally controlled by SI-microforce $\mathbf{F}_{{\rm w}k}$ and not from the outside by any nonsystem microforce.

---

[18] The assumption for $\mathfrak{m}_k$ is the extension of the assumption by Ramsey [4] for $\mathfrak{M}_{\rm eq}$ to NEQ situation.

We now follow the Mec-EQ-P above. It follows from Eq. (53b) that this point represents an extremum in E_k; see Fig. 4. Its *minimum* at $E_k^{\text{seq}} = E_k^{\text{eq}}$ representing a mechanically *stable EQ* point enunciates the *mechanical asymptotic stability principle of minimum energy*. In thermodynamics, stability refers to asymptotic stability in that the system must eventually approach stable equilibrium so that $\boldsymbol{\xi}_k^{\text{E}}(t) \to 0$ as $t \to \infty$ [3]. In this sense, we see that the absolute value $\left|\boldsymbol{\xi}_k^{\text{E}}(t)\right|$ behaves similar to $1/t$ in the figure. The asymptotic approach is a stronger requirement than just imposing stability in which the system never strays far away from stable EQ point.

In contrast, the *maximum of* E_k at $E_k^{\text{ueq}} = E_k^{\text{eq}}$ representing a mechanically *unstable EQ* point enunciates the *mechanical instability principle of maximum energy*. In this case, $\left|\boldsymbol{\xi}_k^{\text{E}}(t)\right|$ behaves similar to t in the figure. Both kinds of points determine the curvature of E_k at E_k^{eq}. The two principles are collectively called *Mec-EQ-P* in this investigation. We now prove the following important theorem emphasizing the physical significance of uniformity of the Mec-EQ point $\mathfrak{m}_{k\text{eq}}$ for thermodynamic stability, which must exist only in $\mathfrak{S}_{\mathbf{X}}$ at $\boldsymbol{\xi}_k^{\text{E}} = 0$, where $\mathfrak{M}_{\text{eq}}$ exists.

Theorem 47. Uniformity Theorem of $\mathfrak{m}_{keq}$: *The Mec-EQ point* $\mathfrak{m}_{keq}$ *of* $\mathfrak{m}_k$ *is the stationary and uniform microstate with no internal flows between the microstates of its uniform subsystems.*

Proof. As $\mathfrak{m}_{k\text{eq}} : (\mathfrak{m}_{k\text{seq}}, \mathfrak{m}_{k\text{ueq}})$ is a microstate of the uniform and time-independent Hamiltonian $\mathcal{H}(\mathbf{X})$ of Σ^{D}, it is a uniform and stationary microstate in $\mathfrak{S}_{\mathbf{X}}$. We consider the microstate $\mathfrak{m}_k(t)$ of $\mathcal{H}(\mathbf{X}, t)$ for Σ^{D} in $\mathfrak{S}_{\mathbf{X}}$ and establish that $\mathfrak{m}_{k\text{eq}} : (\mathfrak{m}_{k\text{seq}}, \mathfrak{m}_{k\text{ueq}})$ is stationary by focusing on Fig. 4. The asymptotic convergence of $\mathfrak{m}_k^{\text{s}}$ to the minimum at $E_{k\text{seq}}$ as $t \to \infty$ means that the minimum of E_k^{s} must be in a stable equilibrium of E_k^{s}, which must also stationary. Thus, the microstate at the minimum must represent the uniform microstate $\mathfrak{m}_{k\text{seq}}$ of the time-independent Hamiltonian $\mathcal{H}(\mathbf{x})$. This justifies calling the uniform microstate of $\mathcal{H}(\mathbf{X})$ the stable EQ microstate. The unstable point of E_k^{u} at the of the red dashed-dot curve $\mathfrak{m}_k^{\text{u}}$ is also a stationary but unstable point, which runs away only if there is some disturbance. As this unstable microstate is stationary, it must be that of the stationary and uniform Hamiltonian $\mathcal{H}(\mathbf{X})$ so it must be identified with $\mathfrak{m}_{k\text{ueq}}$, which justifies identifying $\mathfrak{m}_{k\text{ueq}}$ as an EQ but unstable microstate.

As $\mathfrak{S}_{\mathbf{X}}$ contains no information about the internal structure of Σ^{D}, it cannot be used to understand internal flows for which we need to consider $\mathfrak{S}_{\mathbf{Z}}$ and at least Σ_{E} to justify the remainder part of the theorem. From Eq. (53a), we obtain $\xi_{\text{E}k} = 0$ and $\dot{\boldsymbol{\xi}}^{\text{eq}} = 0$. Using first $\dot{\boldsymbol{\xi}}^{\text{eq}} = 0$ in Eq. (52), we conclude that $\dot{E}_k^{\text{eq}} = 0$, which follows directly from Eq. (51). Using then $\xi_{\text{E}k} = 0$ in Eq. (52) along with $\dot{E}_k^{\text{eq}} = 0$, we conclude that $\dot{E}_{1k_1,2k_2}^{\text{eq}} = 0$. Together, they show that *all* flows cease at E_k^{eq}, which makes $\mathfrak{m}_{k\text{eq}}$ *stationary* and, therefore, *uniform* as above. Any nonzero $\boldsymbol{\xi}_k^{\text{E}}$ is due to nonuniformity, and affects $E_k(\boldsymbol{\xi}) \equiv E_k(\boldsymbol{\xi}_k^{\text{E}})$ as shown in Fig. 4. This completes the proof of the theorem.

It should be clear from the above mechanical proof of the theorem that any time-dependent $\mathfrak{m}_k : (\mathfrak{m}_k^{\text{s}}, \mathfrak{m}_k^{\text{u}})$ must be uniform and stationary only at the equilibrium point $\mathfrak{m}_{k\text{eq}} : (\mathfrak{m}_{k\text{seq}}, \mathfrak{m}_{k\text{ueq}})$ for Σ. Away from it, $\mathfrak{m}_k$ must be nonuniform. We see from Fig. 4 that away from the extremum points, $\mathfrak{m}_k^{\text{s}}$ and $\mathfrak{m}_k^{\text{u}}$ spontaneously evolve to lower microenergies as t increases along the dashed-dot blue and red arrows, respectively. The extremum represents a *uniform* microstate $\mathfrak{m}_{k\text{eq}}$ so the rest of the dashed-dotted curves denote nonuniform microstates $\mathfrak{m}_k$ ($\mathfrak{m}_k^{\text{s}}$ or $\mathfrak{m}_k^{\text{u}}$). Then, $\mathfrak{m}_{k\text{seq}}$ is the (asymptotically) *stable* equilibrium of $\mathfrak{m}_k^{\text{s}}$, where $E_{k\text{seq}}$ is *minimum*. Any perturbation away from $\mathfrak{m}_{k\text{seq}}$ always *restores* $\mathfrak{m}_k^{\text{s}}$ back to $\mathfrak{m}_{k\text{seq}}$ so that $E_k^{\text{s}} \to E_{k\text{seq}}$ spontaneously as shown by the blue arrow. Thus, following Remark 24, $\mathfrak{m}_{k\text{seq}}$ controls $\mathfrak{m}_k^{\text{s}}$-evolution [108] during which $\mathfrak{m}_k^{\text{s}}$ becomes more and more uniform with $dS > 0$. At a mechanically *unstable* equilibrium $\mathfrak{m}_{k\text{ueq}}$ of $\mathfrak{m}_k^{\text{u}}$, $E_{k\text{ueq}}$ is *maximum*; any perturbation from it to $\mathfrak{m}_k^{\text{u}}$ spontaneously *repels* it further away from $\mathfrak{m}_{k\text{ueq}}$. As $\mathfrak{m}_k^{\text{u}}$ *never* returns to $\mathfrak{m}_{k\text{ueq}}$ with E_k^{u} running away from $E_{k\text{ueq}}$, $\mathfrak{m}_{k\text{ueq}}$ becomes a source controlling $\mathfrak{m}_k^{\text{u}}$-evolution along the red arrow during which $\mathfrak{m}_k^{\text{u}}$ becomes more and more nonuniform with $dS < 0$; see Remark 24. Both are deterministic spontaneous $\mathfrak{m}_k$-evolutions, whose directions are controlled by the *principle of mechanical equilibrium* (Mec-EQ-P). ■

6.2. *Temporal Evolution*

By definition, microstates $\{\mathfrak{m}_k(\mathbf{w})\}$ of microenergies $\{E_k(\mathbf{w})\}$ are uniquely determined by the stationary Hamiltonian $\mathcal{H}(\mathbf{w})$; see Definition 36. In contrast, any NEQ microstate $\mathfrak{m}_k(\mathbf{w}, t)$, its probability $p_k(\mathbf{w}, t)$ and microenergy $E_k(\mathbf{w}, t)$ have explicit time dependence as discussed above. As we see in Sect. 5, the explicit time dependence is due to Σ^{D} being nonuniform. Temporal evolution of $\mathfrak{M}(t)$ of energy $E(t)$ in $\mathfrak{S}_{\mathbf{X}}$ is controlled by $\mathfrak{M}_{\text{eq}}$ of energy E_{eq}. As E remains constant in time for an isolated system, we focus on the temporal form of *macrowork function* $E_{\text{w}}(t) = (E_{\text{w}}^{\text{s}}(t), E_{\text{w}}^{\text{u}}(t)) = E_{\text{eq}} - \Delta W$ shown by the solid blue and red curves in Fig. 4, respectively. Their extremum points represent the equilibrium points E_{seq} and E_{ueq} for $E(t)$, respectively. During evolution as $t \to \infty$, $E_{\text{w}}^{\text{s}}(t)$ runs towards E_{seq} along the blue arrows, and $E_{\text{w}}^{\text{u}}(t)$ runs away from E_{ueq} along the red arrows. The former is the behavior of the macrowork function $E_{\text{w}}(t)$ for a stable but NEQ macrostate that terminates in a stable macrostate $\mathfrak{M}_{\text{seq}}$ that is stationary and uniform, and is normally considered in Cl-Th. The latter is that of an unstable and nonuniform macrostate, which runs away from an unstable macrostate $\mathfrak{M}_{\text{ueq}}$ that is uniform but is rarely considered. Similarly, as $t \to \infty$, $E_k^{\text{s}}(t)$ runs towards $E_{k\text{seq}}$ along the blue arrows, and $E_k^{\text{u}}(t)$ runs away from $E_{k\text{ueq}}$ along the red arrows.

7. Stochastic Concepts

7.1. *The BCGM Proposal for Stochasticity*

We now enunciate the BCGM proposal.

BCGM PROPOSAL: While microstates $\{\mathfrak{m}_k\}$ of a mechanical Hamiltonian are deterministic so they are oblivious to any sense of stochasticity, thermodynamic specification of Σ is obtained by appending probabilities to them to describe a macrostate $\mathfrak{M}$ specified by $\{\mathfrak{m}_k, p_k\}$.

The EQ state of Σ^{D} can be made stationary in time so its Hamiltonian $\mathcal{H}(\mathbf{w})$ must also be *stationary* with *no* explicit time dependence provided the motion of Σ^{D} is taken to be *stationary*. This Hamiltonian makes sense only for an isolated system that is shown in Fig. 1(a) for which $\mathbf{X}$ is fixed. For an interacting system in a surrounding medium $\widetilde{\Sigma}$ as shown in Fig. 1(b), its $\mathbf{X}$ can change in time in such a way that both remain in EQ with each other at all times so that the composite isolated system Σ_0 remains stationary.

Implementation of the BCGM proposal requires two basic steps (S1) and (S2), which we now state and describe.

(S1) Describe Σ^{D} mechanically by its *deterministic* $\mathcal{H}$ by specifying $\{\mathfrak{m}_k, E_k\}$ and SI-microwork $\{dW_k\} \doteq -\{dE_k\}$ as discussed in Sect. 4.

Remark 48. *We will usually take the motion of Σ or Σ^D to be* stationary *for the sake of simplicity as the center-of mass motion is not relevant for thermodynamic and mechanical considerations. This is most* *certainly true if they are isolated as shown in Fig. 1(a). However, we may allow them to have relative motion with respect to the medium* $\widetilde{\Sigma}$ *as shown in Fig. 1(b) to capture "frictional" dissipation between them as explicitly demonstrated recently [49]. This will be mentioned clearly when required.*

(S2) Introduce *stochasticity* by appending a probability $p_k,\ k=1,2.\cdots$ to $\mathfrak{m}_k$ to capture eventually capture *dissipation* in $\mathfrak{M}$ of $\overline{\Sigma}$, first identified by Carnot[19] [13], and to identify various *ensemble averages* $\langle\bullet\rangle$ in Eq. (20) for any macrostate.

The EQ state of $\mathcal{H}$ associated with Σ^{D} is specified by the set $\mathfrak{m}_{\mathrm{eq}} \doteq \{\mathfrak{m}_{k\mathrm{eq}}\}$ of its microstates $\mathfrak{m}_{k\mathrm{eq}}$ of microenergies $E_{k\mathrm{eq}}$. As said above, these microstates and microenergies are time independent so they must be identified as EQ microstates and EQ microenergies, respectively. In contrast, when $\mathcal{H}$ has explicit time dependence for Σ^{D}, we identify it as a nonequilibrium (NEQ) Hamiltonian specifying Σ^{D}. In this case, $\mathfrak{m} \doteq \{\mathfrak{m}_k\}$ of its microstates $\mathfrak{m}_k$ and their microenergies E_k also possess explicit time dependence so we identify them as NEQ microstates $\mathfrak{m}_k$ and microenergies, respectively. The NEQ macrostate $\mathfrak{M}(t)$ of Σ also depends on time t in this case.

We use $\mathbf{X}$ to introduce the EQ state space $\mathfrak{S}_{\mathbf{X}}$ in which $\mathfrak{m}_{k\mathrm{eq}}$ and $\mathfrak{M}_{\mathrm{eq}}$ are defined with no explicit time dependence. In contrast, $\mathfrak{m}_k$ and $\mathfrak{M}$ with explicit time dependence in $\mathfrak{S}_{\mathbf{X}}$ refer to NEQ microstates and macrostate, respectively. For simplicity of notation, we will use $\mathfrak{m}_k$ and E_k to refer to both EQ and NEQ microstates and microenergies, and $\mathfrak{M}$ for macrostates if there is no confusion; we also suppress t-dependence unless necessary for clarity.

According to the step (S2), $\mathfrak{m}_k$ appears with probability p_k, but without invoking Mec-EQ-P discussed in Sect. 6. It should be stressed that the deterministic Hamiltonian $\mathcal{H}(\mathbf{x}|\,t)$ is oblivious to p_k so $\mathfrak{m}_k(t)$ is also oblivious to p_k in that all its microquantities such as $E_k(t)$ do not change with p_k. We put no restrictions on possible sets $\{p_k\}$ so the resulting macrostates may have nothing to do with what we encounter in classical thermodynamics (Cl-Th). The resulting thermodynamics that is called *general thermodynamics* (Gen-Th) may not always satisfy the second law $(dS \geq 0)$ that is a fundamental axiom (or assumption) in Cl-Th [3]. By taking $\{p_k\}$ arbitrary will help us to determine the root cause of the second law of Cl-Th and what will cause its violation, both of which are contained in Gen-Th. For it to be thermodynamics, we will need to introduce T following Eq. (11) and S following Eq. (24) in the corresponding Σ. Microstate probabilities are central to statistical thermodynamics and determine the ensemble average such as E introduced above. To specify an EQ macrostate $\mathfrak{M}_{\mathrm{eq}} = \{\mathfrak{m}_{k\mathrm{eq}}, p_{k\mathrm{eq}}\}$ of Σ, we need to ensure that the choice of $p_{k\mathrm{eq}}$ is time independent. All other collections will specify a NEQ macrostate $\mathfrak{M}$. For example, any choice of $p_k \neq p_{k\mathrm{eq}}$ even with $\mathfrak{m}_{k\mathrm{eq}}$ specifies a NEQ macrostate $\mathfrak{M}$ of Σ.

The use of the BCGM proposal is to obtain a viable thermodynamics such as Cl-Th, the most successful thermodynamics to describe EQ processes $\mathcal{P}$. In order to reveal the required conditions for SL and its violation (VSL) in Σ_{M}, we go beyond Cl-Th, and construct a *general thermodynamics* (Gen-Th). To also appreciate the importance of system size, we will relax the macroscopic constraint required for Σ_{M}, and focus on $\overline{\Sigma}$ so that it can denote any isolated system with *any* number of particles $N = 1, 2, \cdots$. To reveal various conditions required for SL and VSL in Σ_{M}, we *reverse* the traditional approach taken in Cl-Th as fully illustrated in Fig. 7 and is explained later in detail in Sect. 14.1.

---

[19] This is the justification of our proposal to call thermodynamic entropy S as Carnot-Clausius entropy; see Sect. 8.

The implementation of the BCGM proposal to obtain a viable thermodynamics for $\Sigma^{\rm D}$ requires two additional steps (S3) and (S4). They are needed to establish the foundations of Cl-Th or Gen-Th. The first three steps form the common core approach in the foundation of the Cl-Th and of our new NEQ thermodynamics (NEQT) identified above as the Gen-Th. However, the step (S4-Gen) differs in a very important way in Gen-Th from the step (S4-Cl) taken in Cl-Th as seen in Fig. 7 in that there is reversal between the roles played by SL and EQ (stable and unstable). We now state these two states.

(S3) The next step is to endow Σ with the *first law* $dE = dQ - dW$ by identifying heat and work as carried out in Sect. 10.3 during any infinitesimal process $\delta\mathcal{P}$ that $\overline{\Sigma}$ undergoes to determine the allowed change $\{dp_k\}$ and to identify the generalized macroheat $dQ \doteq \sum_k E_k dp_k$ in Eq. (85b), a stochastic quantity, see Definition 14, and the generalized macrowork $dW = \sum_k p_k dW_k \doteq -\sum_k p_k dE_k$ in Eq. (85a), a mechanical quantity. Again, (S3) has no ramification for SL so the latter is still not necessarily satisfied. Thus, the resulting thermodynamics goes beyond Cl-Th. We identify it as a general thermodynamics (Gen-Th) noted above.

Step (S4) is broken into two different steps. (S4-Cl) is needed to convert Gen-Th to Cl-Th by imposing SL as an axiom and (S4-Gen) is needed to provide a direct proof of GSL. We now state them.

(S4-Cl) To *properly* choose changes $\{dp_k\}$ to satisfy the *second law* (SL) that controls *dissipation* and to demonstrate *stable equilibrium* in $\overline{\Sigma}$ as is customary; see, for example, [3, 17].

(S4-Gen) To take *arbitrary* $\{p_k\}$ and use the existence of (*stable and unstable*) mechanical equilibrium for $\overline{\Sigma}$ to formulate Gen-Th and to establish the *generalized second law* (GSL).

7.2. *Stability and Dissipation*

There are indirect but strong arguments [3, 12, 14, 15, 17, 18, 109–114] for a deep connection of SL with thermodynamic stability in a *stable* (s) system $\Sigma^{\rm s}$, in which a stable NEQ macrostate $\mathfrak{M}^{\rm s}(t)$ in Fig. 4 asymptotically *converges* along blue arrows to a unique and *stable* equilibrium (SEQ) macrostate $\mathfrak{M}_{\rm seq}$ [18] that is stationary. According to SL, temporal evolution of any arbitrary $\mathfrak{M}^{\rm s}(t)$ will eventually terminate into $\mathfrak{M}_{\rm seq}$ in such systems. As the mechanical evolution of a microstate $\mathfrak{m}_k^{\rm s}$ of $\Sigma^{\rm sD}$ is controlled by (deterministic) Hamiltonian equations of motion, it always undergoes oscillations about its minimum $\mathfrak{m}_{k{\rm seq}}$. The dynamics of $\mathfrak{M}^{\rm s}(t)$ in $\Sigma^{\rm s}$, therefore, cannot be deterministic [84] as noted above. It is customary to call this dynamics *dissipative*, but the term does not seem to have a well-defined meaning, and most certainly has not been clearly defined for an isolated system. Various statements are available in the literature to describe *dissipation* that was first introduced by Thomson [115], some of which are:

1. It is the conversion of mechanical energy of the system into thermal energy with an associated increase in entropy.
2. It is decoherence in energy, *i.e.*, conversion of coherent or directed energy flow into an undirected or more isotropic distribution of energy.
3. Its main effect is an increase in the temperature of the system.
4. It is often used to describe ways in which energy is wasted (lost to $\widetilde{\Sigma}$) in the form of heat.
5. Planck [116], instead of defining it, cites friction as its prime example.

All these statements, some of which may be extended to isolated systems with some leap of imagination, assume that dissipation, which is always *positive*, essentially causes *irreversibility* and *produces* entropy. It is assumed to originate from *dissipative* forces such as friction or viscosity, but what causes these forces or what causes the fixed signature of dissipation has mostly remained unclear. What distinguishes $\Sigma^{\rm s}$ from $\Sigma^{\rm sD}$ is the presence of stochasticity in the former so dissipation is an average concept over stochasticity, not applicable to microstates that evolve under deterministic Hamiltonian equations of motion. It is not clear how a dissipative force can be identified in a spontaneous heat flow (from hot to cold), which is also irreversible. As dissipation is related to some form of energy transformation, there is no direct connection between it and entropy, which is not a form of energy. That necessarily requires introducing some sort of *temperature* in the discussion, which is not properly defined for nonequilibrium macrostates in above statements. As is known, there are many different kinds of NEQ temperature definitions available in the literature, depending on the school of NEQ thermodynamics; see for example [48, Sect. 1] on this point. However, the main drawbacks of these statements are that they are not applicable to an isolated system for which $dE = 0$; see Eq. (88). For example, if E is treated as the mechanical energy, then no part of it can be converted into thermal energy as $dE = 0$. There cannot be a directed flow into the isolated system. Thus, the conventional understanding of dissipation is not only not precise but also not very general, even though the basic idea is commonly accepted that dissipation brings about irreversible processes in $\mathfrak{M}^{\rm s}$ so it asymptotically converges to the stable equilibrium macrostate $\mathfrak{M}_{\rm seq}$ in time [3]. This is an experimental fact, which we express by saying that the spontaneous evolution of $\mathfrak{M}^{\rm s}$ is controlled by the *sink* $\mathfrak{M}_{\rm seq}$. We generalize this experimental observation to also include unstable macrostate $\mathfrak{M}^{\rm u}$ (we add "u" on various symbols to indicate instability), whose spontaneous evolution is controlled by its (unstable) equilibrium macrostate $\mathfrak{M}_{\rm ueq}$, the source, to be introduced later and shown in Fig. 4, in the form of the FUNDAMENTAL PROPOSITION, see Proposition 49, which also includes the spontaneous evolution of their microstates $\mathfrak{m}_{k\rm eq}$, and will be justified in analytical mechanics later.

Proposition 49. FUNDAMENTAL PROPOSITION *The spontaneous evolution of* $\mathfrak{M}$ *(or* $\mathfrak{m}_k$*) is controlled by* $\mathfrak{M}_{eq}$ *(or* $\mathfrak{m}_{keq}$*), where* $\mathfrak{M}_{eq}$ *stands for either* $\mathfrak{M}_{seq}$ *or* $\mathfrak{M}_{ueq}$ *(or* $\mathfrak{m}_{keq}$ *stands for either* $\mathfrak{m}_{kseq}$ *or* $\mathfrak{m}_{kueq}$*).*

Dissipation in an isolated system is further considered in Sect. 10.3, and for an interacting system in the form of Claim 90 is considered in Sect. 16.7.

8. Carnot-Clausius Entropy in Classical Thermodynamics

This section is based on our recent work [76], in which we have argued that even though the idea adiabatic processes, the first law and the concept of entropy were not known to Carnot and that he believed in the now discredited caloric theory, his later writings [13] show that he had abandoned the caloric theory, and that his understanding of thermodynamics was sophisticated enough that he could have discovered the first law. Most importantly, he had foreseen the concept of entropy without realizing and it was left to Clausius to discover it.

8.1. *Carnot's Conjectural Approach*

It is commonly accepted that the concept of entropy was first introduced by Clausius [5, 6]. This is only partially valid as it overlooks the important fact that Clausius was motivated by the contributions of Carnot [13] that are captured in what is now known as the Carnot theorem related to a reversible cycle $\mathcal{P}_{\text{rev,cyc}}$ followed by a Carnot engine. This was recently discussed in our work [76, and references therin], which we follow closely to establish that the germs of Clausius's discovery were already foreseen by Carnot. Therefore, we will identify the conventional entropy as the *Carnot-Clausius entropy* to give Carnot full credit that he deserves; see footnote 19 for justification.

We now discuss the contributions of Carnot and Clausius first.

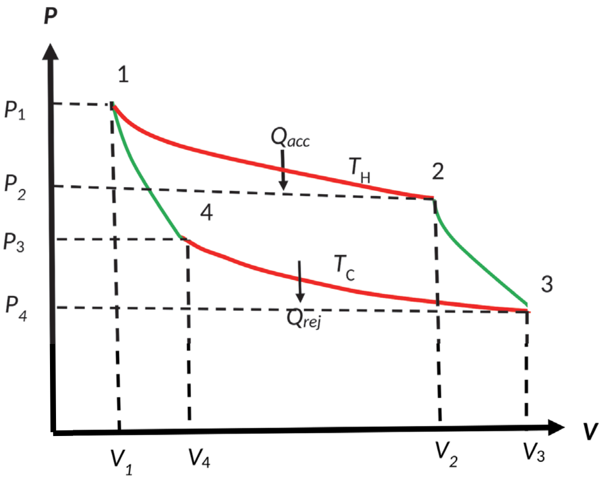

Figure 5. Schematic form of the cycle $\mathcal{P}_{\text{cyc}}$ considered by Carnot, which starts from 1 and comes back to it as follows: $1 \to 2 \to 3 \to 4 \to 1$. We will allow the four processes to be irreversible also for later use. The (reversible or irreversible) processes along $1 \to 2$ and $3 \to 4$ are isothermal at temperatures $T_{0\text{H}}$ and $T_{0\text{C}} < T_{0\text{H}}$, respectively. The (reversible or irreversible) processes along $2 \to 3$ and $4 \to 1$ are adiabatic (no macrohaet transfer) between temperatures $T_{0\text{H}}$ and $T_{0\text{C}}$, and $T_{0\text{C}}$ and $T_{0\text{H}}$, respectively. We will allow the temperature of the engine $T(t)$ to be different from $T_{0\text{H}}$ and $T_{0\text{C}}$ along $1 \to 2$ and $3 \to 4$, respectively, for an irreversible engine. For a reversible engine, these processes remain isothermal as Carnot requires. The accepted macroheat $Q_{\text{acc}} \doteq \Delta_{\text{e}} Q_{\text{acc}}$ and rejected macroheat $Q_{\text{rej}} \doteq \Delta_{\text{e}} Q_{\text{rej}}$ occur along $1 \to 2$ and $3 \to 4$, respectively.

During the days of Carnot and Clausius, the notion of entropy was yet to be discovered so they took T to be primitive concept besides the macroheat. The efficiency of the Carnot engine shown in Fig. 5 is adimensional so it can only depend on the adimensional ratio $\tau \doteq T_{0\text{C}}/T_{0\text{H}}$ of the two isotherms

$$\epsilon^{\text{RC}} = \epsilon(\tau) \tag{54}$$

as noted by Carnot. As he was not yet familiar with the first law, he did not obtain the exact form of ϵ. Had he been aware of this law, he would have anticipated the concept of entropy that was left to Clausius [6] to discover as was recently discussed by us [76], which we discuss below. The discussion is based on his book [13] and his writings so it is based on the information Carnot possessed.

The accepted macroheat $Q_{\text{acc}} \doteq \Delta_{\text{e}} Q_{\text{acc}} > 0$ and rejected macroheat $Q_{\text{rej}} \doteq \Delta_{\text{e}} Q_{\text{rej}} < 0$ occur along $1 \to 2$ and $3 \to 4$, respectively. According to the *Carnot theorem* [13], the efficiency is independent of the choice of the working material, and its four macrostates $1, 2, 3,$ and 4 forming the closed cycle $\mathcal{P}_{\text{cyc}}$, except for the ratio τ of the two isotherms. The only two process macroheats for the entire heat cycle are the latent heats Q_{acc} and Q_{rej}. They determine another adimensional ratio $\rho \doteq Q_{\text{rej}}/Q_{\text{acc}}$ over the cycle so it can also be used to determine the efficiency. The other possible ratio $W/(Q_{\rm acc}+Q_{\rm rej})$ is of quantities that are defined over the entire cycle so it cannot be identified as a ratio of quantities defined over individual isotherms to determine the efficiency. Indeed, the latter ratio turns out to be unity and establishes the first law as we show below in Eq. (60). Let us set

$$W \propto Q_{\rm acc}+Q_{\rm rej}, \tag{55}$$

with some unknown proportionality constant.

As ρ is also determined by the two isotherms, it must be an adimensional function of the above ratio τ:

$$\rho \doteq \rho(\tau). \tag{56}$$

All this can be concluded without the use of the first and the second laws.

