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Nonequilibrium thermodynamics. II. Application to inhomogeneous systems

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We provide an extension of a recent approach to study nonequilibrium thermodynamics [Gujrati, Phys. Rev. E **81**, 051130 (2010), to be denoted by I in this work] to inhomogeneous systems by considering the latter to be composed of quasi-independent subsystems. The system Σ along with the (macroscopically extremely large) medium $\widetilde{\Sigma}$ form an isolated system Σ_0. The fields (temperature, pressure, etc.) of Σ and $\widetilde{\Sigma}$ *differ* unless at equilibrium. We show that the additivity of entropy requires *quasi-independence* of the subsystems, which results from the interaction energies between different subsystems being *negligible* so the energy also becomes additive. The thermodynamic potentials such as the Gibbs free energy that continuously decrease during approach to equilibrium are determined by the fields of the medium and exist no matter how far the subsystems are out of equilibrium, so their fields may not even exist. This and the requirement of quasi-independence make our approach differ from the conventional approach used by de Groot and others, as discussed in the text. We find it useful to introduce the time-dependent Gibbs statistical entropy for Σ_0, from which we derive the Gibbs entropy of Σ; in equilibrium this entropy reduces to the equilibrium thermodynamic entropy. As the energy depends on the frame of reference, the thermodynamic potentials and the Gibbs fundamental relation, but not the entropy, depend on the frame of reference. The possibility of relative motion between subsystems described by their net linear and angular momenta gives rise to viscous dissipation. The concept of internal equilibrium introduced in I is developed further here and its important consequences are discussed for inhomogeneous systems. The concept of internal variables (various examples are given in the text) as variables that cannot be controlled by the observer for nonequilibrium evolution is also discussed. They are important because the concept of internal equilibrium in the presence of internal variables no longer holds if internal variables are not used. The Gibbs fundamental relation, thermodynamic potentials, and irreversible entropy generation are expressed in terms of observables and internal variables. We use these relations to eventually formulate the nonequilibrium thermodynamics of inhomogeneous systems. We also briefly discuss the case when bodies form an isolated system without any medium to obtain their irreversible contributions and show that this case does not differ from when bodies are in an extremely large medium.

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I. INTRODUCTION

A. Nature of the problem

In an earlier paper [1], which we will refer to in this work as I, we have considered some of the consequences of applying the second law of thermodynamics to an isolated system Σ_0, which consists of a macroscopic system of interest Σ containing a fixed number N of particles (atoms or molecules) surrounded by an extremely large medium $\widetilde{\Sigma}$; see Figs. 1 and 2(a). An important consequence of the approach was the realization that the instantaneous fields such as the temperature, pressure, etc., of the system are not the same as those of the medium except when in equilibrium, a fact not commonly appreciated; see, however, Ref. [2]. This realization has motivated this work to obtain a nonequilibrium thermodynamic description of Σ under various conditions. It will be implicitly assumed that the medium is extremely large to be unaffected by the system. (Later in this work, we will also consider Σ to have a fixed volume V instead of N. Furthermore, we will also consider the case of many similar size systems forming an isolated system $\overline{\Sigma}_0$ without the medium $\widetilde{\Sigma}$.) Throughout this work, we will use *body* to refer to any of the three systems Σ_0, $\widetilde{\Sigma}$, and Σ. Quantities pertaining to them will be denoted by a suffix 0, $\sim$ over the top, and without any suffix, respectively, while quantities associated with a body will be denoted without any suffix. Throughout the work, we will say that the system is *open* when it is in a medium. Even though it is not the common usage, this should not cause any confusion as the context will be clear.

To avoid complications due to external shear, we had only considered Σ without external shear in I. This restriction is removed here, but Σ_0 will still have *no* external force to ensure its isolation; see below also. Consider the surface ∂V of the system or any of its subsystems. The force $t_i df$ acting on a surface element df of the surface ∂V equals the stress force $\tau_{ij} n_j df$ (summation over repeated indices implied); here, $\mathbf{n}$ is the outward unit normal at the surface element df on the surface and $t_i = \tau_{ij} n_j$ [3,4] gives the surface traction force which can be used to determine the net force and torque,

$$\mathbf{F} \equiv \oint_{\partial V} \mathbf{t} df, \quad \mathbf{K} \equiv \oint_{\partial V} \mathbf{r}^{(s)} \times \mathbf{t} df,$$

acting on the system, respectively; here, for convenience, $\mathbf{r}^{(s)}$ is taken to be the radius vector of the surface element with respect to the center of mass of the system. The external forces are responsible for the deformation of the system and result in the translation and rotation of the system. Let us consider an infinitesimal volume element dV of mass dm, which is moving with a velocity $\mathbf{v}(t)$ and rotating with an angular velocity $\boldsymbol{\omega}(t)$ with respect to some fixed frame and has an intrinsic angular momentum $\mathbf{m}(t) dV$. The linear and angular momenta of the

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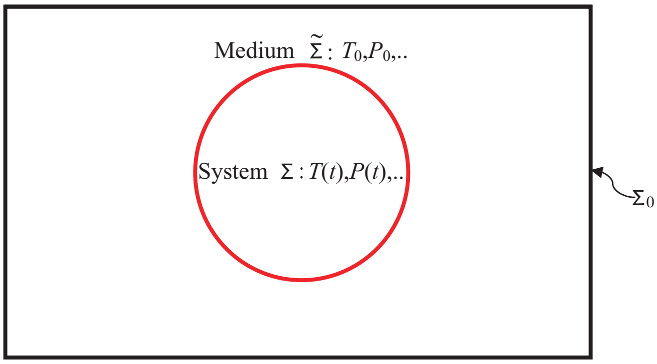
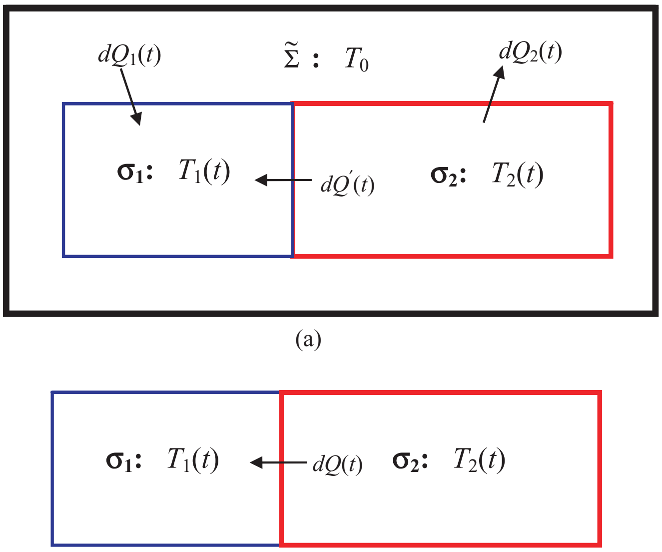


FIG. 1. (Color online) Schematic representation of a macroscopically large system Σ and the medium $\widetilde{\Sigma}$ surrounding it to form an isolated system Σ_0. The system is a very small part of Σ_0. The medium is described by its fixed fields T_0, P_0, etc., while the system, if in internal equilibrium (see text), is characterized by $T(t), P(t)$, and so on.

system in the fixed frame are given by

$$M\mathbf{V}(t) \equiv \int_{V(t)} \mathbf{v}(t)dm, \quad \mathbf{M}(t) \equiv M\mathbf{R}(t) \times \mathbf{V}(t) + \int_{V(t)} \mathbf{r}(t) \times \mathbf{v}(t)dm + \int_{V(t)} \mathbf{m}(t)dV,$$

respectively; here $M = m_0 N$ is the mass of the system (m_0 being the mass of a particle), which is fixed for fixed number of particles N, and $\mathbf{R}(t)$ and $\mathbf{V}(t)$ are the location and the velocity of the center of mass in this frame. If the frame is taken to be the center of mass frame, then $\mathbf{R}(t)$ and $\mathbf{V}(t)$ are zero. In I, the system was *stationary* so its energy represented the *internal energy* of the body. We now allow for relative motions (translation and rotation) between the system and the medium or between subsystems; the energy will no longer represent the internal energy. The relative motions become the additional sources of viscous dissipation due to mechanical forces. The irreversibility due to temperature difference has already been considered in I.



(a)

(b)

FIG. 2. (Color online) We show schematically the two subsystems σ_1 and σ_2 $[T_2(t) > T_1(t)]$ forming the system Σ in an extensively large medium in (a) and by themselves forming an isolated system Σ_0 without an extensively large medium in (b). The heat output $dQ(t)$ in (a) by σ_2 is the sum of $dQ'(t)$ and $dQ_2(t)$, while the heat intake by σ_1 is the sum of $dQ'(t)$ and $dQ_1(t)$. We take T_0 to be the equilibrium temperature for the isolated system in (b). As we are dealing with isolated systems in both cases, the heat input and output must be equal. Therefore, we must have $dQ_1(t) \equiv dQ_2(t)$. The equality of the heat input and output is also true in (b). As the heat transfers between objects do not occur isothermally, there is irreversible entropy generation due to each heat transfer. We will study this issue later in Sec. XI B.

Bouchbinder and Langer [2] also consider a system under external shear but the approach differs. We should also mention earlier very different equilibrium-like attempts by Lubchenko and Wolynes [5] for glasses and by Öttinger [6]. Mention should also be made of a very interesting phenomenological approach by Oono and Paniconi [7] on steady-state thermodynamics, which was later advanced by Sasa and Tasaki [8]. Biot [9] and Keck and Gillespie [10] first introduced the idea of rate controlled constrained equilibrium method to study irreversibility. The idea of surrogate systems was introduced by Gyftopoulos and Beretta [11]. Heterogeneity due to the presence of an interface has been extensively studied by Bedeaux and coworkers; see, for example, Ref. [12]. The classical local nonequilibrium thermodynamics due to de Donder [13–16] is close in spirit to our approach, except that all these works excluding that in Ref. [2], do not explicitly consider the differences in the fields of the system and the medium. There are other versions of nonequilibrium thermodynamics usually known as the extended, rational, and GENERIC (general equation for the nonequilibrium reversible-irreversible coupling) nonequilibrium thermodynamics [6,17,18]; however, we do not discuss these formulations in this work.

According to the second law, the entropy $S_0(t)$ of the isolated system Σ_0 satisfies

$$dS_0(t)/dt \geqslant 0 \tag{1}$$

at each instant t. We assume that Σ_0 is confined to a finite though extremely large volume V_0 [19]. The isolation requires that we *neglect* all interactions, such as gravitational interactions, of Σ_0 with the outside. All relevant interactions must be confined within V_0. This is not to be taken as a weakness of our approach as including the interactions with outside will only make Σ_0 an open system, so our investigation of an open system, which is our primary concern, can then be applied to it. The second law clearly implies that the (thermodynamic) entropy exists even when the system is out of equilibrium. Unfortunately, there is no entropy meter to measure or evaluate the entropy or even the entropy change in a nonequilibrium process. Thus, we find it useful to also consider statistical formulation of entropy valid also for nonequilibrium states. This issue and the related history of the statistical analogs (Boltzmann and Gibbs formulations) of the nonequilibrium entropy have been reviewed recently [19], and references cited therein], and we refer the reader to this for further details. In this work, we will use the Gibbsian definition of entropy in terms of microstates as it contains the Boltzmann entropy formulation as a special case but one can also use the Boltzmann formulation without affecting our conclusions.

B. Important restrictions in I and their removal in the current work

An assumption implicit, but not stated, in I was that there was no relative motion between the system and the medium and that the isolated system was stationary in the laboratory frame of reference; the latter we will denote by $\mathcal{L}$ in this work. Because of the stationary assumption, there is no difference between the energy and the internal energy for Σ_0, $\widetilde{\Sigma}$, and Σ, which is very useful as the entropies depend on the internal energies and not on the energies [20]; the latter contain the contributions from translation and rotation of the body as a whole. Whenever we discuss both energies together in the following, the internal energy will be denoted by a superscript i to distinguish it from the energy, which is denoted without the superscript; otherwise, it will be clear which energy we are considering. The translation of a body as a whole merely affects the energy but not its thermodynamic properties. However, the rotation of a body as a whole gives rise to centrifugal potential energy that modifies the energies of microstates and has to be carefully incorporated into any thermodynamic investigation ([20], see Sec. 34) as we do in Sec. VIII; see also Appendices A and B. The other assumption was the homogeneity of the system, which would be removed here. This is because glasses as nonequilibrium systems normally exhibit both spatial and temporal inhomogeneity; see Refs. [21–23] for some recent investigations. We will also pay close attention to internal variables that were only briefly mentioned but not explored in I.

C. Present goal and the layout

The local nonequilibrium thermodynamics will be the standard formulation with which we will compare and contrast our approach initiated in Ref. [1]. Therefore, for the sake of continuity and clarity, we briefly discuss the classical formulation involving local equilibrium in Sec. II. We discuss the statistical formulation of entropy and averages in Sec. III, which will be exploited whenever it simplifies the discussion. However, the usefulness of the statistical formulation of entropy is evident when the system is out of equilibrium; in this case, there is no way to "measure" or calculate the thermodynamic entropy, but the statistcal entropy can be calculated. In Sec. IV, we discuss the consequences of internal equilibrium and its similarity with and differences from the concept of local equilibrium [13–16]. In particular, we argue in the form of Theorem 1 that a body can only sustain a uniform translation and rotation in internal equilibrium; thus, there will be no relative motion between its various parts. It is assumed here that there are no additional conditions (such as the potential flow in a superfluid) on the velocity. The proof is trivial but the theorem has far-reaching consequences. In this work, we will treat Σ as inhomogeneous by considering it to be composed of a collection of N_{S} *subsystems* $\sigma_k, k = 1,2,\ldots,N_{\mathrm{S}}$ with relative motions and shear forces between them. Each subsystem is still *macroscopically* large so we can introduce a legitimate entropy function s_k; see Sec. X B for further elaboration. Furthermore, each subsystem will be assumed to be in internal equilibrium.

Apart from the *observables* that can be manipulated by the observer, there also appear *internal variables*, see Sec. VII, often needed to describe nonequilibrium states. Therefore, they are also useful in describing glasses, as is well known from the early works of Davies and Jones [24,25]. The internal variables cannot be manipulated by the observer. Specifically, we treat translations and rotations of various parts of a system as internal variables. The alternative approach is to use the traction forces and the strains instead; see, for example, Ref. [2]. The phenomenological ideology introduced by Davies and Jones [24], which has been recently reviewed by Öttinger [6], is by now standard and has been discussed in several textbooks; see, for example, Refs. [26,27]. The observables and internal variables will be collectively called *state variables*; see Sec. III for proper definitions of these terms.

The condition for additivity and quasi-independence is considered in Sec. V, where we prove that the Gibbs entropy formulation in Eq. (8) is also applicable to any body. Various thermodynamic potentials are identified in Sec. VI whose time variations are in accordance with the second law. It is here that we see a clear distinction between our approach and the conventional nonequilibrium theory exploiting the local equilibrium concept [13–16]. Internal variables are discussed in Sec. VII. Using our approach, we prove a well-known result that the chemical potential or the affinity associated with an internal variable must be zero when the system is in equilibrium. This adds credibility to our approach. We also prove that the entropy expressed solely in terms of observables when there are independent internal variables must explicitly depend on time so, while the system is in internal equilibrium with respect to *all* state variables, it is not in internal equilibrium with respect to only observables or only some of them. A system undergoing uniform translation and rotation is studied in Sec. VIII, where we also develop the Gibbs fundamental relation for such a system. We then apply the results to the cases when the homogeneous system and the medium undergo relative translational motion in Sec. IX. An inhomogeneous system with relative motions between its subsystems is studied in the next section. We also discuss in this section the case of several different bodies, each in internal equilibrium, that form an isolated body $\overline{\Sigma}_0$ without a medium; see Fig. 2(b). We discuss a direct method of calculating the irreversible entropy generation in each body in terms of the equilibrium state of all the bodies. We find that the same results are also obtained by bringing all bodies in $\overline{\Sigma}_0$ in contact with a medium as shown in Fig. 2(a) that is chosen with the equilibrium fields such as the equilibrium temperature T_0 of $\overline{\Sigma}_0$. This equivalence is used to prove Theorem 6. All these investigations are extended to include extra observables and internal variables. The final section contains concluding discussion and a brief summary of our results.

II. LOCAL NONEQUILIBRIUM THERMODYNAMICS: A BRIEF REVIEW

In classical local nonequilibrium thermodynamics [13–16], the entropy

$$S \equiv \int_V s(\mathbf{r})dV \tag{2}$$

is always taken to be *additive* [13]; here $s(\mathbf{r})$ is the *local* entropy density per unit volume. The local temperature T and pressure P are assumed continuous functions of the location $\mathbf{r}$ and time t and are postulated to always exist. The *additivity* of the energy E appears as

$$E \equiv \int_V \left[e(\mathbf{r}) + \frac{1}{2} m_0 \rho(\mathbf{r}) \mathbf{v}^2(\mathbf{r}) + \mathbf{m}(\mathbf{r}) \cdot \boldsymbol{\omega}(\mathbf{r}) + \psi(\mathbf{r}) \right] dV, \tag{3}$$

where the terms in the integrand denote the internal energy density, the translational and rotational kinetic energy densities, and the additional energy contribution due to interactions not included in the internal energy density, respectively. The local mass and angular momentum densities are given by $m_0\rho$ and $\mathbf{m}(\mathbf{r})$, respectively; compare with Eq. (73) derived later after limiting it to the volume element dV.