The above discussion of τ and ρ is not what is found in Reflections [13] by Carnot, but he could have very easily concluded them even without knowing the two thermodynamic laws.

However, Carnot [13, p. 61] did claim, see Erlichson [117] also, that

> "the motive power of heat depends also on the quantity of caloric used, and on what may be termed, on what in fact we will call, the *height of its fall*, that is to say, the difference of temperature of the bodies between which the exchange of caloric is made."

We thus conclude, following Carnot and Erlichson, that

$$W \propto Q_{\rm acc}(T_{\rm 0H}-T_{\rm 0C}). \tag{57}$$

Comparing it with Eq. (55), Carnot could have concluded that

$$Q_{\rm acc}+Q_{\rm rej} \propto Q_{\rm acc}(T_{\rm 0H}-T_{\rm 0C}).$$

Taking the proportionality constant $\beta_{\rm 0H} \doteq 1/T_{\rm 0H}$ to yield $Q_{\rm acc}$ on both sides, we obtain

$$Q_{\rm acc}+Q_{\rm rej} = Q_{\rm acc}(1-T_{\rm 0C}/T_{\rm 0H}).$$

Consequently,

$$Q_{\rm rej} = -Q_{\rm acc}T_{\rm 0C}/T_{\rm 0H}, \tag{58}$$

or

$$Q_{\rm acc}/T_{\rm 0H} = -Q_{\rm rej}/T_{\rm 0C} \tag{59a}$$

that define the two Carnot ratios[20] so that

$$Q_{\rm acc}/T_{\rm 0H} + Q_{\rm rej}/T_{\rm 0C} \equiv 0 \tag{59b}$$

emerges as an identity[21]. It is quite possible that the relation between the two macroheats in Eq. (59a) may have motivated Carnot as established from his notes, see Erlichson [76, 117], to eventually abandon

---

[20] These ratios do not apeear in [13], but are useful in our analysis.

[21] Using the negative inverse of $T_{\rm 0C}$ as the proportionality constant also gives the same identity of the Carnot ratios.

the caloric theory later on as $Q_{\rm acc}$ and $Q_{\rm rej}$ do not have the same magnitude as would be the case in the caloric theory. But as we will see, he never had to use Eq. (58) to prove the Carnot Theorem in [13]. We also observe from Eq. (57) by using the proportionality constant $\beta_{0\rm H} \doteq 1/T_{0\rm H}$ that

$$W = Q_{\rm acc}(1 - T_{0\rm C}/T_{0\rm H}) = Q_{\rm acc} + Q_{\rm rej} \equiv Q_{\rm cyc}, \tag{60}$$

which is nothing but the *first law for a cycle*; see Eq. (6), and is precisely the content of the quote by Carnot [13, p. 225]

> Heat is simply motive power, or rather motion which has changed its form. It is a movement among the particles of bodies. Wherever there is destruction of motive power, there is at the same time production of heat in quantity exactly proportional to the quantity of motive power destroyed. Reciprocally, wherever there is destruction of heat, there is production of motive power.

Incidentally, the equality in Eq. (59a) proves that the ratio ρ is independent of the working substance so all reversible Carnot engines have the same efficiency $\epsilon^{\rm RC}$, whose value we now derive.

From Eq. (58), we conclude that

$$\rho = -\tau, \tag{61}$$

and

$$\epsilon^{\rm RC} = 1 - T_{0\rm C}/T_{0\rm H}. \tag{62}$$

The efficiency is independent of the choice of The working substance, and its four macrostates $1, 2, 3,$ and 4 forming a closed cycle $\mathcal{P}_{\rm cyc}$, except for the ratio of the two isotherms as noted above. It simply implies that the ratio

$$\Delta R \doteq Q/T_0 \tag{63}$$

along the two isotherms $1 \to 2$ and $3 \to 4$ has the *same* magnitude but opposite signs, regardless of the choice of $1, 2, 3,$ and 4 forming $\mathcal{P}_{\rm cyc}$ as clearly seen from Eqs. (59a) and (59b). As the two adiabats do not affect the two macroheat exchanges, we conclude that the ratio ΔR has the *same* magnitude but opposite signs along the two processes $\mathcal{P}_{\rm acc} : 1 \to 3$ and $\mathcal{P}_{\rm rej} : 3 \to 1$, respectively. This means that ΔR denotes differences $R(3) - R(1)$ and $R(1) - R(3)$ of a macroquantity R between the two end macrostates at 1 and 3, and 3 and 1, respectively.

8.2. *The Leap by Clausius*

This discovery of the universal feature of ΔR by Carnot is the *precursor* of what Clausius [6] eventually recognized that for any arbitrary thermodynamic *reversible* process along any closed path (cycle) $\mathcal{P}_{\rm rev,cyc}$, see Fig. 6, the ratio

$$dR(t) \doteq dQ(t)/T(t)$$

is no different from Eq. (18), since $dS = dS_{\rm eq}$ and $dQ_{\rm eq} \doteq dQ$, and where the temperature $T(t)$ of Σ is the same as the temperature $T_0(t)$ of $\widetilde{\Sigma}$ in Fig. 1(b) for the two to be in EQ with each other so that

$$T(t) \equiv T_0(t); \tag{64}$$

we have allowed $T_0(t)$ to change during the cyclic process as a generalization of Carnot's original cycle. Clausius [6] introduces the equilibrium entropy function S that satisfies the Clausius equality

$$dQ(t) = T(t)dS(t) \text{ over } \delta\mathcal{P}_{\text{rev}}, \tag{65}$$

where $\delta\mathcal{P}_{\text{rev}}$ is a reversible segment of the reversible cycle $\mathcal{P}_{\text{rev,cyc}}$ so that $\oint_{\mathcal{P}_{\text{rev,cyc}}} dS(t) = 0$, see Eq. (18),

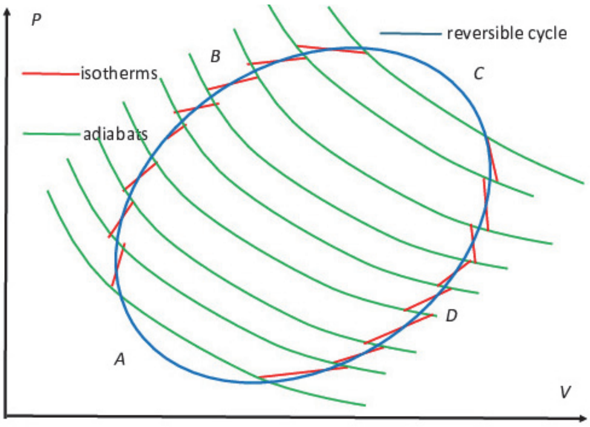

Figure 6. Schematic form of replacing an arbitrary reversible cycle shown in blue by a series of small but exaggerate size RC-cycles placed next to each other. The red segments represent isotherms at infinitesimally different temperatures and green curves denote adiabats sharing consecutive C-cycles. The segment ABC represents $\mathcal{P}_{\text{acc}}$ along which $\Delta_{\text{e}}Q_{\text{acc}}$ is accepted and the segment CDA represents $\mathcal{P}_{\text{rej}}$ along which $\Delta_{\text{e}}Q_{\text{rej}}$ is rejected.

to justify the claim that $S \equiv R$ is a *state function* in EQ so that it comes back to its starting value at the end of the cycle. We identify Eq. (65) as the *Clausius equality*, which was first derived by Clausius for a *reversible* process, and which forms the origin of the *original thermodynamic concept* of $S \equiv R$ of an equilibrium (EQ) macrostate $\mathfrak{M}_{\text{eq}}$ up to an arbitrary constant. This justifies crediting the discovery of S to both Carnot and Clausius as we have done. With its discovery, a movement started in thermodynamics, with entropy being an integral part of it as a state function of observables of the system. Thanks to Carnot [13] and Clausius [6] as noted above, we know how any *arbitrary reversible* cycle (ARC-cycle) $\mathcal{P}_{\text{ARC}}$ shown in blue in Fig. 6 can be turned into a large number of reversible Carnot cycles, with their isothermal temperatures shown by red segments differing from those of their neighboring cycles by *infinitesimal* amounts as originally discussed by Clausius [6], and recently reviewed by us [76]. Because of the decomposition into reversible Carnot cycles, we have added C into ARC as a reminder to denote this particular cycle. We will not go into the detail as it is a common knowledge by now.

The decomposition allowed Clausius to introduce and demonstrate the EQ entropy function (note that in EQ, $dQ(t) = d_{\text{e}}Q(t), d_{\text{i}}Q(t) = 0, d_{\text{i}}S(t) = 0$ and $T = T_0$) so that

$$\Delta S_{\text{cyc}} = \oint_{\mathcal{P}_{\text{ARC}}} dS(t) \doteq \oint_{\mathcal{P}_{\text{ARC}}} dQ(t)/T(t) = 0 \tag{66}$$

for the entropy of an arbitrary reversible cycle that appear in Fig. 6.

8.3. *General Carnot-Clausius Entropy*

The following general statement can be made. Let $\mathfrak{M}_{\text{eq}} = \mathfrak{M}(\mathbf{X})$ be an EQ macrostate of entropy $S_{\text{eq}} = S(\mathbf{X})$. Then, during an *arbitrary* cyclic process $\mathcal{P}_{\text{cyc}}^{(\text{eq})}$ that brings the final macrostate to the initial EQ macrostate $\mathfrak{M}_{\text{eq}0} \doteq \mathfrak{M}(\mathbf{X}_0), \mathbf{X}_0 = \mathbf{X}(t = 0)$ after completing the cycle that may possibly be irreversible, we have the identity

$$\oint_{\mathcal{P}_{\text{cyc}}^{(\text{eq})}} dS(t) \equiv 0; \tag{67}$$

the only requirement is that it brings the system back to $\mathfrak{M}_{\text{eq}0}$, which is encrypted by the additional superscript "eq" within parentheses in $\mathcal{P}_{\text{cyc}}^{(\text{eq})}$, and that $S_{\text{ieq}n(t)} \doteq S(\mathbf{Z}_{n(t)})$ is a unique function of $\mathbf{Z}_{n(t)} \in \mathfrak{S}_{\mathbf{Z}_{n(t)}}$ that parametrizes IEQ NEQ macrostates $\mathfrak{M}_{\text{ieq}n(t)}$ along $\mathcal{P}_{\text{cyc}}^{(\text{eq})}$; we have allowed $\mathbf{Z}_{n(t)}$ to vary in such a way that $n(t)$ can change continuously except that it equals n_{eq} at the start and end of the arbitrary cycle. This manipulation requires extending the Carnot-Clausius entropy concept from EQ macrostate to NEQ macrostates over the remainder of the cycle. A further generalization is to replace $\mathfrak{M}_{\text{eq}0}$ by $\mathfrak{M}_{\text{ieq}0}$ in some given $\mathfrak{S}_{\mathbf{Z}_{n(0)}}$ and an arbitrary hypothetical cyclic process $\mathcal{P}_{\text{cyc}}^{(\text{ieq})}$ that brings the system back to the initial IEQ macrostate $\mathfrak{M}_{\text{ieq}0}$ along a cyclic process.

9. General Formulation of the Statistical Entropy

In this section, we follow the second part of the BCGM proposal and derive a very general formulation of the statistical entropy, see Eq. (24), for a general body Σ_{b}. Later, we show that it is identical to the thermodynamic entropy S. The statistical entropy in this section is denoted by $\mathcal{S}$ to distinguish it from the thermodynamic entropy S. As a consequence, this will also demonstrate that the entropy in general is a *statistical average* defined for a macrostate and not a microstate. Being a property of a macrostate, its instantaneous formulation is oblivious to SL, which is a requirement of a process over time, so it may or may not satisfy SL. Thus, this formulation is useful to develop Gen-Th.

We focus on an arbitrary macrostate $\mathcal{M}(t) \equiv \mathcal{M}(\mathbf{Z}(t), t)$ of Σ_{b} at a given instant t having an explicit dependence on t through some function $f(t)$. To understand this explicit dependence, we denote $\mathbf{Z}(t)$ by $\overline{\mathbf{Z}}$ so that we can separate out the explicit variation due to t, and simply use $\mathcal{M}$ or $\mathcal{M}(t)$ in the following. We also suppress t unless necessary in the following. The macrostate $\mathcal{M}$ refers to the sets of microstates $\mathbf{m} = \{\mathfrak{m}_k(\overline{\mathbf{W}})\}$, with $\mathfrak{m}_k(\overline{\mathbf{W}})$ specified by $(\overline{E}_k, \overline{\mathbf{W}})$, and their probabilities $\mathbf{p} = \{p_k(t)\}$; $\mathfrak{m}_k$ does not uniquely specify $\mathcal{M}(t)$ due to explicit time dependence in the state space $\mathfrak{S}_{\mathbf{Z}}$. For the computation of combinatorics, the probabilities are handled empirically by following Gibbs [14]:

Criterion 50. *We consider a large number $\mathcal{N} = \mathcal{C}W(\overline{\mathbf{Z}})$ of independent* replicas *or* samples *of Σ_b, with $\mathcal{C}$ some large constant integer and $W(\overline{\mathbf{Z}})$ the number of distinct microstates $\mathfrak{m}_k$. The samples should be thought of as identically prepared experimental samples [9].*

The above sample space generalizes Gibbs' *ensemble* for Σ_{b} in $\mathfrak{S}_{\mathbf{Z}}$ in any arbitrary macrostate for which p_k may be time-dependent, instead of the original ensemble that is restricted to an equilibrium body in $\mathfrak{S}_{\mathbf{X}}$. Moreover, we allow some $p_k(t)$'s to be zero so that we can take $W(\overline{\mathbf{Z}})$ to be *fixed* to allow microstates with zero probability to emerge and microstates with nonzero probability to disappear in time as happens in processes such as in classical expansion or compression; the former case was recently discussed by us [35, see Sect. 14] using our newly developed thermodynamic for $\mathcal{M}_{\text{ieq}}$ in the extended state space. This easiest way to handle the situation is by taking $W(\overline{\mathbf{Z}})$ to be its maximum possible value during any process $\mathcal{P}$, which we denote by $W_{\mathcal{P}}$. This allows us to keep $\mathcal{N}$ fixed, which will prove important to allow for the partition of dp_k in Eq. (33) and Remark 31.

9.1. *Simply Connected Sample Space*

Isolated Body

Let $\mathfrak{m}_k$ appear in the ensemble $\mathcal{N}_k(t)$ times and define

$$0 \leq p_k(t) = \mathcal{N}_k(t)/\mathcal{N} \leq 1; \ \sum_{k=1}^{W_{\mathcal{P}}} \mathcal{N}_k(t) = \mathcal{N}. \tag{68}$$

The samples are, by definition, *independent* of each other. Therefore, they can be treated as the "outcomes" of some random "variable," the macrostate $\mathcal{M}$.

The number of ways $\mathcal{W}$ to arrange the $\mathcal{N}$ samples into $W_{\mathcal{P}}$ distinct microstates is

$$\mathcal{W} \equiv \mathcal{N}!/\prod_k \mathcal{N}_k(t)!. \tag{69}$$

We now follow Boltzmann's postulate in Eq. (19a) and take the natural log of $\mathcal{W}$ to obtain an *additive* quantity per sample to introduce the *statistical entropy*

$$\mathcal{S} \equiv (1/\mathcal{N}) \ln \mathcal{W}. \tag{70}$$

Using Stirling's approximation, we see easily that $\mathcal{S}$, which is identified later with the C-C entropy $S(\overline{\mathbf{Z}})$ of Σ_{b}, can be written as the average of the negative of the index of probability defined in Eq. (23)

$$\mathcal{S}(\overline{\mathbf{Z}}, t) \equiv -\langle \eta(t) \rangle \equiv -\sum_{k=1}^{W_{\mathcal{P}}} p_k(t) \ln p_k(t), \tag{71}$$

which was given earlier as Eq. (24); here we have also shown an explicit time-dependence, which is *distinct* from the implicit time-dependence in $\overline{\mathbf{Z}}$. The explicit time-dependence in $\mathcal{S}(\overline{\mathbf{Z}}, t)$ merely reflects the fact that it is not a state function and that $\mathcal{M}$ is not uniquely specified as a $\mathcal{M}_{\mathrm{ieq}}$ in $\mathfrak{S}_{\mathbf{Z}}$. The above derivation is based on fundamental principles and the Boltzmann hypothesis and does not require the body to be in equilibrium; therefore, it is *always* applicable. To the best of our knowledge, even though such an expression has been extensively used in the literature, it has been used *without* any derivation; one simply appeals to this form by appealing to the information entropy [71, 119].Thus, Eq. (71) is a generalization of Eq. (19b) to an arbitrary $\mathcal{M}_{\mathrm{arb}}$.

Remark 51. *The statistical entropy $\mathcal{S}$ appears as an instantaneous ensemble average, see Eq. (21a)*

$$\boldsymbol{\varphi} = \frac{1}{\tau_0} \int_0^{\tau_0} \boldsymbol{\varphi}(t) dt,$$

where $\boldsymbol{\varphi}(t)$ is the value of $\boldsymbol{\varphi}$ at time t [17]. For $\mathcal{M}_{eq}$, both definitions give the same result provided ergodicity holds. The physics of this average is that $\varphi(t)$ at t represents one of the microstate of $\mathcal{M}_{eq}$. As $\mathcal{M}_{eq}$ is invariant in time, these microstates belong to $\mathcal{M}_{eq}$, and the time average is the same as the ensemble average if ergodicity holds. However, for a NEQ macrostate $\mathcal{M}(t)$, which continuously changes with time, the temporal average is not physically meaningful. Only the ensemble average makes any sense at any time as was first pointed out in [79] and is used in this review.

Because of its similarity in form with $S_{\rm G}$ in Eq. (19b), we will refer to $\mathcal{S}(\overline{\mathbf{Z}},t)$ simply as the *Gibbs* or the *statistical entropy*. The distinction between $\mathcal{S}$ and S should be emphasized. The latter appears in the Gibbs fundamental relation, see Sect. 10.6, that relates the energy change dE with the entropy change dS. The concept of microstates is irrelevant for this relation, which is purely thermodynamic. On the other hand, $\mathcal{S}$ is solely determined by $\{\mathfrak{m}_k\}$, and is a statistical quantity. To identify $\mathcal{S}(\overline{\mathbf{Z}},t)$ with the NEQ thermodynamic entropy S requires the following additional steps:

(1) It is necessary to enforce that $\mathcal{S}(\overline{\mathbf{Z}},t)$ satisfies Eq. (1) in Cl-Th during any arbitrary process.

(2) For a body in canonical equilibrium, it is necessary to establish that $\mathcal{S}(t)$ is identical to the equilibrium thermodynamic entropy given by $S_{\rm G}$ [14, 17].

(3) It is necessary to show that $\mathcal{S}(\overline{\mathbf{Z}})$ is identical to $S(\overline{\mathbf{Z}})$ for $\mathcal{M}_{\rm ieq}$.

(4) It is necessary to show that $\mathcal{S}(\overline{\mathbf{Z}},t)$ is identical to $S(\overline{\mathbf{Z}},t)$ for $\mathcal{M}_{\rm nieq}$.

The proof for (2), see [46], is trivial by setting $p_k(t)=p_k^{\rm eq}$, which requires all $p_k(t)$'s to be nonzero at time t. Thus, $W(\overline{\mathbf{Z}})$ must denote the number of microstates with nonzero probabilities at that time, and may be different from $W_{\mathcal{P}}$. We now focus on this t. The maximum possible value of $S(\overline{\mathbf{Z}},t)$ for given $\overline{\mathbf{Z}}$ occurs when $\mathfrak{m}_k$ are *equally probable* (ep):

$$p_k(t)\to p_k^{\rm ep}=1/W(\overline{\mathbf{Z}})>0,\quad \forall\mathfrak{m}_k\in\Gamma_0(\overline{\mathbf{Z}}). \tag{72}$$

In this case, the explicit time dependence in $S(t)$ will *disappear* and we have

$$S_{\max}(\overline{\mathbf{Z}},t)=S_{\rm B}(\overline{\mathbf{Z}})=\ln W(\overline{\mathbf{Z}}), \tag{73}$$

which is identical in form to the Boltzmann entropy in Eq. (19a) for an isolated body in equilibrium, except that the current formulation has been extended to an isolated body out of equilibrium. The only requirement is that all microstates in $W(\overline{\mathbf{Z}})$ are equally probable. The statistical entropy in this case becomes a *state function*, just as the classical entropy is for $\mathcal{M}_{\rm ieq}$ that is fully treated in Sect. 13. This proves (3). The simplest way to understand the physical meaning of Eq. (73) is as follows: Consider $\overline{\mathbf{Z}}\in\mathfrak{S}_{\mathbf{Z}}$ at some time t. As $S(\overline{\mathbf{Z}},t)$ may not be a unique function of $\overline{\mathbf{Z}}$, we look at all possible entropy functions for this $\overline{\mathbf{Z}}$. These entropies correspond to all possible sets of $\{p_k(t)\}$ for a fixed $\overline{\mathbf{Z}}$, and define different possible states $\left\{\mathcal{M}(\overline{\mathbf{Z}})\right\}$. We pick that particular $\overline{\mathcal{M}}(\overline{\mathbf{Z}})\in\left\{\mathcal{M}(\overline{\mathbf{Z}})\right\}$ among these that has the *maximum possible value* of the entropy, which we denote by $S(\overline{\mathbf{Z}})$ or $S(\mathbf{Z}(t))$ without any explicit t-dependence. This entropy is a *state function* $S(\overline{\mathbf{Z}})$ in $\mathfrak{S}_{\mathbf{Z}}$. For a macroscopic body, this occurs when the corresponding microstate probabilities for $\overline{\mathcal{M}}(\overline{\mathbf{Z}})$ are given by $p_k^{\rm ep}$ above. The proof for (4) is by comparing the differential $d\mathcal{S}$ with Eq. (93).

Applying the above formulation to a macrostate characterized by a given $\overline{\mathbf{X}}$ in $\mathfrak{S}_{\mathbf{X}}$ and consisting of microstates $\{\overline{m}_k\}$ with probabilities $\{\overline{p}_k(t)>0\}$, we find that

$$S(\overline{\mathbf{X}},t)\equiv-\sum_{k=1}^{W(\overline{\mathbf{X}})}\overline{p}_k(t)\ln\overline{p}_k(t),\ \sum_{k=1}^{W(\overline{\mathbf{X}})}\overline{p}_k(t)\equiv1, \tag{74}$$

is the entropy of this macrostate, where $W(\overline{\mathbf{X}})$ is the number of distinct microstates $\overline{m}_k$. It should be obvious that

$$W(\overline{\mathbf{X}})\equiv\textstyle\sum_{\boldsymbol{\xi}(t)}W(\overline{\mathbf{Z}}).$$

Again, under the equiprobable assumption $p_k(t) \to \overline{p}_k^{\text{ep}} = 1/W(\overline{\mathbf{X}})$, the above entropy takes its maximum possible value; here,

$$S_{\max}(\overline{\mathbf{X}}, t) = S_{\text{B}}(\overline{\mathbf{X}}) = \ln W(\overline{\mathbf{X}}), \tag{75}$$

which is identical in value to the Boltzmann entropy in Eq. (19a) for an isolated body in equilibrium. The maximum value occurs at $t = \tau_{\text{eq}}$. It is evident that

$$S(\overline{\mathbf{Z}}, t) \leq S_{\text{B}}(\overline{\mathbf{Z}}) \leq S_{\text{B}}(\overline{\mathbf{X}}). \tag{76}$$

We will refer to $S_{\text{B}}(\overline{\mathbf{Z}})$ in terms of $W(\overline{\mathbf{Z}})$ in Eq. (73) as the *time-dependent Boltzmann formulation* of the entropy or simply the Boltzmann entropy [74], whereas $S_{\text{B}}(\overline{\mathbf{X}})$ in Eq. (75) represents the equilibrium (Boltzmann) entropy. It is evident that the Gibbs formulation in Eqs. (71) and (74) supersedes the Boltzmann formulation in Eqs.(73) and (75), respectively, as the former contains the latter as a special limit. However, it should be also noted that there are competing views on which entropy is more general [74, 118]. We believe that the above derivation, being general, makes the Gibbs formulation more fundamental. The continuity of $S(\overline{\mathbf{Z}}, t)$ follows directly from the continuity of $p_k(t)$. The existence of the statistical entropy $S(\overline{\mathbf{Z}}, t)$ follows from the observation that it is bounded above by $\ln W(\overline{\mathbf{Z}})$ and bounded below by 0, see Eq. (73). It should be stressed that $\mathcal{W}$ is not the number of microstates of the $\mathcal{N}$ replicas; the latter is given by $[W(\overline{\mathbf{Z}})]^{\mathcal{N}}$, but these microstates do not satisfy the requirement of nondegeneracy in footnote 2. Thus, the entropy in Eq. (70) should not be confused with the Boltzmann entropy, which would be given by $\mathcal{N} \ln W(\overline{\mathbf{Z}})$. It should be mentioned at this point that Boltzmann uses the combinatorial argument to obtain the entropy of a gas, resulting in an expression similar to that of the Gibbs entropy in Eq. (19b) except that the probabilities appearing in his formulation represents the probability of various discrete states of a particle, and should not be confused with the microstate probabilities used here; see [119]. The approach of Boltzmann is *limited* to that of an ideal gas only and is not general as it neglects the correlations present due to the interactions between particles [74, 78]. On the other hand, our approach is valid for any body with any arbitrary interactions between particles as all microstates in the collection are *independent*.

Interacting System in a Medium and Quasi-independence

The above formulation of $S(\overline{\mathbf{Z}}, t)$ can be applied to Σ, $\widetilde{\Sigma}$, and Σ_0. We assume that Σ, and $\widetilde{\Sigma}$ are *quasi-independent* so that $S_0(t)$ can be expressed as a sum of entropies $S(t)$ and $\widetilde{S}(t)$ of Σ, and $\widetilde{\Sigma}$, respectively:

$$S_0(t) = S(t) + \widetilde{S}(t). \tag{77}$$

The statistical entropies are given by an identical formulation

$$S(t) = -\sum_k p_k(t) \ln p_k(t), \quad \widetilde{S}(t) = -\sum_{\widetilde{k}} \widetilde{p}_{\widetilde{k}}(t) \ln \widetilde{p}_{\widetilde{k}}(t), \tag{78a}$$

and

$$S_0(t) = -\sum_k p_{0k_0}(t) \ln p_{0k_0}(t), \tag{78b}$$

with quasi-independence requiring the approximate equality

$$p_{0k_0} \approxeq p_k(t) \widetilde{p}_{\widetilde{k}}(t). \tag{79}$$

Here, $\mathfrak{m}_k$ with probability p_k denotes a microstate of Σ and $\widetilde{m}_{\widetilde{k}}$ with probability $\widetilde{p}_{\widetilde{k}}$ that of the medium. Then, quasi-additivity condition immediately shows that entropies are additive as given in Eq. (77).

Remark 52. *In the derivation of the above additivity, see [32], we have neither assumed the medium nor the system to be in equilibrium or internal equilibrium; only quasi-independence is assumed.*

In classical thermodynamics, the above concept of quasi-independence (or quasi-noninteracting, *i.e.* approximately noninteracting) is replaced by thermodynamic quasi-independence to make entropies additive [3].