For a simple system containing a fixed number of structureless particles, it is assumed that the functional form of the entropy density is a function only of the local internal energy density e and the local number density ρ; see, for example [13],

$$s(\mathbf{r}) = s[e(\mathbf{r}), \rho(\mathbf{r})]. \tag{4}$$

The local Gibbs free energy density $\widehat{g}$ is given by

$$\widehat{g} = e - Ts + P, \tag{5}$$

whether local equilibrium exists or not. (The unconventional use of the symbol $\widehat{g}$ instead of g will become clear later when we discuss the Gibbs free energy.) However, no direct method of calculating the (thermodynamic) entropy is given in this approach except when local equilibrium exists. In the latter case, one can determine the entropy by using the Gibbs fundamental relation, which, for a simple system with no internal variables, reads [13],

$$Td(s/\rho) = d(e/\rho) + Pd(1/\rho). \tag{6}$$

We instead, first, identify the (statistical analog of the) nonequilibrium entropy in terms of allowed microstate probabilities, see Eq. (8), and then use the concept of *internal equilibrium* to introduce the temperature and pressure; the latter are defined only when there is internal equilibrium [1]. Our approach is *not* local in that we always deal with quantities S, E, etc., related to macroscopically large bodies. As a consequence, all quantities associated with these bodies will not *always* be continuous functions of space at the interfaces. This makes our approach distinct from the traditional local nonequilibrium approach of de Donder [13–16], where these quantities are always treated as continuous. In the latter approach, a system can be broken into subsystems, each sufficiently small to be in internal equilibrium to satisfy the Gibbs fundamental relation. This hypothesis is known as the local equilibrium hypothesis. We add another requirement, that of quasi-independence of the subsystems in our approach, which we believe to be extremely important. *Only this requirement ensures that the entropy remains not only additive but also a state function*; see Sec. V.

A. Helmholtz theorem

It is well known that the local motions for a deformable body can be described as a combination of three distinct types of motions [28,29]: (a) a pure translation, (b) a pure strain, and (c) a pure rotation. This is easily seen by expressing the instantaneous difference in the velocity $\delta\mathbf{v}$ at two nearby points separated by a displacement vector $\delta\mathbf{r}$ as

$$\delta v_i = \psi_{ij}\delta x_j + \widehat{\omega}_{ij}\delta x_j, \tag{7}$$

where the symmetric and the antisymmetric tensors

$$\psi_{ij} \equiv \tfrac{1}{2}(\partial v_i/\partial x_j + \partial v_j/\partial x_i),$$
$$\widehat{\omega}_{ij} \equiv \tfrac{1}{2}(\partial v_i/\partial x_j - \partial v_j/\partial x_i) \equiv e_{ijk}\widehat{\omega}_k$$

represent the rate of strain tensor and the vorticity tensor resulting in the axial vector $\widehat{\boldsymbol{\omega}} = \frac{1}{2}\boldsymbol{\partial} \times \mathbf{v}$, respectively. The first contribution in Eq. (7) represents a pure straining motion while the second contribution represents the components of the vector $\widehat{\boldsymbol{\omega}} \times \delta\mathbf{r}$ due to a rigid-body rotation. For example, a simple shearing motion in which plane layers of the system slide over each other can be treated as a combination of a pure strain (with no rate of volume change) and a rotation [29].

B. Stress tensor

The motion at the local level can also be studied directly by considering the stress tensor. The stress tensor is normally expressed as a sum of the nondissipative and dissipative or viscous contributions [4], $\tau_{ij} = \sigma_{ij} + \sigma'_{ij}$, in which the viscous contribution σ'_{ij} is some function that depends on the velocity gradients $\partial v_i/\partial x_j$, $\partial^2 v_i/\partial x_j \partial x_k$, and so on. In the linear approximation, we see from Eq. (7) that σ'_{ij} depends on ψ_{ij} and $\widehat{\omega}_k$. In general, we can partition σ'_{ij} and τ_{ij} into symmetric and antisymmetric parts, the latter due to the presence of intrinsic rotation of the system [13] and describing the role of the rotational viscosity; see Chapter 12 in the monograph [13]. Of course, there may be symmetry reasons such as the isotropy of the system that would forbid the dependence on vorticity, in which case there would be no antisymmetric part. It is possible to show [13] that the rate of change of the intrinsic angular momentum is determined solely by $\tau^{\mathrm{a}}_{ij} \equiv \frac{1}{2}(\tau_{ij} - \tau_{ji})$. Thus, the absence of τ^{a}_{ij} will imply the conservation of the orbital and intrinsic angular momentum separately.

It is known [13] that τ^{a}_{ij} contributes a term proportional to $\boldsymbol{\tau} \cdot (\widehat{\boldsymbol{\omega}} - \boldsymbol{\omega})$ to the rate of change of the internal energy e and to the entropy production. Here, $\boldsymbol{\tau}$ is the vector associated with $\tau^{\mathrm{a}}_{ij} = e_{ijk}\tau_k$ and $\boldsymbol{\omega}$ represents the angular velocity of rotation of the system; cf. Eq. (3). Thus, this contribution vanishes for uniform rotation $\widehat{\boldsymbol{\omega}} = \boldsymbol{\omega}$, as expected. For $\widehat{\boldsymbol{\omega}} \neq \boldsymbol{\omega}$, there would be precession of the local volume element [30] about the direction of $\boldsymbol{\omega}$, so the rotational viscosity would play an important role until $\widehat{\boldsymbol{\omega}} = \boldsymbol{\omega}$.

III. STATISTICAL ENTROPY AND AVERAGES

A. Isolated system

We have shown elsewhere [31] that the *dimensionless* statistical entropy of an isolated system as a function of time is given by the Gibbs formulation

$$S_0(t) = -\sum_\alpha p_\alpha(t) \ln p_\alpha(t), \tag{8}$$

where $p_\alpha(t)$ is the time-dependent probability of the α-th microstate of the isolated system. It is nondecreasing in time, as reviewed elsewhere [19]. The derivation requires considering $\mathcal{N} p_\alpha(t)$ replicas of the α-th microstate, where $\mathcal{N}$ is the number of replicas in the ensemble. The entropy per replica gives the above entropy. As this formulation contains the Boltzmann formulation, see Eq. (13), we consider the Gibbs formulation to supersede the Boltzmann formulation [19]. But it should be noted here that this issue is far from settled; see, for example, Refs. [32,33] for opposing views.

The collection $\boldsymbol{\alpha} = \{\alpha\}$ of these microstates along with their *nonzero* probabilities represents a *macrostate* $\mathcal{M}_0$ of Σ_0. Customarily, a macrostate is specified by a set of some extensive *observables* $\mathbf{X}_0$; see the discussion in Sec. VII for more details. For an isolated system, these observables remain constant of motion, and the entropy will not change in time if it only depends on $\mathbf{X}_0$. Therefore, we are forced to introduce a set $\mathbf{I}$ of *internal variables* [13–16], to be discussed later in Sec. VII, that cannot be controlled by the observer and that determine the time evolution of the isolated system. We will take these internal variables to be also extensive and call both of them *state variables* and collectively denote them by $\mathbf{Z}$. Taking internal variables as extensive allows us to deal all state variables on equal footing, so the generalization from observables to internal variables becomes almost trivial. In general, microstate probabilities $p_\alpha(t)$ are functions of the state variables $\mathbf{Z}_0$ along with t. As a consequence, the entropy $S_0[\mathbf{Z}_0(t),t]$ is also going to be a function of $\mathbf{Z}_0(t)$ and t. There are situations when the entropy can also depend on some *external parameters*, such as the angular velocity of the rotation of the frame of reference. These parameters need not necessarily be extensive.

While the microstate α, hence, the value of the state variable $\mathbf{Z}_{0\alpha}$ in the microstate α, does not vary with time, the *average* $\mathbf{Z}_0(t)$ for the macrostate varies with t as follows:

$$\mathbf{Z}_0(t) \equiv \sum_\alpha p_\alpha(t)\mathbf{Z}_{0\alpha}. \tag{9}$$

The entropy in Eq. (8) is the *average* of $(-\ln p)$ [19], the negative of the index of probability $\ln p$ introduced by Gibbs. There will be times when we will also use an overbar such as in $\overline{\mathbf{Z}}_0(t)$ to indicate such averages for the sake of clarity. For common thermodynamic quantities such as average energy, volume, etc., the normal practice is to not use the overbar (unless clarity is needed) as it is mostly these average quantities that we deal with.

B. An arbitrary body

It should also be stressed that the microstates for a body remain the same whether the body is isolated or not. We can apply Eqs. (8) and (9) to determine the entropy and the average quantity such as the energy for any body, isolated or not, as follows:

$$S(t) \equiv -\sum_i p_i(t) \ln p_i(t), \tag{10}$$

$$E(t) \equiv \sum_i p_i(t) E_i, \tag{11}$$

where i denotes one of its microstates, whose probability is denoted by $p_i(t) > 0$. In the following, we will always use i to denote a microstate of a body but reserve α to denote the microstate of the isolated system. While we can certainly allow microstates with probabilities $p_\alpha(t) = 0$, $p_i(t) = 0$, we find it convenient to only allow microstates with nonzero probabilities in the sum. Microstates with nonzero probabilities will be identified as *allowed* [19] in this work. While there cannot be any doubt about the validity of the energy average in Eq. (11), one may feel some reservation about Eq. (10) for the entropy of an open system. Therefore, we will give a direct proof of Eq. (10) in Sec. V.

IV. INTERNAL EQUILIBRIUM THERMODYNAMICS

A. Equiprobability concept and consequences

The concept of *internal equilibrium* is similar to the assumption of local equilibrium in the conventional nonequilibrium thermodynamics; see Sec. II. The condition [1,19] for the internal equilibrium is that the entropy has the maximum possible value at each instant for the given *instantaneous* average value $\mathbf{Z}_{\mathrm{IE}} \equiv \mathbf{Z}(t)$ of the state variables of the body. It is easy to see from Eq. (8) or Eq. (10) that this happens *if and only if* all the allowed microstates at that instant are *equiprobable*:

$$p_i(t) = 1/W(t), \quad \forall i, \tag{12}$$

where $W(t)$ is the number of allowed microstates at that instant. This immediately leads to

$$S(t) = \ln W(t), \tag{13}$$

the Boltzmann entropy for a body in internal equilibrium, a very common assumption; see, for example, Refs. [2,10]. Let us follow the consequences of this concept.

(1) Since the entropy is maximum for given $\mathbf{Z}_{\mathrm{IE}}$, there cannot be any *additional* irreversible entropy production for given $\mathbf{Z}_{\mathrm{IE}}$.

(2) When the body is in internal equilibrium, its various parts must be in equilibrium with each other. Otherwise, there would be irreversible entropy generation.

(3) It follows from (2) that all the arguments to follow the consequences of equilibrium can be applied to different parts of the body that are in equilibrium. For example, the arguments that establish that a body in equilibrium can only sustain uniform translation and rotation ([20], Sec. 10) can be applied without any change to a body in internal equilibrium. We state it as a theorem because of its important role here.

Theorem 1. There cannot be any relative motion between different parts of a body for given $\mathbf{Z}_{\mathrm{IE}}$ in the state of internal equilibrium; the whole body can sustain only uniform translation and rotation [20].

Proof. We refer the reader to Landau and Lifshitz ([20]), Sec. 10) for the details. We easily extend their argument by considering our body at some instant t with given $\mathbf{Z}_{\mathrm{IE}} = \mathbf{Z}(t)$. This proves the theorem. ■

The axis of the uniform rotation must be a principal axis of the instantaneous moment of inertia of the body. Otherwise, the body will undergo precession in space [30] and the rotation will not be uniform.

(4) Even with internal equilibrium in the body at each instant, there are both elastic and inelastic or plastic deformations ([34], Sec. 7.4.2) in time, which result in viscoelasticity in the body.

If and only if the body is under internal equilibrium, the derivatives $\mathbf{w}(t)$ of $S(t)$ with respect to $\mathbf{Z}(t)$,

$$\mathbf{w}(t) \equiv \beta(t)\mathbf{W}(t) \equiv [\partial S(t)/\partial \mathbf{Z}(t)]_{\mathbf{Z}'(t)}, \tag{14}$$

where $\beta(t) \equiv 1/T(t)$ and where $\mathbf{Z}'(t)$ denotes all other elements of $\mathbf{Z}(t)$ except the one used in the derivative, have the significance of the *fields* $\mathbf{y}(t)$ or *affinities* $\mathbf{a}(t)$:

$$\begin{aligned} \mathbf{y}(t) &\equiv \beta(t)\mathbf{Y}(t) \equiv [\partial S(t)/\partial \mathbf{X}(t)]_{\mathbf{Z}'(t)}, \\ \mathbf{a}(t) &\equiv \beta(t)\mathbf{A}(t) \equiv [\partial S(t)/\partial \mathbf{I}(t)]_{\mathbf{Z}'(t)}. \end{aligned} \tag{15}$$

In particular, the temperature $T(t)$ and the pressure $P(t)$ are defined in the standard manner,

$$\begin{aligned} y_E(t) &\equiv \beta(t) = [\partial S(t)/\partial E(t)]_{\mathbf{Z}'(t)}, \\ y_V(t) &\equiv \beta(t)P(t) = [\partial S(t)/\partial V(t)]_{\mathbf{Z}'(t)}. \end{aligned} \tag{16}$$

The pair of quantities $\mathbf{Z}(t),\mathbf{W}(t)$ or $\mathbf{Z}(t),\mathbf{w}(t)$ are called *conjugate* to each other. We will refer to $\mathbf{W}(t)$ or $\mathbf{w}(t)$ as *generalized fields* or, simply, *fields* if no confusion arises.

The definitions of the generalized fields give us an alternative way to interpret internal equilibrium. We imagine bringing the body in *contact* with another medium whose generalized fields are exactly equal to those of the body at that instant t,

$$\mathbf{w}_{\mathrm{IE}} \equiv \beta_{\mathrm{IE}}\mathbf{W}_{\mathrm{IE}} \equiv [\partial S(t)/\partial \mathbf{Z}(t)]|_{\mathbf{Z}_{\mathrm{IE}}};$$

here $\beta_{\mathrm{IE}} \equiv 1/T_{\mathrm{IE}}$ and the symbol $|_{\mathbf{Z}_{\mathrm{IE}}}$means that the derivative is evaluated at $\mathbf{Z}_{\mathrm{IE}} = \mathbf{Z}(t)$. To distinguish this medium from the medium $\widetilde{\Sigma}$ that is characterized by $\mathbf{W}_0 = (T_0,P_0,\ldots)$, we denote the new medium by $\widetilde{\Sigma}_{\mathrm{IE}}$ or $\widetilde{\Sigma}(\mathbf{W}_{\mathrm{IE}})$. The body, which now represents the system Σ in internal equilibrium with state variable $\mathbf{Z}_{\mathrm{IE}}$, is in equilibrium with the medium $\widetilde{\Sigma}_{\mathrm{IE}}$. On the other hand, if we isolate the system, only the observables $\mathbf{X}_{\mathrm{IE}}$ will remain constant, but $\mathbf{I}(t)$ will not remain fixed at its value $\mathbf{I}_{\mathrm{IE}}$. Thus, when internal variables are present, $\mathbf{Z}_{\mathrm{IE}}$ can be kept fixed only by bringing the body in contact with the medium $\widetilde{\Sigma}_{\mathrm{IE}}$. It is clear now that the instantaneous state of the system with $\mathbf{Z}_{\mathrm{IE}}$ must not be confused with a surrogate system [11].

B. The zeroth and the second law

All the above discussion can be easily extended to a system consisting of various subsystems σ_k, each in internal equilibrium. Let us consider the isolated system $\overline{\Sigma}_0$ shown in Fig. 2(b), which consists of two subsystems σ_1 and σ_2 whose instantaneous temperatures are $T_1(t)$ and $T_2(t) > T_1(t)$, respectively. Let their respective energies be $E_1(t)$ and $E_2(t)$, with their sum $\overline{E}_0$ a constant. We consider *all* other observables fixed for both subsystems. The irreversible entropy gain for $\overline{\Sigma}_0$ is $[\beta_1(t) \equiv 1/T_1(t),\beta_2(t) \equiv 1/T_2(t)]$

$$d_{\mathrm{i}}^{(Q)}\overline{S}_0 = dQ[\beta_1(t) - \beta_2(t)] > 0 \tag{17}$$

during an infinitesimal heat transfer $dQ = -dE_2$ from the hotter subsystem to the colder subsystem. The inequality follows from the second law. Here, $F_{\mathrm{Q}}(t) \equiv \beta_1(t) - \beta_2(t)$ plays the role of the thermodynamic force $F_Q(t)$ driving the heat transfer; compare with Eq. (20). As $\overline{\Sigma}_0$ is isolated, $d_{\mathrm{i}}^{(Q)}\overline{S}_0$ is also the entropy change $d\overline{S}_0 = dS_1 + dS_2$, with the subsystem entropy changes given by

$$dS_1 = \beta_1(t)dQ, \quad dS_2 = -\beta_2(t)dQ.$$

At this moment, it is important to follow another important consequence of the thermodynamic force $F_Q(t)$, which vanishes if and only if the system has come to *thermal equilibrium*. During equilibration process, its signature *cannot* change. This is the *zeroth* law of thermodynamics in terms of the instantaneous temperatures of the two subsystems: *the instantaneous temperature plays the role of a thermodynamic temperature in that the heat always flows from a hotter body to a colder body*, a well-known result.