Remark 53. *The above formulation of the additivity of statistical entropies will not remain valid if the two are not quasi-independent. From this, we also conclude that the additivity will also not be true of the thermodynamic entropies under this condition.*

9.2. *Disjoint Sample Space (Component Confinement)*

The consideration of dynamics resulting in the simple connectivity of the sample (or phase) space has played a pivotal role in developing the kinetic theory of gases [16, 74], where the interest is at high temperatures [9, 17, 79, 81]. As dynamics is very fast here, it is well known that the ensemble entropy agrees with its temporal formulation. However, at low temperatures, where dynamics becomes sluggish as in a glass [106, 107, 120, 121], the body can be *confined* into disjoint components. Sample (or phase) space confinement at a phase transition such as a liquid-gas transition is well known in equilibrium statistical mechanics [9, 17, 79]. It also occurs when the body undergoes symmetry breaking such as during magnetic transitions, crystallizations, etc. But confinement can also occur under nonequilibrium conditions, when the observational time scale τ_{obs} becomes shorter than the equilibration time τ_{eq} [106, 107, 120, 121], such as for glasses, whose behavior and properties have been extensively studied. In the following, we will focus on Σ_{b}. The issue has been recently considered by us [9], where only energy as an observable was considered. The discussion is easily extended to the present case when confinement occurs for whatever reasons into one of the thermodynamically significant number of disjoint components $\Gamma_\lambda, \lambda = 1, 2, 3 \cdots, \mathcal{C}$, each component corresponding to the same set $\overline{\mathbf{Z}}$. Such a situation arises, for example, in Ising magnets at the ferromagnetic transition., where the system is either confined to Γ_+ with positive magnetization or Γ_- with negative magnetization. Even a weak external magnetic field $|H| \to 0$, that we can *control* as an observer, will allow the system to make a choice between the two parts of Γ. It just happens that in this case $\mathcal{C} = 2$ and is thermodynamically insignificant. The situation with glasses or other amorphous materials is very different [120], In the first place, Γ is a union of *thermodynamically significant* number $\mathcal{C} \sim e^{cN}, c > 0$, disjoint components. In the second place, there is no analog of a symmetry breaking field. Therefore, there is no way to prepare a sample in a given component Γ_λ. Thus, the samples will be found in all different components. Taking into consideration disjointedness of the components generalizes the number of configurations in Eq. (69) to

$$\mathcal{W} \equiv \mathcal{N}!/\prod_{\lambda,k_\lambda} \mathcal{N}_{k_\lambda}(t)!,$$

where $\mathcal{N}_{k_\lambda}$ denotes the number of sample in the microstate $\mathfrak{m}_{k_\lambda}$ in the λ-th component. In terms of $p_{k_\lambda} = \mathcal{N}_{k_\lambda}(t)/\mathcal{N}$, this combination immediately leads to

$$S(t) \equiv (/\mathcal{N}) \ln \mathcal{W} = -\textstyle\sum_\lambda \sum_{k_\lambda} p_{k_\lambda}(t) \ln p_{k_\lambda}(t), \tag{80}$$

for the statistical entropy of the system and has already been used earlier [9, see Sec. 4.3.3] by us. From what has been said above, this statistical entropy is also the thermodynamic entropy of a nonequilibrium macrostate under component confinement for which the entropy is a state function of $\overline{\mathbf{Z}}$. Therefore, as before, we take S to be the general expression of the nonequilibrium thermodynamic entropy and use S in place of S. Introducing

$$p_{\lambda}(t) \equiv \sum\nolimits_{k_{\lambda}} p_{k_{\lambda}}(t),$$

it is easy to see [9] that

$$S(t) = \sum\nolimits_{\lambda} p_{\lambda}(t) S_{\lambda}(t) + S_{\mathcal{C}}(t).$$

Here, the entropy of the component Γ_{λ} in terms of the reduced microstate probability $\widehat{p}_{k_{\lambda}} \equiv p_{k_{\lambda}}/p_{\lambda}$ is

$$S_{\lambda}(t) = -\sum\nolimits_{k_{\lambda}} \widehat{p}_{k_{\lambda}}(t) \ln \widehat{p}_{k_{\lambda}}(t) \tag{81}$$

so that the first contribution is its average over all components. The second term is given by

$$S_{\mathcal{C}}(t) = -\sum\nolimits_{\lambda} p_{\lambda}(t) \ln p_{\lambda}(t), \tag{82}$$

and represents the *component entropy*. It is this entropy that determines the residual entropy [79] in disordered systems for $\Sigma_{\mathrm{b}} = \Sigma$ that is discussed in Sect. 15.

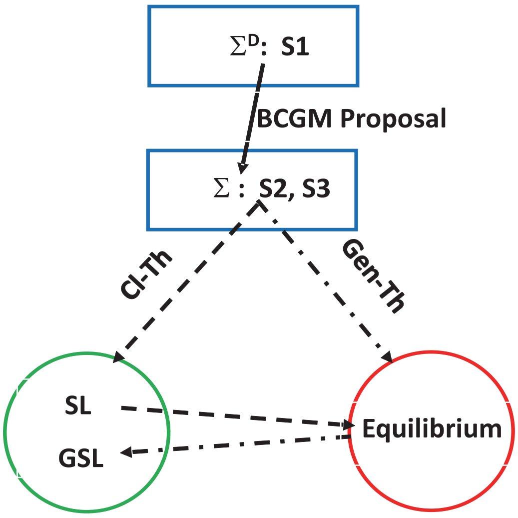

Figure 7. Reverse approaches in Cl-Th and Gen-Th by accepting S1, S2, and S3; see Sect. . In the former, one assumes the second law (SL) to justify (stable) equilibrium, usually called stability, as indicated by dashed arrows. In the latter, one assumes (stable or unstable) equilibrium to justify the generalized second law (GSL) as shown by dashed-dot arrows.. We find it useful to replace equilibrium stability by simply equilibrium, which can be stable or unstable, in Cl-Th as we wish to extend it to negative temperatures..

10. Thermodynamical Setup for Σ

10.1. *Implementing (S2)-(S3)*

In order to reveal the required conditions for SL and its violation (VSL) in Σ_{M}, we take a separate path than that taken in Cl-Th as fully illustrated in Fig. 7, and construct a *general thermodynamics* (Gen-Th) that is unconstrained by requiring SL so that it allows both SL and VSL. To also appreciate the importance of system size, we relax the macroscopic constraint required for Σ_{M}, and focus on $\overline{\Sigma}$ so that it can denote any system with any number of particles $N = 1, 2, \cdots$. We always denote a macroscopically large system by $\overline{\Sigma}_{\mathrm{M}}$ in which we *reverse* the traditional approach taken in Cl-Th as shown in Fig. 7 to reveal various conditions required for SL and VSL; see also Sect. 14.1.

As explained earlier in Sect. 7.1 and later in Sect. 14.1, implementation of the BCGM proposal to ascribe stochasticity to Σ^{D} requires the two steps (S1) and (S2).

We now elaborate on the (ensemble) averaging in (S2) as introduced in Eq. (20), which is valid for a Σ of any size; see Remark 15.

Remark 54. *Following Remark 15, we recognize that there is no restriction on the size of* $\overline{\Sigma}$ *in ensemble averages in Eq. (20) so they are valid for a system of any size, such as a coin having 2 outcomes. The ensemble for the coin consists of many trials and determines their probabilities. This also means that various versions of the first law in Sect. (10.4) are also valid for any size of* $\overline{\Sigma}$.

Let us pause for a moment to consider useful averages. The first one is related to the average of E_k in Eq. (44b) when the system is composed of two quasi-independent subsystems. The (average) energy E of the system is easily seen to be given by

$$E = N(n_1 e_1 + n_2 e_2) = Ne \tag{83}$$

in terms of average energies of the system and subsystems. For a nonuniform system, $e_1 \neq e_2$. For a uniform system, $e_1 = e_2 = e$ as expected. The next one is to consider $\xi_{\mathrm{E}k}$ introduced in Eq. (50). The corresponding ensemble average is given by

$$\xi_{\mathrm{E}} = E_1/n_1 - E_2/n_2, \tag{84a}$$

where we use the quasi-independence $p_k \simeq p_{1k_1} p_{2k_2}$, see Eq. (79), and $E_l \doteq \sum_{k_l} p_{jk_l} E_{jk_l}$, $l = 1, 2$. Thus, microstate internal variable $\boldsymbol{\xi}_k^{\mathrm{E}}$ is replaced by its average

$$\boldsymbol{\xi}^{\mathrm{E}} \doteq (\xi_{\mathrm{E}}, \boldsymbol{\xi}) \tag{84b}$$

to represent the complete set of internal variables for uniquely specifying the macrostate $\mathfrak{M}_{\mathrm{ieq}}$; compare this with $\boldsymbol{\xi}_k^{\mathrm{E}}$ in Eq. (45), which uniquely specifies $\mathfrak{m}_{\mathrm{ieq}k}$.

Conclusion 55. *The work parameter set for the macrostate* $\mathfrak{M}_{ieq}$ *is* $\mathbf{W} = (\mathbf{w}, \boldsymbol{\xi}^E)$, *while it is* $\mathbf{W}_k = (\mathbf{w}, \boldsymbol{\xi}_k^E)$ *in Eq. (47) for the microstate* $\mathfrak{m}_{ieqk}$. *The state variable* $\mathbf{Z} = (E, \mathbf{W})$ *determines the state space* $\mathfrak{S}_{\mathbf{Z}}$ *in which* $\mathfrak{M}_{ieq}$ *is uniquely specified without any explicit time dependence and is written as* $\mathfrak{M}(\mathbf{Z})$. *For a proper subset* $\boldsymbol{\xi}'^E \subset \boldsymbol{\xi}^E$ *so that we deal with a smaller state space* $\mathfrak{S}_{\mathbf{Z}'} \subset \mathfrak{S}_{\mathbf{Z}}$, $\mathfrak{M}_{ieq}$ *acquires an explicit time dependence, is identified as NIEQ state, and is expressed as* $\mathfrak{M}(\mathbf{Z}', t)$. *In the same way,* $S_{ieq} \equiv S(\mathbf{Z})$ *acquires an explicit time dependence in* $\mathfrak{S}_{\mathbf{Z}'} \subset \mathfrak{S}_{\mathbf{Z}}$, *written as* $S(\mathbf{Z}', t)$, *and represents the entropy of a NIEQ state* $\mathfrak{M}(\mathbf{Z}', t)$. *The same reasoning shows that any NEQ state, which include IEQ and NIEQ states, can be expressed as* $\mathfrak{M}(\mathbf{X}, t)$ *having its entropy written as* $S(\mathbf{X}, t)$ *in* $\mathfrak{S}_{\mathbf{X}}$.

Thus, (S2) takes us from a microstate specification to an average specification of a macrostate $\mathfrak{M}$ but without any thermodynamics such as the first and the second law. We now turn to them.

10.2. *Statistical Macrowork and Macroheat*

The discussion above for Σ^{D} is easily extended to discussing a thermodynamic system Σ associated with it by simply attaching p_k to $\mathfrak{m}_k$. This then allows us to describe an arbitrary macrostate $\mathfrak{M}_{\text{arb}}$ by considering ensemble averages over p_k. The ensemble average

$$dW \doteq \langle dW\rangle = \textstyle\sum_k p_k dW_k = -\sum_k p_k dE_k \tag{85a}$$

determines the SI-macrowork dW. We observe a very important fact of the above definition of dW. It is defined at fixed set $\{p_k\}$, which implies that the entropy S in Eq. (24) remains constant over $\delta\mathcal{P}$. This means that dW above is a purely mechanical quantity as is widely appreciated in Cl-Th; it is the negative of the energy change in an *isentropic* process. We warn the reader that in Cl-Th, one uses adiabatic process, instead of isentropic process, to determine the mechanical work. But this is valid only for an equilibrium process; see also footnote 25 and Sect. 16.8. As we are also treating NEQ processes here, we prefer to identify the isentropic process with a mechanical process.

The first law version using this SI-macrowork in Eq. (6) can be used to identify the SI-macroheat $dQ = dE + dW$, which is easily seen to be given by

$$dQ \doteq \langle dQ\rangle \equiv \textstyle\sum_k E_k dp_k = \sum_k \left(E_k \dfrac{dp_k}{p_k}\right) p_k, \tag{85b}$$

where dQ_k in $\langle dQ\rangle$ is identified (but not uniquely) by

$$dQ_k \doteq (E_k + c)\frac{dp_k}{p_k}, \tag{85c}$$

with c an arbitrary real or complex constant for the simple reason that

$$\left\langle \frac{dp}{p}\right\rangle = \textstyle\sum_k dp_k \equiv 0, \tag{86}$$

which ensures that the choice of c does not affect thermodynamics in anyway.

With the introduction of p_k to determine dW and dQ, we have a SI-specification of the first law for $\mathfrak{M}_{\text{arb}}$ of Σ, to which we now turn.

10.3. *Statistical Formulations of the First Law*

The additional steps (S3) is needed to establish the foundations of Cl-Th or Gen-Th to endow Σ with the *first law* $dE = dQ - dW$ in terms of generalized macroheat and macrowork [122, 123] that are identifying above during any infinitesimal process $\delta\mathcal{P}$ that Σ undergoes. The generalized macroheat dQ in Eq. (85b), is a stochastic quantity, see Definition 14, and the generalized macrowork dW in Eq. (85a) is a mechanical quantity. Again, (S3) has no ramification for SL so the latter is still not necessarily satisfied; see Fig. 7. It follows from the SI-macroenergy E in Eq. (21b) is valid for any $N \geq 1$ and for any arbitrary macrostate $\mathfrak{M}_{\text{arb}}$. It follows from this that

$$dE = \textstyle\sum_k E_k dp_k + \sum_k p_k dE_k. \tag{87}$$

From Eq. (41b) in Sect. 4, we observe that the second sum gives the negative of the SI-macrowork dW in Eq. (85a) as the ensemble average of SI-microwork dW_k given in Eq. (38) or ((41d)). We identify the first sum, which is $dE + dW$, with SI-macroheat dQ as the ensemble average of SI-microheat dQ_k in Eq. (85b).

Conclusion 56. *We emphasize that the above identifications of dE, dW and dQ do not require any size restriction on Σ, do not need any notion of temperature or entropy, and are valid for any arbitrary macrostate $\mathfrak{M}_{arb}$.*

We thus obtain the statement of the *first law* in Eq. (6) for Σ. This completes the step (S3). It should be clear that dQ and dW are the primary concepts in the first law and Gen-Th, making them equivalent as both are independent of SL ($dS \geq 0$). We see from Eq. (36) that $dE_k \equiv 0$ for uniform microstates so $dW \equiv 0$.

10.4. *Various Forms of the First law*

The first law in Eq. (6) is in terms of SI-macroheat and SI-macrowork. But the same law can also be expressed by exchange quantities $d_{\mathrm{e}}Q$ and $d_{\mathrm{e}}W$ in Eq. (7), and by irreversible quantities $d_{\mathrm{i}}Q$ and $d_{\mathrm{i}}W$ in Eq. (8). To do so, we first use Eq. (33) and identify

$$d_\alpha W \doteq -\textstyle\sum_k p_k d_\alpha E_k, d_\alpha Q \doteq \textstyle\sum_k p_k E_k d_\alpha \eta_k,$$

where

$$d_\alpha \eta_k \doteq d_\alpha p_k / p_k$$

for d_α denoting d, d_{e}, and d_{i}.

Recalling the arbitrariness in the definition of dQ_k in Eq. (85c), which also appears in the summands in $d_{\mathrm{e}}Q$ and $d_{\mathrm{i}}Q$, it is easily seen that

$$\textstyle\sum_k d_\alpha p_k \equiv 0.$$

It is well known that $d_{\mathrm{i}}E \equiv 0$ for the simple reason that no internal process can affect the energy of the system; it can only change due to exchanges with the medium [25]. Therefore, the partitioning $dE \equiv d_{\mathrm{e}}E + d_{\mathrm{i}}E \equiv d_{\mathrm{e}}E$ so that $dE = d_{\mathrm{e}}Q - d_{\mathrm{e}}W$ is the standard form of the first law in Cl-Th, which is identical to the one in Eq. (7) in terms of exchange quantities. In contrast, Eq. (6) is the first law for SI-quantities. Subtracting Eq. (7) from Eq. (6) and using Eq. (33), we immediately conclude that

$$d_{\mathrm{i}}E = d_{\mathrm{i}}Q - d_{\mathrm{i}}W = 0, \tag{88}$$

which is the *first law for internal processes*.

10.5. *The Irreversibility Principle*

The first law for internal processes ($d_{\mathrm{i}}E \equiv 0$) in a system Σ of any size immediately leads to the *irreversibility principle* (Irr-P) [34, 46] expressed by the identity $d_{\mathrm{i}}Q \equiv d_{\mathrm{i}}W \gtreqless 0$ that was given in Eq. (9) and that *intertwines* these seemingly unrelated macroquantities (stochastic versus deterministic) similar to intertwining of electric and magnetic fields in the Maxwell theory; see also Sect. 14.3.

While they have the same sign, their sign is not fixed yet so SL is still not necessarily satisfied. For the latter, we need to take the last step (S4) shown by the two bottom arrows in Fig. 7. By taking two different paths alone these arrows, we can either formulate NEQ Cl-Th using (S4-Cl) or a NEQ Gen-Th using (S4-Gen) for any possible $\mathfrak{M}_{\text{arb}}$; compare Eq. (9).

Equations (7) and (88) also gives rise to Eq. (9), which is called the *irreversibility principle* (Irr-P) [22] because of its basic importance in Gen-Th as it is a very surprising result in that it relates two quantities of *disparate* nature: a purely mechanical quantity $d_{\text{i}}W$ and a purely stochastic quantity $d_{\text{i}}Q$, akin to relating electric and magnetic fields in the Maxwell theory of electromagnetism during any arbitrary process including a cyclic process such as a Carnot engine.

Claim 57. *Irr-P states that internal macrowork d_iW and internal macroheat d_iQ are equal so that they are fully converted into each other, and have the same* fixed *sign during any process $\mathcal{P}$; see Definition 20. As it follows from the first law, the full conversion cannot be violated.*

Remark 58. *This claim should not be confused with the general statement in classical thermodynamics that states that (exchange) macrowork d_eW can be fully converted into exchange macroheat d_eQ but not the other way around, as is well known from the work by Carnot [13] as already discussed Sect. 8.*

From Irr-P follows three conclusions about the sign of $d_{\text{i}}Q$ and $d_{\text{i}}W$. of Irr-P above depending on the sign of the irreversible work. Either it is positive or it is negative. What is meant by irreversibility here is that it cannot change is sign in a thermodynamic process

Irr-P(+) They are both nonnegative over the entire process:

$$d_{\text{i}}W \geq 0 \Longleftrightarrow d_{\text{i}}Q \geq 0,$$

which is nothing but the *principle of dissipation*. It is this principle that is considered to be the hallmark of the second law: dissipated macrowork gives rise to internally generated macroheat [22], and has been established by considering the SI-microwork $d_{\text{i}}W_k$ and its ensemble average in Sect. 6.

Irr-P(-) They are both nonpositive over the entire process:

$$d_{\text{i}}W < 0 \Longleftrightarrow d_{\text{i}}Q < 0,$$

which is nothing but the violation of the principle of dissipation.

Irr-P(?) They both have changing but same signs over the entire process:

$$d_{\text{i}}W \gtrless 0 \Longleftrightarrow d_{\text{i}}Q \gtrless 0.$$

This is the violation of the irreversibility principle; see Definition 20.

10.6. *Gibbs Fundamental Relation in Gen-Th*

It is worth emphasizing that the entire discussion so far in this section is general and applies to any $N \geq 1$ and any macrostate $\mathfrak{M}_{\text{arb}}$ in any state space. Also, SL has not been imposed as step (S4) has not been implemented yet so we are concerned with Gen-Th. We now wish to establish that the Gibbs fundamental relation for S and E codify Gen-Th for any $\mathfrak{M}_{\text{arb}}$, and not just for $\mathfrak{M}_{\text{eq}}$ and $\mathfrak{M}_{\text{ieq}}$ as done, for example, in [35] but with (S4-Cl) imposed. Here, we will relax this imposition.

We now restrict the discussion to $\mathfrak{M}_{\text{ieq}}$ in $\mathfrak{S}_{\mathbf{Z}}$ but without imposing (S4). The entropy S_{ieq} is a state function $S(\mathbf{Z})$. In any process $\mathcal{P}$, the change in it can be expressed as the Gibbs fundamental relation for S:

$$dS = (\partial S/\partial E)dE + (\partial S/\partial \mathbf{W}) \cdot d\mathbf{W}, \tag{89a}$$

where we have separated the first term due to dE so that we can invert the above identity to express it as the Gibbs fundamental relation for E:

$$dE = (\partial E/\partial S)dS + (\partial E/\partial \mathbf{W}) \cdot d\mathbf{W}. \tag{89b}$$

The intensive partial derivatives that identify the *fields* in the above two equations are related to each other:

$$\frac{\partial E}{\partial S} = \frac{1}{\partial S/\partial E}, \frac{\partial E}{\partial \mathbf{W}} = -\frac{\partial E/\partial S}{\partial S/\partial \mathbf{W}}. \tag{90}$$

To make further progress, we consider Eq. (41a) for dE_k and take its ensemble average. We immediately recognize from Eq. (85a) that the last term in Eq. (89b) is nothing but the negative of dW. Comparison with Eq. (6) then identifies the first term as dQ.

We now consider a non-IEQ macrostate $\mathfrak{M}_{\text{nieq}}$ with $S(\mathbf{Z}', t)$ in $\mathfrak{S}_{\mathbf{Z}'} \subset \mathfrak{S}_{\mathbf{Z}}$, with missing internal variable $\boldsymbol{\xi}''$ so that we can express

$$dE = (\partial E/\partial S)dS + (\partial E/\partial \mathbf{W}') \cdot d\mathbf{W}' + (\partial E/\partial t)dt, \tag{91}$$

with the new derivatives being related as below:

$$\frac{\partial E}{\partial \mathbf{W}'} = -\frac{\partial E/\partial S}{\partial S/\partial \mathbf{W}'}, \frac{\partial E}{\partial t} = -\frac{\partial E/\partial S}{\partial S/\partial t}. \tag{92}$$

By using $\mathfrak{S}_{\mathbf{X}}$ instead of $\mathfrak{S}_{\mathbf{Z}}$ so that $\mathbf{W}'$ is identified with $\mathbf{w}$ and $\boldsymbol{\xi}''$ with $\boldsymbol{\xi}$, we replace Eq. (91) by

$$dE = (\partial E/\partial S)dS + (\partial E/\partial \mathbf{w}) \cdot d\mathbf{w} + (\partial E/\partial t)dt, \tag{93}$$

with derivatives related as in Eq. (92) but with $\mathbf{W}'$ replaced by $\mathbf{w}$.

We thus conclude that

Conclusion 59. *Eqs. (89b), (91), and (93) provide the generalization of the conventional EQ Gibbs fundamental relation for $\mathfrak{M}_{eq}$ to all possible $\mathfrak{M}_{arb}$ in all possible state spaces to justify that Gen-Th provides the most general thermodynamics. The first term in the right side of each equation is the macroheat term dQ and the rest of the terms represent the macrowork dW including the time term if present; see Eq. (42a) for dW_k.*

11. Hierarchy among Relaxation Times in the Enlarged State Spaces

We now justify the Fundamental Proposition 49 about the spontaneous evolution of an arbitrary macrostate $\mathfrak{M}_{\text{arb}}$ that is controlled by $\mathfrak{M}_{\text{eq}} = (\mathfrak{M}_{\text{seq}}, \mathfrak{M}_{\text{ueq}})$ and discuss the nature of evolution in time. For this, we classify state variables in a hierarchical manner as below. To begin with, we focus on an isolated system, whose macrostate is uniquely specified as $\mathfrak{M}_{\text{ieq}}$ in $\mathfrak{S}_{\mathbf{Z}}$ and we wish to study its evolution in time. This should not be of a concern as internal variables describe internal nonuniformity so they can be studied in an isolated system. Later, we will be considering an interacting system.

Conclusion 60. *We easily conclude from Eqs. (73), (75), and (76) that the entropy increases as the number of internal variables decreases and decreases as the latter increases. Thus, the two evolutions are in opposite directions regarding the number of internal variables. In the former, the system becomes more and more uniform and entropy increase; in the latter, it becomes more and more nonuniform and the entropy decreases.*

We now explain the physics behind the two distinct evolutions. We first focus on a stable system Σ^{s} so that $\mathfrak{M}_{\mathrm{ieq}}$ evolves into $\mathfrak{M}_{\mathrm{seq}}$ in time $t \gtrapprox t_{\mathrm{eq}}$. In IEQ states, $\boldsymbol{\xi}$ has had enough time $\tau_{\mathrm{obs}} = \tau_{\mathrm{ieq}} < \tau_{\mathrm{eq}}$ for $\mathfrak{M}_{\mathrm{ieq}}$ to emerge out of $\mathfrak{M}_{\mathrm{arb}} = \mathfrak{M}$. But for $\tau_{\mathrm{obs}} < \tau_{\mathrm{ieq}}$, the states in $\mathfrak{S}_{\mathbf{Z}}$ have not had enough time for $\mathfrak{M}_{\mathrm{ieq}}$ to emerge so that their entropy is a nonstate function, which will continue to increase if the system is left isolated until it reaches $S_{\mathrm{ieq}}(\mathbf{X}, \boldsymbol{\xi})$ and becomes a state function. The affinity $\mathbf{A}$ corresponding to $\boldsymbol{\xi}$ is nonzero in $\mathfrak{M}_{\mathrm{ieq}}$. If there were other internal variables $\boldsymbol{\xi}', \boldsymbol{\xi}'', \boldsymbol{\xi}''', \cdots$ in the system, with relaxation times $\tau', \tau'', \tau''', \cdots$, respectively, that are distinct from $\boldsymbol{\xi}$, then these must have equilibrated during τ_{ieq} so that their affinities $\mathbf{A}', \mathbf{A}'', \mathbf{A}''', \cdots$ have vanished, implying that they are no longer independent of $\mathbf{X}$ ($\mathbf{A}' = \partial S/\partial \boldsymbol{\xi}' = 0$). This means that they have *disappeared* so the entropy does not depend on them. It is clear that τ_{ieq} forms an upper bound for the relaxation times $\tau', \tau'', \tau''', \cdots$. Thus, they play no role in $\mathfrak{S}_{\mathbf{Z}}$.

When the process is carried out somewhat faster ($\tau_{\mathrm{obs}} < \tau_{\mathrm{eq}}$) than that required for obtaining $\mathfrak{M}_{\mathrm{eq}}$, then $\boldsymbol{\xi}$ has not had enough time to "equilibrate" as we have discussed earlier [45, 46] and $\mathbf{A} \neq 0$. Even if S does not depend on the inactive $\boldsymbol{\xi}', \boldsymbol{\xi}'', \boldsymbol{\xi}''', \cdots$ (which we denote by the equilibrated group $\boldsymbol{\xi}_{\mathrm{E}}$ below), we have shown by the Tool-Narayanaswamy concept of the fictive temperature [34, see Sect, 8] that $\boldsymbol{\xi}_{\mathrm{E}}$ affects the thermodynamics of the system indirectly, a fact that does not seem to have been appreciated. For the moment, we will not consider the internal variables $\boldsymbol{\xi}_{\mathrm{E}}$.

The discussion below is somewhat abstract and intricate, and requires patience on the part of the reader. The set-theoretic notation is perfectly suited for the abstract nature of the discussion. Some readers may find the set-theoretic notation cumbersome, but this is the price we must pay to make the discussion comprehensive but compact. To simplify our discussion, we *assume* that all internal variables in $\boldsymbol{\xi}$ are divided into *nonoverlapping* groups $\boldsymbol{\xi}_n$ indexed by $n = 1, 2, \cdots$. We further assume that all internal variables in $\boldsymbol{\xi}_n$ have the same relaxation time τ_n so that they equilibrate and are no longer independent of $\mathbf{X}$ for $\Delta t \gtrsim \tau_n$. The relaxation times depend strongly on $\mathbf{X}$. Let us also define $\boldsymbol{\xi}_0 = \mathbf{X}$ in order to compactify our notation below. Because of this, we can include $\boldsymbol{\xi}_0 = \mathbf{X}$ whenever we speak of internal variables from now on, unless clarity is needed.

Remark 61. *To investigate the evolution of $\boldsymbol{\xi}_0$, we need to consider an interacting system so that $\mathbf{X}(t)$ can change with time. This is what we will do below.*

The groups $\boldsymbol{\xi}_n, n = 0, 1, 2, \cdots$ are indexed by n so that τ_n's appear in a *decreasing* order (with $\tau_0 = \tau_{\mathrm{eq}}$):

$$\tau_0 > \tau_1 > \tau_2 > \cdots . \tag{94}$$

The relaxation times form a discrete set and not a continuum for simplicity. It is important that the set $\{\mathbf{W}\}$ has a finite though large number of elements for a physically sensible thermodynamic specification of the system; having an enormous number of elements will make the specification unnecessarily too complex and completely useless for thermodynamics. We now introduce the sequence of state spaces $\{\mathfrak{S}_n\}$, where $\mathfrak{S}_n, n = 0, 1, 2, \cdots$ is spanned by the *union*

$$\boldsymbol{\xi}^{(n)} \doteq \cup_{k=1}^{n} \boldsymbol{\xi}_k, n \geq 1,$$

of all $\boldsymbol{\xi}_k, k \leq n$, with relaxation times $\tau_k > \tau_{n+1}$, with $\boldsymbol{\xi}^{(0)}$ (not to be confused with $\boldsymbol{\xi}_0 = \mathbf{X}$) denoting an *empty* set, so that

$$\mathbf{Z}_n \doteq (\mathbf{X}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \cdots, \boldsymbol{\xi}_n) \equiv (\boldsymbol{\xi}_0, \boldsymbol{\xi}^{(n)}), n \geq 0.$$

Thus, $\mathfrak{S}_0 = \mathfrak{S}_{\mathbf{X}}$, formed by $\mathbf{Z}_0 = \boldsymbol{\xi}_0 = \mathbf{X}$, is relevant when $\tau_0 > \tau_{\text{obs}} > \tau_1$. Similarly, $\mathfrak{S}_1$, formed by $\mathbf{Z}_1 = (\boldsymbol{\xi}_0, \boldsymbol{\xi}^{(1)}) = (\mathbf{X}, \boldsymbol{\xi}_1)$, is relevant when $\tau_1 > \tau_{\text{obs}} > \tau_2$, and so on. It is clear from the construction that the state spaces $\mathfrak{S}_n, n = 0, 1, 2, \cdots$ are ordered with *increasing* dimensions:

$$\mathfrak{S}_0 \subset \mathfrak{S}_1 \subset \mathfrak{S}_2 \subset \cdots. \tag{95}$$

The longest relaxation time in $\mathfrak{S}_n$ is τ_0 corresponding to $\boldsymbol{\xi}_0 = \mathbf{X}$ and the shortest relaxation time is τ_n corresponding to $\boldsymbol{\xi}_n$. Any $\boldsymbol{\xi}_k, k > n$ with relaxation time shorter than τ_n need not be considered as it has already equilibrated and does not affect any state in $\mathfrak{S}_n$. We can summarize this conclusion as the following

Proposition 62. *The additional internal variable $\boldsymbol{\xi}_k$ in $\mathfrak{S}_k$ relative to $\mathfrak{S}_{k-1}$ equilibrates and plays no role (i.e., is absent by disappearing) in all smaller state spaces $\mathfrak{S}_l, l \leq k-1$ but participate in all state spaces $\mathfrak{S}_l$ larger than $\mathfrak{S}_{k-1}$, i.e., $l \geq k$.*

Proof. See the discussion above. ■

Let us consider some observation time τ_{obs} used to observe a state $\mathfrak{M}$ of an interacting system. We can always find a pair of *neighboring* state spaces $\mathfrak{S}_{n+1} \supset \mathfrak{S}_n, n \geq 0$ satisfying

$$\tau_{n+1} < \tau_{\text{obs}} < \tau_n; \tag{96}$$

the two sides define a *window* $\Delta t_n \doteq \tau_n - \tau_{n+1}$ in which τ_{obs} must lie. As $\tau_{\text{obs}} > \tau_{n+1}$, all $\boldsymbol{\xi}_k$'s, $k > n$, do not have to be considered to describe the state $\mathfrak{M}$ as they have already equilibrated (cf. the discussion of $\grave{\boldsymbol{\xi}}$ above); thus, $\mathfrak{S}_k, k > n$, play no role in describing $\mathfrak{M}$. As $\tau_{\text{obs}} < \tau_n$, we need to consider all $\boldsymbol{\xi}_k, k \leq n$ to describe $\mathfrak{M}$. We must, therefore, use $\mathfrak{S}_n$ to describe $\mathfrak{M}$ for a τ_{obs} in this window; we denote $\mathfrak{M}$ by $\mathfrak{M}(\mathbf{Z}_n)$ for clarity in this section. Among all the states in $\mathfrak{S}_n$, there are IEQ states $\mathfrak{M}_{\text{ieq}}(\mathbf{Z}_n)$ for which $S = S_{\text{ieq}}(\mathbf{Z}_n)$. This happens when $\tau_{\text{obs}} \simeq \tau_{\text{ieq}}(\mathbf{Z}_n) \leq \tau_n$, $\tau_{\text{ieq}}(\mathbf{Z}_n)$ denoting the time required for $\mathfrak{M}(\mathbf{Z}_n)$ to evolve into $\mathfrak{M}_{\text{ieq}}(\mathbf{Z}_n)$; we will also use $\tau_{\text{ieq}}^{(n)}$ or simply τ_{ieq} to denote $\tau_{\text{ieq}}(\mathbf{Z}_n)$ in $\mathfrak{S}_n$ if no confusion will arise. For $n = 0$, $\tau_{\text{ieq}}(\mathbf{Z}_0)$ simply refers to τ_{eq}. There exists IEQ states $\mathfrak{M}_{\text{ieq}}(\mathbf{Z}_n)$ in $\mathfrak{S}_n$ for which $\boldsymbol{\xi}_n$ is no longer independent of $\mathbf{X}$; for these states, $\tau_{\text{obs}} \simeq \tau_{\text{ieq}}(\mathbf{Z}_{n-1}, \boldsymbol{\xi}_n(\mathbf{X})) \equiv \tau_{\text{ieq}}(\mathbf{Z}_{n-1})$. However, $\boldsymbol{\xi}_n \to \boldsymbol{\xi}_n(\mathbf{X})$ as $t \to \tau_n$ even if $\mathfrak{M}(\mathbf{Z}_{n-1})$ in $\mathfrak{S}_{n-1}$ has not turned into $\mathfrak{M}_{\text{ieq}}(\mathbf{Z}_{n-1})$. As achieving internal equilibrium will take some additional time, we have $\tau_{\text{ieq}}(\mathbf{Z}_{n-1}) > \tau_n$. We thus conclude that (with $\tau_{\text{ieq}}^{(0)}$ representing τ_{eq})

$$\tau_{\text{ieq}}^{(n)} < \tau_{\text{ieq}}^{(n-1)}, n > 0, \tag{97}$$

which will be assumed in this work. We now consider the window

$$\tau_1 < \tau_{\text{obs}} < \tau_0. \tag{98}$$

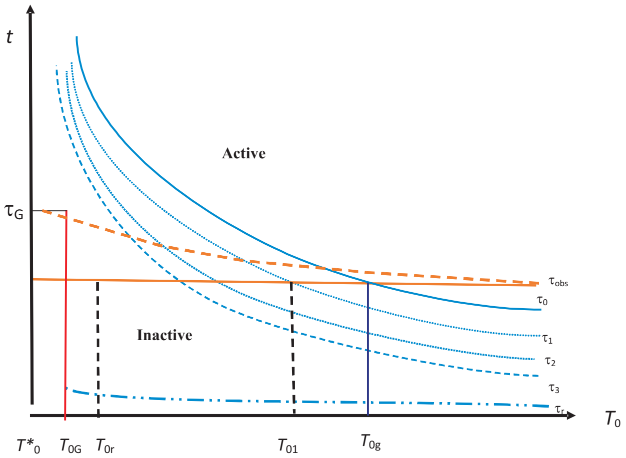

Figure 8. Schematic form of relaxation times $\{\tau_n\}$ as a function of the temperature T_0 for a fixed pressure P_0 of the medium. This figure will play an important role in the discussion of vitrification later. At low enough temperatures near $T_0^* < T_{0\text{G}}$, relaxation times become extremely large so that there is practically no relaxation over a long period of time. However at $T_0 > T_{0\text{g}}$, all internal variables have equilibrated over τ_{obs} in the figure. We have drawn τ_{obs} as a red solid horizontal line when it does not change, and as a red broken line when it increases, as T_0 is reduced.

As $\tau_0 > \tau_{\text{obs}} > \tau_1$, $\boldsymbol{\xi}_1$ has already equilibrated so it need not be considered, but $\boldsymbol{\xi}_0 = \mathbf{X}$ has not yet equilibrated. Thus, the entropy must be a function only of the observables $\mathbf{X}$, which we must write as $S_{\text{ieq}}(\mathbf{X}(t))$ as it continues to vary; see Remark 61. As $\tau_{\text{obs}} \to \tau_0$, $\mathbf{X}(t) \to \mathbf{X}_{\text{eq}}$, S_{ieq} continues to increase until it finally reaches S_{eq}; there is no explicit time dependence as *all* $\boldsymbol{\xi}_k$'s, $k > 0$, have equilibrated; see also Landau and Lifshitz [17] and Wilks [124], where NEQ states with respect to the medium are treated as IEQ states in $\mathfrak{S}_{\mathbf{X}}$. This is the most common way NEQ states in the literature are treated when internal variables are not invoked. This is only possible when τ_{obs} satisfies Eq. (98). We now consider the remaining case

$$\tau_{\text{obs}} \geq \tau_0. \tag{99}$$

This situation corresponds to the quasistatic case so that even $\boldsymbol{\xi}_0 = \mathbf{X}$ has equilibrated to $\mathbf{X}_{\text{eq}}$ and we are dealing with an EQ state

$$S = S_{\text{eq}} = S(\mathbf{X}_{\text{eq}}).$$

We know that $\{\tau_n\}$ depend on the state of the system. In vitrification that is of our primary interest in Sect. 15, they depend on the temperature T_0. It is commonly believed that τ_n's increase with decreasing T_0 as shown in Fig. 8, where we show them as a function of T_0. From this figure, we observe that for a given τ_{obs}, drawn as a solid or broken line in red, $\boldsymbol{\xi}_{\text{E}}$ correspond to the internal variables that lie in the *inactive* zone lying below τ_{obs}. (Recall that $\boldsymbol{\xi}_0 = \mathbf{X}$ is now included in internal variables.) They have all equilibrated and have disappeared. The *active* zone corresponds to internal variables that lie above τ_{obs}. They have not equilibrated and are still present. For higher temperatures ($T_0 > T_{0\text{g}}$), all internal variables are inactive. At lower temperature, some of them become active and make the system out of equilibrium. At very low temperatures, all internal variables become active for their NEQ role. We will discuss this figure further in Sec. 15.

We now come to an unstable isolated system Σ^{u}. As the evolution of $\mathfrak{M}^{\text{u}}$ runs away from $\mathfrak{M}_{\text{ueq}}$, which represents a uniform macrostate, it becomes more and more nonuniform and the entropy continues to decrease as we see in Conclusion 60.

12. NEQ Temperature T

We now introduced the operational definition of NEQ temperature, which has been one of the outstanding problems of NEQT, see Ruelle [125, for example], and which is required for the formulation of Gen-Th, the new NEQ statistical thermodynamics.

12.1. *Fundamental Clausius Identity* $dQ = TdS$

Temperature is one of the three most important stochastic concepts and its physics for $\mathfrak{M}_{\text{eq}}$ has been well understood for some time, where it is defined by the standard thermodynamic relation [17].

$$T_{\text{eq}} \doteq \partial E_{\text{eq}}/\partial S_{\text{eq}}, \tag{100}$$

its existence for NEQ $\mathfrak{M}$ has not been validated for everyone. We believe that Theorem 65 settles this dispute in a convincing manner by extending the EQ definition above to any NEQ macrostate $\mathfrak{M}$ in any state space. In this, we are motivated by Planck [116] to introduce such a T, who believed that there should exist a unifying approach to identify NEQ temperature for any system with or without memory effects. Such a temperature was apparently first introduced by Landau [126] for partial set of the degrees of freedom (dof). We have discussed this issue earlier in [32,35], where we have considered $\mathfrak{M}_{\text{ieq}}$ in $\mathfrak{S}_Z$. The discussion here is applicable to any arbitrary NEQ macrostate $\mathfrak{M}$ in any state space so the following definition is very general.

Definition 63. *We introduce the concept of NEQ temperatures* $T(\mathbf{Z})$ *in* $\mathfrak{S}_{\mathbf{Z}}$ *and* $T(\mathbf{Z}', t)$ *in in* $\mathfrak{S}_{\mathbf{Z}'}$ *by the derivatives of the relevant entropies*

$$T(\mathbf{Z}) \doteq (\partial E/\partial S)(\mathbf{Z}), T(\mathbf{Z}', t) \doteq (\partial E/\partial S)(\mathbf{Z}', t), \tag{101}$$

which are not *constrained by whether SL is satisfied or not. They can have positive and negative values.*

Claim 64. *Identifying the first term in Eq. (89b) with* dQ *has a very important consequence of introducing* T*, which relating* dQ *with* dS*; see Theorem 66 below.*

The above definition of $T(\mathbf{Z})$ should be compared with the inverse temperature definition β in Eq, (112) later in Sect. 13.2. By taking $\mathbf{Z}' = \mathbf{X}$, we also define the NEQ temperature $T(\mathbf{X}, t)$ in $\mathfrak{S}_{\mathbf{X}}$.

As noted below and discussed elsewhere [31,32,35], the above definition satisfies all the properties of a *thermodynamic temperature* we deem important; see Criterion 69. In the following, we will use $T(t)$ or simply T to denote all these thermodynamic temperatures.

Theorem 65. *All thermodynamic temperatures,* $T(\mathbf{Z})$ *in* $\mathfrak{S}_{\mathbf{Z}}$*,* $T(\mathbf{Z}', t)$ *in* $\mathfrak{S}_{\mathbf{Z}'}$*, and* $T(\mathbf{X}, t)$ *in* $\mathfrak{S}_{\mathbf{X}}$ *are identical in values:*

$$T(\mathbf{Z}) \equiv T(\mathbf{Z}', t) \equiv T(\mathbf{X}, t). \tag{102}$$

Proof. The proof follows from observing that $(\partial E/\partial S)_{\mathbf{W}}$ is the same as $(\partial E/\partial S)_{\mathbf{W}',t}$,which follows from the equality of Eq. (41e) with Eq. (43a). ■

The extension that we have defined in Definition 63 establishes the following

Theorem 66. *Definition 63 results in the* fundamental Clausius identity

$$dQ(t) = T(t)dS(t), \tag{103}$$

for any $\mathfrak{M}$ in any state space, where $T(t)$ is the properly defined NEQ temperature of the system above, $dQ(t)$ the SI macroheat, and $dS(t)$ the SI entropy change.

Proof. From the above definition of T and the identification of dQ immediately justifies the above important identity. This completes the proof. ■

Eq. (103) is the generalization of the Clausius equality in Eq. (65) to an arbitrary (reversible or irreversible) process, and has a simple heuristic justification for a macroscopic system Σ_{M}. As $dQ(t)$ and $dS(t)$ are SI extensive quantities that are stochastic in nature, they must be related linearly. The proportionality constant is the temperature $T(t)$ as its definition suggests. This thus justifies the introduction of T in the first equation in Eq. (11). The definition in Eq. (101) and Theorem 65 justifies the second equation in Eq. (11).

The classical concept of Carnot-Clausius entropy satisfies the *Clausius equality*

$$d_{\mathrm{e}}S(t) = d_{\mathrm{e}}Q(t)/T_0(t), \tag{104}$$

in terms of MI-quantities that are the instantaneous temperature $T_0(t)$ of, and the exchange quantities controlled by, the medium $\widetilde{\Sigma}$, see Fig. 1(b). In terms of SI-quantities, it is replaced by the fundamental Clausius identity in Eq. (103) in Theorem 66, which is valid for any arbitrary macrostate $\mathfrak{M}_{\mathrm{arb}}$. In NEQ macrostates $\mathfrak{M}$, irreversibility plays an important role and results in dissipation that are captured by $d_{\mathrm{i}}Q(t)$ and $d_{\mathrm{i}}S(t)$ see Eq. (33).

12.2. *Relation between T and SL*

We now discuss the relationship of this NEQ thermodynamic temperature with SL.

Conjecture 67. *The conventional SL, i.e., the inequality $d_iS \geq 0$ in Eq. (27), as a nonstrict inequality does not require any knowledge of thermodynamic SI-temperature T of the system. Therefore, the conventional wisdom [4, see, for example] is that SL must not change regardless of whether T is positive or negative; see his quote below Eq. (27).*

This explains the common belief that SL is a universal law of Nature as discussed above so that a spontaneous process with $dS < 0$ will *never* occur for any $T \gtrless 0$. We believe that this conventional wisdom has never been questioned, so we pose the following

Problem 68. *Do* positive *and* negative *temperatures both satisfy SL as is commonly believed [4, for example]?*

We wish to emphasize that negative temperatures are not physically impossible [4, 17, 127, 128] even in EQ situations, see Eq. (100), in a region where E_{eq} decreases with S_{eq} or S_{eq} decreases with E_{eq}. This definition is extended to NEQ macrostates in Eqs. (101) and (103).

As the second law is *postulated* to be part of classical thermodynamics (Cl-Th) [3, 12], we always demand or impose the constraint

$$d_{\text{i}}S \geq 0 \Longrightarrow d_{\text{i}}Q \geq 0 \tag{105}$$

in Cl-Th, see [35], so SL is satisfied in it. The inequality $d_{\text{i}}Q \geq 0$, though not obvious, has been demonstrated to hold as a consequence of SL in various publications; for example, see Theorem 4 on p. 473 in [48]. For an isolated system, Eq. (105) is replaced by

$$dS \geq 0 \Longrightarrow dQ \geq 0, \tag{106}$$

which immediately asserts this to be valid only for $T \geq 0$; however, see Eq. (17) and Ramsey's quote mentioned above.

12.3. *A No-Go Theorem for SL-Violation*

As we will see that GSL asserts that $dQ \geq 0$ for an isolated system can *never* be violated in the BCGM approach, we are forced to conclude that

$$T < 0, dS < 0 \Longrightarrow dQ \geq 0, \tag{107}$$

which contradicts Ramsey [4]. Thus, under GSL, we obtain the following No-Go Theorem [21]

$$dS \begin{cases} \quad \geq 0 \text{ for } T \geq 0; \\ dS \ngeq 0 \text{ for } T < 0, \end{cases} \tag{108}$$

so that $dS < 0$ for negative T must not be considered a violation of SL.

12.4. *A Digression on the NEQ Temperature T*

While the concept of the macrowork is quite familiar from mechanics as we have discussed in Sect. 10.2, the concept of the macroheat also discussed there is peculiar to thermodynamics in view of Eq. (103). In EQ thermodynamics, where the concepts of entropy, temperature, and macroheat are well established in EQ thermodynamics, the macroheat dQ_{eq} is directly proportional to the change dS_{eq}, and the constant of proportionality determines the EQ temperature T_{eq} in Eq. (100). A Σ in thermal equilibrium with a $\widetilde{\Sigma}$ at T_0 obviously has the same temperature T_0. The temperature for an isolated system in equilibrium is also well defined [17, for example]; its inverse is identified with the energy derivative of the *equilibrium* entropy as shown in Eq. (100). The definition is valid for *all* EQ systems, even those containing gravitational interaction. This is confirmed by the fact that Bekenstein used it to identify the temperature of an isolated black hole [129, 130]. The formulation is valid both classically and quantum mechanically [17].

The EQ definition of the temperature in $\mathfrak{S}_{\mathbf{X}}$ is formally identical as a derivative to those in Eq. (101) for any $\mathcal{M}$, which are valid in NEQT [9, 26, 31–33, 35, 45, 46, 122, 123] in various state spaces that are used to specify Σ. It is important to realize that the notion of a NEQ temperature is an absolute necessity for the *Clausius statement* of the second law that the exchanged macroheat flows spontaneously from hot to cold to be meaningful.

It is clear from the above discussion that macrowork is the isentropic change in the energy, while macroheat is the energy change due to the entropy change. This is not as surprising a statement as it appears, since a mechanical system Σ^{D} is usually thought of as a system for which the entropy concept is not meaningful as the entropy S^{D} remains constant (isentropic) in any mechanical process $\mathcal{P}^{\mathrm{D}}$. Planck [116] had already suggested that the temperature should be defined for NEQ macrostates just as the entropy should be defined for them if we need to carry out a thermodynamic investigation of a NEQ system; see also Landau [126]). This then allows the possibility that the notion of temperature can be separately applied, for example, to vibrational and configurational dof in glasses that are known to be out of equilibrium with each other [105] in that they are ascribed different temperatures. This means that macroheat would be exchanged between them until they come to equilibrium, but this is internally exchanged. But there seems to be a lot of confusion about the meaning of the entropy and temperature in NEQT [29, 39, 40, 118, 131–137, for example], where different definitions lead to different results. In contrast, the meaning of entropy and fields in equilibrium thermodynamics has no such problem.

We agree with Planck and believe that there must exist a unifying approach to identify the temperature for $\mathcal{M}_{\mathrm{arb}}$; see Definition 5, with or without memory effects in $\mathfrak{S}_{\mathbf{Z}}$. The inverse temperature defined above in Eq. (101) includes nonIEQ-macrostates in $\mathfrak{S}_{\mathbf{Z}}$ for which S is not a state function, but can be extended to them so as to accommodate memory effects as we do in [35] to which we refer the reader for full detail. Here, we basically summarize the relevant discussion in the form of

Criterion 69. *The identification of temperature in $\mathcal{M}_{arb}$ must satisfy some stringent but obvious criteria:*

C1 It must be intensive and must reduce to the temperature determined by Eq. (101) for $\mathcal{M}_{\mathrm{arb}}$ even for an isolated system.

C2 It must cover negative temperatures [4] that are commonly observed for some dof such as nuclear spins in a system. As these dof are not involved in any macroscopic motion [17, Sec. 73], there is no kinetic energy involved. Most common occurrence of a negative temperature is when the above spin dof are out of equilibrium with the other dof such as lattice vibrations in the system.

C3 It must satisfy the Clausius statement that macroheat between two objects always flows spontaneously from hot to cold for positive temperatures. When negative temperatures are considered, macroheat must flow from a system at a negative temperature to a system at a lower temperature, which may be positive or negative‘.

C4 It must be a global rather than a local property of the system so that we can differentiate hot and cold between two different systems.

The above Criterion is justified by Theorem 9 and its proof in our publication [35]. The first criterion ensures that the new temperature is an extension of the conventional notion of the temperature that is valid when the entropy is a state function. This means that the new notion of temperature is valid for any arbitrary macrostate. In addition, it must exist even for an isolated system. The second criterion ensures that our formalism includes negative temperatures that may occur in a lattice system. The third criterion ensures compliance with the second law for interacting systems. This is a very important criterion, which *every notion of temperature must satisfy*. The last criterion ensures that the temperature is associated with the entire system by enlarging the state space to always deal with a uniform system. Then Theorem 65 ensures that the same time-dependent temperature also works in the presence of missing $\boldsymbol{\xi}''$. By extension, the concept of a NEQ temperature can be also applied to different dof of a system such as a glass under the assumption that they are weakly interacting in accordance with the approach taken by Landau [126]. This results in the Tool-Narayanaswamy relation derived in [31] a while back.

Before we close this discussion, we wish to point out major differences between the NEQ temperature T in the Gen-Th and its other definitions. We first consider Cl-Th. The most important theories belonging to this class are the classical local irreversible thermodynamics [27], the rational thermodynamics [23], and the extended irreversible thermodynamics [40]. We refer the reader to [29, 40] for excellent reviews on these theories that use local densities of energy e and entropy s. They are continuum theories, and can all be classified as continuum Cl-Th to be denoted by the CCl-Th here. They differ in the choice of their state spaces. Considering the local entropy and energy densities s and e, the inverse local temperature is defined as $\partial s/\partial e$, and differs from the global temperature in Eq. (101). We have discussed the differences

1. In the Local-NEQT, each local volume element is in EQ so the local temperature is the EQ temperature of the volume element, and differs from T, which is a global temperature.

2. In the Rational-NEQT, the temperature is taken as a primitive quantity along with the entropy. Because of the memory effect, the temperature at any time depends on the entire history. Thus, it is a local analog of the global temperature of $\mathcal{M}_{\text{nieq}}$ in the Gen-Th, but the latter is defined thermodynamically.

3. In the Extended-NEQT, the fluxes are part of the state variables so the local temperature also depends on them. Assuming the total entropy to also depend on the fluxes [40, see Eq. (5.66), for example], one can identify the global analog of the temperature. However, as fluxes are MI-quantities, this temperature cannot be compared with the SI-temperature in the Gen-Th.

4. There is a recent attempt [138] to introduce another NEQ temperature by using fluctuation theorems to determine the entropy generation, which is then related to the Gouy-Stodola theorem. It is limited to an interacting Σ in a medium $\widetilde{\Sigma}$ so does not apply to an isolated system. In addition, its validity is limited to the situation when the Gouy-Stodola theorem is valid as discussed recently in [44].

13. General Thermodynamics (Gen-Th)

13.1. *Uniqueness of S_{ieq} and T*

We now discuss the importance of the concept of IEQ microstates $\mathfrak{M}_{\text{ieq}} \doteq \mathfrak{M}(\mathbf{Z})$ in $\mathfrak{S}_{\mathbf{Z}}$ with $n = n_{\text{ieq}}$, which is in many important ways similar to $\mathfrak{M}_{\text{eq}} \doteq \mathfrak{M}(\mathbf{X})$ as we now discuss. We first establish the *uniqueness* of $\mathfrak{M}_{\text{ieq}}$ and its entropy S_{ieq} in $\mathfrak{S}_{\mathbf{Z}}$ to support such a similarity. Let us assume that we divide Σ into a finite number of nonoverlapping EQ subsystems $\{\Sigma_l\}$ such that $\cup_l \Sigma_l = \Sigma$. Without loss of generality, we assume that the subsystems are not in EQ with each other (their fields are not identical) so that Σ is in a NEQ macrostate $\mathfrak{M}$. Let $\lambda_{\text{corr}}^{(l)}$ denote the correlation length of Σ_l, and we define $\lambda_{\text{corr}} = \max\left\{\lambda_{\text{corr}}^{(l)}\right\}$ to denote the maximum correlation length determining quasi-independence required for *entropy additivity* as discussed in Sect. 1.2; see Eq. (109a). For this, we need to take the linear size $\Delta l_l \gtrsim \lambda_{\text{corr}}$ of Σ_l. The EQ microstate $\mathcal{M}_{\text{eq}}^{(l)}$ of Σ_l is uniquely described in $\mathfrak{S}_{\mathbf{X}}$. The additivity of entropy gives S_{ieq} that must be a function of $\{\mathbf{X}_l\}$. Moreover, since each $\mathcal{M}_{\text{eq}}^{(l)}$ has a unique EQ entropy $S_l(\mathbf{X}_l)$, S_{ieq} also has a *unique* value

$$S_{\text{ieq}}(\{\mathbf{X}_l(t)\}) = \textstyle\sum_l S_l(\mathbf{X}_l(t)). \tag{109a}$$

Theorem 70. *S_{ieq} has the unique maximum possible value for given $\{\mathbf{X}_l\}$, just as $S_l(\mathbf{X}_l)$ has its unique possible value, the EQ value $S_{eq}^{(l)} = S_l(\mathbf{X}_l(t))$, for given $\mathbf{X}_l$.*

Proof. As each $S_l(\mathbf{X}_l)$ has the unique maximum value S_{eq} in for given $\mathbf{X}_l$ in $\mathfrak{S}_{\mathbf{X}}$, their sum in S_{ieq} above also has the maximum value for given $\{\mathbf{X}_l\}$. ■

However, we need to express S_{ieq} in $\mathfrak{S}_{\mathbf{Z}}$, which requires expressing S_{ieq} in terms of $\mathbf{X}(t) = \sum_l \mathbf{X}_l(t)$ and additional independent linear combinations $\boldsymbol{\xi}(t) = \cup_l \boldsymbol{\xi}_l(t)$ made from the set $\{\mathbf{X}_l\}$ as already discussed in Sect. 5 to ensure that $S(\mathbf{Z}(t))$ depends on the *same* number n_{ieq} of state variables as there are in $S_{\text{ieq}}(\{\mathbf{X}_l(t)\})$. This *uniquely* defines

$$S_{\text{ieq}} \doteq S(\mathbf{Z}(t)) = \textstyle\sum_l S_l(\mathbf{X}_l(t)) \tag{110}$$

in $\mathfrak{S}_{\mathbf{Z}}$ in terms of the unique values $S_l(\mathbf{X}_l(t))$. It is a mathematical identity between the two different expressions having the same value. We can also take Σ_l's to be in $\mathcal{M}_{l\text{ieq}}$'s in $\mathfrak{S}_{\mathbf{Z}_l}$'s so that $S_l(\mathbf{Z}_l(t))$ are also uniquely defined. Then, the same reasoning as above also proves the

Corollary 71.

$$S(\mathbf{Z}(t)) = \textstyle\sum_l S_l(\mathbf{Z}_l(t)) \tag{111}$$

is unique and has maximum possible value by ensuring that the number of arguments n_{ieq} are the same on both sides above.

We now prove the following central theorem on the existence of NEQ entropy for any $\mathcal{M}_{\text{ieq}}$ with n^* independent state variables.

Theorem 72. *Existence Theorem: The SI-entropy $S(\mathbf{Z}(t))$ for any $\mathcal{M}_{ieq}$ exists, is additive, and has a unique thermodynamic temperature $T_{ieq} \doteq T(\mathbf{Z})$ in Eq. (101) in $\mathfrak{S}_{\mathbf{Z}}$.*

Proof. According to the postulates of classical thermodynamics, EQ entropies exist in $\mathfrak{S}_{\mathbf{X}}$ and are continuous. Therefore, Eq. (109a) proves the existence of the entropy $S(\mathbf{Z}(t))$ for any $\mathcal{M}_{\text{ieq}}$ in the state space $\mathfrak{S}_{\mathbf{Z}}$, and is continuous. It follows from the existence of $S(\mathbf{Z}(t))$ that $\mathcal{M}_{\text{ieq}}$ has a unique thermodynamic temperature T. In addition, $S(\mathbf{Z}(t))$ is also additive as follows from Eq. (111). This proves the theorem. ■

To make S_{ieq} a *state function* for Σ_{M} in $\mathfrak{S}_{\mathbf{Z}}$ requires an important *restriction* on $\{p_k\}$, but not on $\{dp_k\}$. We now put a *particular* form of restriction on $\{p_k\} = \left\{p_k^{\text{ieq}}\right\}$ for $\mathfrak{M}$ in $\mathfrak{S}_{\mathbf{Z}}$ that ensures that S is a state function and that $\mathfrak{M}$ is identical to $\mathfrak{M}_{\text{ieq}}$. This also means that E becomes a *state function* of its S and $\mathbf{W}$ for Σ_{M}; see Sect. 10.6. Because of entropy additivity, neither is a state function for Σ_{E} in $\mathfrak{S}_{\mathbf{Z}}$.