The above result can be easily generalized to many bodies forming $\overline{\Sigma}_0$ by introducing the concept of an effective instantaneous temperature for $\overline{\Sigma}_0$. To do this, we proceed as follows. Consider the above two subsystems. The heat dQ vanishes as the two subsystems approach equilibrium. Let T_0 denote the equilibrium temperature. We can associate an effective temperature $T(t)$ intermediate between $T_1(t)$ and $T_2(t)$, as discussed in I, for $\overline{\Sigma}_0$. For this, we momentarily assume that the two subsystems are thermally insulated from each other and that $\overline{\Sigma}_0$ is not isolated. We imagine adding a certain amount of energy $dE = dE_1 + dE_2$ to $\overline{\Sigma}_0$; here dE_1 and dE_2 denote the energies that are added to the two subsystems. As shown in I, the effective instantaneous temperature of $\overline{\Sigma}_0$ is given by [see Eq. (30) there]

$$\beta(t) = \beta_1(t)x(t) + \beta_2(t)[1 - x(t)], \tag{18}$$

where $x(t) \equiv dE_1/dE$. We now revert to the isolated system $\overline{\Sigma}_0$. As it approaches equilibrium, $T(t) \to T_0$; however, the differences $\Delta T(t) \equiv T(t) - T_0$, $\Delta T_1(t) \equiv T_1(t) - T_0$ and $\Delta T_2(t) \equiv T_2(t) - T_0$ cannot change their signature during the equilibration period. Moreover, the signatures of $dQ_1 \equiv dQ$ and $\Delta T_1(t)$ and of $dQ_2 \equiv -dQ$ and $\Delta T_2(t)$ are opposite at all times during the equilibration period. The extension to many bodies is straightforward: the signatures of $\Delta T_k(t) \equiv T_k(t) - T_0$ and of heat gain dQ_k for the k-th body *cannot* change during equilibration. The extension will prove useful below.

We now bring $\overline{\Sigma}_0$ (now denoted by Σ) to be in thermal contact with a medium at a fixed temperature T_0, as shown in Fig. 2(a), to form the isolated system Σ_0. We take T_0 to be the equilibrium temperature of $\overline{\Sigma}_0$ above. The infinitesimal heat given out by the hotter subsystem is now $dQ = dQ' + dQ_2$. The heat gained $dQ' + dQ_1$by the colder subsystem will now shown to be exactly the heat loss dQ, since we are dealing with an isolated system Σ_0. Thus, $dQ_1 = dQ_2$. We present this claim as a theorem.

Theorem 2. When the medium is at the equilibrium temperature of $\overline{\Sigma}_0$, then the medium does not contribute to any heat transfer between the subsystems so the entropy of the medium remains constant.

Proof. We, first, note that when the two subsystems have come to equilibrium in the presence of the medium, then the two subsystems are in the same equilibrium state as in $\overline{\Sigma}_0$. If the total heat given by σ_2 is ΔQ in the present case, then the heat gained by σ_1 must also be ΔQ just as was for $\overline{\Sigma}_0$. It then follows that the total heat ΔQ_2 given by σ_2 to the medium must be exactly equal to the total heat ΔQ_1 gained by σ_1. Therefore, the total heat change $\Delta\widetilde{Q} \equiv \Delta Q_2 - \Delta Q_1$ for the medium must be identically zero. If we now treat the two subsystems as the single system Σ at its effective temperature $T(t)$, then from what we have said above, it follows that the signature of instantaneous heat change $d\widetilde{Q}$ of the medium and of $\Delta T(t) \equiv T(t) - T_0$ cannot change as Σ comes to equilibrium. Therefore, at each instant,

$$d\widetilde{Q} \equiv dQ_2 - dQ_1 \equiv 0,$$

which proves the first part of the theorem. As the instantaneous entropy change of the medium is given by $d\widetilde{S} \equiv d\widetilde{Q}/T_0$, we also find that the entropy of the medium remains constant during the entire process. This completes the proof. ■

As $d_{\mathrm{i}}^{(Q)}S = d_{\mathrm{i}}^{(Q)}S_0 = d_{\mathrm{i}}^{(Q)}\overline{S}_0 > 0$, bringing $\overline{\Sigma}_0$ in Fig. 2(b) in contact with a medium, characterized by the equilibrium temperature T_0 of $\overline{\Sigma}_0$ does not affect the irreversible entropy production. The arguments are easily extended to many subsystems and to other field variables. We will not pause here to do that.

Let the volumes of the two subsystems adjust as they come to equilibrium. All other extensive observables are considered fixed. The same reasoning as above then results in

$$d_{\mathrm{i}}^{(V)}S = dV(t)[y_{V1}(t) - y_{V2}(t)] > 0 \tag{19}$$

in terms of the volume change $dV(t)$ of σ_1; $y_V(t)$ is defined in Eq. (16). The corresponding thermodynamic force $F_V(t) \equiv y_{V1}(t) - y_{V2}(t)$ vanishes when the system comes to *mechanical* and *thermal equilibrium*. In general, the thermodynamic force is given by

$$F_Z(t) \equiv F[w(t)] \equiv w(t) - w_0, \tag{20}$$

with w_0 representing the equilibrium value of w corresponding to the state variable Z.

C. Maxwell relations

As the concept of internal equilibrium does not differ much from the concept of equilibrium, it should not come as a surprise that there are analogs of Maxwell relations. For a system characterized by only S and V (fixed N), equilibrium Maxwell relations can be compactly written by using the numerators of Jacobians as

$$\partial(T_0,S,N) = \partial(P_0,V,N);$$

see Ref. [35] for details. We now consider a system in internal equilibrium. For simplicity, we assume that only one internal variable, to be denoted by ξ instead of I, characterizes this system. To simplify the notation, we will suppress N. The system is in equilibrium with the medium $\widetilde{\Sigma}(\mathbf{W}_{\mathrm{IE}})$. We then have conventional Maxwell relations $\partial(T,S,\xi) = \partial(P,V,\xi)$, $\partial(T,S,V) = \partial(A,\xi,V)$, and $\partial(P,V,S) = -\partial(A,\xi,S)$ obtained by replacing T_0, P_0, A_0 with $T(t) = T_{\mathrm{IE}}$, $P(t) = P_{\mathrm{IE}}$, $A(t) = A_{\mathrm{IE}}$. From this, it follows that "nonequilibrium" Maxwell relations when the system is in the medium $\widetilde{\Sigma}(\mathbf{W}_0)$ become

$$\frac{\partial(T,S,\xi)}{\partial(P_0,S,\xi)} = \frac{\partial(P,V,\xi)}{\partial(P_0,S,\xi)}, \frac{\partial(T,S,\xi)}{\partial(T_0,V,\xi)} = \frac{\partial(P,V,\xi)}{\partial(T_0,V,\xi)}, \tag{21}$$

and so on. More details will be given in the following publication in this issue.

D. Statistical nature of the approach

Our approach is truly a statistical mechanical approach. The averages and other moments of all state variables required to identify the microstates and the entropy are determined for the macrostate in terms of the microstate probabilities; the latter do not even have to satisfy the requirement for internal equilibrium. For example, the average fluctuation in $\mathbf{Z}$ for a body is given by

$$[\Delta\mathbf{Z}(t)]^2 \equiv \sum_i p_i(t)[\mathbf{Z}_i - \overline{\mathbf{Z}}(t)]^2, \tag{22}$$

where

$$\overline{\mathbf{Z}}(t) \equiv \sum_i p_i(t)\mathbf{Z}_i \tag{23}$$

is the average $\overline{\mathbf{Z}}$ for the body; compare with Eq. (9). These averages, which include the entropy and volume, for example, exist at all times, even if the system is not in internal equilibrium. Therefore, these quantities are on equal footing in our approach. Accordingly, their role turns out to be identical to those of internal variables; see I.

V. ADDITIVITY OF ENTROPY AND QUASI-INDEPENDENCE

For simplicity of discussion, we consider all bodies to be stationary in this section, so we deal only with internal energies. As noted in Sec. III, we take the entropy of an isolated body to be given by the Gibbs statistical formulation in Eq. (8), regardless of whether it is in equilibrium. There is no reason to believe that this formulation also applies to a body under all conditions, though its applicability in equilibrium is not in dispute [20]. We now prove that this formulation also applies to any body under a very mild condition that is always taken for granted. We will specifically consider our system Σ at some instant t, but the conclusion is valid for all bodies. Let us consider all allowed microstates of Σ with fixed number of particles N; we index these microstates by $i = 1,2,\ldots,W(t)$. We use $\widetilde{\alpha}$ to denote the microstates of $\widetilde{\Sigma}$ whose number of particles $\widetilde{N}$ is also fixed. A specification of the microstates i and $\widetilde{\alpha}$ gives a unique microstate α of the isolated system Σ_0. Hence, the number of *allowed* microstates $W_0(t)$ of the Σ_0 is the product

$$W_0(t) = W(t)\widetilde{W}(t), \tag{24}$$

where $W(t)$ and $\widetilde{W}(t)$ are, respectively, the number of all allowed microstates of Σ and $\widetilde{\Sigma}$ associated with the state variables $\mathbf{Z}(t)$ and $\widetilde{\mathbf{Z}}(t)$, respectively.

Let E_0, $E(t)$, and $\widetilde{E}(t)$ denote the internal energies of Σ_0, Σ, and $\widetilde{\Sigma}$, respectively, and $E_0^{(\mathrm{int})}(t)$ the mutual interaction energy between Σ and $\widetilde{\Sigma}$ at some instant t. For short-ranged interactions, this energy is determined by the surface $\partial V(t)$ of

Σ. For convenience, we assume that this entire area is exposed to the surrounding medium, as shown in Fig. 1. If long-ranged interactions are also present, or if the system size is very small, this energy may depend on the entire volume $V(t)$ of Σ. In all cases, this energy is defined by the following identity:

$$E_0 \equiv E(t) + \widetilde{E}(t) + E_0^{(\mathrm{int})}(t). \tag{25}$$

Because of the smallness of Σ relative to Σ_0, $E(t) \ll \widetilde{E}(t)$. If it happens that

$$\left|E_0^{(\mathrm{int})}(t)\right| \ll |E(t)|, \tag{26}$$

we call Σ and $\widetilde{\Sigma}$ *quasi-independent*. For quasi-independence, the linear size of the system must be at least as large as, but hopefully larger than, the longest correlation length in the system; the latter is obtained by considering the two-point correlation function between fluctuations in any observable. In this case, we can neglect their mutual interactions, which is a common practice in the discipline [20]. The quasi-independence of the system and the medium holds to a very high degree of accuracy for all short-ranged interactions [1], provided the system itself is macroscopically large so the ratio of its surface to volume is insignificant. In most cases, this will also ensure that the correlation length is small compared to the size of the system. If there are also long-ranged interactions, then we can still have quasi-independence, provided these interactions are relatively weak and shielding occurs and that Eq. (26) and the condition on the correlation length hold simultaneously. Thus, we have the additivity of the energies

$$E_0 \equiv E(t) + \widetilde{E}(t) \tag{27}$$

as a consequence of *quasi-independence*. In this case, the microstates of Σ and $\widetilde{\Sigma}$ are independent of each other to a very high degree of accuracy and we have

$$p_\alpha(t) = p_i(t)p_{\widetilde{\alpha}}(t).$$

From it follows the additivity of entropies

$$S_0(t) = S(t) + \widetilde{S}(t), \tag{28}$$

where the two terms represent the entropies of the system and the medium

$$S(t) = -\sum_i p_i(t)\ln p_i(t), \quad \widetilde{S}(t) = -\sum_{\widetilde{\alpha}} p_{\widetilde{\alpha}}(t)\ln p_{\widetilde{\alpha}}(t), \tag{29}$$

respectively. This demonstration justifies the additivity of entropies and the additivity of energies. Note that we have neither assumed the medium nor the system to be in internal equilibrium in the above demonstration. Thus, *the additivity principle is more fundamental than the requirement of internal equilibrium*. It is easy to see that the additivity holds true for any number of quasi-independent bodies in Σ_0, each of which has its entropy given by an expression identical in form to that of $S(t)$ in Eq. (29). It is easy to see that for an equilibrium body, $S(t)$ reduces to the equilibrium thermodynamic entropy.

If quasi-independence fails, then Eq. (26) is violated. In this case, the entropy $S_0(t)$ will be strictly less than the entropy in Eq. (28). We denote their difference by $S_0^{(\mathrm{int})}(t) \leqslant 0$ [36], which is defined by the following identity:

$$S_0(t) \equiv S(t) + \widetilde{S}(t) + S_0^{(\mathrm{int})}(t). \tag{30}$$

This identity reduces to Eq. (28) provided

$$\left|S_0^{(\mathrm{int})}(t)\right| \ll S(t); \tag{31}$$

compare with Eq. (26). This inequality will in general hold only if the interaction energy is also negligible.

If the strong inequality in Eq. (31) is not satisfied, we have lost the additivity property of the entropy. Let us assume that the strong inequality is satisfied for some large size of Σ. As the size decreases, which is what will happen on the way to considering physically infinitesimal volume elements used in Eq. (2), there comes a point where the strong inequalities in Eqs. (26) and (31) are violated. This will destroy the additivity of the entropy in Eq. (28), which occurs at intermediate sizes of the system, somewhere between the macroscopic size where Eqs. (26) and (31) are valid, and small local or microscopic size containing a small number dN of particles. For example, for $dN \approx 10^{18}$, the surface-to-volume ratio for the volume element dV is about 10^{-6}, implying an almost imperceptible error in neglecting the interaction entropy $S_0^{(\mathrm{int})}(t)$, provided the linear size of this region is large compared to not only the interparticle separation ([3], p. 1) but also the correlation length in the system. Under these conditions, the integrand in Eq. (2) truly refers to a "physically" infinitesimal volume element containing a very large number of particles. In this sense, our starting premise is similar to that adopted in the conventional nonequilibrium thermodynamics [13–16], except that we require quasi-independence, which imposes the strong condition that not only the interaction energy be small but also that the linear size be at least as large as the correlation length. At present, there is some evidence that the correlation length in a glass forming system appears to increase as the system approaches the glass transition [37]. In general, we expect correlation length in any nonequilibrium body to increase as the temperature is lowered. If true, this requirement may prove very important, especially at low temperatures.

As we will be interested in considering parts of Σ as subsystems in this work, the additivity of their entropy requires that their mutual interaction energies be also negligibly small compared to their individual internal energies and that their linear sizes be at least as large as the correlation lengths. In general, we should consider all state variables such as V. We must have an analogous condition such as $|V_0^{(\mathrm{int})}(t)| \ll V(t)$ for V, where $V_0^{(\mathrm{int})}(t)$ is defined similar to $E_0^{(\mathrm{int})}(t)$ in Eq. (25), for each one of them. These requirements put a strong condition on the sizes of subsystems.

VI. THERMODYNAMIC POTENTIALS

A. Fixed N

We assume the medium to be in internal equilibrium. Under this very weak assumption for $\widetilde{\Sigma}$, its field variables are well defined and are unaffected by whatever processes happen to be going on within the system Σ or whether Σ is homogeneous or inhomogeneous. When the number of particles N in Σ is held fixed, the appropriate thermodynamic potential is, as shown in

I, the Gibbs free energy,

$$G(T_0,P_0,t) = E(t) - T_0S(t) + P_0V(t), \tag{32}$$

which *differs* from the local Gibbs free energy [13–16] in Eq. (5); the latter is related to $\widehat{G}(t)$,

$$\widehat{G}(t) \equiv \widehat{H}(t) - T(t)S(t),\ \widehat{H}(t) \equiv E(t) + P(t)V(t), \tag{33}$$

which can be defined *only* when the system is under internal equilibrium and not otherwise. It was shown to increase with time [1] during relaxation,

$$d\widehat{G}(t)/dt \geqslant 0, \tag{34}$$

in a cooling process. As it does not always decrease with time, it cannot represent the Gibbs free energy; see also Eq. (22) of I. The particular form for $G(t)$ follows from the second law and remains valid even if the system is so far out of equilibrium that its temperature and pressure cannot be defined; see also Landau and Lifshitz ([20], see Sec. 20). Therefore, the Gibbs free energy does *not* represent a state function of the system. In an engineering context, this quantity is also known as *exergy* or *availability* [38].

It was shown in I that $G(t)$ continuously decreases as the system relaxes toward equilibrium, a result quite well known in classical thermodynamics [20] as follows:

$$dG(t)/dt \leqslant 0. \tag{35}$$

It, finally, becomes identical to the equilibrium Gibbs free energy at the current temperature and pressure T_0,P_0. If we abruptly change the temperature T_0' and pressure P_0' of the system in some state A', where the system was in equilibrium, to a new state A where the temperature and pressure are T_0,P_0, respectively, at time $t=0$, then the *initial* values of the energy, volume, and entropy in A remain equal to their respective equilibrium values in the previous state A' as the microstate probabilities $p_\alpha(t)$ at $t=0$ have not had any time to change. Thus, initially $G(0) = E_A' - T_0S_A' + P_0V_A'$ in A; the quantities with a prime are the equilibrium values in the state A'. The Gibbs free energy decreases in accordance with Eq. (35) and eventually becomes equal to its new equilibrium value $G_A = E_A - T_0S_A + P_0V_A$, where the quantities with the subscript A denote the equilibrium values in the new state A. It should be noted that the equilibrium Gibbs free energy in the state A' before the abrupt change is $G_A^{'} = E_A' - T_0'S_A' + P_0'V_A'$ so the Gibbs free energy undergoes a discontinuity at $t=0$ due to the abrupt change:

$$\Delta G_A^{'} = (T_0' - T_0)S_A' - (P_0' - P_0)V_A'.$$

Its magnitude and sign has nothing to do with the second law as the abrupt change is not due to a spontaneous process.