In the state space $\mathfrak{S}_{\mathbf{Z}'} \subset \mathfrak{S}_{\mathbf{Z}}$, neither S nor E is a state function as there will be an explicit time dependence due to missing internal variable $\boldsymbol{\xi}''$; see Sect. 4.3.

13.2. Gen-Th of $\mathfrak{M}_{arb}$

In this section, we focus on $\mathcal{M}_{\text{arb}}$ in $\mathfrak{S}_{\mathbf{Z}'}$ as it changes in time with $\mathbf{Z}'(t)$ during a process $\mathcal{P}$ containing only IEQ-macrostates. However, we will suppress the suffix "ieq" in this section to simplify the notation. We let $\mathbf{w} = (V, \cdots)$ by not exhibiting other observables below; they can be easily included. Then, E is a function of $S, V, \cdots, \boldsymbol{\xi}$, and possibly t, with N held fixed. Introducing the fields, see Eq. (90),

$$\begin{aligned}
&(\partial E/\partial S) = \beta(t) \doteq T(t),\\
&(\partial E/\partial V) = -P(t), \cdots,\\
&(\partial E/\partial \xi') = -\mathbf{A}'(t),
\end{aligned} \tag{112}$$

we can write down the Gibbs fundamental relation in Eq. (93) as $dE(t) = T(t)dS(t) - dW(t)$, where

$$dW(t) = P(t)dV(t) + \cdots + \mathbf{A}'(t)\cdot d\boldsymbol{\xi}'(t) - (\partial E/\partial t)dt. \tag{113}$$

We have allowed both signs of T, which does not seem to have any connection with SL. This is not correct as we will soon see when we implement (S4-Gen). We also emphasize that T_{ieq} is the SI thermodynamic temperature of Σ, since it has been shown to satisfy all the requirements of an EQ and a NEQ thermodynamic temperature in [35], which we discuss later in this review for its importance.

Remark 73. *For any $\mathcal{M}_{arb}$, $\mathfrak{S}_{\mathbf{Z}'}$ contains $\mathfrak{S}_{\mathbf{X}}$ and other state spaces as proper subspaces that emerge during relaxation. In EQ, internal variables become superfluous as they are no longer independent after being equilibrated as discussed in Sect. 11. Thus, as $\mathcal{M}_{arb}$ relaxes towards $\mathcal{M}_{eq}$, internal variables gradually equilibrate (become nonactive) and are no longer independent of $\mathbf{X}$ so $\mathfrak{S}_{\mathbf{Z}}$ gradually reduces to $\mathfrak{S}_{\mathbf{X}}$ when complete equilibration has occurred over τ_{eq}.*

We further simplify the notation by suppressing the argument t and reexpress the Fundamental Clausius identity for $\mathcal{M}_{\text{arb}}$ in Eq. (103) as

$$dQ = T_0 d_{\text{e}}S + T_0 d_{\text{i}}S + (T - T_0)dS, \tag{114a}$$

$$dQ = d_{\text{e}}Q + T_0 d_{\text{i}}S + (T - T_0)dS, \tag{114b}$$

using the Clausius equality in Eq. (104). From this and Eq. (9), we conclude that

$$d_{\text{i}}Q = d_{\text{i}}W = \left\{ \begin{array}{l} T_0 d_{\text{i}}S + (T - T_0)dS \\ T d_{\text{i}}S + (T - T_0)d_{\text{e}}S \end{array} \right. \gtreqless 0, \tag{115}$$

which can be used to express $d_{\text{i}}S$ in terms of

$$d_{\text{i}}W \doteq (P - P_0)dV + \cdots + \mathbf{A}' \cdot d\boldsymbol{\xi}' - (\partial E/\partial t)dt \tag{116}$$

as follows

$$T_0 d_{\text{i}}S = (T_0 - T)dS + d_{\text{i}}W; \tag{117a}$$

$$T d_{\text{i}}S = (T_0 - T)d_{\text{e}}S + d_{\text{i}}W. \tag{117b}$$

But what is most remarkable about Eq. (103) is that it provides a purely *mechanical definition* of stochastic entropy change that holds in all kinds of processes in Nature. As the two terms in the right side of the above equations are of independent origin (stochastic versus mechanical), they must independently satisfy the irreversibility principle. We thus conclude that

$$(T_0 - T)dS \gtreqqless 0, (T_0 - T)d_{\rm e}S \gtreqqless 0. \tag{118}$$

In the rest of this section, we do not include the missing terms in $\mathbf{w}$ to simplify the discussion. But including them is trivial.

Enthalpy

Let us consider the enthalpy

$$H(S, V, \boldsymbol{\xi}', t|P_0) = E(S, V, \boldsymbol{\xi}', t) + P_0 V \tag{119}$$

[31,32] in terms of the external pressure P_0 of the medium. We can treat $H(S, V, \boldsymbol{\xi}|P_0)$ as an SI-quantity by treating P_0 as an external parameter. It is easy to see that

$$dH = TdS - d_{\rm i}W + VdP_0. \tag{120}$$

The above differential clearly shows that the enthalpy H is a function of $S, V, \boldsymbol{\xi}', t$ and P_0. Recall that for an EQ state, $H(S, P_0)$ is not a function of V so it is a Legendre transform of $E(S, V)$ with respect to V. In other words, $\partial H/\partial V = 0$. What we see from above that, for a NEQ states, H is not a Legendre transform of E with respect to V. This is clearly seen by evaluating

$$\partial H/\partial V = P - P_0 \neq 0,$$

as the pressure difference need not vanish in an irreversible process. Despite this, dH has no irreversible component, despite of the presence of $d_{\rm i}Q$, see Eq. (116) as we easily find that

$$dH = TdS - d_{\rm i}Q + VdP_0 = d_{\rm e}Q + VdP_0, \tag{121}$$

regardless of the number and nature of the internal variables; we have used here Eq. (9). Thus, dH contains terms on the right side that are controllable from outside the system. As such, it does not have any spontaneous or irreversible relaxation. For an isobaric process, $dP_0 = 0$ so dH reduces to

$$dH = d_{\rm e}Q \tag{122}$$

The above equality, which is well known for a reversible process, remains valid no matter how irreversible an isobaric process is. Thus, it must remain valid for not only supercooled liquids and glasses but also if SL is violated.

Gibbs Free Energy

Let us now consider the Gibbs free energy $G(S, V, \boldsymbol{\xi}', t|T_0, P_0) \doteq E(S, V, \boldsymbol{\xi}', t) - T_0 S + P_0 V$ [31,32] in terms of the external temperature T_0 and pressure P_0 of the medium. As is the case with the enthalpy, the Gibbs free energy is also not a Legendre transform of $E(S, V, \boldsymbol{\xi}', t)$ with respect to S and V. We easily find that

$$dG = -T_0 d_{\rm i}S - SdT_0 + VdP_0, \tag{123}$$

in which the first term can be identified as $d_{\rm i}G \doteq -T_0 d_{\rm i}S$ and the remainder as $d_{\rm e}G \doteq -SdT_0 + VdP_0$. At fixed T_0 and P_0, we have

$$dG = d_{\rm i}G = -T_0 d_{\rm i}S \gtreqless 0.$$

We observe that dG is controlled by the irreversibility in a NEQ system such as a glass in a medium. For positive $T_0 > 0$, the Gibbs free energy decreases during spontaneous relaxation during which $d_{\rm i}S > 0$ as will be established soon in Sect. 15.

13.3. *Elucidating Irreversibility and Dissipation by SI-First Law*

We now draw a very important distinction between the SI-version of the first law in Eq. (6) and its MI-version in Eq. (7). The latter is the one used in Cl-Th and contains only exchange quantities so it contains no information about the irreversible contributions $d_{\rm i}Q$ and $d_{\rm i}W$, even though it is applicable to any process, reversible or not. As these contributions are nonzero in an irreversible process, they can only be accounted for by including them explicitly under consideration. Therefore, irreversibility in Cl-Th is accounted for after imposing the step (S4-Cl) to include SL as a *separate law* for irreversibility. In contrast, the SI-formulation of the first law in Eq. (6) in Gen-Th allows us to directly include our generalized form of irreversibility, see Definition 20. Thus, Gen-Th has SL and its violation already built in its formulation so there is no need to impose irreversibility as a separate law. We now clarify this point.

To do so, we express Eq. (6) differently in Gen-Th to clearly show irreversible contributions by highlighting exchange or MI-contributions:

$$dE = T_0 d_{\rm e}S - d_{\rm e}W + Td_{\rm i}S + (T - T_0)d_{\rm e}S - d_{\rm i}W.$$

The first two terms on the right equals dE as seen from Eq. (7). Therefore, the last three terms must vanish, which is nothing but the general Irr-P in Eq. (9) determining the amount of dissipation, which measures the amount of lost work $W_{\rm lost}$ in a stable system but not an unstable system.

Definition 74. *The amount of dissipation D during any $\mathcal{P}$ for a system Σ of any size is given by Eq. (10).*

This measures is equivalently given by Eq. (115) for any elemental process $\delta\mathcal{P}$. In our approach, irreversibility simply means here that $d_{\rm i}W = d_{\rm i}Q$ has in general the same fixed signature throughout any $\mathcal{P}$ or $\delta\mathcal{P}$; see Definition 20. As Gen-Th does not impose SL in its framework, there is no constraint on the sign of the irreversible macrowork $d_{\rm i}W$ or macroheat $d_{\rm i}Q$. We introduce two new entropy differential contributions

$$d_{\rm i}W = Td_{\rm i}S^{\rm (w)} \gtreqless 0, Td_{\rm i}S^{\rm (h)} = (T_0 - T)d_{\rm e}S \gtreqless 0 \tag{124}$$

that are related to the macrowork irreversibility $d_{\rm i}W$ and the entropy irreversibility due to entropy (or heat) exchange, respectively. The first component is defined for any Σ but the second component is only defined for $\Sigma_{\rm M}$, in which exchange and additivity have to operate. It is easy to see that they form two complementary parts of $d_{\rm i}S$ as an identity

$$d_{\rm i}S \equiv d_{\rm i}S^{\rm (w)} + d_{\rm i}S^{\rm (h)}. \tag{125}$$

13.4. *Consequences of Gen-Th for* $dS > 0$ *and* $dS < 0$

We apply Gen-Th to a macrostate $\mathfrak{M}$ of an isolated Σ_{M} used in Example 44. We consider the results in Eq. (50), in which $\xi_{\text{E}k}$ must be replaced by its ensemble average $\xi_{\text{E}} \doteq E_1/n_1 - E_2/n_2$; the latter denotes internal macroheat exchange between the two subsystems at fixed volumes of subsystems as shown below. A simple calculation using the state function $S(E, \boldsymbol{\xi}_{\text{E}}, \xi_{\text{V}})$ and $dE = 0$ yields

$$dS = n_1 n_2[(\beta_1 - \beta_2)d\xi_{\text{E}} + (\beta_1 P_1 - \beta_2 P_2)d\xi_{\text{V}}], \tag{126}$$

where β_1, P_1, and β_2, P_2 are the inverse temperature and pressure of $\Sigma_{1\text{M}}$ and $\Sigma_{2\text{M}}$, respectively, and $\beta \doteq 1/T = n_1\beta_1 + n_2\beta_2$ is the inverse global temperature of Σ. The two terms on the right side in Eq. (126) represent entropic contributions due to the two internal variables ξ_{E} and ξ_{V} in Gen-Th; each must be nonnegative for SL or negative for its violation. In terms of $dE_1 = -dE_2$ as the macroenergy change and $dV_1 = -dV_2$ as the volume change of $\Sigma_{1\text{M}}$, we have

$$d\xi_{\text{E}} = \frac{1}{n_1 n_2}dE_1, d\xi_{\text{V}} = \frac{1}{n_1 n_2}dV_1. \tag{127}$$

We thus see that the first term in Eq. (126) is due to energy flow between the two subsystems. Using $\gamma \doteq -1/T$ introduced by Ramsey [4], whose numerical values define the "hotness" of Σ_{M} as it increases from $-\infty$ to $+\infty$ covering positive and negative temperatures, Eq. (126) becomes

$$dQ = TdS = -(\Delta\gamma/\gamma)dE_1 - (\Delta(\gamma P)/\gamma)dV_1 \tag{128}$$

for Σ_{M} in Gen-Th, where $\Delta\gamma \doteq (\gamma_2 - \gamma_1)$, and $\Delta(\gamma P) \doteq (\gamma_2 P_2 - \gamma_1 P_1)$; $\Delta\gamma > 0$ means that $\Sigma_{2\text{M}}$ is hotter than $\Sigma_{1\text{M}}$, and vice-versa. For GSL to hold, we require dS in $dQ = TdS$ to be ≥ 0 for $T > 0$ ($\gamma < 0$) and < 0 for $T < 0$ ($\gamma > 0$). For GSL violation, we require $dS < 0$ for $T > 0$ and $dS > 0$ for $T < 0$. Both situations are considered above. Let us consider just the first term above to be specific by setting $dV_1 = 0$. We consider various scenarios; (a) and (b) refer to $\mathfrak{M}^{\text{s}}$ having $T > 0$, and (c) and (d) refer to $\mathfrak{M}^{\text{u}}$ having $T < 0$. The analysis here is more extensive compared to an earlier preliminary and incomplete investigation [48], where the issue of catastrophic evaluation was first discussed.

(a) For $dQ = dW > 0$ and $T > 0$, we must have $dE_1 > 0$ for $\mathfrak{M}^{\text{s}}$ so that macroheat flows from hot to cold as expected in which it converges to $\mathfrak{M}_{\text{seq}}$ due to an *attractive* SI-macroforce $\mathbf{F}^{\text{seq}}$ pointing towards SEQ. The SI-evolution of $\mathfrak{M}^{\text{s}}$ is spontaneous due to $\mathbf{F}^{\text{seq}}$ pointing towards its sink $\mathfrak{M}_{\text{seq}}$ as seen from the blue arrows. Therefore, as expected in this case, $dS > 0$ so Cl-Th and Gen-GSL-Th remain valid. This is the most common situation.

(b) For $dQ = dW < 0$ and $T > 0$, $dE_1 < 0$ so that macroheat flows from cold to hot, and $\mathfrak{M}^{\text{s}}$ runs away from $\mathfrak{M}_{\text{seq}}$ due to some *repulsive* macroforce $\mathbf{F}^{\text{s}}_{\text{repu}}$ along green arrows, distinct from the SI-macroforce $\mathbf{F}^{\text{seq}}$, to eventually converge to $\mathfrak{M}^{\text{s}}_{\text{cata}}$ by becoming more and more nonuniform. The evolution of $\mathfrak{M}^{\text{s}}$ is not spontaneous as is in (a) and $\mathfrak{M}_{\text{seq}}$ is no longer the sink. In this case, $dS < 0$ (VSL), but we also violate GSL (Gen-GSL-Th), but the violation is because of nonspontaneous processes.

(c) For $dQ = dW > 0$ but $T < 0$ for $\mathfrak{M}^{\text{u}}$, $dE_1 < 0$ so that macroheat flows from cold to hot and Σ_{M} becomes more and more nonuniform because of the instability in it as discussed earlier. The spontaneous evolution of $\mathfrak{M}^{\rm u}$ from its source $\mathfrak{M}_{\rm ueq}$ under the *repulsive* SI-macroforce $\mathbf{F}^{\rm ueq}$ along the red arrows is catastrophic in that it converges to a catastrophic macrostate $\mathfrak{M}_{\rm cata}^{\rm u}$ corresponding to an extremely large $\iota = \iota_{\rm cats}$. In this case, $dS < 0$ so it appears that SL is violated, but GSL (Gen-GSL-Th) remains valid. However, as the process remains spontaneous, $dS < 0$ must not be considered as violating SL; GSL remains satisfied. In this scenario, $\mathfrak{m}_k^{\rm u}$ runs away from $\mathfrak{m}_{k{\rm ueq}}$ but terminates in a *catastrophe* in which $\mathfrak{m}_k^{\rm u}$ becomes extremely nonuniform.

(d) For $dQ = dW < 0$ and $T < 0$, we must have $dE_1 > 0$ so that macroheat flows from hot to cold in $\mathfrak{M}^{\rm u}$. In this case, $\mathfrak{M}^{\rm u}$ nonspontaneously converges to $\mathfrak{M}_{\rm ueq}$ due to an *attractive* macroforce $\mathbf{F}_{\rm attr}^{\rm u}$, which is distinct from the repulsive SI-macroforce $\mathbf{F}^{\rm ueq}$, with $dS > 0$ so SL seems to remain valid but not Gen-GSL-Th. As $\mathfrak{M}_{\rm ueq}$ is no longer the source for $\mathfrak{M}^{\rm u}$-evolution in the nonspontaneous process that is not covered by SL, $dS > 0$ must not be taken as validating SL; GSL fails as expected.

We analyze nonspontaneous processes (b) and (d) further. As these processes are not controlled by SL, they cannot be taken as examples of violating SL. We first consider (b). As $\mathfrak{M}^{\rm s}$ runs away from its sink $\mathfrak{M}_{\rm seq}$ to a new macrostate $\mathfrak{M}'^{\rm s}$, the latter further runs away from $\mathfrak{M}^{\rm s}$ by its $\xi_{\rm E}$ deviating further from their values in $\mathfrak{M}^{\rm s}$. Thus, we get successive macrostates $\mathfrak{M}^{(p){\rm s}}, p = 0, 1, 2, \cdots$ which run away from the sink farther and farther, during which $dS^{(p)}$ remains non-positive as p increases. Therefore, the evolution to $\mathfrak{M}_{\rm cata}^{\rm s}$ is *catastrophic* in that it makes $\Sigma_{\rm M}$ highly nonuniform due to unexplained nonsystem repelling macroforce $\mathbf{F}_{\rm repu}^{\rm s}$ that mutilates $\mathfrak{M}_{\rm seq}$. It follows from the stability of $\mathfrak{M}^{\rm s}$ considered here that $\Sigma_{1{\rm M}}$ and $\Sigma_{2{\rm M}}$ are also stable so their specific heats at constant volume are nonnegative. As $dE_1 = -dE_2 < 0$, the disparity $\Delta\gamma$ continues to increase with $\Sigma_{2{\rm M}}$ getting more hot and $\Sigma_{1{\rm M}}$ getting more cold, until $\Delta\gamma$ takes its maximum value $\Delta\gamma_{\rm cata}$ in $\mathfrak{M}_{\rm cata}^{\rm s}$. We now consider (d), where a similar discussion can also be carried out for $\mathfrak{M}^{\rm u}$ but with different conclusions. Here, $\mathfrak{M}^{\rm u}$ gets more uniform but the uniformity is not due to any SI-macroforce so the evolution is not governed by SL. It should be clear from the discussion that GSL seems to capture spontaneous processes at both positive and negative temperatures. In this sense, GSL subsumes SL. The discussion is easily extended to include the second term in Eq. (128) with same conclusions that remain consistent with Lemma 80. We now summarize our conclusions from Gen-Th.

C1 $dS > 0$ is *not* always a consequence of spontaneous processes. In (d), it is a consequence not only of negative T but also of negative dW performed by nonsystem forces that result in a nonspontaneous process. This process is not controlled by SL so $dS > 0$ has no significance of spontaneity.

C2 $dS < 0$ in (b) and (c) shows that it is *not* always a consequence of nonspontaneous processes. In (b), it is a consequence only of negative dW performed by nonsystem forces that result in a nonspontaneous process such as during the creation of internal constraints as explained by Callen [3] and below. Again, this process is not controlled by SL, while SI-macrowork $dW > 0$ or the removal of the internal constraint is controlled by SL so $dS < 0$ in (c) has no significance for SL-violation.

C3 From (a) and (c), we observe that GSL is *always* a consequence of spontaneous processes, but *fails* for nonspontaneous processes in (b) and (c).

14. Implementing (S4-Gen) in Gen-Th and GSL

The first three steps (S1), (S2), and (S3) form the common core approach in the foundation of the Cl-Th and of our newly developed Gen-Th. However, the step (S4-Gen) differs in a very important way in Gen-Th from the step (S4-Cl) taken in Cl-Th as seen in Fig. 7 in that there is reversal between the roles played by SL and EQ (stable and unstable).

14.1. *Adopting A Reverse Approach*

We first elaborate on the distinction between (S4-Cl) used Cl-Th and (S4-Gen) to be used here so that we can appreciate the importance of our new approach. These steps were introduced in Sect. 7.1. The content of Fig. 7 can be explicitly summarized by the following table

$$\begin{array}{l}\text{Cl-Th } (\Sigma_{\text{M}})\text{: (S1, S2, S3), (S4-Cl) SL}\Longrightarrow\text{Stable EQ}\\ \text{Gen-Th } (\Sigma)\text{: (S1, S2, S3), (S4-Gen) EQ}\Longrightarrow\text{GSL}\end{array} \tag{129}$$

that contrasts the two approaches. It is clear that the two steps are the reverse of each other. Our approach is to impose the principle of mechanical EQ through (S4-Gen) in order to prove GSL. It also requires considering microstates to take the statistical mechanical approach for Gen-Th for a system of any size and which can be either stable or unstable. We have already established Irr-P in Eq. (9) without using (S4-Gen). With incorporating (S4-Gen), we prove the following Claim 75 and establish GSL as a *generalization* of SL to *all* temperatures. On the other hand, in Cl-Th, SL is accepted as a law, which is then used to justify stability of the system; unstable systems are not considered. However, as SL is adopted as an axiom [3], there is no way to understand or decipher why SL should be a law of Nature. Thus, our approach is more general than that for constructing Cl-Th.

Claim 75. *We impose Mech-EQ-P in Sect. 6.2 through (S4-Gen) that was introduced in Sect. 7.1 to force the restriction on the signatures of the two components in Eq. (124), and their relationship with the SI-temperature T that can be positive or negative to justify GSL and the concept of dissipation δD as originally proposed by Thomson [115] and recently discussed in the publication [44] for spontaneous processes*

$$\delta D \doteq d_i W = T d_i S^{(w)} \geq 0, T d_i S^{(h)} = (T_0 - T) d_e S \geq 0. \tag{130}$$

Implementing (S4-Gen) allows us to establish the *generalized second law* (GSL) within Gen-Th that was presented in Eq. (13); the new law restricts the inequality in Eq. (9) as follows:

$$d_{\text{i}} W \equiv d_{\text{i}} Q \geq 0 \text{ (Gen-Th+ S4-Gen)}, \tag{131a}$$

which finally justifies Eq. (14).

Remark 76. *We find it convenient to focus on an isolated system in Fig. 1(a) to simplify our discussion so we will establish the equivalent form*

$$dQ = T dS \equiv dW \geq 0 \textit{ (Gen-Th+S4-Gen)} \tag{132}$$

of Eq. (131a) in the following. The reason is simple. When we must deal with an interacting system in a medium, see Fig. 1(b), the irreversibility appears in the system alone so $dQ_0 = d_i Q$ and $dW_0 = d_i W$ for the isolated system Σ_0.

Remark 77. *As dQ is nothing but TdS in all cases, it establishes for the first time how T becomes a central player for dissipation and physical irreversibility.*

14.2. Irreversibility Principle for an Isolated Σ

We observe that $dE = d_{\rm i}E = 0$ in Σ, see Eq. (88), so that

$$E = \textstyle\sum_k p_k(t)E_k(t) \equiv \sum_k p_k^{\rm eq}E_k^{\rm eq} = E_{\rm eq}, \tag{133}$$

where $p_k^{\rm eq}$ is the probability of $\mathfrak{m}_{k\rm eq}$ of microenergy $E_k^{\rm eq}$, and $E_{\rm eq}$ is the macroenergy of $\mathfrak{M}_{\rm eq}$. The *irreversibility principle* (Irr-P) during any $\delta\mathcal{P}$ provides the *mechanical formulation* by dW of the stochasticity inherent in the thermodynamic process through dQ.

Claim 78. *The set $\{E_k\}$ for a given system remains fixed in $\mathfrak{S}_{\mathbf{Z}}$ so the signature of dQ in Eq. (85b) can be reversed by changing $\{dp_k\}$ to $\{-dp_k\}$ for a given $\{p_k\}$. This also means that the sign of dS also reversed.*

We conclude from the above claim that the stochasticity, *i.e.*, the change $\{dp_k\}$ in dQ, see footnote 6, is strongly constrained in form for any $\mathcal{P}$ by the mechanical work dW and the first law. This constraint is the backbone of Irr-P. It is derived under steps (S1-S3) and is valid for an isolated Σ of any size. Thus, Irr-P is not an independent principle (law) in Gen-Th. We see from Eq. (36) that $dE_k \equiv 0$ for uniform microstates so E_k cannot change for the uniform Σ. Accordingly, $dW \equiv 0$. The first law then enforces that $dQ \equiv 0$. However, it is easy to see that it is not possible for the macroenergy E in Eq. (133) to remain invariant in general for all possible choices of time-dependent $p_k(t)$ and constant $\{E_k\}$ that result in a time-dependent macrostate $\mathfrak{M}$ that was introduced earlier as uniform NEQ macrostate after Definition 36. Thus,

Remark 79. *Uniform NEQ macrostates that must have time-dependent probabilities cannot satisfy energy conservation for Σ so they are irrelevant in thermodynamics. The situation can only be salvaged by allowing uncontrollable weak interactions with the outside even for the isolated system as discussed elsewhere [9] as no system is really isolated in Nature.*

The following simple example clarifies the above Remark. Consider a Σ containing two microstates with distinct microenergies E_1, E_2 and probabilities p_1, p_2, respectively. The change in the energy due to probability changes at fixed microenergies is

$$dE = (E_1 - E_2)dp_1.$$

It is easy to see that, for nonzero dp_1 for time-dependent probabilities, dE cannot vanish.

As the signature of dQ and the stochasticity is controlled by the signature of dW, we turn to the microwork done during the $\mathfrak{m}_{k\rm eq}$-controlled evolution of $\mathfrak{m}_k(t)$ along its *spontaneous* trajectory γ_k in a thermodynamic process $\mathcal{P}$ in $\mathfrak{S}_{\mathbf{X}}$. The accumulated microwork along γ_k in step (S1) follows from Eq. (39) by the microenergy change ΔE_k along γ_k. In step (S2), its ensemble average over $\mathcal{P}$ yields the SI-macrowork

$$\Delta W = \int_{\mathcal{P}} dW \equiv \textstyle\sum_k \displaystyle\int_{\gamma_k} p_k dW_k \doteq <\Delta W> \tag{134}$$

in Gen-Th; it remains valid even if p_k remains constant over γ_k. The cumulative formulation of Eq. (9) is the cumulative Irr-P

$$\Delta Q = \Delta W, \tag{135}$$

where ΔQ is given by

$$\Delta Q = \sum\nolimits_k \int\limits_{\gamma_k} p_k E_k d\eta_k, \tag{136}$$

and exists (*i.e.*, nonzero) if and only if p_k does not remain constant during $\mathcal{P}$[22].

Temporal evolution of $\mathfrak{M}(t)$ in $\mathfrak{S}_{\mathbf{X}}$ is controlled by $\mathfrak{M}_{\text{eq}}$ of energy E_{eq} and the nature of energy $E(t)$; the temporal form of $E(t) = (E^{\text{s}}(t), E^{\text{u}}(t))$ is shown by the solid blue and red curves in Fig. 4, respectively. But a better understanding of dissipation is obtained by also focusing on the evolution of microstates, whose energies $E_k^{\text{s}}(t)$ and $E_k^{\text{u}}(t)$ are shown by the dashed-dot blue and red curves in Fig. 4, respectively. The extremum points of these curves represent the equilibrium points E_{seq} and E_{ueq} for $E(t)$, and $E_{k\text{seq}}$ and $E_{k\text{ueq}}$ for $E_k(t)$, respectively. During evolution as $t \to \infty$, $E^{\text{s}}(t)$ runs towards E_{seq} along the blue arrows, and $E^{\text{u}}(t)$ runs away from E_{seq} along the red arrows. The former is the behavior of the macroenergy for a stable but NEQ macrostate, which terminates in a stable equilibrium (SEQ) macrostate $\mathfrak{M}_{\text{seq}}$ that is stationary and uniform, and is normally considered in classical thermodynamics. The latter is that of an unstable and nonuniform macrostate, which runs away from an unstable equilibrium (UEQ) macrostate $\mathfrak{M}_{\text{ueq}}$ that is uniform but is rarely considered in classical thermodynamics. Similarly, as $t \to \infty$, $E_k^{\text{s}}(t)$ runs towards $E_{k\text{seq}}$ along the blue arrows, and $E_k^{\text{u}}(t)$ runs away from $E_{k\text{ueq}}$ along the red arrows.

14.3. *Generalized Second Law (GSL)*

After imposing (S4-Gen) on Gen-Th results in a new thermodynamics that we have identified as Gen-GSL-Th for Σ, for the simple reason that (S4-Gen) leads to GSL as we now discuss. The extremum and the form of $\{E_k\}$ determine the extremum and the form of the macrowork function E_{w} for $\mathfrak{M}$ shown by continuous curves in Fig. 4. To understand this better, we consider the ensemble average $\mathbf{F} = \langle \mathbf{F} \rangle$. By definition,

$$\mathbf{F} \doteq \sum\nolimits_k p_k \mathbf{F}_{\text{w}k} = 0$$

at the extremum. As this must hold for any $\{p_k\}$, this requires that $\mathbf{F}_{\text{w}k} = 0$ for every microstate $\mathfrak{m}_k$. This thus shows that the averaging also generalizes microstate Mec-EQ-P to the *thermodynamical principle of (stability and instability) equilibrium* (Th-EQ-P) for $\mathfrak{M}$ in Gen-GSL-Th, according to which the extremum E_{eq} of E_{w} controls $\mathfrak{M}$-evolution. We must not confuse this evolution with that produced by *intervention* required to prepare nonuniform $\mathfrak{M}$ out of uniform $\mathfrak{M}_{\text{eq}}$ by internal constraints as introduced in Sect. 3.4; see also [3,77]. As $\mathfrak{m}_{k\text{ueq}}$ is, in effect, physically equivalent to a "nonexistent" microstate because of its instability, $\mathfrak{M}_{\text{ueq}}$ is also physically nonexistent[23] [59, 110]. Because of this, Cl-Th only deals

---

[22] For an interacting system Σ, we need determine $\Delta_{\text{i}} W = \int_{\mathcal{P}} d_{\text{i}} W \equiv \sum_k \int_{\gamma_k} p_k d_{\text{i}} W_k \doteq < \Delta_{\text{i}} W >$ and $\Delta_{\text{i}} Q = \sum_k \int_{\gamma_k} p_k E_k d_{\text{i}} \eta_k$ so that $\Delta_{\text{i}} Q = \Delta_{\text{i}} W$ from Irr-P.

[23] Any realistic isolated system has a boundary separating it from its exterior so it is not truly isolated from the exterior.

with $\mathfrak{M}^{\rm s}$ having the sink $\mathfrak{M}_{\rm seq}$ to which it asymptotically converges[24]. Despite this, we also consider $\mathfrak{M}^{\rm u}$ to obtain additional and surprising information at the microstate level that is not available in Cl-Th, and allows for a reformulation of SL for negative T as discussed earlier. Without (S4-Gen), Gen-Th also describes GSL-violation ($dQ = dW < 0$), see Eq. (9), and SL-violation ($dS < 0$) for Σ. We justify the emergence of GSL within Gen-Th of Σ; accordingly, we do not impose any restriction on possible $\{p_k\}$. We focus on Σ and prove the following Lemma 80 for an equilibrium point of a mechanical $\mathfrak{m}_k$ and a thermodynamic $\mathfrak{M}$.

Lemma 80. *During $\mathfrak{m}_{keq}$-controlled spontaneous evolution of $\mathfrak{m}_k$ of Σ^D in Gen-GSL-Th, $\mathfrak{m}_k$ performs* nonnegative *microwork. ΔW_k as $\mathfrak{m}_k \to \mathfrak{m}_k^{'}$. Performing ensemble average with arbitrary $\{p_k\}$ then determines thermodynamic stability (instability) of the resulting macrostate $\mathfrak{M} = (\mathfrak{M}^s, \mathfrak{M}^u)$ in Σ, which spontaneously performs* nonnegative *macrowork ΔW in Gen-GSL-Th as $\mathfrak{M} \to \mathfrak{M}^{'}$ during some spontaneous process $\mathcal{P}$. Dissipation is the nonnegative macroheat $\Delta Q = \Delta W$.*

Proof. (a) Microstate Evolution: The *extremum* of E_k at $E_{k\rm eq}$ represents $\mathfrak{m}_{k\rm eq} = (\mathfrak{m}_{k\rm seq}, \mathfrak{m}_{k\rm ueq})$ that is uniform in $\mathfrak{S}_{\mathbf{X}}$; see Uniformity Theorem 47. We now consider a nonuniform $\mathfrak{m}_k = (\mathfrak{m}_k^{\rm s}, \mathfrak{m}_k^{\rm u})$ away from $\mathfrak{m}_{k\rm eq}$ as it spontaneously evolves to $\mathfrak{m}_k^{'} = (\mathfrak{m}_k^{'\rm s}, \mathfrak{m}_k^{'\rm u})$, see red and blue arrows in Fig. 4. During this evolution, E_k spontaneously *decreases* to $E_k^{'}$ so that $\Delta E_k = -\Delta W_k \doteq E_k^{'} - E_k \leq 0$. Thus, $\mathfrak{m}_k$ performs spontaneous *nonnegative* microwork during its evolution towards $\mathfrak{m}_k^{'}$ given by Eq. (39).

(b) Macrostate Evolution: We now average over $\mathfrak{m}_k^{\rm s}$ and $\mathfrak{m}_k^{\rm u}$ using arbitrary p_k to obtain macroquantities of $\mathfrak{M}^{\rm s}$ and $\mathfrak{M}^{\rm u}$, respectively, in Gen-GSL-Th. The mechanical equilibrium microstate $\mathfrak{m}_{k\rm eq}$ determines the thermodynamic EQ macrostate $\mathfrak{M}_{\rm eq} = (\mathfrak{M}_{\rm seq}, \mathfrak{M}_{\rm ueq})$. The macroenergy $E \doteq < E >$ gives $E_{\rm eq} \doteq < E_{\rm eq} >$ for thermodynamic EQ and uniform macrostate $\mathfrak{M}_{\rm eq}$ in $\mathfrak{S}_{\mathbf{X}}$. The spontaneous process $\mathfrak{M} \to \mathfrak{M}^{'}$ results in the nonnegative spontaneous macrowork given by Eq (134). Thus, dissipated macroheat $\Delta Q = \Delta W \geq 0$. This completes the proof. ■

Remark 81. *The inequality $dW \geq 0$ is satisfied in any* spontaneous *infinitesimal process controlled by Mec-EQ-P as part of (S4-Gen). This proves Eq. (132). As a consequence, $dW < 0$ must only happen in any* nonspontaneous *infinitesimal process that violates Mec-EQ-P. The above proof only uses the behavior of E_k in Fig. 4. We recall that there is no sign restriction on ΔW_k and ΔW in Gen-Th of Σ. The fixed sign of $dW \geq 0$ in any process $\mathcal{P}$ is due to spontaneous irreversible processes [28], which according to Irr-P is dissipated or wasted as macroheat dQ to ensure unchanging E.*

We now prove the main Theorem.

Theorem 82. *We consider Σ in $\mathfrak{S}_{\mathbf{X}}$. The spontaneous $\mathfrak{M}_{eq}$-evolution of any $\mathfrak{M}$ in Gen-GSL-Th during which it either converges to the sink $\mathfrak{M}_{seq}$ for $\mathfrak{M}^s$ or runs away from the source $\mathfrak{M}_{ueq}$ for $\mathfrak{M}^u$ directly leads to GSL in Eq. (13), making it internally consistent with analytical mechanics. A violation of GSL requires $\Delta W < 0$ that cannot occur in Σ so the theorem is a No-Go Theorem for GSL violation. Emergence of $\Delta S < 0$ due to instability in the spontaneous evolution in $\mathfrak{M}^u$ is not a violation of SL because of its negative T. Violation of GSL and SL make them inconsistent with analytical mechanics and the BCGM proposal, and require forcing Σ to evolve along the opposite directions of the red and blue arrows as shown by the green arrows by manipulating the system externally.*

---

[24] For example, the behavior for the stable equilibrium is at the heart of Cahn-Hilliard equation for the energy in which the square of the gradient term is included to account for the interfacial energy due to nonuniformity, or a similar term in the Ginzburg-Landau equation.

Proof. In Gen-GSL-Th, the isolated Σ in $\mathfrak{M} \neq \mathfrak{M}_{\mathrm{eq}}$ either spontaneously relaxes as t increases to $\mathfrak{M}_{\mathrm{seq}}$ during which $dS \geq 0$ or runs off from $\mathfrak{M}_{\mathrm{ueq}}$ during which $dS \leq 0$. As $\mathfrak{M} \to \mathfrak{M}'$, we have $\Delta W \geq 0$ from Lemma 80. It then follows from Eq. (13) that the corresponding spontaneous macroheat $\Delta Q \doteq \int_{\mathfrak{M}}^{\mathfrak{M}'} TdS$ is nonnegative for any $\mathfrak{M}$ in Σ, and establishes its consistency with Mech-EQ-P of analytical mechanics. A GSL-violation requires $dQ < 0$ that can only happen if $dW < 0$ such as along the double green arrow in Fig. 4 near $\mathfrak{M}_{\mathrm{seq}}$. As this evolution violates Lemma 80, it is *nonspontaneous* and cannot occur in Σ. This makes any GSL violation *impossible* and turns the theorem into a No-Go theorem for GSL-violation as discussed in Sect. 12.3. The requirement $dQ \geq 0$ is consistent with $T \geq 0$ and $dS \geq 0$ for $\mathfrak{M}^{\mathrm{s}}$, and $T < 0$ and $dS < 0$ for $\mathfrak{M}^{\mathrm{u}}$, and justifies Eq. (17). The instability in $\mathfrak{M}^{\mathrm{u}}$ and $\Delta S < 0$ during its spontaneous evolution does not imply violating SL. It is also clear that any violation of GSL cannot occur in Σ as they are inconsistent with analytical mechanics and the BCGM proposal. This completes the proof. ■

The claims also apply to Σ_{E} and Σ_{M} in $\mathfrak{S}_{\mathbf{Z}}$ without any change. The following calculation clarifies the claims for a one-particle system in $\mathfrak{S}_{\mathbf{X}}$. We also conclude that the stochasticity $\{dp_k\}$, see Claim 78, is determined by the sign of dW and cannot be reversed without violating GSL.

14.4. *A Simple Example*

It is instructive to consider, as an example, a two-level particle as our system Σ. The entropy is $S = -p_1 \ln p_1 - p_2 \ln p_2$, where $p_1$and p_2 are the probabilities of the two levels. Then, $dS = \ln[(1-p_1)/p_1]dp_1$. The maximum of S occurs at $p_1 = p_2 = 1/2$, which represents the EQ point. For any other value of p_1, the behavior is different for $dS > 0$ and $dS < 0$. In the former case, dS brings p_1 and p_2 closer to the EQ point making it a sink, while in the latter case, $p_1$and p_2 move away from the EQ point making it a source. This is consistent with our discussion above and brings out the difference of $\mathfrak{M}^{\mathrm{s}}$ two $\mathfrak{M}^{\mathrm{u}}$ vividly. To make the example more interesting, we need to associate energies to the two level. We capture nonuniformity of the system by adding small contributions ϵ_1 and ϵ_2 to the equilibrium energies e_1 and $e_2 > e_1$, respectively, so that $E_1 = e_1 + \epsilon_1$ and $E_2 = e_2 + \epsilon_2$. We also take $p_1 = 1/2 - \delta$ and $p_2 = 1/2 + \delta$, with δ a small quantity. We keep only leading order terms. For $\epsilon_1 > 0$ and $\epsilon_2 > 0$, we are considering $\mathfrak{M}^{\mathrm{s}}$; see the blue solid curve. Along the blue arrow, we have $dW \approx (\epsilon_1 + \epsilon_2)/2$, and $dQ \approx (e_1 - e_2)\delta$. From Irr-P, we have $(e_2 - e_1)\delta + (\epsilon_1 + \epsilon_2)/2 = 0$, which is the condition for $dE = 0$, as is easily seen from equating $E_{\mathrm{eq}} = (e_1 + e_2)/2$, and $E \approx E_{\mathrm{eq}} + (e_2 - e_1)\delta + (\epsilon_1 + \epsilon_2)/2$, and $\delta < 0, dS > 0$, making the system more uniform and $T > 0$. For $\epsilon_1 < 0$ and $\epsilon_2 < 0$, we are considering $\mathfrak{M}^{\mathrm{u}}$; see the red solid curve. Along the red arrow, we again have $dW > 0$ but $dS < 0$ as system becomes more nonuniform. In both cases, $dQ > 0$ so GSL remains intact, but the behavior of $dS < 0$ shows that $T < 0$ as expected.

Our proof of GSL should be contrasted with the current situation of proving $dS \geq 0$ without ever mentioning T; one usually recourses to ad-hoc assumptions like molecular chaos or master equations [15, 90]. The real significance of our reverse approach becomes very transparent and unravels many mysteries of SL by recognizing *fluctuating* dW_k as the *primitive* mechanical concept that completely captures the stochasticity in dQ and the importance of T for SL. Their intertwining provides the basis for the famous *fluctuation-dissipation theorem* [108, 139]. To paraphrase Kubo [108], the internal relationship between the frictional force in Brownian motion resulting in dQ and the random microscopic driving forces resulting in $\{dW_k\}$ is,

> " ... in fact, a very general matter, which is manifested in the so-called fluctuation-dissipation theorem ... because both come from the same origin."

We also observe that the concepts of generalized macrowork and macroheat are very different from those considered in [140] and [141], where these concepts refer to exchange microquantities with a medium, which is absent for our isolated system Σ[25], so they vanish; see also [142–145]. Our concepts are intrinsic to Σ and are nonzero in NEQ $\mathfrak{M}$. Nevertheless, the generalized macrowork according to Irr-P is completely converted into generalized macroheat but not the other way around as our microscopic approach will justify. This makes dW the primary concept and dQ the secondary concept. To our knowledge, our reverse approach with Micro-BCGM proposal has never been used before to directly prove SL ($dS \geq 0$) for $T \geq 0$ and its extension requiring a *reformulation* $dS < 0$ for $T < 0$; the latter contradicts the conventional wisdom [4]; see his quote below Eq. (27). In addition, GSL also disproves that instability causes SL violation.

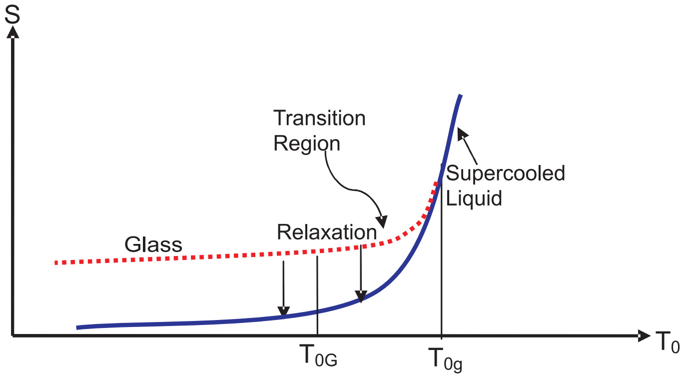

Figure 9. Schematic behavior of the entropy: equilibrated supercooled liquid (solid curve) without any relaxation and a glass (dotted curve) during vitrification as a function of the temperature T_0 of the medium. Structures appear to freeze (over an extremely long period of time) at and below $T_{0\mathrm{G}}$; see text. The transition region between $T_{0\mathrm{g}}$ and $T_{0\mathrm{G}}$ over which the liquid turns into a glass has been exaggerated to highlight the point that the glass transition is not a sharp point. For all temperatures $T_0 < T_{0\mathrm{g}}$, the glassy state undergoes isothermal (fixed T_0) structural relaxation in time towards the supercooled liquid shown by the downwards arrows. The instantaneous temperature $T(t)$ of the glass decreases towards the T_0 during relaxation, and so does the entropy during isothermal relaxation. The entropy of the supercooled liquid is shown to extrapolate to zero, but that of the glass to a positive value S_{R} at absolute zero per our assumption. The possibility of an ideal glass transition, which does not affect our conclusion, will result in a singular form of the solid curve.

15. Vitrification in Gen-GSL-Th ($T > 0$)

15.1. *Entropy Bound*

We now apply Gen-GSL-Th of the last section to the vitrification process, which is carried out at some cooling rate as follows. The discussion in this section is an elaboration and extension of what we have discussed earlier [46, 146–150] and follows the approach first used by Bestul and Chang [151] and later

---

[25] The concepts of generalized macrowork and macroheat are confused with their exchange macroanalogs in [140–142]. We postpone to discus these issues in Sect. 16.8.

by Sethna and coworkers [152]. All temperatures in this section are taken to be positive so GSL refers to the conventional SL as discussed above.

The temperature of the medium is isobarically changed by some small but fixed ΔT_0 from the current value to the new value, and we wait for (not necessarily fixed) time τ_{obs} at the new temperature to make an instantaneous measurement on the system before changing the temperature again. At some temperature $T_{0\text{g}}$, see Fig. 9, the relaxation time τ_{relax}, which continuously increases as the temperature is lowered, becomes equal to τ_{obs}. Just below $T_{0\text{g}}$, the structures are not yet frozen; they "freeze" at a lower temperature $T_{0\text{G}}$ (not too far from $T_{0\text{g}}$) to form an amorphous solid with a viscosity close to 10^{13} poise. This solid is identified as a *glass*, which we assume to be in a NEQ macrostate $\mathfrak{M}_{\text{ieq}}$ in IEQ. The location of both temperatures depends on the rate of cooling, i.e. on τ_{obs}. Over the glass transition region between $T_{0\text{G}}$ and $T_{0\text{g}}$ shown in Fig. 9, the NEQ liquid gradually turns from an EQ supercooled liquid[26] at or above $T_{0\text{g}}$ into a glass at or below $T_{0\text{G}}$, a picture already known since Tammann [106]. Over this region, some dynamical properties such as the viscosity vary continuously but very rapidly. However, thermodynamic quantities such as the volume or the enthalpy change continuously but slowly. As the observation time τ_{obs} is increased, the equilibrated supercooled liquid continues to lower temperatures before the appearance of $T_{0\text{g}}$. In the *hypothetical limit* $\tau_{\text{obs}} \to \infty$, it is believed that the equilibrated supercooled liquid will continue to lower temperatures without any interruption, and is shown schematically by the solid blue curve in Fig. 9. We overlook the possibility of the supercooled liquid ending in a spinodal [153]. It is commonly believed that this entropy will vanish at absolute zero ($S_{\text{SCL}}(0) \equiv 0$), as shown in the figure[27]. As we are going to be interested in $S_{\text{SCL}}(T_0)$ over $(0, T_{0\text{g}})$, we must also acknowledge the possibility of an ideal glass transition in the system. If one believes in an ideal glass transition, then there would be a singularity in $S_{\text{SCL}}(T_0)$ at some positive temperature $T_{\text{K}} < T_{0\text{G}}$, below which the system will turn into an ideal glass whose entropy will also vanish at absolute zero [106]. The possibility of an ideal glass transition, which has been discussed in a recent review elsewhere [121], will not be discussed further in this work. All that will be relevant in our discussion here is the fact that the entropy vanishes in both situations ($S_{\text{SCL}}(0) \equiv 0$). However, it should be emphasized that the actual value of $S_{\text{SCL}}(0)$ has no relevance for the theorems we derive below.

It is a common practice to think of the glass transition to occur at a point that lies between $T_{0\text{g}}$ and $T_{0\text{G}}$. We have drawn entropy curves (Glass and SCL) in Fig. 9 for a process of vitrification in a cooling experiment. The entropy curves $S_{\text{g}}(T_0, t)$ for Glass emerges out of $S_{\text{SCL}}(T_0)$ at $T_{0\text{g}}$ for a given τ_{obs} in such a way that it lies above that of SCL for all $T_{0\text{g}} > T_0 \geq 0$. At any nonzero temperature T_0, $S(T_0, t)$ approach $S_{\text{SCL}}(T_0)$ from above during *isothermal (fixed temperature of the medium) relaxation*; see the two downward vertical arrows.

The concept of internal equilibrium is also a common practice now-a-days for glasses [106, 107]. Employing the concept of internal equilibrium provides us with an instantaneous Gibbs fundamental relation, see Eq. (89b), which determines instantaneous temperature, pressure, etc. of the system; see footnote 27.

---

[26] The supercooled liquid (SCL) is in a metastable macrostate so it has higher entropy relative to the crystaline EQ macrostate. It si customary to assume SCL to have extremely long lifetime so it is also described as a macrostate that is uniqly desribed in $\mathfrak{S}_{\mathbf{X}}$, jus as the crystal.

[27] The arguments of entropies in this section are the temperaure of the medium and possibly time t, State variables are not shown, but we asssume the macrostate of the glass to be $\mathfrak{M}_{\text{ieq}}$ in $\mathfrak{S}_{\mathbf{Z}}$ as noted above.

We now prove the entropy bounds

$$S_{\mathrm{R}} \equiv S(0) > S_{\mathrm{expt}}(0) > S_{\mathrm{SCL}}(0). \tag{137}$$

in the form of Theorems 83 and 84. We will only consider isobaric cooling (we will not explicitly exhibit the pressure in this section), which is the most important situation for glasses. The process is carried out along some path from an initial state $\mathfrak{M}_{\mathrm{ieqA}}$ at temperature $T_{0\mathrm{A}}$ in the supercooled liquid state which is still higher than $T_{0\mathrm{g}}$ to the state $\mathfrak{M}_{\mathrm{ieqA0}}$ at absolute zero; the latter depends on the path $\mathfrak{M}_{\mathrm{ieqA}} \to \mathfrak{M}_{\mathrm{ieqA0}}$, which is implicit in the following [28]. The change dS between two neighboring macrostates on such a path is [26–28, 31–33]

$$dS(t) = -d_{\mathrm{e}}Q(t)/T_0 + d_{\mathrm{i}}S \equiv C_P dT_0/T_0 + d_{\mathrm{i}}S; \tag{138}$$

here, $d_{\mathrm{e}}Q(t)$ represents the macroheat exchange by the glass to the medium at time t whose temperature at that instant is T_0, and $d_{\mathrm{i}}S > 0$ represents the irreversible entropy generation in the irreversible process of spontaneous relaxation. In general, it contains, in addition to the contribution from the irreversible heat transfer with the medium, contributions from all sorts of viscous dissipation going on *within* the system and normally require the use of internal variables [26–28, 31, 32]. The strict inequality $d_{\mathrm{i}}S > 0$ occurs only for a physically realistic irreversible process such as in a glass; see Remark 81.

Theorem 83. *The experimentally observed (extrapolated) non-zero entropy $S_{expt}(0)$ at absolute zero in a vitrification process is a* strict lower bound of the residual entropy *of any system:*

$$S_R \equiv S(0) > S_{expt}(0).$$

Proof. We have along $\mathfrak{M}_{\mathrm{ieqA}} \to \mathfrak{M}_{\mathrm{ieqA0}}$

$$S(0) = S(T_0) + \int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{e}}S + \int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{i}}S, \tag{139}$$

where we have assumed that there is no latent heat in the vitrification process. The first integral is easily determined experimentally since it is expressible in terms of the exchange heat

$$\int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{e}}S = -\int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{e}}Q/T_0.$$

The second integral is always *positive*, but almost impossible to measure, see Eq. (117a), which is

$$\int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{i}}S = \int_{\mathrm{A}}^{\mathrm{A}_0} [\{T_0 - T(t)\}\, dS(t) + d_{\mathrm{i}}W(t)]/T_0 > 0. \tag{140}$$

It involves knowing SI-temperaure, SI-pressure and SI-fugacity of the glass, which is not easily measurable. Since the residual entropy S_{R} is, by definition, the entropy $S(0)$ at absolute zero, we obtain the important result, see Eq. (138),

$$S_{\mathrm{R}} \equiv S(0) > S_{\mathrm{expt}}(0) \doteq S(T_{0\mathrm{A}}) + \int_{T_{0\mathrm{A}}}^{0} C_P dT_0/T_0. \tag{141}$$

This proves Theorem 83. ■

---

[28] In the following, we will simply use A and A_0 in place of $\mathfrak{M}_{\mathrm{ieqA}}$ and $\mathfrak{M}_{\mathrm{ieqA0}}$, respectively, to simplify notaion if formulas.

The irreversibility during vitrification does not allow for the determination of the entropy exactly, because evaluating the integral in Eq. (140) is not feasible [32, 106]. The forward inequality

$$S_{\mathrm{R}} - S_{\mathrm{expt}}(0) = \int_{\mathrm{A}}^{\mathrm{A}_0} d_{\mathrm{i}}S > 0$$

is due to the irreversible entropy generation from all possible sources [26–28, 31–33]. The inequality is made strict as we are treating the NEQ glass with $\tau_{\mathrm{obs}} < \tau_{\mathrm{relax}}(T_0)$ and clearly establishes that the residual entropy at absolute zero must be strictly larger than the "experimentally or calorimetrically measured" $S_{\mathrm{expt}}(0)$.

Theorem 84. *The calorimetrically measured (extrapolated) entropy during processes that occur when* $\tau_{obs} < \tau_{relax}(T_0)$ *for any* $T_0 < T_{0g}$ *is larger than the hypothetical supercooled liquid entropy at absolutely zero*

$$S_{expt}(0) > S_{SCL}(0).$$

Proof. Let $\dot{Q}_{\mathrm{e}}(t) \equiv d_{\mathrm{e}}Q(t)/dt$ be the rate of net heat loss by the system during $\tau_{\mathrm{obs}} < \tau_{\mathrm{relax}}(T_0)$ as it relaxes isothermally at some fixed T_0. For each temperature interval $dT_0 < 0$ below $T_{0\mathrm{g}}$, we have

$$\begin{aligned} |d_{\mathrm{e}}Q| &= \int_0^{\tau_{\mathrm{obs}}} \left|\dot{Q}_{\mathrm{e}}\right| dt < |\Delta_{\mathrm{e}}Q|_{\mathrm{eq}T_0} \\ &\doteq \int_0^{\tau_{\mathrm{relax}}(T_0)} \left|\dot{Q}_{\mathrm{e}}\right| dt,\ T_0 < T_{0\mathrm{g}} \end{aligned}$$

where $|\Delta_{\mathrm{e}}Q|_{\mathrm{eq}T_0} > 0$ denotes the net heat loss by the system to come to equilibrium, i.e. become supercooled liquid during cooling at T_0. For $T_0 \geq T_{0\mathrm{g}}$, $dQ \equiv dQ_{\mathrm{eq}}(T_0) \doteq C_{P,\mathrm{eq}}dT_0$. Thus, the entropy loss observed experimentally with $\tau_{\mathrm{obs}} < \tau_{\mathrm{relax}}(T_0)$ is less than the entropy loss if the system is allowed to come to SCL at each temperature T_0. We thus conclude that

$$S_{\mathrm{expt}}(0) > S_{\mathrm{SCL}}(0). \tag{142}$$

This proves Theorem 84. ■

The strict inequality above is the result of the fact that glass is in a NEQ macrostate $\mathfrak{M}_{\mathrm{ieq}}$ in the proper state space $\mathfrak{S}_{\mathbf{Z}}$.

The difference $S_{\mathrm{R}}-$ $S_{\mathrm{expt}}(0)$ would be larger, more irreversible the process is. The quantity $S_{\mathrm{expt}}(0)$ can be determined calorimetrically by performing a cooling experiment. We take $T_{0\mathrm{A}}$ to be the melting temperature $T_{0\mathrm{M}}$, and uniquely determine the entropy of the supercooled liquid at $T_{0\mathrm{M}}$ by adding the entropy of melting to the crystal entropy $S_{\mathrm{CR}}(T_{0\mathrm{M}})$ at $T_{0\mathrm{M}}$. The latter is obtained in a unique manner by integration along a reversible path from $T_0 = 0$ to $T_0 = T_{0\mathrm{M}}$:

$$S_{\mathrm{CR}}(T_{0\mathrm{M}}) = S_{\mathrm{CR}}(0) + \int_0^{T_{0\mathrm{M}}} C_{P,\mathrm{CR}}dT_0/T_0,$$

here, $S_{\mathrm{CR}}(0)$ is the entropy of the crystal at absolute zero, which is traditionally taken to be zero in accordance with the third law, and $C_{P,\mathrm{CR}}(T_0)$ is the isobaric heat capacity of the crystal. This then uniquely determines the entropy of the liquid to be used in the right hand side in Eq. (141). We will assume that $S_{\mathrm{CR}}(0) = 0$. Thus, an experimental determination of $S_{\mathrm{expt}}(0)$ is required to give the *lower bound* to the residual entropy in Eq. (137). Experimental evidence for a non-zero value of $S_{\text{expt}}(0)$ is abundant as discussed by several authors; see for example the textbooks [106, 107]. However, Eq. (142) gives a mathematical justification of $S_{\text{expt}}(0) > 0$. The strict inequality proves immediately that the residual entropy *cannot* vanish for glasses, which justifies the curve Glass in Fig. 9.