B. Fixed V

Instead of keeping N fixed, let us keep its volume V fixed so the volume of the medium is also kept fixed. The number of particles $\widetilde{N}$ of the medium is no longer fixed. We follow the steps similar to those in I and identify a new thermodynamic potential $\Omega(t) \equiv E(t) - T_0S(t) - \mu_0N(t)$, $[\beta_0\mu_0 = -(\partial\widetilde{S}/\partial\widetilde{N})|_{\mathbf{X}_0}$, with $\mathbf{X}_0$ representing E_0,V_0,N_0, and $\beta_0 \equiv 1/T_0]$, which also uses the fields of the medium and whose time variation obeys

$$d\Omega(t)/dt \leqslant 0.$$

C. Fixed N and V

If both N and V are kept fixed, we conclude that the Helmholtz free energy $F(t) \equiv E(t) - T_0S(t)$ continuously decreases as the system reaches equilibrium:

$$dF(t)/dt \leqslant 0.$$

VII. INTERNAL VARIABLES

A suitable macrostate description of a body requires a set of *independent* macroscopic observables that can be controlled by an experimentalist and whose values will allow him to differentiate between different macrostates of the body. It normally happens that experimentalists have a far less number of external controls than the possible extensive variables that can be used to characterize the macrostates. Thus, one does not characterize a macrostate by specifying all of the relevant extensive system quantities. For example, for a single component system, one normally uses E, V, and N to specify the macrostate if there are no external shearing forces, which we assume. Usually, one considers a system with fixed N; E and V then can be controlled by the two external variables T_0 and P_0 associated with the medium. However, these external variables need not necessarily control the local or internal structures in the system at all times during its evolution toward equilibrium. As Frenkel has observed, the local structures can be important when considering the structural relaxation in a glass or other nonequilibrium systems ([39], p. 208). For example, one can consider the average numbers of neighbors and next-neighbors of a given particle to describe the local structure in the system. The corresponding conjugate variables, normally identified as "chemical potentials" or "affinity" for these internal variables usually vanish in equilibrium. Frenkel goes on and calculates viscoelastic effects due to structural changes and compares them with Maxwell's model of elastic relaxation or an RC circuit. This investigation by Frenkel [39] shows that internal variables can play an important role in the temporal evolution in some systems such as glasses. As such, they become an integral part of the description of any nonequilibrium system and determine the relaxation of the system ([3], Sec. 78). We have already seen their importance in Sec. III. The internal variables are also called hidden variables or internal order parameters.

To introduce the concept of internal variables in a logical way, let us consider the isolated system Σ_0 for which one can identify a set of *conserved* quantities, i.e., integrals of motion. For a mechanical system of s degrees of freedom, the number of such integrals of motion are $2s-1$ [30]. Of these integrals of motion, those that are *additive* play an important role in thermodynamics and statistical mechanics. The notable ones are the energy, and linear and angular momenta of the system, among others such as the polarization, magnetization, and so on. For the moment, let us consider Σ_0 to be stationary. Its macrostate $\mathcal{M}_0$ is characterized by constant extensive observables $\mathbf{X}_0$. Let us consider the energy E_0, which is an integral of motion. It usually happens (see below for an example) that there are many different components $E_0^{(k)}$ of the energy whose total sum is the energy E_0,

$$E_0 \equiv \sum_{k=1}^{n+1} E_0^{(k)}(t), \tag{36}$$

where $n+1>1$ is the number of energy components. Only n of the components are independent for a given E_0, which we take to be given by $k=1,2,\ldots,n$. We will denote this set by an n vector $\mathbf{I}_0(t)$. It is E_0 that is a constant of motion, not the individual components $E_0^{(k)}(t)$; the latter will continue to change as the system evolves in time while maintaining Eq. (36). Let $W_0(\mathbf{X}_0,t)$ denote the number of allowed microstates corresponding to the macrostate $\mathcal{M}_0$ at time t. At each instant t, the microstates in $W_0(\mathbf{X}_0,t)$ can be partitioned into groups according to the possible values of $E_0^{(k)}(t)$. Let $W_0[\mathbf{X}_0,\mathbf{I}_0(t),t]$ denote the number of allowed microstates for a given $\mathbf{Z}_0(t)$. These microstates define a new macrostate, which we denote by $\mathcal{N}_0$. Obviously,

$$W_0(\mathbf{X}_0,t) \equiv \sum_{\mathbf{I}_0(t)} W_0[\mathbf{X}_0,\mathbf{I}_0(t),t]. \tag{37}$$

As the system evolves, different components $E_0^{(k)}(t)$ of $\mathbf{I}_0(t)$ evolve in time t, but $\mathbf{X}_0$ remains fixed. Thus, a better understanding of the evolution of the system can be obtained by monitoring how the various components $E_0^{(k)}(t)$ change in time. For this, it is better to use $\mathbf{Z}_0 \equiv [\mathbf{X}_0,\mathbf{I}_0(t)]$ to identify the macrostate $\mathcal{N}_0$ even though individual $E_0^{(k)}(t)$ cannot be controlled by the observer. As E_0 can be controlled by the observer, it is still the choice observable to be used for identifying a macrostate. This is even more true for the isolated system for which E_0 is a constant of motion. The n components of $\mathbf{I}_0(t)$ then play the role of *internal variables* in developing nonequilibrium thermodynamics of the isolated system.

It is evident that the same "extended" description is applicable to any body Σ. The only difference between any body and an isolated system is that not all elements of $\mathbf{X}$ remain constant for the former. Some of the observables, denoted by $\mathbf{X}'$ are controlled by external field parameters $\mathbf{Y}_0'$ (such as T_0, P_0, μ_0, etc.) of the medium so they do not remain fixed but continue to fluctuate about their mean $\mathbf{X}'(t)$ that keeps changing in time. However, at least one of the extensive observables such as N must be kept *constant* to quantify the *size* of the system [40]. The observables $\mathbf{X}'(t)$ may be replaced by $\mathbf{Y}_0'$, with the remaining observables remaining constant. We will denote the latter observables by $\mathbf{C}$ to remind us that they are constant. A body can be either specified by $\mathbf{X}'(t),\mathbf{C}$ or $\mathbf{Y}_0',\mathbf{C}$. However, for the sake of convenience, we will continue to use $\mathbf{X}(t)$ rather than $\mathbf{X}'(t),\mathbf{C}$ or $\mathbf{Y}_0',\mathbf{C}$. Let us now consider Σ, which is not in internal equilibrium, so it undergoes internal deformation due to relative motions between its various parts or other dissipation. If there are external strains on the system, they can be controlled by us from the outside. Hence, they will not be considered as internal variables. However, internal stresses acting on various parts of the system are beyond our control and must be treated as internal variables in describing the system. As said earlier, we can describe the internal forces acting on each part in terms of translation and rotation of its various parts; see Sec. II A. These motions must be described by the use of suitable internal variables, such as the linear and angular momenta, as was discussed in Sec. I B.

As the internal variables are uncontrollable, it is commonly believed that their affinity in equilibrium must vanish. We prove this as a theorem.

Theorem 3. The affinity of an internal variable must vanish in equilibrium.

Proof. It is sufficient to prove the theorem for an isolated system. Also, we will prove it for the energy components in Eq. (36). The extension to the general case is a trivial extension and will not be done here. As we are dealing with equilibrium, we consider only equilibrium values of all the quantities obtained by suppressing the argument t as they are stationary. We now construct the following partition function for the isolated system

$$Z_0(\mathbf{X}_0,\mathbf{A}_0) \equiv \sum_{\mathbf{I}_0} W_0(\mathbf{X}_0,\mathbf{I}_0)\exp\left\{-\sum_{k=1}^{n} a_0^{(k)} I_0^{(k)}\right\},$$

where $\mathbf{a}_0$ is the the n-vector $\{a_0^{(k)}\}$ equilibrium affinity. Such a partition function correctly describes the situation in which the n internal variables are not constant but keep changing from microstate to microstate. We now observe that this partition function reduces to the equilibrium value $W_0(\mathbf{X}_0)$ in Eq. (37) (where we take the limit $t\to\infty$), provided

$$A_0^{(k)} \equiv 0, \quad k=1,2,\ldots,n,$$

for each of the internal variable in the set $\mathbf{I}_{0,\mathrm{eq}}$. This proves the theorem. ■

The above theorem deals with equilibrium affinities and says nothing about the affinities of the internal variables when the system is out of equilibrium.

Let α denote one of the allowed microstates associated with the macrostate $\mathcal{M}_0$ and α' one of the allowed microstates associated with the macrostate $\mathcal{N}_0$. Then, using their probabilities $p_\alpha(t)$ and $p_{\alpha'}(t)$, we can determine the entropies $S_0(\mathbf{X}_0,t)$ and $S_0[\mathbf{X}_0,\mathbf{I}_0(t),t]$ of the two macrostates. For a macroscopically large system, the following standard statistical mechanical arguments can be used to highlight the maximum of the summand in Eq. (37). Let the maximum of the summand be denoted by $M_0(t)$, which occurs for some particular value $\bar{\mathbf{I}}_0(t)$ of $\mathbf{I}_0(t)$:

$$M_0(t) \equiv W_0[\mathbf{X}_0,\bar{\mathbf{I}}_0(t),t].$$

We separate the maximum contribution from the sum and rewrite Eq. (37) as follows:

$$W_0(\mathbf{X}_0,t) \equiv M_0(t)\left\{1+\sum_{\mathbf{I}_0(t)\neq\bar{\mathbf{I}}_0(t)} W_0[\mathbf{X}_0,\mathbf{I}_0(t),t]/M_0(t)\right\},$$

where the sum is over all remaining $\mathbf{I}_0(t)$. It is normally the case that the ratio in the above sum is vanishingly small for a macroscopic system and that the sum can be neglected. Thus,

$$W_0(\mathbf{X}_0,t) \approx W_0[\mathbf{X}_0,\bar{\mathbf{I}}_0(t),t]. \tag{38}$$

For a macroscopically large body, the above equation is formally valid, except that we must replace $\mathbf{X}_0$ with $\mathbf{X}(t)$ and $\bar{\mathbf{I}}_0(t)$ with $\bar{\mathbf{I}}(t)$:

$$W[\mathbf{X}(t),t] \approx W[\mathbf{X}(t),\bar{\mathbf{I}}(t),t]. \tag{39}$$

We now prove an important theorem about the nature of the entropy.

Theorem 4. The entropy expressed only in terms of the observables when (independent) internal variables are present must explicitly depend on t.

Proof. We first consider the isolated system Σ_0. For $\overline{\mathbf{I}}_0(t)$ to be independent of (constant) $\mathbf{X}_0$, it must surely have an explicit dependence on time: $\overline{\mathbf{I}}_0(t) \equiv \overline{\mathbf{I}}_0(\mathbf{X}_0,t)$. Let us assume that there is an explicit t dependence in both W_0 functions in Eq. (38). As the entropy of the macrostate $\mathcal{M}_0$ is given by the sum over all allowed microstates $W_0(\mathbf{X}_0,t)$ in Eq. (10), it must explicitly depend on t. Thus, the theorem is satisfied. If, however, neither of the W_0 functions in Eq. (38) have any explicit t dependence, then this is possible only if $\overline{\mathbf{I}}_0(t)$ becomes a function of $\mathbf{X}_0$ as the left side is only a function of $\mathbf{X}_0$. Since $\mathbf{X}_0$ is constant, $\overline{\mathbf{I}}_0(t)$ itself must be constant. The latter is the situation in equilibrium: $\overline{\mathbf{I}}_{0,\mathrm{eq}} = \overline{\mathbf{I}}_0(\mathbf{X}_0) =$ constant. As $\overline{\mathbf{I}}_0 \equiv \overline{\mathbf{I}}_{0,\mathrm{eq}}$ is no longer an independent variable, this case is not covered by the theorem. The entropy in this case is given by the Boltzmann formulation, cf. Eq. (13), and we have $S_0(\mathbf{X}_0) \approx S_0(\mathbf{X}_0,\overline{\mathbf{I}}_0) =$ const, which follows from Eq. (38).

Let us now consider the special case when the macrostate $\mathcal{N}_0$ satisfies the condition of internal equilibrium. In this case, $W_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t),t]$ should be written as $W_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t)]$ with $\overline{\mathbf{I}}_0(t)$ having an explicit time dependence. The entropy is again given by the Boltzmann formula $S_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t)] = \ln W_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t)]$. It now follows from Eq. (38) that $W_0(\mathbf{X}_0,t)$ must have an explicit time dependence due to the explicit t dependence of $\overline{\mathbf{I}}_0(t)$ in $W_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t)]$. Thus, $S_0(\mathbf{X}_0,t)$ will have an explicit t dependence even though $S_0[\mathbf{X}_0,\overline{\mathbf{I}}_0(t)]$ does not. This proves the theorem for an isolated system.

Let us now consider any body such as Σ. Again, $\overline{\mathbf{I}}(t)$ must be a function of $\mathbf{X}(t)$ and t to remain independent of $\mathbf{X}(t)$. Let us assume that there is an explicit t dependence in the W functions in Eq. (39). As the entropy of the body is given by the sum over all allowed microstates $W[\mathbf{X}(t),t]$, it must explicitly depend on t. If, however, neither of the W functions have any explicit t dependence, then $\overline{\mathbf{I}}(t)$ becomes a function of $\mathbf{X}(t)$. In this case, it is not independent of $\mathbf{X}(t)$. This situation is, then, not relevant for the theorem.

The remaining possibility, the one in which $\overline{\mathbf{I}}(t)$ is independent of $\mathbf{X}(t)$, but $W[\mathbf{X}(t),\overline{\mathbf{I}}(t)]$ has no explicit t dependence due to internal equilibrium, is very important. Fixing $\mathbf{X}_{\mathrm{IE}} \equiv \mathbf{X}(t)$ allows us to think of the body as an isolated system. Now we can use the argument given above for the isolated system to validate the theorem. Thus, we conclude that even if the macrostate $\mathcal{N}$ is in internal equilibrium, the corresponding macrostate $\mathcal{M}(t)$ is not in internal equilibrium.

This proves the theorem. ■

It follows from the above discussion that a general thermodynamic state can be taken to be a function of internal variables along with other observables and time t when we deal with nonequilibrium states. For a body in which many of the observables are controlled by external field parameters $\mathbf{Y}_0$ (such as T_0, P_0, etc.) of the medium, we can express $\overline{\mathbf{I}}_{\mathrm{eq}}$ either as $\overline{\mathbf{I}}_{\mathrm{eq}} = \overline{\mathbf{I}}(\mathbf{X}'_{\mathrm{eq}},\mathbf{C})$ or as $\overline{\mathbf{I}}_{\mathrm{eq}} \equiv \overline{\mathbf{I}}(\mathbf{Y}'_0,\mathbf{C})$. Away from equilibrium, $\overline{\mathbf{I}}[\mathbf{X}'(t),\mathbf{C}]$ differs from $\overline{\mathbf{I}}_{\mathrm{eq}}$. It is then treated as *independent* and plays an important role during relaxation as the body strives to reach equilibrium. Thus, it is not surprising that internal variables are employed to specify the macrostate of a nonequilibrium body; this fact has been recognized for quite some time [13–16].

Internal variables can also be related to the presence of internal degrees of freedom in the particles of interest. The internal degrees are more common in polymers but can also occur in small molecules in the form of rotation about some internal axes. An example will clarify the point much better. Consider a polymerization process resulting in a system of polydisperse linear polymer chains of average molecular weight $\overline{M}$ in a solution [41]. The model is defined on a lattice of N sites and volume $V = Nv_0$, with v_0 a constant representing the volume occupied by a lattice site. One normally uses E, V, $\overline{M}$, defined below, and the number of chains p as the standard observables that can be used to identify the macrostate (equilibrium or not) of the polymer solution. In turn, these quantities are controlled by the temperature, pressure, and the initiation-termination and propagation rates; the last two can be related to the initiation-termination activity controlling the number of end groups, two for each polymer, and the middle-group activity. These activities determine the corresponding affinity or "chemical potentials." Let $N_{\mathrm{m}} \equiv N - N_{\mathrm{v}}$ denote the number of monomers, each monomer occupying a lattice site, in terms of the number of voids or sites not covered by monomers N_{v} so $\overline{M} \equiv N_{\mathrm{m}}/p$. In terms of the number of middle groups $N_{\mathrm{M}} \equiv N_{\mathrm{m}} - 2p$, or N_{m}, the number of chemical bonds in the p polymers is given by $N_{\mathrm{B}} \equiv N_{\mathrm{M}} + p = N_{\mathrm{m}} - p$.

There are two kinds of energy in the model [41]. One kind of energy is due to mutual interactions of voids (v) with the end (E) and middle (M) groups, and the mutual interactions between chemically unbonded M and E. Let $N_{ij}, i, j =$ v, M, or E, denote the number of nearest-neighbor contacts ij, $i \neq j$, and ε_{ij} the corresponding interaction energies, respectively. The other kind of energy is due to intrachain gauche bonds (g) and hairpin turns (hp). The energies are E_{g} for gauche bonds and E_{hp} for hairpin turns. Let N_{g} and N_{hp} denote the number of gauche bonds and hairpin turns and ε_{g} and $\varepsilon_{\mathrm{hp}}$ their energies. In addition, there is a mutual interaction energy between two parallel (chemical) bonds, which may belong to the same or different polymers. Let N_{P} denote the number parallel bonds, each of energy ε_{P}. Then,

$$\begin{aligned} E &\equiv \sum_{i\neq j:\mathrm{v,M,E}} \varepsilon_{ij}N_{ij} + \varepsilon_{\mathrm{g}}N_{\mathrm{g}} + \varepsilon_{\mathrm{hp}}N_{\mathrm{hp}} + \varepsilon_{\mathrm{P}}N_{\mathrm{P}} \\ &\equiv \sum_{i\neq j:\mathrm{v,M,E}} E_{ij} + E_{\mathrm{g}} + E_{\mathrm{hp}} + E_{\mathrm{P}}, \end{aligned} \tag{40}$$

where we have introduced $E_{ij}, E_{\mathrm{g}}, E_{\mathrm{hp}}$, and E_{P} with obvious definitions. We, thus, observe that the energy can be partitioned into six extensive energies, five of which can be taken as internal variables.

To summarize, we conclude that the quantities that *cannot* be controlled by the observer can be identified as the *internal variables*. This statement should not be taken literally as what is considered uncontrollable today may not remain so in the future. Thus, to some degree, the decision to identify the internal variables is left to the observer. For us, any variable that cannot be controlled to have a fixed value when the system is out of equilibrium will be taken as an internal variable [42].

It should also be noted that the number of internal variables is not unique for a given body. For example, to describe local structures in a monatomic system [39], one can consider any number of neighboring particles (neighbors, next-neighbors, next-to-next neighbors, and so on). Thus, a choice will have to be made to see how many of them are useful in a given experiment or investigation. This certainly gives rise to an additional complication in the study of nonequilibrium system.