By considering the state A_0 above to be a state A_0 of the glass in a medium at some arbitrary temperature T_0' below $T_{0\mathrm{g}}$, we can get a generalization of Eq. (141):

$$S(T_0') > S_{\text{expt}}(T_0') \doteq S(T_0) + \int_{T_0}^{T_0'} C_P dT_0/T_0. \tag{143}$$

We again wish to remind the reader that all quantities depend on the path $\mathrm{A}\to\mathrm{A}_0$, which we have not exhibited. By replacing T_0 by the melting temperature $T_{0\mathrm{M}}$ and T_0' by T_0, and adding the entropy $\widetilde{S}(T_{0\mathrm{M}})$ of the medium on both sides in the above inequality, and rearranging terms, we obtain (with $S_{\mathrm{L}}(T_{0\mathrm{M}}) = S_{\mathrm{SCL}}(T_{0\mathrm{M}})$ for the liquid)

$$S_{\mathrm{L}}(T_{0\mathrm{M}}) + \widetilde{S}(T_{0\mathrm{M}}) \leq S(T_0) + \widetilde{S}(T_{0\mathrm{M}}) - \int_{T_{0\mathrm{M}}}^{T_0} C_P dT_0/T_0, \tag{144}$$

where we have also included the equality for a reversible process. This provides us with an independent derivation of the inequality given in Langer and Sethna [152].

It is also clear from the derivation of Eq. (142) that the inequality can be generalized to any temperature $T_0 < T_{0\mathrm{g}}$ with the result

$$S_{\text{expt}}(T_0) > S_{\mathrm{SCL}}(T_0), \tag{145}$$

with $S_{\text{expt}}(T_0) \to S_{\mathrm{SCL}}(T_0)$ as $T_0 \to T_{0\mathrm{g}}$ from below.

While we have only demonstrated the forward inequality, the excess $S_{\mathrm{R}} - S_{\text{expt}}(0)$ can be computed in NEQ thermodynamics [26–28, 31, 32], which provides a clear prescription for calculating the irreversible entropy generation. The calculation will, of course, be system-dependent and will require detailed information. Gutzow and Scmelzer [107] provide such a procedure with a single internal variable but under the assumption of equal temperature and pressure for the glass and the medium. However, while they comment that $d_{\mathrm{i}}S \geq 0$ whose evaluation requires system-dependent properties, their main interest is to only show that it is negligible compared to $d_{\mathrm{e}}S$.

We have proved Theorems 83 and 84 by considering only the system without paying any attention to the medium. For Theorem 83, we require the second law. This is also true of Eq. (143). The proof of Theorem 84 requires the constraint $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$ for any $T_0 < T_{0\mathrm{g}}$, which leads to a NEQ state. The same is also true of Eq. (145).

We have focused on the system in this section. This does not mean that the conclusion would be any different had we brought the medium into our discussion. This is seen from the derivation of the inequality in Eq. (144) from Eq. (143).

15.2. *Isothermal Relaxation*

We wish to consider *isothermal* relaxation in a cooling experiment carried out isobarically at a fixed pressure P_0 of $\widetilde{\Sigma}'$, in which the system is in equilibrium at its temperature T_0'. We change to a different medium $\widetilde{\Sigma}$ at $T_0 < T_0', P_0$ and bring Σ in its contact. Initially, the temperature $T\,(0)$ of Σ is $T\,(0) = T_0' > T_0$ so it is out of equilibrium with the new medium and its temperature $T(t)$ will strive to get closer to T_0 as we wait for Σ to come to equilibrium with $\widetilde{\Sigma}$:

$$T(t) > T_0 \tag{146}$$

during relaxation.

The initial entropy $S(T_0, 0) = S_{\text{SCL}}(T_0') > S_{\text{SCL}}(T_0)$. If the system is now allowed to equilibrate, it will undergo spontaneous (isothermal) relaxation at fixed T_0 so that $S(T_0, t) \to S_{\text{SCL}}(T_0)$ in time. Thus, the entropy of the glass is supposed to decrease. This is what we expect intuitively as the arrows show in Fig. 9. We now wish to consider such a relaxation and determine the behavior of thermodynamic functions such as the entropy, enthalpy, etc. using IEQ thermodynamically we have introduced above. We prove two additional theorems in this section. The theorems are general even though we have in mind NEQ states including glasses obtained under the condition $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$ for any $T_0 < T_{0\text{g}}$. We consider the system to be in internal equilibrium with temperature $T(t)$, pressure $P(t)$, etc. We remind the reader that all processes that go on within the medium occur at constant temperature T_0, pressure P_0, etc. Thus, there will not be any irreversible process going on within the medium. All irreversible processes will go on within the system.

We will exploit below the *strict* inequalities in Eq. (140) to derive a bound on the rate of entropy variation. For a system out of equilibrium, the instantaneous entropy $S(t)$ and volume $V(t)$ seem to play the role [31] of "internal variables," whose "affinities" are given by the corresponding thermodynamic forces $T_0 - T(t)$ and $P(t) - P_0$, respectively. This fact is not commonly appreciated in the glass literature to the best of our knowledge. Even during an isobaric vitrification, there is no fundamental reason to assume that the pressure P of the system is always equal to the external pressure P_0. However, it is a common practice to assume the two to be the same, which may not be a poor approximation in most cases. We will not generally make such an approximation in this work.

We now state Theorem 85.

Theorem 85. *The entropy of a glass reaches that of the supercooled liquid from above during relaxation at fixed* T_0, P_0 *of the mediums. Thus,*

$$S > S_{SCL},$$

so that the entropy variation in time has a unique direction as shown by the downward arrows *in Fig. 9.*

Proof. It follows from the relaxation (fixed T_0, P_0) of any NEQ macrostate from $T > T_0$ to T_0,

$$dS(t)/dt < 0 \tag{147a}$$

due to stability (nonnegative heat capacity;)the inequality turns into an equality once equilibrium is reached. In other words, during relaxation,

$$S(T_0, P_0, t) \to S^{+}_{\text{SCL}}(T_0, P_0); \tag{147b}$$

the plus symbol is again to indicate that the glass entropy reaches $S_{\text{SCL}}(T_0, P_0)$ from above. This completes the proof of Theorem 85. ■

The above discussion justifies the claim by Goldstein [154] for the reality of the residual entropy, which was to rebut the claim by Kievelson and Reiss [155]. Any theory, such as the one proposed in [155–158] and known as the *entropy loss view* of the glass transition, in which $S(T_0, P_0, t)$ drops below $S_{\mathrm{SCL}}(T_0, P_0)$ so that

$$S(T_0, t) \leq S_{\mathrm{SCL}}(T_0). \tag{148}$$

In this case, during relaxation, $dS(t) > 0$ so that $(T_0 - T(t))dS(t) < 0$ in direct conflict with the nonnegative contribution in Eq. (118), a consequence of the second law. Such a theory then violates the second law as first pointed out by Goldstein [154].

We now prove the following theorem [34]:

Theorem 86. *For a glass, we must have $H(T_0, P_0, t) > H_{SCL}(T_0, P_0)$ at all $T_0 < T_{0g}$, where $S > S_{SCL}$.*

Proof. According to Eqs. (146) and (130), we conclude that $d_{\mathrm{e}}Q = T_0\, d_{\mathrm{e}}S < 0$ [cf. Eq. (138)] while relaxation is going on and vanishes as $T(t) \to T_0^+$. It then follows from Eq. (122) that

$$dH(t)/dt \leq 0, \tag{149}$$

a result that is consistent with experimental observations [105]. This completes the proof of the theorem.

It follows from the behavior of the Gibbs free energy $G(t) = H(t) - T_0 S(t)$ during relaxation $(dG(t)/dt \leq 0)$ that $dH \leq T_0\, dS$ in an isothermal relaxation, *i.e.*,

$$|dH(t)/dt| \geq T_0\, |dS(t)/dt| \tag{150a}$$

and

$$H(T_0) - H_{\mathrm{SCL}}(T_0) \geq T_0[S(T_0) - S_{\mathrm{SCL}}(T_0)]; T_0 < T_{0\mathrm{g}}, \tag{150b}$$

The equality holds at $T_0 = T_{0\mathrm{g}}$.

From Eqs. (120) and (130), we also have

$$|dH(t)/dt| \geq T\, |dS(t)/dt|\,. \tag{150c}$$

The last bound is tighter than the bound in Eq. (150a) and reduces to the equality obtained earlier [31] where $\boldsymbol{\xi}$ was neglected. This equality there was used to infer Eq. (147a). We have just established that the conclusion remains unaltered even if we consider internal variables. ■

In summary, the isothermal relaxation originates from the tendency of the glass to come to thermal equilibrium during which its temperature $T(t)$ approaches T_0 from above in time. The relaxation process results in the lowering of the corresponding Gibbs free energy in time, as expected due to the second law. But it also results in the lowering of the corresponding entropy as shown in Fig. 9, and the enthalpy during vitrification; the latter is observed experimentally [105]. These issues have been discussed by us in a separate publication [159].

16. Summary and Discussion

We are ready to summarize our novel approach to understand irreversibility, conditions required for the validity of SL, and its violation by following the BCGM proposal and focusing on an isolated system. As a consequence of this approach, we obtain a generalization GSL of the second law, which is valid for a system of any size. We also highlight our findings and discuss their tantalizing consequences.

16.1. *Operational Defnition of Internal Variables and $\mathfrak{S}_{\mathbf{Z}}$*

The concepts of uniform and nonuniform Hamiltonians are introduced for the first time in the field of NEQT. They prove very useful to operationally and uniquely identify internal variables, both mechanically and thermodynamically, to specify the extended state space $\mathfrak{S}_{\mathbf{Z}}$, in which $\mathfrak{m}_{k\mathrm{ieq}}$ and $\mathfrak{M}_{\mathrm{ieq}}$ with no explicit time dependence are defined. Our approach is distinct from the ad hoc and phenomenological uses of internal variables in prior approaches [23–33, 106, 107]. In a state space $\mathfrak{S}_{\mathbf{Z}'}$ where internal variable $\boldsymbol{\xi}''$ is missing, we are also able to consider time dependent $\mathfrak{m}_k(t)$ and $\mathfrak{M}(t)$. We are able to formulate a generalized NEQ thermodynamics (Gen-Th), which is not incumbered by SL so that we deal with any process satisfying SL and VSL. Gen-Th is codified by generalized Gibbs fundamental relations discussed in Sect. 10.6. Imposing SL on Gen-Th and applying it to $\mathfrak{M}_{\mathrm{ieq}}$ results in the macroscopic NEQT, Gen-GSL-Th, that is fully discussed in [35] earlier so we have not visited it here. Rather, we have expanded the discussion to any arbitrary macrostate $\mathfrak{M}_{\mathrm{arb}}$ in Sect. 13.2. As Gen-Th is formulated by taking into consideration microstates, it also is a formulation of the corresponding statistical thermodynamics Gen-STh by identifying statistical specification of macroworks $d_\alpha W$ and macroheats $d_\alpha Q$, $d_\alpha = d.d_{\mathrm{e}}$, and d_{i}, in Sect. 10.4, and microstate evolution in Sect.

16.2. *NEQ Entropy and Temperature*

Two of the outstanding unsolved problems in NEQT have been to uniquely identify NEQ entropy S and temperature T. As reviewed here, there are competing schools of thought about both issues. We believe that we have finally unambiguously resolved both issues for any arbitrary macrostate $\mathfrak{M}_{\mathrm{arb}}$. Regarding the entropy, we have first identified S_{ieq} for Σ_{M} uniquely, see Sect. 13.1 by considering a collection of subsystems Σ_l, each in its own EQ macrostate, and using entropy additivity in Eq. (109a) to establish the uniqueness of S_{ieq}, which shares many of the properties of S_{eq} known from EQ thermodynamics. Then the definition of $T_{\mathrm{ieq}} \doteq T(\mathbf{Z})$ in Eq. (101) shows that it is the time-independent and unique thermodynamic temperature of $\mathfrak{M}_{\mathrm{ieq}}$. A similar definition of time-dependent temperature $T(\mathbf{Z}', t)$, similar to $T(\mathbf{X}, t)$, in the same equation is also a thermodynamic temperature, and their equality is established by Theorem 65 in Sect. 12.

However, SL is introduced in terms of dS in Cl-Th as a law independent of the first law, with temperature playing no role. Therefore, SL is erroneously assumed to hold for both positive and negative temperatures; see for example [4]. We avoid this limitation by formulating GSL, see Eq. (13), in terms of dQ and not dS for an isolated system. The use of the fundamental Clausius identity in Eq. (103) allows GSL to be expressed in terms of dS, but T remains an integral part of GSL. Our earlier work [21, 22] establishes that stable macrostates $\mathfrak{M}^{\mathrm{s}}$ correspond to $T \geq 0, dS \geq 0$, and unstable macrostates $\mathfrak{M}^{\mathrm{u}}$ correspond to $T < 0, dS < 0$. In both cases, $dQ \geq 0$ so GSL is not violated.

16.3. *Stability and Instability*

What causes the convergence for $\mathfrak{M}^{\mathrm{s}}$ is not understood theoretically in Cl-Th as mentioned above, where the traditional approach is to postulate the existence of $\mathfrak{M}_{\mathrm{seq}}$ in the state space of Σ_{M}, postulate SL in the form of entropy maximum principle [3, see for example, Chap. 4], and then prove thermodynamic stability [17] by following $\mathfrak{M}^{\mathrm{s}}$-evolution ($\mathfrak{M}^{\mathrm{s}} \to \mathfrak{M}_{\mathrm{seq}}$ as $t \to \infty$) described above. However, $\mathfrak{M}^{\mathrm{u}}$-

evolution is never considered in Cl-Th, which we overcome in this study. As SL results in stability, a SL-violation strongly suggests, but not yet verified, thermodynamic *instability* for its cause. However, our conclusion contradicts this scenario. so we also consider rarely studied unstable macrostate $\mathfrak{M}^{\mathrm{u}}$ *emerging* out of $\mathfrak{M}_{\mathrm{ueq}}$ along red arrows; however, see [4] as exception. All arrows in Fig. 1 point towards *increasing* time t, during which we need to investigate the behavior of entropy (increasing or decreasing) as $\mathfrak{M}^{\mathrm{s}}$ or $\mathfrak{M}^{\mathrm{u}}$ becomes less or more nonuniform. This will allow us to identify the conditions required for SL and VSL in the isolated system Σ, which is our main goal.

16.4. *Reverse Approach, Mec-EQ-P, and Irreversibility*

We introduced the thermodynamical principle of (stability and instability) equilibrium (Th-EQ-P) in Sect. 14.3 from ensemble averaging the mechanical equilibrium principle of energy (Mec-EQ-P) over microstates that is introduced and discussed in Sect. 6. For $\mathfrak{M}^{\mathrm{s}}$, Th-EQ-P is a consequence of SL that is accepted as an axiom [3, for example] in Cl-Th for Σ_{M} as is well known. We do not follow this route as our focus is to look deeper at the root cause of SL. Instead, by taking the reverse approach, see Eq. (129), we prove not only Th-EQ-P for $\mathfrak{M}^{\mathrm{s}}$ and $\mathfrak{M}^{\mathrm{u}}$ but also GSL ($dQ = dW \geq 0$ in Eq. (13)) for Σ by imposing (S4-GSL), *i.e.*, Mec-EQ-P, of analytic mechanics in Gen-GSL-Th; see Fig. 7 also. GSL turns out to be a consequence of analytical mechanics and the first law. It is not a different law as is commonly thought of SL in Cl-Th. This shows the strength of our reverse approach. As $\mathfrak{m}_k^{\mathrm{s}}$ and $\mathfrak{M}^{\mathrm{s}}$ asymptotically converge to $\mathfrak{m}_{k\mathrm{seq}}$ and $\mathfrak{M}_{\mathrm{seq}}$, respectively, by removing nonuniformity gradually, $S(t)$ continuously increases ($dS > 0$) and reaches its *maximum* [34], with nonuniformity gradually decreasing and vanishing at the stable equilibrium point. As $\mathfrak{m}_k^{\mathrm{u}}$ and $\mathfrak{M}^{\mathrm{u}}$ runs away from $\mathfrak{m}_{k\mathrm{ueq}}$ and $\mathfrak{M}_{\mathrm{ueq}}$, respectively, by increasing nonuniformity gradually, $S(t)$ continuously decreases and reaches some *minimum* S_{cats} $(dS > 0)$, even though GSL remains valid.

With (S4-GSL) imposed in Gen-Th, BCGM proposal imposes a very strong constraint of *nonnegativity* on dW_k for $\overline{\Sigma}$. The nonnegative average dW through Irr-P in Eq. (9) determines dQ, which imposes a restriction on $\{dp_k\}$ to have a particular form $\left\{dp_k^{\mathrm{GSL}}\right\}$ to ensure $dQ \geq 0$, see footnote

. As a side remark, we observe another important consequence of the impossibility of GSL violation that is captured by the *No-Go* Theorem 82, according to which any GSL-violation requires *rejecting* (S4-Gen), *i.e.,* Mec-EQ-P of analytical mechanics, a prospect that has not been recognized so far. This consequence is a disaster for the foundation of thermodynamics, and has not been recognized so far. Indeed, the violation cannot be taken as a viable possibility as it defies analytic mechanics. The conclusion provides not only a tantalizing insight into SL-violation in Σ_{M} for the first time by recognizing that its violation at $T > 0$[29] requires rejecting analytical mechanics, but is also a testament to the robustness of the BCGM proposal. This elevates Mec-EQ-P to be of *primary* relevance for thermodynamic foundation of GSL/SL in Gen-GSL-Th, and clarifies the significance of "asymptotic approach to stable equilibrium" for a thermodynamic system in $\mathfrak{M}^{\mathrm{s}}$ in time after being momentarily disturbed [3,59,110,118] from $\mathfrak{M}_{\mathrm{seq}}$, which forms the cornerstone of Cl-Th. We also extend GSL/SL now to cover $\mathfrak{M}^{\mathrm{u}}$, where negative T plays an important role. Thus, SL must always be stated along with T, a fact that has not been appreciated so far. Indeed, it is dQ and not dS that controls irreversibility. Irreversibility in Σ_0 makes its relaxation to $\mathfrak{M}_{0\mathrm{eq}}$ acyclic, see footnote 8, as seen in Fig. 2. Even for a stable Σ_0^{s}, the relaxation cannot give rise to a

---

[29] It is for $T > 0$ where all SL violations have been noted.

cyclic process. The only way to perform a cyclic process is to drive $\overline{\Sigma}$ that generates a nonspontaneous process in $\overline{\Sigma}$ by an external work agent, a work medium $\tilde{\Sigma}$ as in Fig. 3. We postpone a discussion of it to a future publication.

16.5. *GSL/SL*

Gen-Th for an isolated Σ always satisfies the first law $dE = 0$, see 10.3, from which follows Irr-P in (S2), for any $\{p_k\}$ that determines dW. Irr-P *intertwines* dW and dQ, but without imposing restrictions on dp_k [21, 22] so dQ has either sign but always determined by dW. It is here the relevance of *microscopic* Mec-EQ-P for $\{\mathfrak{m}_k\}$, which has not been properly recognized so far, becomes central in our reverse approach.

Conclusion 87. *Mec-EQ-P is finally identified as the* root cause *of the stochastic principle of GSL/SL that is surprisingly and completely determined by* mechanical works $\{dW_k \geq 0\}$ *and* dW *alone in Gen-GSL-Th for* $\overline{\Sigma}$.

Thus,

Conclusion 88. GSL is a consequence of analytical mechanics*, with* $dQ \geq 0$ *directly related to* $dS \gtreqqless 0$ *depending on* $T \gtreqqless 0$*, respectively. This conclusion provides a direct proof of SL for* $\mathfrak{M}^s$ *for* $T \geq 0$ *and* $dS \geq 0$*, and extends it to* $\mathfrak{M}^u$ *for* $T < 0$ *and* $dS \leq 0$*, a very tantalizing extension, which corrects a common* misconception *of SL about negative* T *[4].*

As negative temperatures are not physically impossible [4, 17, 127, 128], it is quite surprising to realize that $dS < 0$ is *not* a violation of SL, if $T < 0$. This has not been recognized before our recent work [21, 22]. Thus,

Conclusion 89. *Gen-GSL-Th of* Σ *supersedes Cl-Th for* Σ_M*. In addition, violation of GSL (any temperature) and SL (positive temperature) cannot be taken as a viable possibility within the BCGM proposal.*

It is clear from Theorem 82 that $dS \gtreqqless 0$ alone without any reference to T cannot be used to describe SL or its violation, a point that has not been appreciated so far and highlights the role of T for SL.

16.6. *Violation of GSL/SL and IC*

Let us consider a nonspontaneous evolution requiring $T \geq 0$ and $dS < 0$ for $\mathfrak{M}^{\mathrm{s}}$, and $T < 0$ and $dS > 0$ for $\mathfrak{M}^{\mathrm{u}}$. In both cases, $dQ < 0$. During this evolution, $\mathfrak{M}^{\mathrm{s}}$ becomes less and less uniform ($dS < 0$) and $\mathfrak{M}^{\mathrm{u}}$ becomes more and more uniform ($dS > 0$). Thus, $\mathfrak{M}^{\mathrm{s}}$ runs off from the uniform sink $\mathfrak{M}_{\mathrm{seq}}$ *catastrophically* to asymptotically approach an extremely *nonuniform* macrostate $\mathfrak{M}^{\mathrm{s}}_{\mathrm{cats}}$ so that $S^{\mathrm{s}}_{\mathrm{cats}} << S_{\mathrm{seq}}$ as if $\mathfrak{M}_{\mathrm{seq}}$ is *unstable*. Similarly, $\mathfrak{M}^{\mathrm{u}}$ runs towards and terminates in the uniform source $\mathfrak{M}_{\mathrm{ueq}}$ along the direction opposite to red arrows with S increasing to S_{ueq} as if $\mathfrak{M}_{\mathrm{ueq}}$ is *stable*. Both possibilities require some external agent as discussed above in Sect. 3.4, see Fig. 3, for $T > 0$ ($T < 0$) to obtain $dS < (>) 0$ by "*manipulating* $\mathfrak{M}_{\mathrm{seq}}$ ($\mathfrak{M}_{\mathrm{ueq}}$) " to drive $\mathfrak{M}^{\mathrm{s}}$ ($\mathfrak{M}^{\mathrm{u}}$) run away from (towards) the sink $\mathfrak{M}_{\mathrm{seq}}$ ($\mathfrak{M}_{\mathrm{ueq}}$) in a nonspontaneous manner; see Sect. 13.4, where various possibilities are discussed. If $\overline{\Sigma}$ in Fig. 3(b) is now detached from any surroundings, the result will be an internal constraint discussed by

Callen [3], removal of which will initiate spontaneous processes to increase the entropy in accordance with GSL/SL as it must. A similar situation occurs in the demon paradox [19, 161, 162], in which the demon starts manipulating $\mathfrak{M}_{\text{seq}}$ in a nonspontaneous manner as discussed recently [77, 163, 164]. Thus, there cannot be a genuine GSL/SL violation in $\overline{\Sigma}$, which is consistent with the No-Go theorem; see Theorem 82.

16.7. *Dissipation*

One of our goals listed in Sect. 1.3 is to obtain a proper measure of dissipation, which according to Thomson [115] is nothing but lost work W_{lost} without introducing of any "temperature-like" concept but intimately intertwining it with irreversibility. The traditional concept of W_{lost} in Cl-Th only applies to a NEQ process $\mathcal{P}_{12}$ between two EQ macrostates as shown in Fig. 2. We have generalized this concept to any arbitrary NEQ process $\mathcal{P}$ between any two possibly NEQ macrostates. Then the measure of lost work is given by $\Delta_{\text{i}}W$ given in footnote 22. As our concept of irreversibility is more general than the one used in a stable system, see Definition 20, where $d_{\text{i}}\mathfrak{Q}^{\text{s}}$ has a fixed sign, so it does not apply to irreversibility in an unstable system, where $d_{\text{i}}\mathfrak{Q}^{\text{u}}$ has the opposite sign; see Eq. (9). Then, the measure of dissipation in Gen-Th over $\mathcal{P}$ is given by Eq. (10); for an infinitesimally small segment $\delta\mathcal{P}$, it is given in Eq. (130). It is clear from Eq. (117b) that dissipation δD is not simply proportional to $Td_{\text{i}}S$. which we express as

Claim 90. *Dissipation measured by dissipated macroheat or lost macrowork is not always proportional to the irreversible entropy d_iS. The difference is the irreversible macroheat $Td_iS^{(h)}$ generated due to macroheat exchange.*

As expressing δD in terms of entropy changes requires knowing T, which can be of any sign, it is more general and useful to express it in terms of $d_{\text{i}}W$ as

$$\delta D \doteq d_{\text{i}}W \gtreqless 0,$$

in Gen-Th so that it becomes oblivious to T. This form is general and valid for all temperatures. The difference $Td_{\text{i}}S - d_{\text{i}}Q$, see the bottom of Eq. (115), is the irreversible macroheat $d_{\text{i}}Q^{(\text{h})} \doteq Td_{\text{i}}S^{(\text{h})}$ generated due to exchange macroheat;. To understand the significance of $Td_{\text{i}}S^{(\text{h})}$, we turn to the discussion in Sect. 13.4 in which we treat the two subsystems Σ_1 and Σ_2 forming an isolated system. We treat them to denote Σ and $\tilde{\Sigma}$, respectively, and take the limit $n_1 \to 0$ and $n_2 \to 1$. We consider the first term in Eq. (128) by not allowing any change in their volumes so $d\xi_{\text{V}} = 0$. This term is precisely the macrowork $d_{\text{i}}W_{\xi_{\text{E}}}$ done by the internal variable ξ_{E} and must be equal to $d_{\text{i}}Q^{(\text{h})}$ according to Irr-P. They can be of any sign, but must be nonnegative according to GSL. They have been discussed in that section including all possible cases.

In Gen-GSL-Th, δD must remain nonnegative

$$\delta D \doteq d_{\text{i}}W \geq 0;$$

thus, it cannot be violated in any spontaneous process as follows from GSL. We now focus on the cases (a) and (c) in Sect. 13.4 for both signs of the temperature; in both cases, $d_{\text{i}}W_{\xi_{\text{E}}} \geq 0$. Our approach has thus reproduced the well-known result in classical thermodynamic [28] for positive T. The important observation, however, is that

$$Td_{\text{i}}S \geq d_{\text{i}}Q; \tag{151}$$

the equality occurs only when there is no macroheat exchange between Σ and $\tilde{\Sigma}$. This inequality is not always appreciated in the literature. We now point out an important aspect of dissipation in the interacting case, which is either measure by the lost macrowork $d_{\rm i}W$ or equivalently by dissipated macroheat $d_{\rm i}Q$. We see that the dissipated macroheat or lost macrowork is not identical to $Td_{\rm i}S$ as was the case for an isolated $\Sigma_{\rm M}$ for which $d_{\rm i}S = dS$ and Eq. (103) holds.

The observation that the irreversible macroheat $Td_{\rm i}S^{(\rm h)}$ must be subtracted from $Td_{\rm i}S$ for δD is not inconsistent with our previous observation in Eq. (48) and the discussion of it. However, Eq. (48) has a much deeper consequence, which states that variation of $\xi_{{\rm E}k}$ does not generate any SI-microwork $d_{\rm i}W_{k{\rm E}}$ so it does not generate any macroscopic dissipation[30], although its average $\xi_{\rm E}$ creates irreversible entropy generation $d_{\rm i}d_{\rm i}S^{(\rm h)}$. We conclude by pointing out that fluctuations that are integral part of any statistical analysis have not been taken into account. It would be an interesting exercise to incorporate them and follow their consequences in the mechanical approach that we have introduced here. Another interesting extension is to apply the approach to metastable macrostates.

16.8. *Confusing $\Delta_{\rm e}W_k$ with ΔW_k in Fluctuation Theorems*

We now return to footnote 25 to discuss the confusion that is wide spread in both classical [140–142, 167–169, for example] and quantum [170, for example] NEQT. All these attempts were made before the introduction of generalized macrowork dW and macroheat dQ by us. All prevailing forms of thermodynamics were used to the exchange macrowork $d_{\rm e}W$ and macroheat $d_{\rm e}Q$ so it was the version of the first law in Eq. (7) that was familiar to the workers in the field, and not the one in Eq. (6) in terms of SI-macroquantities. As we have seen, they differ by the internal/irreversible macroquantities $d_{\rm i}W$ and $d_{\rm i}Q$. While Eq. (87) was well known in NEQT, its physics was not understood as we have presented in Sect. 10.2. Confusing Eq. (87) with (7), allowed the following *mistaken identification*

$$d_{\rm e}Q \overset{?}{\doteq} \textstyle\sum_k E_k dp_k, d_{\rm e}W \overset{?}{\doteq} -\textstyle\sum_k p_k dE_k. \tag{152}$$

which is incorrect as we see from Sect. 10.2.

Claim 91. *The mistaken identification above simply means that there is no irreversibility as $d_iW \equiv 0$ and $d_iQ \equiv 0$. Thus, the above identification is correct only for a reversible process $\mathcal{P}_{rev}$.*

The above error was completely overlooked in the modern approach to NEQT. As $\Delta_{\rm i}W$ represents the lost work $W_{\rm lost}$, the above identification simply means that there is no lost work, thus confirming Claim 91.

The problem came to the surface when Jarzynski [142] made a famous claim that the identity that he discovered to capture $W_{\rm lost}$ was an identity for a NEQ process $\mathcal{P}$. Cohen and Mauzerall [171, 172] immediately pointed out several issues with the Jarzynski identity to cast doubts on its NEQ nature. But even they were not aware of the fact that Jarzynski had also assumed no irreversibility by using the mistaken identification; see Claim 91. It was left to Gujrati to finally point the error for the first time in [143–145]. The issue was later discussed further in [48, see Sect. 15]. The lesson is that the correct equivalence of Eq. (87) is with Eq. (6).