Our approach allows us to associate affinity in a formal sense with all internal variables as is done in the classical nonequilibrium thermodynamics [13–16]. As observed by Landau and Lifshitz [3], the use of internal variables in a modern way can be traced to Mandelstam and Leontovich [43]; see also Pokrovski [44]. Under the internal equilibrium assumption, Prigogine addresses the issue of internal variables (orientation of a molecule, deformation due to flow, elastic deformation, etc.) in Sec. 11, Chap. III, of his classic book [16], or in Sec. 10.4 in the modern version [15], and couples them to their "chemical potentials" or affinities. Indeed, Prigogine and Mazur were the first one to do this in their classic paper [45]; see also Coleman and Gurtin [46]. The issue of the internal variables is also discussed in Sec. 6, chap. 10 in Ref. [13]. Pokrovski [44] provides a very illuminating discussion of internal variables and their role in determining the internal energy. More recently, the idea has also been visited by Bouchbinder and Langer [2]. We will treat internal variables as additional thermodynamic extensive quantities or "observables" similar to the number of chemical species in chemical reactions that can be controlled by affinities or chemical potentials.

VIII. THERMODYNAMICS OF A SIMPLE ROTATING BODY

A. General case

We will find it convenient for later use to consider observing a body in different frames of reference; see also Appendices A and B. For concreteness, we consider the body with no internal variables and no other observables in addition to E, V, and N; the latter can be added easily as we will discuss later. We will consider three special frames: the laboratory frame denoted by $\mathcal{L}$, an intermediate frame $\mathcal{I}$, with its axes parallel to those of and moving with respect to $\mathcal{L}$ with a velocity $\mathbf{V}(t)$, and a frame $\mathcal{C}$ with its origin common with $\mathcal{I}$ and rotating with respect to it with an angular velocity $\boldsymbol{\Omega}(t)$. Let $\mathbf{R}(t)$ denote the location of the origins of $\mathcal{I}$ and $\mathcal{C}$ in the laboratory frame $\mathcal{L}$ at time t with $\mathbf{R}(t=0)=0$ and $\mathbf{r}_{\mathcal{C}}(t),\mathbf{v}_{\mathcal{C}}(t)$ the coordinate and velocity of a particle of Σ in the $\mathcal{C}$ frame at that time, respectively. The coordinate $\mathbf{r}_{\mathcal{L}}$ in the laboratory frame $\mathcal{L}$ is given by

$$\mathbf{r}_{\mathcal{L}} \equiv \mathbf{R} + \mathbf{r}_{\mathcal{C}} \tag{41}$$

and its velocity is given by Eq. (A1). The energy of the particle in the two frames are related as shown in Eq. (A4). Let us consider $\mathcal{I}$ to be the frame in which the center of mass of the body is at the origin. Applying the above two relations to all the particles in the body and averaging over all allowed microstates [19], as explained later in Sec. VIII B, we find that the energy of the body in the three frames are related as shown in Eqs. (B5) and (B8):

$$E_{\mathcal{C}} = E_{\mathcal{L}} - \mathbf{P}^2/2M - \mathbf{M}\cdot\Omega = E_{\mathcal{I}} - \mathbf{M}\cdot\Omega, \tag{42a}$$

$$E_{\mathcal{I}} = E_{\mathcal{L}} - \mathbf{P}^2/2M, \tag{42b}$$

where $\mathbf{P}$ and $\mathbf{M}$ are introduced in Eq. (B2). We have not used the overbar to express the statistical averages as explained in Sec. VIII B but is implied.

We, first, prove Theorem 5.

Theorem 5. The entropy of a body is the same in all three frames $\mathcal{L}$, $\mathcal{I}$, and $\mathcal{C}$.

Proof. To prove the theorem, we proceed as follows. We focus on a body with *fixed* V and N at some instant t only for simplicity of the argument and presentation. The extension to considering other extensive variables is trivial. Consider observing the body simultaneously at t in these frames. It is evident that, corresponding to each pair $\mathbf{r}_{\mathcal{L}},\mathbf{p}_{\mathcal{L}}$ of the coordinates and momenta of a given particle in the laboratory frame $\mathcal{L}$ at this moment, there is a unique pair $\mathbf{r}_{\mathcal{I}},\mathbf{p}_{\mathcal{I}}$ and $\mathbf{r}_{\mathcal{C}},\mathbf{p}_{\mathcal{C}}$ in the other two frames. This is true of all the particles. The collection of $\{\mathbf{r},\mathbf{p}\}$ of all the particles defines a point in the phase space. In classical statistical mechanics, an allowed microstate $i(=i_{\mathcal{L}},i_{\mathcal{I}}$, or $i_{\mathcal{C}})$ of the body is identified by a small volume element of size $(2\pi\hbar)^{3N}$ containing $\{\mathbf{r},\mathbf{p}\}$. Corresponding to each i in one frame, there exists a *unique* microstate in the other two frames. The uniqueness of microstate mapping ensures that their probabilities are equal,

$$p_{i_{\mathcal{L}}} = p_{i_{\mathcal{I}}} = p_{i_{\mathcal{C}}}. \tag{43}$$

Let $W(t) \equiv W(E_{\mathcal{C}},t)$ denote the number of all allowed microstates of energy $E_{\mathcal{C}}$ in the $\mathcal{C}$ frame at time t, and let and $\boldsymbol{p}_{\mathcal{C}}(t)$ the set of their probabilities (not to be confused with momenta $\mathbf{p}_{\mathcal{C}}$, etc.). Because of Eq. (43), we find that not only $W(t) \equiv W(E_{\mathcal{C}},t) \equiv W(E_{\mathcal{L}},t) \equiv W(E_{\mathcal{I}},t)$ but also the set of their probabilities $\boldsymbol{p}_{\mathcal{C}}(t) \equiv \boldsymbol{p}_{\mathcal{L}}(t) \equiv \boldsymbol{p}_{\mathcal{I}}(t)$; however, their energies differ as given by Eq. (42). This immediately shows that the entropies according to Eq. (8) are equal in the three frames as follows:

$$S_{\mathcal{C}}(E_{\mathcal{C}},t) = S_{\mathcal{I}}(E_{\mathcal{I}},t) = S_{\mathcal{L}}(E_{\mathcal{L}},t), \tag{44}$$

whether the body is in internal equilibrium or not. This proves the theorem. ■

It should be noted that the center-of-mass kinetic energy $\mathbf{P}^2/2M$ is the same for all allowed microstates in $W(t)$. Similarly, it follows from Eq. (B10) that even $\mathbf{M}\cdot\boldsymbol{\Omega}$ is the same for all allowed microstates in $W(t)$; see also the discussion leading to the second equation in Eq. (48). Thus, the three energies differ only by some constants at each instant t.

It follows from Eq. (44) that there is no reason to use different subscripts to distinguish the entropies. Accordingly, we will use S to represent the entropies in different frames; their energy arguments will, of course, depend on the frame of reference. The arguments $\mathbf{V}$ and $\boldsymbol{\Omega}$ above are actually external parameters that are not extensive. We will show below that the entropies in the $\mathcal{I}$ and $\mathcal{L}$ frames are actually functions of extensive quantities $\mathbf{P}$ and $\mathbf{M}$ that are conjugate to $\mathbf{V}$ and $\boldsymbol{\Omega}$, respectively; cf. Eq. (14). If we specialize and assume the existence of the internal equilibrium, then all allowed microstates are equally probable, and the three entropies are each equal to $S(t) = \ln W(t)$; see Eq. (13).

B. Statistical averaging over allowed microstates

We now investigate the consequences of statistical averaging over allowed microstates and show that its consequences are the same as expressed in Eqs. (42) and (44). We, first, note that $\mathbf{M}$ in Eq. (B2) depends on the coordinates and momenta of the particles, but this is not the case with $\mathbf{P}$, even though both are extensive quantities. As $E_{\mathcal{C}}$ in Eq. (B5) or (42a) is for a microstate determined by the coordinates and momenta of the particles, we need to average it using microstate probabilities in Eq. (12). Averaging over various allowed microstates relates the average energies in the two frame. We use an overbar, see Eq. (23), to denote the average. We find that the same form also describes the desired relation between the average energies,

$$\begin{aligned}\overline{E}_{\mathcal{C}}(t) &= \overline{E}_{\mathcal{L}}(t) - \mathbf{P}^2(t)/2M - \overline{\mathbf{M}}(t)\cdot\Omega(t)\\ &= \overline{E}_{\mathcal{I}}(t) - \overline{\mathbf{M}}(t)\cdot\Omega(t),\end{aligned} \tag{45}$$

where $\overline{E}_{\mathcal{I}}(t) = \overline{E}_{\mathcal{L}}(t) - \mathbf{P}^2(t)/2M$. The momentum $\mathbf{P}$, of course, does not require any averaging as noted above. We can also take the statistical average of Eq. (B3a) to obtain

$$\begin{aligned}\overline{E}_{\mathcal{C}}(t) = \overline{E}_{\mathcal{L}}(t) - \mathbf{P}^2(t)/2M - \sum_j m_j\overline{\mathbf{r}_j\cdot(\mathbf{v}_j\times\Omega)}\\ -\frac{1}{2}\sum_j m_j\overline{(\Omega\times\mathbf{r}_j)^2},\end{aligned} \tag{46}$$

where the two sums are over all the particles in the body. Here $\mathbf{r}_j$ and $\mathbf{v}_j$ are the instantaneous position and velocity of the jth particle in a microstate with respect to the $\mathcal{C}$ frame; we have suppressed the subscript $\mathcal{C}$ from $\mathbf{r}_j$ and $\mathbf{v}_j$ for the sake of notational simplicity. In the last equation, the third contribution is due to the relative motion of the particles with respect to the $\mathcal{C}$ frame. Indeed, the average of Eq. (B4) immediately yields

$$\overline{\mathbf{M}}(t)\cdot\Omega(t) = \sum_j m_j\overline{\mathbf{r}_j\cdot(\mathbf{v}_j\times\Omega)} + \sum_j m_j\overline{(\Omega\times\mathbf{r}_j)^2}. \tag{47}$$

The first contribution in Eq. (47) vanishes when the body is in internal equilibrium because of the absence of any relative motion in that case; see Theorem 1.

As $\overline{E}_{\mathcal{I}}$ does not depend on $\mathbf{V}$, a similar averaging of Eqs. (B9) and (B10) gives us

$$\begin{aligned}[\partial\overline{E}_{\mathcal{C}}(t)/\partial\mathbf{V}(t)]_{\overline{E}_{\mathcal{I}},V,N,\Omega} &= 0,\\ [\partial\overline{E}_{\mathcal{C}}(t)/\partial\Omega(t)]_{\overline{E}_{\mathcal{I}},V,N} &= -\overline{\mathbf{M}}(t).\end{aligned} \tag{48}$$

Comparing the above equations with the equations in the Appendix A, we see that there is no reason to make a distinction between $\mathbf{M}(t)$, used in the proof above, and $\overline{\mathbf{M}}(t)$ or between $\overline{E}_{\mathcal{L}}(t)$ and $E_{\mathcal{L}}(t)$, etc., used above in the proof. This justifies not using overbars to indicate statistical averages in Eq. (42).

Since the entropy $S(t)$ is the same for fixed $\overline{E}_{\mathcal{I}}$, V, N, and $\mathbf{\Omega}$, we can express the above two derivatives at fixed S instead of fixed $\overline{E}_{\mathcal{I}}$ as follows:

$$\begin{aligned}[\partial\overline{E}_{\mathcal{C}}(t)/\partial\mathbf{V}(t)]_{S,V,N,\Omega} &= 0,\\ [\partial\overline{E}_{\mathcal{C}}(t)/\partial\Omega(t)]_{S,V,N,\mathbf{V}} &= -\overline{\mathbf{M}}(t).\end{aligned} \tag{49}$$

The above equation is similar to the well-known result [20, Sec. 11] in equilibrium statistical mechanics whereby the statistical average of the derivatives of the energy with respect to external parameters ($\mathbf{V}$ and $\mathbf{\Omega}$) should be taken at *constant entropy* and other extensive quantities. We have extended this result to internal equilibrium now. Introducing the standard derivatives

$$\begin{aligned}[\partial\overline{E}_{\mathcal{C}}(t)/\partial S(t)]_{V,N,\mathbf{V},\mathbf{\Omega}} &= T(t),\\ [\partial\overline{E}_{\mathcal{C}}(t)/\partial V(t)]_{S,N,\mathbf{V},\mathbf{\Omega}} &= -P(t)\end{aligned} \tag{50}$$

for the body, we can write down the following differential identity:

$$d\overline{E}_{\mathcal{C}} = T(t)dS(t) - P(t)dV(t) - \overline{\mathbf{M}}\,(t)\cdot d\mathbf{\Omega}(t). \tag{51}$$

It should be noted that, because of Eq. (48), the average energy $\overline{E}_{\mathcal{C}}(t)$ does not depend on the velocity of the frames $\mathcal{I}$ and $\mathcal{C}$. Thus, there is no reason to keep $\mathbf{V}$ fixed in the various derivatives in Eq. (50).

Using $\overline{E}_{\mathcal{I}} = \overline{E}_{\mathcal{C}} + \overline{\mathbf{M}}\cdot\mathbf{\Omega}$, we find that

$$d\overline{E}_{\mathcal{I}} = T(t)dS(t) - P(t)dV(t) + \mathbf{\Omega}(t)\cdot d\overline{\mathbf{M}}(t), \tag{52}$$

which is an extension of the result given by Landau and Lifshitz [20, Sec. 26] to the internal equilibrium. The point to note is that the entropy $S(t)$ in the $\mathcal{I}$ frame is a function of the conjugate variable $\overline{\mathbf{M}}(t)$ instead of $\mathbf{\Omega}(t)$. Using $\overline{E}_{\mathcal{L}}(t) = \overline{E}_{\mathcal{C}}(t) + \mathbf{P}(t)^2/2M + \overline{\mathbf{M}}(t)\cdot\mathbf{\Omega}(t)$, we find an additional contribution due to $\mathbf{V}$,

$$\begin{aligned}d\overline{E}_{\mathcal{L}}(t) = T(t)dS(t) - P(t)dV(t)\\ + \mathbf{V}(t)\cdot d\mathbf{P}(t) + \mathbf{\Omega}(t)\cdot d\overline{\mathbf{M}}(t),\end{aligned} \tag{53}$$

which is in terms of all extensive quantities. The additional contribution due to the momentum differential $d\mathbf{P}(t)$ is due to the velocity of the body as a whole and has important consequences in the laboratory frame. For example, such a contribution is needed to describe the flow of a superfluid in which the normal and superfluid components have different velocities so the superfluid cannot be considered at rest in any frame ([3], see Eq. (130.9)). This term is also responsible for the frictional contribution due to relative motion.

It follows from Eq. (53) that the *drift velocity* of the center of mass and the angular velocity of the body are given by

$$\begin{aligned}[\partial\overline{E}_{\mathcal{L}}(t)/\partial\mathbf{P}(t)]_{S,V,N,\overline{\mathbf{M}}} &= \mathbf{V}(t);\\ [\partial\overline{E}_{\mathcal{L}}(t)/\partial\overline{\mathbf{M}}(t)]_{S,V,N,\mathbf{P}} &= \mathbf{\Omega}(t).\end{aligned} \tag{54}$$

We observe that the entropy in the laboratory frame $\mathcal{L}$ is a function of the extensive conjugate quantities $\mathbf{P}(t)$ and $\overline{\mathbf{M}}(t)$ rather than the external parameters $\mathbf{V}$ and $\mathbf{\Omega}$.

From now on, we will not use the overbar to show statistical averages for the sake of notational simplicity.

It is clear from Eq. (51) that we must treat $E_{\mathcal{C}}(t)$ as a function of $S(t)$, $V(t)$, and $\mathbf{\Omega}(t)$ for constant N. Alternatively, we must treat $S(t)$ as a function of $E_{\mathcal{C}}(t)$, $V(t)$, and $\mathbf{\Omega}(t)$,

$$S_{\mathcal{C}}(t) \equiv S_{\mathcal{C}}[E_{\mathcal{C}}(t),V(t),\mathbf{\Omega}(t),N], \tag{55}$$

which is identical to the functional dependence shown in Eq. (44), except that we no longer have an explicit t dependence because of internal equilibrium. The important point to observe is that the entropy is a function of not only the energy in the $\mathcal{C}$ frame but is also a function of the angular velocity of the reference frame when rotation is involved.

C. Same temperature and pressure in different frames

We now make an important observation. It follows from Eqs. (52) and (53) that

$$[\partial E_{\mathcal{I}}(t)/\partial S(t)]_{V,N,\mathbf{M}} = [\partial E_{\mathcal{L}}(t)/\partial S(t)]_{V,N,\mathbf{P},\mathbf{M}} = T(t), \quad (56)$$

obtained by differentiating with respect to $S(t)$. Similar equations are obtained when we differentiate with respect to $V(t)$,

$$[\partial E_{\mathcal{I}}(t)/\partial V(t)]_{S,N,\mathbf{M}} = [\partial E_{\mathcal{L}}(t)/\partial S(t)]_{S,N,\mathbf{V},\mathbf{M}} = -P(t). \quad (57)$$

These equations are identical to the derivatives in Eq. (50) and show that the instantaneous temperature $T(t)$ and the instantaneous pressure $P(t)$ are the same in the three frames. Moreover, it is the same entropy function $S(t)$ that appears in Eqs. (51)–(53).

IX. A HOMOGENEOUS SYSTEM WITH TRANSLATIONAL MOTION

A. Thermodynamic potentials under arbitrary conditions

1. *Fixed N*

Before we discuss an inhomogeneous body, let us consider a homogeneous body which is moving as a whole with a linear momentum $\mathbf{P}$. We still assume that Σ_0 is at rest so the linear momentum $\widetilde{\mathbf{P}}$ of the center of mass of $\widetilde{\Sigma}$ is $-\mathbf{P}$. For simplicity, we will assume the absence of overall intrinsic rotation for Σ and $\widetilde{\Sigma}$ individually. The latter is easily incorporated as we do in the next section. The orbital angular momentum $\mathbf{L}_0$ of Σ_0 in terms of the locations $\mathbf{R}$ and $\widetilde{\mathbf{R}}$ of the centers of mass of Σ and $\widetilde{\Sigma}$, respectively, always vanishes since $\mathbf{P}$ and $\mathbf{R}-\widetilde{\mathbf{R}}$ are collinear: $\mathbf{R}\times\mathbf{P}-\widetilde{\mathbf{R}}\times\mathbf{P} = 0$.

The (average) internal energies of Σ and $\widetilde{\Sigma}$ in their center-of-mass frames (the $\mathcal{C}$ frame) are

$$E^{\mathrm{i}} = E - \mathbf{P}^2/2M, \quad \widetilde{E}^{\mathrm{i}} = \widetilde{E} - \mathbf{P}^2/2\widetilde{M},$$

where E and $\widetilde{E}$ denote their total energies in the laboratory frame $\mathcal{L}$, respectively; see Eq. (42). However, because of the extreme large size of $\widetilde{\Sigma}$, its mass $\widetilde{M}$ satisfies the inequality $\widetilde{M} \gg M$, so we can replace $\widetilde{E}^{\mathrm{i}}$ with $\widetilde{E}$ without any appreciable error. The entropy S of Σ is a function of the internal energy $\widetilde{E}^{\mathrm{i}}$; however, this is not relevant for our argument here if we are only interested in identifying the appropriate thermodynamic potential for the system. The energy $E_0 = E + \widetilde{E}$ of Σ_0 remains constant in time. As discussed above, the additivity of energy ensures that the entropies are also additive. In the laboratory frame $\mathcal{L}$, the entropies of the Σ and $\widetilde{\Sigma}$ are obtained by considering their entropies in respective rest frames $\mathcal{C}$ and $\widetilde{\mathcal{C}}$; they are $S(E^{\mathrm{i}},V,N,t)$ and $\widetilde{S}(\widetilde{E}^{\mathrm{i}},\widetilde{V},\widetilde{N},t)$, respectively. We then have

$$\begin{aligned} S_0(E_0,V_0,N_0,t) &= S(E^{\mathrm{i}},V,N,t) + \widetilde{S}(\widetilde{E}^{\mathrm{i}},\widetilde{V},\widetilde{N}) \\ &\simeq S(E^{\mathrm{i}},V,N,t) + \widetilde{S}(\widetilde{E},\widetilde{V},\widetilde{N}). \quad (58) \end{aligned}$$

We now expand and follow the steps, as shown in I, which are unaffected by the motion of Σ. We obtain

$$S_0(t) - \widetilde{S} \simeq S(E^{\mathrm{i}},V,N,t) - E(t)/T_0 - P_0V(t)/T_0$$

in terms of the energy and volume of the system. We can now identify the Gibbs free energy and enthalpy in the laboratory frame $\mathcal{L}$ in terms of the energy of the system as follows:

$$G(t) = E(t) - T_0S(t) + P_0V(t), \quad H(t) = E(t) + P_0V(t); \quad (59)$$

compare with the Gibbs free energy in Eq. (32). Thus, the second law in terms of the Gibbs free energy remains unchanged and is given by Eq. (35).

In the center-of-mass frame $\mathcal{C}$ of the system, the Gibbs free energy and the enthalpy of the system are given by

$$G^{\mathrm{i}}(t) = E^{\mathrm{i}}(t) - T_0S(t) + P_0V(t), \quad H^{\mathrm{i}}(t) = E^{\mathrm{i}}(t) + P_0V(t). \quad (60)$$

The temperature and the pressure of the medium are not affected by the choice of the frame as noted near the end of Sec. VIII. Similarly, the entropy of the system is unaffected by the choice of the frame as shown by Theorem 5.

2. *Fixed V*

Following the procedure given in Sec. VI, we find that the correct thermodynamic potential now in $\mathcal{L}$ and $\mathcal{C}$, respectively, are given by

$$\Omega(t) \equiv E(t) - T_0S(t) - \mu_0N(t),$$
$$\Omega^{\mathrm{i}}(t) \equiv E^{\mathrm{i}}(t) - T_0S(t) - \mu_0N(t).$$

3. *Fixed N and V*

The correct thermodynamic potentials in $\mathcal{L}$ and $\mathcal{C}$ are given, respectively, by the Helmholtz free energy

$$F(t) \equiv E(t) - T_0S(t), \quad F^{\mathrm{i}}(t) \equiv E^{\mathrm{i}}(t) - T_0S(t).$$

B. Extension to many state variables

From now on, we will list E, V, and N for any body separately and use $\mathbf{X}'$ and $\mathbf{Z}'$ to denote the rest of the observables and state variables, respectively. We will fix only the number of particles $N,\widetilde{N}$. Then $\widetilde{S}(\widetilde{E}^{\mathrm{i}},\widetilde{V},\widetilde{N})$ in Eq. (58) must be written as $\widetilde{S}(\widetilde{E}^{\mathrm{i}},\widetilde{V},\widetilde{N},\widetilde{\mathbf{Z}}')$. Carrying out the expansion in terms of small quantities as in I, and introducing the "chemical potential vector" $\boldsymbol{\mu}_0$ and the "affinity vector" $\mathbf{a}_0 \equiv \beta_0\mathbf{A}_0$

$$(\partial\widetilde{S}/\partial\widetilde{\mathbf{X}}')|_0 = -\beta_0\boldsymbol{\mu}_0, \quad (\partial\widetilde{S}/\partial\widetilde{\mathbf{I}})|_0 = \beta_0\boldsymbol{A}_0 = 0, \quad (61)$$

for $\widetilde{\Sigma}$ allows us to identify a new thermodynamic potential $G^{\mathbf{X}}(t) \equiv -T_0[S_0(E_0,V_0,N_0,\mathbf{Z}'_0,t) - \widetilde{S}(E_0,V_0,\widetilde{N},\mathbf{Z}'_0)]$,

$$\begin{aligned} G^{\mathbf{X}}(t) &= E(t) - T_0S(t) + P_0V(t) + \boldsymbol{\mu}_0\cdot\mathbf{X}'(t) \\ &= G(t) + \boldsymbol{\mu}_0\cdot\mathbf{X}'(t), \quad (62) \end{aligned}$$

in the laboratory frame $\mathcal{L}$. Here, $|_0$ corresponds evaluating the derivative at E_0, V_0, N_0, $\mathbf{Z}'_0$ ($\mathbf{X}'_0$ and $\mathbf{I}'_0$). As E_0, V_0, N_0, $\mathbf{X}'_0$, and $\widetilde{N}$ are constant, we have

$$\frac{d}{dt}\widetilde{S}(E_0,V_0,\widetilde{N},\mathbf{Z}'_0) = \left(\frac{\partial\widetilde{S}}{\partial\mathbf{I}_0}\right)\bigg|_0 \cdot \frac{d\mathbf{I}_0(t)}{dt} = 0.$$

Thus, $\widetilde{S}(E_0,V_0,\widetilde{N},\mathbf{Z}_0')$ is a constant, and the second law tells us that

$$T_0 dS_0/dt = -dG^{\mathrm{X}}/dt \geqslant 0 \tag{63}$$

in any spontaneous process. In the $\mathcal{C}$ frame, we will instead have

$$\begin{aligned} G^{\mathrm{iX}}(t) &= E^{\mathrm{i}}(t) - T_0 S(t) + P_0 V(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t) \\ &= G^{\mathrm{i}}(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t). \end{aligned} \tag{64}$$

The analogs of the thermodynamic potential $\Omega(t)$ and $F(t)$ are

$$\Omega^{\mathrm{X}}(t) = \Omega(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t), \quad \Omega^{\mathrm{iX}}(t) = \Omega^{\mathrm{i}}(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t),$$
$$F^{\mathrm{X}}(t) = F(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t), \quad F^{\mathrm{iX}}(t) = F^{\mathrm{i}}(t) + \boldsymbol{\mu}_0 \cdot \mathbf{X}'(t),$$

respectively. Again, we have

$$d\Omega^{\mathrm{X}}/dt \leqslant 0, \quad dF^{\mathrm{X}}/dt \leqslant 0, \tag{65}$$

in any spontaneous process.

C. Gibbs fundamental relation for a system under internal equilibrium

1. Absence of $\mathbf{Z}'(t)$

We assume that Σ is in internal equilibrium. We then can immediately write down the Gibbs fundamental relation as $T(t)dS = dE^{\mathrm{i}}(t) + P(t)dV(t) - \mu(t)dN(t)$, which can be rearranged to give

$$dE^{\mathrm{i}}(t) = T(t)dS - P(t)dV(t) + \mu(t)dN(t). \tag{66}$$

Using Eq. (45), we have

$$dE = T(t)dS + \mathbf{V} \cdot d\mathbf{P} - P(t)dV(t) + \mu(t)dN(t) \tag{67}$$

for the energy $E(t)$. This has some important consequences that will be extremely useful in the following. The first consequence is that it allows us to think of $S(E^{\mathrm{i}},V,N)$ as a function of four variables $S(E,\mathbf{P},V,N)$ as follows:

$$T(t)dS = dE - \mathbf{V} \cdot d\mathbf{P} + P(t)dV(t) - \mu(t)dN(t).$$

This equation is the Gibbs fundamental relation relating the entropy with $E(t)$ rather than $E^{\mathrm{i}}(t)$. The second consequence is that the *drift velocity* $\mathbf{V}$ (of the center of mass) of the system is given a thermodynamic interpretation in terms of the derivative at fixed E, V, and N,

$$(\partial S/\partial \mathbf{P}) = -\beta(t)\mathbf{V}(t). \tag{68}$$

2. Inclusion of $\mathbf{Z}'(t)$

Introducing the instantaneous chemical potential vector $\boldsymbol{\mu}(t)$ associated with $\mathbf{X}'$ and the affinity vector $\mathbf{A}$ associated with $\mathbf{I}$,

$$(\partial S/\partial \mathbf{X}') = -\beta(t)\boldsymbol{\mu}(t), \quad (\partial S/\partial \mathbf{I}) = \beta(t)\mathbf{A}(t), \tag{69}$$

we find the Gibbs fundamental relation to be

$$\begin{aligned} T(t)dS &= dE^{\mathrm{i}}(t) + P(t)dV(t) - \mu(t)dN(t) \\ &\quad - \boldsymbol{\mu}(t) \cdot d\mathbf{X}'(t) + \mathbf{A}(t) \cdot d\mathbf{I}(t) \qquad (70\mathrm{a}) \\ &= dE(t) - \mathbf{V}(t) \cdot d\mathbf{P}(t) + P(t)dV(t) - \mu(t)dN(t) \\ &\quad - \boldsymbol{\mu}(t) \cdot \mathbf{X}'(t) + \mathbf{A}(t) \cdot d\mathbf{I}(t). \qquad (70\mathrm{b}) \end{aligned}$$

X. INHOMOGENEOUS SYSTEM WITH RELATIVE MOTION

A. Subsystems undergoing relative motion

We consider Σ_0 to be stationary but will allow relative motions between Σ and $\widetilde{\Sigma}$ so they each will possess linear and angular momenta that individually must cancel out as follows:

$$\mathbf{P} + \widetilde{\mathbf{P}} = 0, \quad \mathbf{M} + \widetilde{\mathbf{M}} = 0. \tag{71}$$

We will also treat Σ as inhomogeneous and assume that it can be decomposed into a *collection* of a large number N_S of *quasi-independent subsystems* σ_k, $k = 1,2,\ldots,N_S$, which may be in different macrostates to allow for inhomogeneity. The subsystem k is still *macroscopically* large so there is a legitimate entropy function s_k for its macrostate $\mathcal{M}_k$ characterized by the state variables e_k^{i},n_k,v_k, and $\mathbf{z}_k'$ via Gibbs's formulation $s_k(e_k^{\mathrm{i}},\boldsymbol{\omega}_k,n_k,v_k,\mathbf{z}_k',t) \equiv -\sum_{\alpha_k} p_{\alpha_k}(t) \ln p_{\alpha_k}$, in terms of the probability $p_{\alpha_k}(t)$, where α_k denotes one of the allowed microstates of σ_k in the macrostate $\mathcal{M}_k$. These entropies satisfy the *additive property*

$$S(E^{\mathrm{i}},\boldsymbol{\Omega},N,V,\mathbf{Z}',t) = \sum_{k=1}^{N_S} s_k\big(e_k^{\mathrm{i}},\boldsymbol{\omega}_k,n_k,v_k,\mathbf{z}_k',t\big). \tag{72}$$

Using the entropy s_k, we can introduce the appropriate thermodynamic functions, but care must be exercised in identifying these functions in the lab frame $\mathcal{L}$, where the experiments are done. The energies depend on the frame of reference, which will result in different values of the energies and thermodynamic potentials in different frames. We will also be interested in the rotating frame $\mathcal{C}_k$ attached to the center of mass of σ_k, which is translating with a linear velocity $\mathbf{v}_k(t)$ and rotating with an angular velocity $\boldsymbol{\omega}_k(t)$.

If each subsystem is in *internal equilibrium*, then all allowed microstates are *equiprobable*: $p_{\alpha_k}(t) = 1/W_k$, $\alpha = 1,2,\ldots,W_k(t)$ so $s_k(t) = \ln W_k(t)$; here $W_k(t)$ represents the number of allowed microstates of the subsystem σ_k at time t. It then follows from Theorem 1 that such a subsystem is uniformly translating with a linear velocity $\mathbf{v}_k(t)$ and rotating with an angular velocity $\boldsymbol{\omega}_k(t)$ so this subsystem is *stationary* in its frame $\mathcal{C}_k$.

B. System under arbitrary conditions

We, first, consider the general case when the subsystems is not necessarily in internal equilibrium. The internal energy for each subsystem σ_k is related to its energy e_k in the laboratory frame $\mathcal{L}$,

$$e_k^{\mathrm{i}} \equiv e_k - \mathbf{p}_k^2/2m_k - \mathbf{m}_k \cdot \boldsymbol{\omega}_k; \tag{73}$$

see Eq. (45). Alternatively, we can use Eq. (46) to express this relation as

$$\begin{aligned} e_k^{\mathrm{i}} = e_k - \mathbf{p}_k^2/2m_k - \sum_{j_k} m_{j_k}\mathbf{r}_{j_k} \cdot (\mathbf{v}_{j_k} \times \boldsymbol{\omega}_k) \\ - \frac{1}{2}\sum_{j_k} m_{j_k}(\boldsymbol{\omega}_k \times \mathbf{r}_{j_k})^2, \end{aligned} \tag{74}$$

where each sum is over n_k particles in the subsystem k. The third term in the last equation vanishes when the subsystem is in internal equilibrium as commented earlier. We also have the additivity laws

$$V=\sum v_k,\quad N=\sum n_k,\quad \mathbf{X}=\sum \mathbf{x}_k,\quad \mathbf{I}=\sum \mathbf{i}_k,\tag{75a}$$

$$E=\sum e_k=\sum\left(e_k^{\mathrm{i}}+\mathbf{p}_k^2/2m_k+\mathbf{m}_k\cdot\boldsymbol{\omega}_k\right),\tag{75b}$$

$$\mathbf{P}=\sum \mathbf{p}_k,\quad \mathbf{M}=\sum(\mathbf{m}_k+\mathbf{r}_k\times\mathbf{p}_k),\tag{75c}$$

at each instant t. The angular momentum $\mathbf{l}_k\equiv\mathbf{r}_k\times\mathbf{p}_k$ is the orbital angular momentum of σ_k with $\mathbf{r}_k$, $\mathbf{p}_k$ representing the location and momentum of the center of mass of σ_k, respectively, and should not be confused with its intrinsic angular momentum $\mathbf{m}_k$ introduced in Eq. (B2). We should emphasize that the additivity of the energy requires that the interaction energy between subsystems be negligible. As a consequence, we do not have the contribution analogous to $\psi(\mathbf{r})dV$ in Eq. (3). This distinguishes our approach with that taken in local nonequilibrium thermodynamics [13–16].

We keep n_k fixed for simplicity so N is also fixed and allow e_k^{i}, v_k, and $\mathbf{z}_k'$ to vary in time. As usual, we assume internal equilibrium for the medium. As usual, we have, for Σ_0,

$$E_0=\widetilde{E}+E,\quad V_0=\widetilde{V}+V,\quad N_0=\widetilde{N}+N,$$

$$\mathbf{X}_0'=\widetilde{\mathbf{X}}'+\mathbf{X}',\quad \mathbf{I}_0=\widetilde{\mathbf{I}}+\mathbf{I}.$$

For the medium, its energy is related to its internal energy according to Eq. (45) as follows:

$$\widetilde{E}^{\mathrm{i}}\equiv\widetilde{E}-\widetilde{\mathbf{P}}^2/2\widetilde{M}-\widetilde{\mathbf{M}}\cdot\widetilde{\boldsymbol{\Omega}}=E-\mathbf{P}^2/2M-\mathbf{M}^2/2\widetilde{I},\tag{76}$$

where, according to Eq. (71), we have taken $\widetilde{\mathbf{M}}=-\mathbf{M}$ and where $\widetilde{I}$ is the moment of inertia of the medium about its axis of rotation. The axis of rotation must be one of its principal axes of rotation; see the comment after the proof of Theorem 1 in Sec. IV. The contribution for the medium coming from the internal motion, which is similar to the third contribution in Eq. (74), vanishes because of its uniform translation and rotation in accordance with Theorem 1. The contribution similar to the last term in Eq. (74) is the standard rotational kinetic energy of the medium treated as a rigid body. The angular momentum $\widetilde{\mathbf{M}}$ is given by

$$\widetilde{M}_i=\widetilde{I}_{ij}\widetilde{\Omega}_j=-M_i.$$

Assuming that the motions are finite, we conclude that $\widetilde{M}_i$ must be finite. Therefore, for an extremely large medium, $\widetilde{\boldsymbol{\Omega}}$ and $\widetilde{\mathbf{V}}$ must be extremely small, which ensure that the last two terms in Eq. (76) are extremely small. This allows us to approximate

$$\widetilde{E}\simeq\widetilde{E}^{\mathrm{i}}\tag{77}$$

without any appreciable error. As far as the system is concerned, the relationship between its internal energy and the energy is still given by Eq. (B5),

$$E^{\mathrm{i}}\equiv E-\mathbf{P}^2/2M-\mathbf{M}\cdot\boldsymbol{\Omega},\tag{78}$$

except that the system may not be uniformly translating and rotating about any of its principal axis of inertia. We take $\widetilde{N}$ and N as constants but allow for E, V, and $\mathbf{Z}'$ ($\mathbf{X}$ and $\mathbf{I}$) to change with time. We now recall that the expansion of $\widetilde{S}(\widetilde{E}^{\mathrm{i}},\widetilde{\boldsymbol{\Omega}},\widetilde{N},\widetilde{V},\widetilde{\mathbf{Z}}')$, see I, does not require any knowledge of what is happening with the system Σ. For example, we have *not* assumed internal equilibrium in the system or that it is inhomogeneous. Thus, the conclusions arrived at there, in particular, the identifications of various thermodynamic potentials, do no change because the system is now inhomogeneous.