---

[30] $d_{\rm i}W_{\xi_{\rm E}} = d_{\rm i}Q^{(\rm h)}$ above must not be confused with the ensemble average $d_{\rm i}W_{k{\rm E}}$. The former originates from dE_1, which from the first law contains macroheat, but the latter does not.

16.9. *Some Open Problems*

Before we end, we turn some of the important issues that have remained unanswered in this review with the hope that they could be answered in near future.

For a nonuniform isolated system Σ^{D}, its Hamiltonian $\mathcal{H}(\mathbf{x}|\,\mathbf{w},t)$ has an explicit time dependence, which seems to be counterintuitive as it contradicts the "well-known" result of analytical mechanics. The resolution of this puzzle is that the "well-known" result is only valid for a uniform isolated system as is clear from Eq. (36), where we must set $\dot{\mathbf{w}}=0$. To the best of my knowledge, we are the first to investigate nonuniform systems having the above time-dependence that results from internal processes due to nonuniformity and not due to any external source. This becomes clear from Eqs. (41a) and (43a). Thus, there is no paradox. Our resolution requires operationally defined internal variables due to nonuniformity, which requires Σ^{D} not smaller than $\Sigma^{\mathrm{D}}_{\mathrm{M}}$, in extended state space. However, Eq. (42a) in $\mathfrak{S}_{\mathbf{X}}$ can be applied to Σ^{D} of any size including the one with a single particle in in Sect. 14.4. The question that is left open is whether it is possible to operationally describe nonuniformity without introducing internal variables as we have done to deal with Σ^{D} smaller than $\Sigma^{\mathrm{D}}_{\mathrm{M}}$,provide.

Our derivation of GSL was limited by using the extensive state variable $\mathbf{W}$ that was the same for all microstates. This makes $\mathbf{F}_{\mathrm{w}k}$ in Eq. (41b) fluctuating over $\mathfrak{m}_k$. It would be interesting to extend the derivation in which some components of $\mathbf{W}$ are replaced by their conjugate fields in $\boldsymbol{x}$ discussed in Sect. 1.2 that are kept the same for all microstates. This exercise will make the corresponding extensive variable fluctuating over $\mathfrak{m}_k$. Both specifications have already been studied in [48, see, for example, Section 12.5 there] so no new techniques are required to make the transition.

It will be interesting to extend our approach to E_k and its temporal evolution with multiple EQ points such as in glasses that result is a disjoint phase space, see Sect. 15, and to explore their relevance for justifying E also having multiple EQ points that are commonly used phenomenologically to study metastability such as in glasses [173]. Another important question that we have not addressed is to operationally identify internal variables for a disjoint phase space, which should be welcomed.

Acknowledgments

I am grateful to Alain Le Mehaute for his invitation to contribute to the project Lîla-Entropie.

References

[1] L.D. Landau and E.M. Lifshitz, *Mechanics*, Third Ed., Pergamon Press, Oxford (1976).

[2] E. Fermi, *Thermodynamics*, Dover, New York (1956).

[3] H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (2nd ed.), John Wiley & Sons, New York, 1985.

[4] N.F. Ramsey, Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures, Phys. Rev. **103**, 20 (1956).

[5] Clausius, R., Über die Wärmeleitung gasförmiger Körper. *Ann. Physik*, **115**, 1 (1862).

[6] R. Clausius, *The Mechanical Theory of Heat*. Macmillan, London (1879).

[7] H.S. Leff, *Energy and Entropy: A Dynamic Duo*, CRC Press, Boca Raton, FL (2020).

[8] S.W. Angrist and L.G. Hepler, Loren G., *Order and Chaos – Laws of Energy and Entropy*, Basic Books, New York (1967).

[9] P.D. Gujrati, Loss of Temporal Homogeneity and Symmetry in Statistical Systems: Deterministic Versus Stochastic Dynamics, Symmetry **2**, 1201 (2010).

[10] R. Giles, Mathematical foundations of thermodynamics, Pergamon Press, Oxford, UK (1964).

[11] E.H. Lieb and J. Yngvason, A Guide to Entropy and the Second Law of Thermodynamics, Notices Of the AMS, **45**, 571 (1999).

[12] E.H. Lieb and J. Yngvason, The Mathematics of the Second Law of Thermodynamics, *Phys. Rep*. **310**, 1 (1999).

[13] S. Carnot, *Reflections on the Motive Power of Heat*, Ed. R.H. Thurston, 2nd revised edition, John Wiley & Sons, N.Y. (1897).

[14] J.W. Gibbs, *Elementary Principles in Statistical Mechanics*, Scribner's Sons, N.Y. (1902).

[15] Tolman, R. C., *The Principles of Statistical Mechanics*,Oxford University, London, UK (1959).

[16] L. Boltzman, *Lectures on Gas Theory*, University of California Press: Berkeley, CA, USA (1964); see also, L. Boltzmann, über die Beziehung zwischen dem Zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung resp. den Sätzen über das Wärmegleichgewicht, Wien Ber. **76**, 373 (1877).

[17] L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Vol. 1, Third Edition, Pergamon Press, Oxford (1986).

[18] G. Gallavotti, *Statistical Mecahanics, A Short Treatise*, Springer-Verlag, Berlin (1999).

[19] J.C. Maxwell, *Theory of Heat*, Longmans, Green, and Co., London (1902).

[20] P. Ehrenfest, P. and T. Ehrenfest, (1990). *The Conceptual Foundations of the Statistical Approach in Mechanics*, Cornell University Press, Ithaca, NY (1959).

[21] P.D. Gujrati, A No-Go Theorem of Analytical Mechanics for the Second Law Violation, arXiv:2406.17007.

[22] P.D. Gujrati, Mechanical Foundations of the Generalized Second Law and the Irreversity Principle, Foundations **4**, 560 (2024).

[23] B.D. Coleman, Thermodynamics of materials with memory. Arch. Rat. Mech. Anal. **17**, 1 (1964).

[24] B.D. Coleman, Thermodynamics with Internal State Variables, *J. Chem. Phys*. 47, 597 (1967,1967).

[25] I. Prigogine, *Thermodynamics of Irreversible Processes*, Wiley-Interscience, New York (1971).

[26] Th. De Donder and P.V. Rysselberghe, *Thermodynamic Theory of Affinity: A Book of Principles,* Oxford University Press, Oxford, England (1936).

[27] S.R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics***,** First Edition, Dover, New York (1984).

[28] D. Kondepudi and I. Prigogine, *Modern Thermodynamics*, John Wiley and Sons, West Sussex (1998).

[29] G.A. Maugin, *The Thermomechanics of Nonlinear Irreversible Behaviors: An Introduction*, World Scientific, Singapore (1999).

[30] E. Bouchbinder; J. Langer, Nonequilibrium thermodynamics of driven amorphous materials. I. Internal degrees of freedom and volume deformation, Phys. Rev. E **80**, 031131 (2009).

[31] P.D. Gujrati, Nonequilibrium thermodynamics: Structural relaxation, fictive temperature, and Tool-Narayanaswamy phenomenology in glasses, Phys. Rev. E **81**, 051130 (2010); P.D. Gujrati, arXiv:0910.0026.

[32] P.D. Gujrati, Nonequilibrium thermodynamics. II. Application to inhomogeneous systems, Phys. Rev. E **85**, 041128 (2012); P.D. Gujrati, arXiv:1101.0438.

[33] P.D. Gujrati and P. P. Aung, Nonequilibrium thermodynamics. III. Generalization of Maxwell, Clausius-Clapeyron, and response-function relations, and the Prigogine-Defay ratio for systems in internal equilibrium, Phys. Rev. E **85**, 041129 (2012); P.D. Gujrati, arXiv:1101.0431.

[34] P.D. Gujrati, Hierarchy of Relaxation Times and Residual Entropy: A Nonequilibrium Approach, *Entropy* **20**, 149 (2018).

[35] P.D. Gujrati, A Review of the System-Intrinsic Nonequilibrium Thermodynamics in Extended Space (MNEQT) with Applications, Entropy, **23**, 1584 (2021).

[36] P.D. Gujrati, Non-equilibrium Entropy in an Extended State Space, 627-669, *Frontiers in Entropy Across the Disciplines: Panorama of Entropy: Theory, Computation, and Applications*, Willi Freeden and M Zuhair Nashed , Eds., World Scientific, Singapore (2022).

[37] J. Katz, Thermodynamics of self-gravitating systems, Found. Phys. **33**, 223-269 (2003).

[38] W.H. Schottky, *Thermodynamik*, Julius Springer, Berlin, Germany (1929).

[39] W. Muschik, Discrete systems in thermal physics and engineering: a glance from non-equilibrium thermodynamics, *Continuum Mech. Thermody*. **33**, 2411 (2021).

[40] J. Casas-Vázquez, D. Jou, Temperature in non-equilibrium states: A review of open problems and current proposals. Rep. Prog. Phys. **66**, 1937 (2003).

[41] A.I. Arnold, *Mathematical Methods of Classical Mechanics*, Second Ed, Springer-Verlag, New York (1989).

[42] Davies, R.O.; Jones, G.O. Thermodynamic and kinetic properties of glasses. Adv. Phys. **2**, 370 (1953).

[43] N.G. Chetaev, *Theoretical Mechanics*, Springer-Verlag, Berlin (1989).

[44] P.D. Gujrati, Irreversibility, Dissipation, and Its Measure: A New Perspective, Symmetry, **17**, 232 (2025).

[45] P.D. Gujrati, Nonequilibrium Entropy, arXiv:1304.3768.

[46] P.D. Gujrati, On Equivalence of Nonequilibrium Thermodynamic and Statistical Entropies, *Entropy*, **17**, 710 (2015).

[47] D.A. Lavis, Boltzmann, Gibbs, and the Concept of Equilibrium, Philos. Sci., **75**, 682 (2008).

[48] P.D. Gujrati, Foundations of Nonequilibrium Statistical Mechanics in Extended State Space, *Foundations*, 3, 419 (2023).

[49] P.D. Gujrati, First-principles nonequilibrium deterministic equation of motion of a Brownian particle and microscopic viscous drag, *Phys. Rev.* E **102**, 012140 (2020).

[50] B.C. Eu, *Kinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized Hydrodynamics,* Vol. 1, Springer, Switzerland (2016).

[51] O.K. Rice, *Statistical Mechanics, Thermodynamics and Kinetics*, W.H. Freeman, San Francisco, USA (1967).

[52] J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes*; Springer: New York, NY, USA (1987).

[53] R. Balian, *From Microphysics to Macrophysics*, Vol. 1, Springer-Verlag, Berlin (1991).

[54] G.D.C. Kuiken, *Thermodynamics of Irreversible Processes*, John Wiley, Chichester (1994).

[55] H.C. Ottinger, *Beyond Equilibrium Thermodynamics*, Wiley, Hoboken (2005).

[56] S. Kjelstrum and D. Bedeaux, *Nonequilibrium Thermodynamics of Heterogeneous Systems*, World-Scientific, Singapore (2008).

[57] D.J. Evans and G. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Second edition, Cambridge University Press, Cambridge (2008).

[58] F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, Inc. New York (1965).

[59] L.C. Woods, *The Thermodynamics of Fluids Systems*, Oxford University Press, Oxford (1975).

[60] J. Kestin, *A Course in Thermodynamics*, vols. 1 & 2, *Revised Printing,* McGraw-Hill Book Company, New York (1979).

[61] J.R. Waldram, *The Theory of Thermodynamics*, Cambridge University, Cambridge (1985).

[62] L.D. Landau, E.M. Lifshitz, *Quantum Mechanics*, Third Edition, Pergamon Press, Oxford (1977).

[63] J. von Neumann, *Mathematical Foundations of Quantum Mechanics*, Princeton University Press, N.J. (1996).

[64] M.H. Partovi, Entropic Formulation of Uncertainty for Quantum Measurements Phys. Rev. Lett. **50**,1883 (1983).

[65] J.D. Beckenstein, Black Holes and Entropy, Phys. Rev. D **7**, 2333 (1973).

[66] J.D. Beckenstein, Statistical black-hole thermodynamics, Phys. Rev. D **12**, 3077 (1975).

[67] B. Schumacker, Quantum coding, Phys. Rev. A **51**, 2738 (1995).

[68] C.H. Bennet, The thermodynamics of computation—a review, Int. J. Theor. Phys. **21**, 905 (1982).

[69] R. Landauer, Irreversibility and Heat Generation in the Computing Process, IBM J. Res. Develop. **5**, 183 (1961).

[70] N. Wiener, *Cybernetics, or Control and Communication in the Animal and the Machine*, John Wiley and Sons, New York (1948).

[71] C.E. Shannon, A Mathematical Theory of Communication, Bell Syst. Tech. **27**, 379 (1948).

[72] L. Szilard, über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen, Z. Phys. **53**, 840 (1929); English translation in [73], p. 110.

[73] H.S. Leff and A.F. Rex, eds. *Maxwell's Demon 2 : Entropy, Classical and Quantum Information, Computing*, CRT Press, Boca Raton, FL. (2018).

[74] J.L. Lebowitz, Statistical mechanics: A selective review of two central issues, Rev. Mod. Phys. **71**, S346 (1999).

[75] E.H. Lieb and J. Yngvason, The entropy concept for non-equilibrium states, Proc. R. Soc. A, **469**, 20130408 (2013); arXiv:1305.3912.

[76] P.D. Gujrati, Carnot Theorem Revisited: A Critical Perspective, Entropy **27**, 346 (2025).

[77] P.D. Gujrati, Overlooked Work and Heat of Intervention and the Fate of Information Principles of Szilard and Landauer, arXiv:2205.02373v2.

[78] Jaynes, E.T. Gibbs vs Boltzmann Entropies. Am. J. Phys. **33**, 391 (1965).

[79] P.D. Gujrati, Where is the residual entropy of a glass hiding? arXiv:0908.1075.

[80] S.A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids*, Interscience Publishers, New York (1965).

[81] P.D. Gujrati, Poincare Recurrence, Zermelo's Second Law Paradox, and Probabilistic Origin in Statistical Mechanics, arXiv:0803.0983.

[82] P.D. Gujrati, Irreversibility, Molecular Chaos, and A Simple Proof of the Second Law, arXiv:0803.1099.

[83] D. Searles and D. Evans, Fluctuations relations for nonequilibrium systems, Aust. J. Chem., **57**, 1119 (2004).

[84] J. Keizer, On the kinetic meaning of the second law of thermodynamics, J. Chem. Phys. **64**. 4466 (1976).

[85] A. Einstein, "Autobiographical Notes," in *Albert Einstein: Philosopher-Scientist*, P. A. Schilpp, Ed., Library of Living Philosophers, Evanston, IL (1949).

[86] A.S. Eddington, *New Pathways In Science*, Macmillan Company, Cambridge, The University Press (1935).

[87] I. Prigogine, A. Grecos, and Cl. George, On the relation of dynamics to statistical mechanics, Cel. Mech. **16**, 487 (1977).

[88] L. Boltzmann, L. Weitere Studien ¨uber das W¨armegleichgewicht unter Gasmolek¨un, Sitzungberichte der Akademie der Wissenschaften zu Wien, mathematischnaturwissenschaftliche Klasse, **66**, 275 (1872). English translation in Brush [89], pp. 262-349.

[89] S.G. Brush, *The kinetic theory of gases*, London: Imperial College Press (2003).

[90] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, 3rd ed. North Holland, Amsterdam (2007).

[91] X.Y. Fu, An approach to realize Maxwell's hypothesis, *Energy Convers. Mgmt*. **22**, 1 (1982).

[92] D.J. Evans, E. Cohen, and G. Morriss, Probability of second law violations in shearing steady states, Phys. Rev. Lett. **71**, 2401 (1993).

[93] D.J. Evans and D.J. Searles, Equilibrium microstates which generate second law violating steady states, Phys. Rev. E **50**, 1645 (1994).

[94] G. Moddel, A. Weerakkody, D. Doroski, and D. Bartusiak, Casimir-cavity-induced conductance changes, Phys. Rev. Res. **3**, L022007 (2001).

[95] E. Gerstner, Second law broken, Nature (2002); https://doi.org/10.1038/news020722-2.

[96] G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles, and D.J. Evans, Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales, Phys. Rev. Lett. **89**, 050601 (2002).

[97] V. Capek and D. Sheehan, *Challenges to the Second Law of Thermodynamics*: *Theory and Experiment*, Springer, Berlin (2005).

[98] G.W. Ford and R. F. O'Connell, A Quantum Violation of the Second Law?, Phys. Rev. Lett. **96**, 020402 (2006).

[99] G. D'Abramo, The peculiar status of the second law of thermodynamics and the quest for its violation, Stud. Hist. Philos. Sci. B - Stud. Hist. Philos. Mod. Phys. **43**, 226 (2012); arXiv:1101.5056v5.

[100] B. Pandey, Configuration entropy of the cosmic web: can voids mimic the dark energy?, MNRAS **471**, L73 (2017).

[101] D. Ebler, S. Salek, and G. Chiribella, Enhanced Communication with the Assistance of Indefinite Causal Order, Phys. Rev. Lett. **120**, 120502 (2018).

[102] L.M. Procopio, F. Delgado, M. Enriquez, N. Belabas, and J.A. Levenson, Sending classical information via three noisy channels in superposition of causal orders, *Phys. Rev*. A **101**, 012346 (2020).

[103] J.W. Lee, Type-B Energy Process: Asymmetric Function-Gated Isothermal Electricity Production, *Energies*, **15**, 7020 (2022).

[104] X. Liu, D. Ebler, and O. Dahlsten, Thermodynamics of Quantum Switch Information Capacity Activation, Phys. Rev. Lett. **129**, 230604 (2022).

[105] *The Glass Transition and the Nature of the Glassy State,* M. Goldstein and R. Simha, Eds., Ann. N.Y. Acad. Sci. Vol. 279 (1976).

[106] S.V. Nemilov, *Thermodynamic and kinetic aspects of the vitreous state*, CRC Press, Boca Raton (1995).

[107] I.S. Gutzow and J.W.P. Schmelzer, T*he Vitreous State: Thermodynamics, Structure*, *Rheology*, *and Crystallization*, 2nd enlarged edition, Springer, Heidelberg (2013).

[108] R. Kubo, The fluctuation-dissipation theorem, Rep. Prog. Phys. **29**, 255 (1966).

[109] C.M. Dafermos, The second law of thermodynamics and stability, Arch. Ration. Mech. Anal. **70**, 167 (1979).

[110] J. Kestin, *A course in Thermodynamics*, Vol. II, Revised printing, Hemisphere Publishing Corporation, Washington (1979).

[111] R.L. Fosdick and K.R. Rajgopal, Thermodynamics and stability of fluids of third grade, Proc. R. Soc. Lond. A **339**, 351 (1980).

[112] L. Gavassino, M. Antonelli, and B. Haskell, Thermodynamic Stability Implies Causality, Phys. Rev. Lett. **128**, 010606 (2022); arXiv:2105.14621v2.

[113] C. Rovelli, How causation is rooted into thermodynamics, *arXiv*:2211.00888v2.

[114] M. Capela, H. Verma, F. Costa, and L.C. Céleri, Indefinite causal order is not always a resource for thermodynamic processes, *arXiv*:2208.03205v2; see also Reassessing thermodynamic advantage from indefinite causal order, Phys. Rev. A **107**, 062208 (2023).

[115] William Thomson, (Lord Kelvin), On a Universal Tendency in Nature to the Dissipation of Mechanical Energy (Google Books) (URL), Proceedings of the Royal Society of Edinburgh for April 19, 1852, also Philosophical Magazine, Oct. 1852, also Mathematical and Physical Papers, vol. i, art. 59, pp. 511. https://zapatopi.net/kelvin/papers/on_a_universal_ tendency.html

[116] M. Planck, Über die Begründung des zweiten Hauptsatzes der Thermodynamik, Akad. Wiss., Sitzungsber. Preuss. Phys. Math. Kl. 453 (1926).

[117] H. Erlichson, Sadi Carnot, 'Founder of the Second Law of Thermodynamics," Eur. J. Phys. **20**, 183 (1999).

[118] D. Ruelle, *Statistical Physics*, W.A. Benjamin, Inc., Reading, Massachusetts (1983).

[119] E.T. Jaynes, Information Theory and Statistical Mechanics, Phys. Rev. **106**, 620 (1957); Information Theory and Statistical Mechanics. II, ibid. **108**, 171 (1957).

[120] R.G. Palmer, Broken ergodicity, Adv. Phys. **31**, 669 (1982).

[121] P.D. Gujrati, Energy gap Model of Glass Formers: Lessons Learned from Polymers, *Modeling and Simulation in Polymers*, ed. P.D. Gujrati and A.I. Leonov, Wiley-VCH,Weinheim (2010).

[122] Gujrati, P.D. Generalized Non-equilibrium Heat and Work and the Fate of the Clausius Inequality, arXiv:1105.5549.

[123] Gujrati, P.D. Nonequilibrium Thermodynamics. Symmetric and Unique Formulation of the First Law, Statistical Definition of Heat and Work, Adiabatic Theorem and the Fate of the Clausius Inequality: A Microscopic View, arXiv:1206.0702.

[124] J. Wilks, *The Third Law of Thermodynamics*; Oxford University Press: London, UK (1961).

[125] Ruelle, D. What physical quantities make sense in nonequilibrium statistical mechanics? *Boltzmann's Legacy*; Gallavotti, G., Reiter,W.L., Yngvason, J., Eds.; European Mathematical Society: Zürich, Switzerland (2008).

[126] L.D. Landau, The transport equation in the case of Coulomb interactions. Zh. Eksp.Teor. Fiz. **7**, 203 (1937).

[127] E. Purcell and R. Pound, A Nuclear Spin System at Negative Temperature, Phys. Rev. **81**, 279 (1951).

[128] E. Abraham and O. Penrose, Physics of negative absolute temperatures, Phys. Rev. E *95*, 012125 (2017).

[129] Hawking, S.W. Particle creation by black holes. Commun. Math. Phys. **43**, 199 (1975).

[130] J.D. Bekenstein, Black Holes and Entropy. Phys. Rev. D **7**, 2333 (1973).

[131] W. Muschik, Aspects of Non-Equilibrium Thermodynamics; World Scientific: Singapore (1990).

[132] W. Muschik and G. Brunk, A concept of non-equilibrium temperature. Int. J. Engng Sci. **15**, 377 (1977).

[133] W. Muschik, C. Papenfuss, and H. Ehrentraut, A sketch of continuum thermodynamics. J. Non-Newton. Fluid Mech. **96**, 255 (2001).

[134] G.P. Morris and L. Rondoni, Definition of temperature in equilibrium and nonequilibrium systems. Phys. Rev. E **59**, R5 (1999).

[135] W.G. Hooverand C.G. Hoover, Nonequilibrium temperature and thermometry in heat-conducting f4 models. Phys. Rev. E **77**, 041104 (2008).

[136] Y. Oono and M. Paniconi, Steady State Thermodynamics. Prog.Theor. Phys. Suppl. **130**, 29 (1998).

[137] J. Keizer, Heat, work, and the thermodynamic temperature at nonequilibrium steady states. J. Chem. Phys. **82**, 2751 (1985).

[138] Lucia, U.; Grisolia, G. Nonequilibrium Temperature: An Approach from Irreversibility. Materials **14**, 2004 (2021).

[139] H.B. Callen and T.A. Welton, Irreversibility and Generalized Noise, *Phys. Rev.* **83**, 34 (1951).

[140] U. Seifert, Stochastic thermodynamics: principles and perspectives, *Eur. Phys. J.* B **64**, 423 (2008).

[141] K. Sekimoto, *Stochastic Energetics*, Lecture Notes in Physics 799, Springer, Heidelberg (2010).

[142] C. Jarzynski, Nonequilibrium equality for free energy differences, Phys. Rev. Lett. **78**, 2690 (1997).

[143] P.D. Gujrati, Nonequilibrium Work and its Hamiltonian Connection for a Microstate in Nonequilibrium Statistical Thermodynamics: A Case of Mistaken Identity, arXiv:1702.00455.

[144] P.D. Gujrati, Jarzynski Equality and its Special Trajectory Ensemble Average Demystified, arXiv:1802.08084.

[145] P.D. Gujrati, Jensen Inequality and the Second Law, Phys. Lett. A **385**, 126460 (2020).

[146] P.D. Gujrati, Comment on "Comment on: On the reality of residual entropies of glasses and disordered crystals" [J. Chem. Phys. 129, 067101 (2008)], arXiv:0909.0238.

[147] P.D. Gujrati, Comment on "Non-equilibrium entropy of glasses formed by continuous cooling" [J. Non-Cryst. Solids 355 (2009) 600], arXiv:0909.0734.

[148] P.D. Gujrati, A Rigorous Derivation of the Entropy Bound and the Nature of Entropy Variation for Non-equilibrium Systems during Cooling, arXiv:1101.5623.

[149] P.D. Gujrati, Is Structural Relaxation During Vitrification the Inverse of the Glass Transition?, arXiv:1103.0219.

[150] P.D. Gujrati, Some Rigorous Results Relating Nonequilibrium, Equilibrium, Calorimetrically Measured and Residual Entropies during Cooling, arXiv:1304.5764.

[151] A. B. Bestul and S. S. Chang, Limits on Calorimetric Residual Entropies of Glasses, J. Chem. Phys. **43**, 4532 (1965).

[152] S.A. Langer and J.P. Sethna, Entropy of Glasses, Phys. Rev. Lett. **61**, 570 (1988).

[153] P.D. Gujrati, S.S. Rane and A. Corsi, Significance of the free volume for metastability, spinodals, and the glassy state: An exact calculation in polymers, Phys. Rev. E **67**, 052501 (2003).

[154] Goldstein, M. On the reality of residual entropies of glasses and disordered crystals. J. Chem. Phys. **128**, 154510 (2008).

[155] D. Kivelson and H. Reiss, Metastable systems in thermodynamics: Consequences, role of constraints. J. Phys. Chem. B **103**, 8337 (1999).

[156] P.K. Gupta and J.C. Mauro, Comment on: “On the reality of residual entropies of glasses and disordered crystals [J. Chem. Phys. **128**, 154510 (2008)]”. J. Chem. Phys. **129**, 067101 (2008).

[157] P.K. Gupta and J.C. Mauro, The configurational entropy of glass. J. Non-Cryst. Solids **355**, 595 (2009).

[158] H. Reiss, Apparent entropy, residual entropy, causality, metastability, constraints, and the glass transition. J. Non-Cryst. Solids **355**, 617 (2009).

[159] P.D. Gujrati, The Glass transition and the entropy crisis: A modern perspective*, Encyclopedia of Glass Science, Technology, History, and Culture*, P. Richet, R. Conradt, A. Takada, J. Dyon, Eds.; Wiley-VCH:Weinheim, Germany (2021); https://doi.org/10.1002/9781118801017.ch3.3.

[160] M. Campisi, Statistical mechanical proof of the second law of thermodynamics based on volume entropy, Studies in History and Philosophy of Modern Physics, **39**, 181 (2008).

[161] C.G. Knott, *Life and Scientific Work of Peter Guthrie Tait,* Cambridge University Press, London, 1911; p. 213.

[162] M. von Smoluchowski, Experimentell nachweisbare, der üblichen Thermodynamik widersprechende Molekularphänomene, *Phys. Zeitschrift* **13**, 1069 (1912).

[163] P.D. Gujrati, Maxwell's Demon must remain sebservient to Clausius's statement, *arXiv*:2112.12300v2.

[164] P.D. Gujrati, Maxwell's Conjecture of the Demon creating a Temperature Difference is False, *arXiv*:2205.02313.

[165] J.D. Beckenstein, Generalized second law of thermodynamics in black-hole physics, *Phys. Rev*. D **9**, 3292 (1974).

[166] G.L. Sewell, On the generalised second law of thermodynamics, *Phys. Lett*. A **122**, 309 (1987).

[167] G.E. Crooks, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, Phys. Rev. E **60**, 2721 (1999).

[168] L.P. Pitaevskii, Rigorous results of nonequilibrium statistical physics and their experimental verification, Physics-Uspekhi **54**, 625 (2011).

[169] H. Spohn and J.L. Lebowitz, Irreversible Thermodynamics for Quantum Systems Weakly Coupled to Thermal Reservoirs, Adv. Chem. Phys. **38**, 109 (1978).

[170] R. Alicki, The quantum open system as a model of the heat engine, J. Phys. A **12**, L103 (1979).

[171] E.G.D. Cohen and D. Mauzerall, A note on the Jarzynski equality, J. Stat. Mech. P07006 (2004).

[172] E.G.D. Cohen and D. Mauzerall, The Jarzynski equality and the Boltzmann factor, Mol. Phys. **103**, 21 (2005).

[173] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles*, princeton University Press, Princeton, N.J. (1997).