Let us introduce

$$g_k\equiv e_k-T_0s_k+P_0v_k,\quad g_k^{\mathrm{i}}\equiv e_k^{\mathrm{i}}-T_0s_k+P_0v_k\tag{79}$$

for the subsystem σ_k so the additivity remains intact,

$$G=\sum_k g_k,\quad G^{\mathrm{i}}=\sum_k g_k^{\mathrm{i}}.$$

Let us also introduce

$$g_k^{\mathbf{x}}\equiv e_k-T_0s_k+P_0v_k+\mathbf{x}_k'\cdot\boldsymbol{\mu}_0,$$

$$g_k^{\mathrm{i}\mathbf{x}}\equiv e_k^{\mathrm{i}}-T_0s_k+P_0v_k+\mathbf{x}_k'\cdot\boldsymbol{\mu}_0.$$

Because of the quasi-independence of various subsystems, Eq. (63) immediately leads to

$$dg_k^{\mathbf{x}}/dt\leqslant 0.\tag{80}$$

Thus, $g_k^{\mathbf{x}}(t)$ can be identified as the generalized Gibbs free energy of the subsystem σ_k in the laboratory frame $\mathcal{L}$. For $\mathbf{x}_k'=0$, $g_k(t)$ can be identified as the Gibbs free energy of the subsystem σ_k in the laboratory frame $\mathcal{L}$. Comparing this definition with the definition in Eq. (5) used in the conventional nonequilibrium thermodynamics, we see that the discrepancy in the two Gibbs free energy has not disappeared by taking into account the inhomogeneity inherent in the system.

It may be argued that the above identification of g_k in Eq. (79) is based on considering the entire system in contact with the medium. One can, alternatively, consider a particular subsystem σ in contact with the medium and the remaining subsystems. However, a little bit of reflection shows that this will not affect the behavior of g_k for the simple reason that the remaining subsystems still form a very small part of the isolated system so they *cannot* affect the internal equilibrium of the medium. To see this more clearly, let us introduce a new medium $\widetilde{\Sigma}'$ consisting of $\widetilde{\Sigma}$ and the remaining subsystems. Only for the sake of simplicity do we again consider $\mathbf{X}=0$. The argument can be easily extended to include them. Let $\widetilde{S}'$ denote the entropy and $\widetilde{E}'^{\mathrm{i}}\simeq\widetilde{E}'$, $\widetilde{V}'$, and $\widetilde{N}'$ the internal energy, volume, and the number of particles of $\widetilde{\Sigma}'$, the latter of which is kept fixed. Expanding this entropy in terms of the small quantities e^{i} and v of the chosen subsystem requires calculating the derivatives $\partial\widetilde{S}'/\partial\widetilde{E}'|_{E_0,V_0}$ and $\partial\widetilde{S}'/\partial\widetilde{V}'|_{E_0,V_0}$. Because of the small size of the system relative to the original medium $\widetilde{\Sigma}$, these derivatives do not differ from $\partial\widetilde{S}/\partial\widetilde{E}|_{E_0,V_0}$ and $\partial\widetilde{S}/\partial\widetilde{V}|_{E_0,V_0}$, respectively. Thus, using $e=E_0-\widetilde{E}'$ for the energy of the subsystem σ_k, we find that $\widetilde{S}'(\widetilde{E}^{\mathrm{i}\prime},\widetilde{\boldsymbol{\Omega}},\widetilde{N}',\widetilde{V}')=\widetilde{S}(E_0,\widetilde{N},V_0)-(e-P_0v)/T_0$. Using this in $S_0(E_0^{\mathrm{i}},N_0,V_0,t)=s(e^{\mathrm{i}},\boldsymbol{\omega},n,v,t)+\widetilde{S}'(\widetilde{E}^{\mathrm{i}\prime},\widetilde{\boldsymbol{\Omega}},\widetilde{N}',\widetilde{V}')$, where $\boldsymbol{\omega}$ is the angular velocity of the $\mathcal{C}$ frame of the selected subsystem, allows us to identify

$$g\equiv e-T_0s+P_0v\tag{81}$$

as the Gibbs free energy of the particular subsystem σ. It now follows from Eq. (1) that

$$dg/dt\leqslant 0,$$

a property we expect from the Gibbs free energy. Incidentally, this also provides an independent justification of the inequality in Eq. (80).

In terms of g_k^{i}, we immediately have

$$G^{\mathrm{i}} = \sum_k \left(g_k^{\mathrm{i}} + \mathbf{p}_k^2/2m_k + \mathbf{m}_k \cdot \Omega_k\right),$$

which is expected in view of the sum rule in Eqs. (75b) and (78).

C. System under internal equilibrium

The above derivation uses only the second law and the assumption that the medium satisfies the condition of internal equilibrium. In general, the differential ds_k of the entropy of the subsystem σ_k is given by

$$\begin{aligned} ds_k = {}& \frac{\partial s_k}{\partial e_k} de_k^{\mathrm{i}} + \frac{\partial s_k}{\partial v_k} dv_k + \frac{\partial s_k}{\partial n_k} dn_k \\ & + \frac{\partial s_k}{\partial \mathbf{\Omega}_k} \cdot d\mathbf{\Omega}_k + \frac{\partial s_k}{\partial \mathbf{z}_k'} \cdot d\mathbf{z}_k'(t) + \frac{\partial s_k}{\partial t} dt; \end{aligned}$$

cf. Eqs. (44) and (55). If we now assume internal equilibrium so s_k does not have an explicit t dependence, we can get rid of the last term above. In this case only, the remaining derivatives identify the field variables $1/T_k, P_k/T_k, -\mu_k/T_k, \mathbf{m}_k/T_k, -\boldsymbol{\mu}^{(k)}/T_k$, and $\mathbf{A}^{(k)}/T_k$, respectively, of σ_k. These derivatives then allows us to obtain the Gibbs fundamental relations for the k-th subsystem, which follow from Eqs. (70a) and (70b),

$$\begin{aligned} de_k^{\mathrm{i}}(t) = {}& T_k(t)ds_k(t) - P_k(t)dv_k(t) + \mu_k(t)dn_k(t) - \mathbf{m}_k(t) \\ & \cdot d\mathbf{\Omega}_k(t) + \boldsymbol{\mu}^{(k)}(t) \cdot d\mathbf{x}_k(t) - \mathbf{A}^{(k)}(t) \cdot d\mathbf{i}_k(t) \end{aligned} \tag{82}$$

and

$$\begin{aligned} de_k = {}& T_k(t)ds_k(t) + \mathbf{v}_k(t) \cdot d\mathbf{p}_k(t) + \omega_k(t) \cdot d\mathbf{m}_k(t) \\ & - P_k(t)dv_k(t) + \mu_k(t)dn_k(t) + \boldsymbol{\mu}^{(k)}(t) \\ & \cdot d\mathbf{x}_k(t) - \mathbf{A}^{(k)}(t) \cdot d\mathbf{i}_k(t); \end{aligned} \tag{83}$$

compare with Eq. (53). This allows us to think of the entropy $s_k(e_k^{\mathrm{i}}, \mathbf{\Omega}_k, n_k, v_k, \mathbf{z}_k', t)$ as a function,

$$s_k(e_k, \mathbf{p}_k, \mathbf{m}_k, n_k, v_k, \mathbf{z}_k', t),$$

so the drift and the angular velocities in internal equilibrium are given by

$$\begin{aligned} \beta_k(t)\mathbf{v}_k(t) &= -\partial s_k(t)/\partial \mathbf{p}_k(t), \\ \beta_k(t)\omega_k(t) &= -\partial s_k(t)/\partial \mathbf{m}_k(t), \end{aligned} \tag{84}$$

$\beta_k(t) \equiv 1/T_k(t)$. However, different subsystems will undergo relative motions with respect to each other as $\mathbf{v}_k(t)$ and $\omega_k(t)$ differ for them. In addition, $T_k(t)$, $P_k(t)$, $\boldsymbol{\mu}^{(k)}(t)$, and $\mathbf{A}^{(k)}(t)$ differ from each other and will result in viscous dissipation and, consequently, entropy production as they approach equilibrium with each other and with the medium. We now turn to this issue.

XI. REVERSIBLE AND IRREVERSIBLE CONTRIBUTIONS

A. General considerations: Bodies in a medium

In equilibrium, the coefficients of the differential quantities in Eq. (83) take their constant values of the medium. Writing $ds_k(t) \equiv d_{\mathrm{re}}s_k(t) + d_{\mathrm{ir}}s_k(t)$ as a sum of the change in the entropy $d_{\mathrm{re}}s_k(t)$ due to reversible exchange with the medium and the production of the entropy $d_{\mathrm{ir}}s_k(t) \geqslant 0$ due to irreversible processes within the system, we have

$$\begin{aligned} d_{\mathrm{re}}s_k = {}& \beta_0[de_k(t) - \mathbf{V}_0(t) \cdot d\mathbf{p}_k(t) - \Omega_0 \cdot d\mathbf{m}_k(t) \\ & + P_0 dv_k(t) - \mu_0 dn_k(t) - \boldsymbol{\mu}_0 \cdot d\mathbf{x}_k(t)] \end{aligned}$$

and

$$\begin{aligned} d_{\mathrm{ir}}s_k = {}& F[\beta_k(t)]de_k(t) + F[-\beta_k(t)\mathbf{v}_k(t)] \cdot d\mathbf{p}_k(t) \\ & + F[-\beta_k(t)\boldsymbol{\omega}_k(t)] \cdot d\mathbf{m}_k(t) + F[\beta_k(t)P_k(t)]dv_k(t) \\ & + F[-\beta_k(t)\mu_k(t)]dn_k(t) + F[-\beta_k(t)\boldsymbol{\mu}^{(k)}] \cdot d\mathbf{x}_k(t) \\ & + F[\beta_k(t)\mathbf{A}^{(k)}] \cdot d\mathbf{i}_k(t) \end{aligned} \tag{85}$$

$$\geqslant 0, \tag{86}$$

where $F_k \equiv F[w_k] = w_k(t) - w_{k0}$ is the thermodynamic force, see Eq. (20), at time t associated with $z_k(t)$. According to the second law of thermodynamics, not only $d_{\mathrm{ir}}s_k \geqslant 0$ but each term in Eq. (85) is non-negative,

$$F[w]\,dz \geqslant 0,$$

where z and w form a conjugate pair. In terms of these pairs, we can express the two parts of the entropy as follows:

$$ds_k = \mathbf{w}_k \cdot d\mathbf{z}_k, \quad d_{\mathrm{re}}s_k = \mathbf{w}_{0k} \cdot d\mathbf{x}_k, \quad d_{\mathrm{ir}}s_k = \mathbf{F}[\mathbf{w}_k] \cdot d\mathbf{z}_k, \tag{87}$$

which is the general form of the entropy differential and its two components.

We can similarly express $de_k \equiv d_{\mathrm{re}}e_k(t) + d_{\mathrm{ir}}e_k(t)$, where

$$\begin{aligned} d_{\mathrm{re}}e_k = {}& T_0 ds_k(t) + \mathbf{V}_0(t) \cdot d\mathbf{p}_k(t) + \mathbf{\Omega}_0 \cdot d\mathbf{m}_k(t) \\ & - P_0 dv_k(t) + \mu_0 dn_k(t) + \boldsymbol{\mu}_0 \cdot d\mathbf{x}_k(t) \end{aligned}$$

and

$$\begin{aligned} d_{\mathrm{ir}}e_k = {}& F[T_k(t)]ds_k(t) + F[\mathbf{v}_k(t)] \cdot d\mathbf{p}_k(t) + F[\omega_k(t)] \cdot d\mathbf{m}_k(t) \\ & - F[P_k(t)]dv_k(t) + F[\mu_k(t)]dn_k(t) + F[\boldsymbol{\mu}^{(k)}] \cdot d\mathbf{x}_k(t) \\ & - F[\mathbf{A}^{(k)}] \cdot d\mathbf{i}_k(t). \end{aligned}$$

The generalized form for the Gibbs fundamental relation is, evidently,

$$\begin{aligned} de_k &= T_k ds_k - \mathbf{W}_k \cdot d\mathbf{z}^{\mathrm{e}}, \quad d_{\mathrm{re}}e_k = T_0 ds_k - \mathbf{W}_{0k} \cdot d\mathbf{z}', \\ d_{\mathrm{ir}}e_k &= F[T_k]ds_k - \mathbf{F}[\mathbf{W}_k] \cdot d\mathbf{z}^{\mathrm{e}}, \end{aligned}$$

where $\mathbf{z}^{\mathrm{e}}$ represents all state variables except the energy e_k and where $\mathbf{W}_k = T\mathbf{w}$ and $\mathbf{W}_0 = T_0\mathbf{w}_0$.

It is easy to see that performing the Legendre transform to obtain the Gibbs free energy in Eq. (79) affects only the form of $d_{\mathrm{re}}s_k$ but leaves $d_{\mathrm{ir}}s_k$ unaffected. Thus, it is easy to see that

$$dg_k(t) \equiv d_{\mathrm{re}}g_k(t) + d_{\mathrm{ir}}g_k(t),$$

where

$$\begin{aligned} d_{\mathrm{re}}g_k = {}& -s_k(t)dT_0 + \mathbf{V}_0(t) \cdot d\mathbf{p}_k(t) + \mathbf{\Omega}_0 \cdot d\mathbf{m}_k(t) \\ & + v_k(t)dP_0 + \mu_0 dn_k(t) + \boldsymbol{\mu}_0 \cdot d\mathbf{x}_k(t) \end{aligned}$$

and

$$d_{\mathrm{ir}}g_k \equiv d_{\mathrm{ir}}e_k.$$

B. Bodies forming a finite isolated system without a medium

We now consider a collection of bodies of comparable sizes forming an isolated system $\overline{\Sigma}_0$; the presence of the overbar implies that no medium is present. In this case, we cannot treat any of the bodies as a (macroscopically extensively large) medium with a fixed field $\mathbf{Y}_0$. As the collection strives toward equilibrium, their field variables continue to change in time. This causes a problem in identifying reversible contributions to various quantities. To solve this problem, we discuss below a simple case; the generalization to more complex situation will be trivial.

1. Two bodies

Let us consider the simplest possible case of two comparable bodies 1 and 2 in internal equilibrium at temperature T_1 and $T_2 > T_1$, respectively, that are brought in thermal contact at time $t = 0$ to form the isolated body $\overline{\Sigma}_0$. We will simplify the discussion by assuming that all other extensive observables in addition to the energy are held fixed. The case of two bodies in the shape of rectangular cuboid along the x axis are shown schematically in Fig. 3(a), with the rectangular interface of area A lying in the yz plane. Let $dQ(t) = dE(t)$ be the infinitesimal heat given to body 1 by body 2 at time t. As the amount of heat is infinitesimal, it does not alter the instantaneous temperatures $T_1(t), T_2(t)$ of the bodies in any significant way so the entropy of $\overline{\Sigma}_0$ changes by

$$d\overline{S}_0(t) = d_{\mathrm{i}}\overline{S}_0(t) = dQ(t)[1/T_1(t) - 1/T_2(t)] > 0. \quad (88)$$

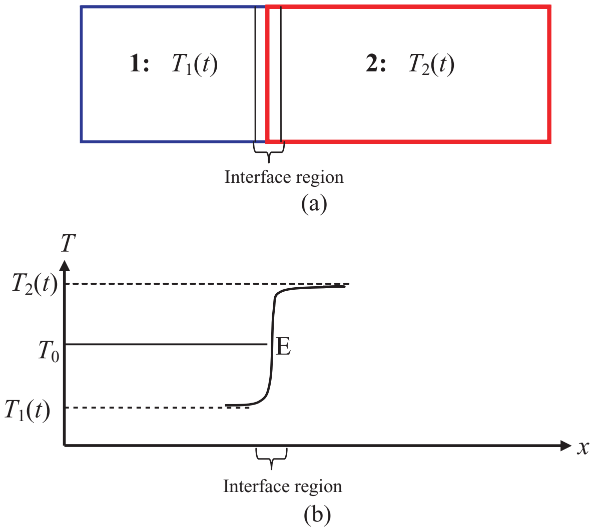


FIG. 3. (Color online) We show in (a) a simplified situation in which two bodies 1 and 2 in thermal contact are allligned along the x axis. Initially, the two bodies are in internal equilibrium at temperatures T_1 and $T_2 > T_1$. Their contact interface is taken to be a plane orthogonal to the x axis as shown in the figure, but the discussion is valid for any shape of the interface. In reality, however, any interface is an interface region of some very small width Δx over which the temperature continuously changes between $T_1(t)$ and $T_2(t)$ so there is a very narrow region of width $dx \ll \Delta x$ around a point E on the x axis, where the temperature is exactly T_0, the equilibrium temperature of the two bodies, as shown in (b) for the simple case shown in (a).

If the system above were not isolated, then Eq. (88) would still give the entropy change due to the direct flow of heat between the two bodies, but there would also be changes in the entropy of the system and each of the bodies due to heat exchange with the medium or other bodies. These entropy changes will also have their own irreversible entropy generations.

The quantity $d_{\mathrm{i}}\overline{S}_0(t)$ in Eq. (88) is the irreversible entropy generation in the two bodies, but says nothing about the irreversible entropy generation within each body, which is described by $d_{\mathrm{i}}s_k \equiv d_{\mathrm{ir}}s_k$ in Eq. (85); note that $d_{\mathrm{e}}s_k \equiv d_{\mathrm{re}}s_k$ as is seen easily. What can we say about the irreversible entropy generation $d_{\mathrm{i}}S_1$ and $d_{\mathrm{i}}S_2$ (in the spirit of $d_{\mathrm{i}}s_k$) within each of the two bodies in $\overline{\Sigma}_0$? This question, to the best of our knowledge, is not answered within the local thermodynamics approach. To obtain the desired result, we introduce the equilibrium temperature T_0 of $\overline{\Sigma}_0$. We now discuss two alternative approaches to determine the individual entropy generation on the way to prove Theorem 6. We require that the entropy generation in each body must vanish when the bodies come to equilibrium.

a. Medium $\widetilde{\Sigma}$ at T_0. We insert the two bodies in an extensively large medium $\widetilde{\Sigma}$ kept at a fixed temperature T_0, with all three bodies now forming a new isolated system Σ_0. The situation is schematically shown in Fig. 4. There is no direct contact between the two bodies, as shown. Despite this, the heat loss $dQ(t) \geqslant 0$ by the body 2 to $\widetilde{\Sigma}$ is completely transferred to body 1 as shown earlier when proving Theorem 2. An alternative is to insert the medium between the two bodies along the x axis [but not surrounding them from all sides as was the case in Fig. 2(a)] with the same effect of transferring the entire heat $dQ(t)$ from body 2 to body 1. The width of the medium along the x axis may be infinitesimally small of order dx but must have a macroscopically large cross-sectional area in the yz plane to ensure its constant temperature T_0 at all times. In all cases, the entropy of the medium does not change. Therefore, the irreversible entropy generation in Σ_0 is identical to the irreversible entropy generation in $\overline{\Sigma}_0$. This artificial introduction of $\widetilde{\Sigma}$ can now be exploited to obtain the

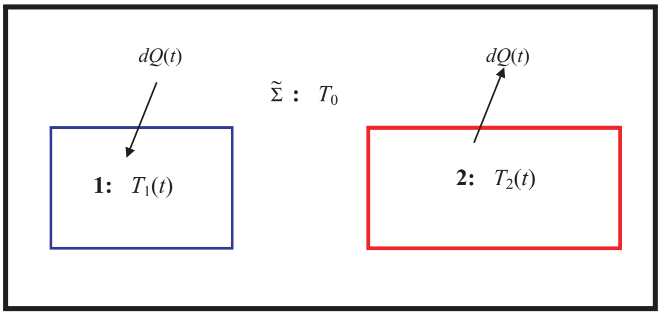


FIG. 4. (Color online) A schematic representation of the isolated system Σ_0 consisting of the two bodies 1 and 2, not in thermal contact, surrounded by an extensively large medium $\widetilde{\Sigma}$, which is so large that the presence of 1 and 2 does not alter its internal temperature, which, therefore, remains constant. We choose $\widetilde{\Sigma}$, as explained in the text, to be at the equilibrium temperature T_0 of $\overline{\Sigma}_0$. In the case $\widetilde{\Sigma}$ is at a different temperature T_0', then the two $dQ(t)$ should be replaced by $dQ_{1,\mathrm{net}}$ and $dQ_{1,\mathrm{net}} \neq dQ_{1,\mathrm{net}}$; see text.

irreversible entropy generation in each body. The result is

$$\begin{aligned} d_{\mathrm{i}}S_1(t) &= dQ(t)[1/T_1(t) - 1/T_0], \\ d_{\mathrm{i}}S_2(t) &= dQ(t)[1/T_0 - 1/T_2(t)]. \end{aligned} \tag{89}$$

This is identical to, and, therefore, a direct demonstration of the validity of, Eq. (85) applied to each of the bodies. From now on, we will simply apply Eq. (85) whenever necessary. These entropy productions vanish in equilibrium, as required.

b. Medium $\widetilde{\Sigma}$ not at T_0. If we introduce a medium held at a constant temperature $T_0^{'} \neq T_0$, then the equilibrium will occur at $T_0^{'}$, and we would end up with a different final state of $\Sigma_0^{'}$. In this case, the heat $dQ_{1,\mathrm{net}}(t)$ given to body 1 differs from the heat given out $dQ_{2,\mathrm{net}}(t)$ by body 2 in Fig. 4. The same situation also occurs if we think of the medium inserted between the two bodies as described above. In relation to Fig. 2(a), we note that $dQ_{1,\mathrm{net}}(t) \equiv dQ_1(t) + dQ'(t) \neq dQ_{2,\mathrm{net}}(t) \equiv dQ_2(t) + dQ'(t)$, giving $dQ_1(t) \neq dQ_2(t)$. The irreversible entropy generation in the two bodies are, using Eq. (85), now

$$\begin{aligned} d_{\mathrm{i}}S_1(t) &= dQ_{1,\mathrm{net}}(t)[1/T_1(t) - 1/T_0'], \\ d_{\mathrm{i}}S_2(t) &= dQ_{2,\mathrm{net}}(t)[1/T_0' - 1/T_2(t)], \end{aligned}$$

in all cases. Even for Fig. 4 or for the case of the medium sandwiched between the two bodies, we can think of a heat transfer $dQ'(t)$ between the two bodies as if they were in thermal contact. It is now possible to express $d_{\mathrm{i}}S(t) \equiv d_{\mathrm{i}}S_1(t) + d_{\mathrm{i}}S_1(t)$ by

$$\begin{aligned} d_{\mathrm{i}}S(t) = dQ'(t)[1/T_1(t) - 1/T_2(t)] + dQ_1(t) \\ \times [1/T_1(t) - 1/T_0'] + dQ_2(t)[1/T_0' - 1/T_2(t)]. \end{aligned} \tag{90}$$

Notice that for $T_0' > T_2(t) > T_1(t)$, $dQ_1(t) > 0$ and $dQ_2(t) < 0$. Similarly, for $T_0' < T_1(t)$, $dQ_1(t) < 0$ and $dQ_2(t) < 0$. Thus, each of the last two irreversible entropy generation contributions above is non-negative, as expected. We will see below that the last two contributions are absent in the local theory.

c. Extension to many bodies. The above approach can now be extended to many bodies at different instantaneous temperatures T_k forming an isolated system $\overline{\Sigma}_0$. Let T_0 denotes the final temperature of $\overline{\Sigma}_0$. Let us choose a medium $\widetilde{\Sigma}$ at T_0 that surrounds the collection of bodies $\{\sigma_k\}$ to form an isolated system Σ_0. The generalization of above result is

$$d_{\mathrm{i}}s_k(t) = dQ_k(t)[1/T_k(t) - 1/T_0], \tag{91}$$

where $dQ_k(t)$ denotes the net infinitesimal heat added to the k-th body σ_k between t and $t + dt$. The irreversible entropy generation in the isolated system Σ_0 is

$$dS_0(t) \equiv \sum_k ds_k(t) + d\widetilde{Q}(t)/T_0 = \sum_k d_{\mathrm{i}}s_k(t) = d_{\mathrm{i}}S(t),$$

as it must be for an isolated system; here $d\widetilde{Q}(t)$ is the net heat added to the medium, and we have used the obvious fact

$$\sum_k dQ_k(t) + d\widetilde{Q}(t) = 0.$$

It is quite clear that the discussion is easily extended to include other extensive variables which results in the expression for $d_{\mathrm{i}}S_k(t)$, which is identical in form to the expression $d_{\mathrm{i}}s_k(t)$ in Eq. (85).

d. Without any medium. One may feel uneasy that the introduction of the fictitious medium $\widetilde{\Sigma}$ has changed the problem. To be convinced that this is not the case, we recognize that its introduction does not affect the heat $dQ_k(t)$, which determines the entropy generation and because one ends with the correct equilibrium state of each body. The importance of this trick is that it allows us to use all the results we have found by the use of a medium. To offer an even stronger argument, we now provide an alternative proof without the introduction of the medium so we can feel comfortable not only in associating a medium in the case when finite-size bodies form an isolated system but also in the validity of Eq. (85).

We revert to the simple case of two bodies in thermal contact. In reality, the interface or the contact region between the two bodies is not a sharp boundary with a discontinuity in temperature; rather, it is a narrow region [12] of width Δx over which the temperature rapidly changes from $T_1(t)$ to $T_2(t)$, as shown in Fig. 3(b). Thus, there exists a point E over this region where the temperature is precisely T_0. It is possible that the location of the point E along the x axis changes with time, but this fact is irrelevant for the discussion. The relevant fact is that the temperature in a very narrow width $dx \ll \Delta x$ around and including this point will remain constant in time. Thus, any heat passing through this region passes through unaffected and no irreversibility will occur in this region. If we take a narrow neighborhood of a point whose temperature differs from T_0, its temperature will eventually converge to T_0, as equilibrium is approached either by local absorption or generation of heat. Thus, irreversibility will occur in these regions. We take the region where the temperature is greater than T_0 along on the side of 2 to be the part of the body 2, while the region with the temperature less than T_0 on the side of 1 to be the part of the body 1. From the quasi-independence of the two bodies, it is clear that the inclusion of the narrow region around E will not significantly affect the instantaneous temperatures $T_1(t)$ and $T_2(t)$. The heat lost $dQ(t)$ by body 2 is transferred through the region around E to body 1 at a *constant* temperature T_0 and we obtain $d_{\mathrm{i}}S_1(t)$ and $d_{\mathrm{i}}S_2(t)$ given in Eq. (89).

The discussion can be easily extended to a collection of many bodies, except that we must use T_0 to denote the equilibrium temperature of the collection to obtain the expressions in Eq. (91). It is only with this choice can the irreversible entropy production in each body will vanish in equilibrium with the understanding that T_0 represents the equilibrium temperature of the system $\overline{\Sigma}_0$. Thus, we conclude that we can consider an isolated inhomogeneous body as a body embedded in a medium without affecting any of the consequences.

e. Comparison with local thermodynamics. The same result as in Eq. (88) is also obtained in the local thermodynamics; see, for example, ([16], Eq. (3.14)). In the limit in which the interfacial region between the two subsystems is infinitesimal in width along the x direction, we can obtain the continuum analog of the irreversible entropy generation *between* the two neighboring regions. Denoting $T_1(t)$ by $T(x,t)$ and $T_2(t)$ by $T(x + dx,t) \simeq T(x,t) + (\partial T/\partial x)dx$, we have $dS_0(t) \simeq dQ(t)\,[\partial(1/T)/\partial x]\,dx$ for conduction. Dividing and multiplying by the cross-sectional area A of the interface, and using Adx as the volume of the interfacial region, we have, for the rate σ of entropy production per unit interfacial volume,

$$\sigma(x,t) = \dot{q}(t)[\partial(1/T)/\partial x], \tag{92}$$

where $\dot{q}(t) = \dot{Q}(t)/A$ denotes the heat flux. This expression [in three dimensions, the result will contain $\boldsymbol{\partial}(1/T)$] in this limit is a standard result for the entropy production due to heat conduction in local thermodynamics.

It should be stressed that our derivation of $\sigma(x,t)$ above is independent of how long the two subsystems are along the x axis but assumes implicitly that $T(x,t)$ has a Taylor series expansion. It is also obvious that $\sigma(x,t)$ must be zero outside the interfacial region. Thus, $\sigma(x,t)$ should be correctly identified as the rate of entropy per unit volume in the *interfacial region*. Therefore, as it follows from the discussion immediately following Eq. (88), the derivation says nothing about how much of the irreversible entropy is generated within each body. The issue is avoided in local thermodynamics by assuming that the entire volume of the system is composed only of such interfacial regions. This is contrary to the basic postulate of local equilibrium according to which each local region has a well-defined temperature $T(t)$, while the interfacial regions have nonzero gradients of the temperature.

We also observe that the form of $\sigma(x,t)$ in Eq. (92) is valid only for the case when Eq. (88) is valid. It is not valid for the case covered in Eq. (90). This is the case when the equilibrium temperature T_0' of the system differs from the equilibrium temperature T_0 of the two bodies under consideration if treated as isolated bodies. Thus, the above expression $\sigma(x,t)$ will not be valid if our system consists of a large number of bodies so the irreversible entropy generation between any two bodies in contact will be given by Eq. (90). In this case, the expression explicitly contains the equilibrium temperature of the system in the last two terms, which is not the case with $\sigma(x,t)$ in Eq. (92).

C. General case

We are now in a position to provide a proof of Theorem 6. We consider the entropy change $ds^{(p)}$ and its two components in a given subsystem associated with the p-th generalized field $W^p(t)$ due to the change dz^p. It is given by

$$ds^{(p)} = \frac{W(t)}{T(t)}dz^p, \quad d_{\rm re}s^{(p)} = \frac{W_0}{T_0}dz^p,$$
$$d_{\rm ir}s^{(p)} = F\left[\frac{W(t)}{T(t)}\right]dz^p \geqslant 0,$$

where $F[w]$ is given in Eq. (20). This then leads us to Theorem 6.

Theorem 6. An isolated system Σ is no different than the same system Σ in an extensively large medium $\widetilde{\Sigma}(\mathbf{Y}_0,\mathbf{A}_0)$, provided the medium is appropriately chosen to represent the equilibrium state (in terms of $\mathbf{Y}_0,\mathbf{A}_0$) of the isolated system Σ.

In particular, the reversible entropy change and the irreversible entropy generation in the two cases (a) and (b) in Fig. 2 are exactly the same, as they both depend on the equilibrium conjugate variables $\mathbf{Y}_0,\mathbf{A}_0$ of the system or subsystems. It should be evident that this theorem is a generalization of Theorem 2.

XII. DISCUSSION AND CONCLUSIONS

We have extended our previous work in I to inhomogeneous systems taking into account the differences in fields for Σ and $\widetilde{\Sigma}$ that result in the thermodynamic forces. Each body is characterized by a set of extensive state variables $\mathbf{Z}(t)$, and some constant parameters $\mathbf{C}$, some of which may be external parameters and need not be extensive. Examples of $\mathbf{C}$ may be the number of particles in the system that characterize the system or the translational and the angular velocities of the frame of reference in which the observations are made. Examples of the state variables are mechanical quantities such as energy, volume, translational and angular momenta, etc., of a body and of the internal variables are various kinds of energy, the translational and angular momenta of its various parts, and so on. The source of irreversibility due to the temperature difference was considered in I. We now allow for relative translational and rotational motions among subsystems that give rise to irreversibility due to mechanical forces. We then generalize the discussion to the thermodynamic forces $F\,[w]$ associated with the all possible observables and internal variables.

A. Quasi-independence and additivity of entropy and energy

It is required that various bodies be quasi-independent, as shown in Sec. V for the *additivity* of the entropy and of energy. Unless the quasi-independence property holds, the entropy of a body cannot be expressed as a sum of the entropies of its parts, with each entropy depending only on the properties of the part alone. As the thermodynamic entropy cannot be measured in an irreversible process, the only choice we have is to use a statistical formulation of entropy, which can always be determined by or at least formally defined in terms of some basic quantities pertaining to the macrostate of the system of interest. We use the Gibbs formulation [19] of entropy, see Eq. (8), for an isolated system [19], but we show in Sec. V that it is also applicable to any body. We use the statistical formulation to develop a nonequilibrium thermodynamics for an inhomogeneous system.

B. Internal equilibrium and irreversible entropy generation

For some body B out of equilibrium with the medium $\widetilde{\Sigma}(\mathbf{Y}_0,0)$, its entropy $S(B) = S[\mathbf{X}(t),\mathbf{I}(t),t]$ usually has an *explicit* dependence on time in addition to the implicit time dependence; we will suppress this time dependence in $\mathbf{X}(t),\mathbf{I}(t)$ in the following for notational simplicity. (We will assume, as discussed in Ref. [40], that at least one observable, which we take to be the number of particles N in the body, is held fixed and is not contained in $\mathbf{X}$.) Thus, such an entropy will continue to change (increase if the body is isolated) for *given* state variables. For a homogeneous body, this will happen if the state variables in $\mathbf{X}$ and $\mathbf{I}$ do not uniquely specify its state, and there are other internal variables not contained in $\mathbf{I}$. This is a consequence of a simple generalization of Theorem 4. The other possibility is that the body is not homogeneous.

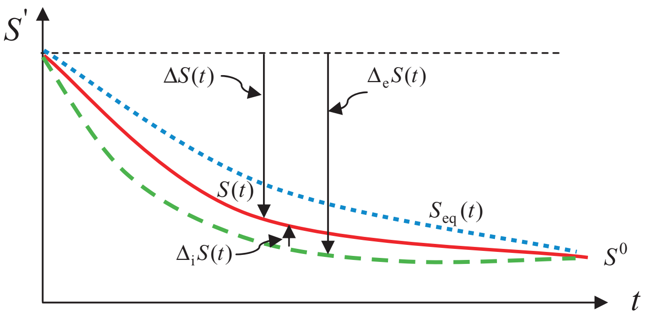


FIG. 5. (Color online) Schematic form of the entropy $S(t)$ (solid curve) and $S_{\rm eq}(t)$ (dotted upper curve; see text) in a cooling experiment. Both curves start from S' at $t = 0$ and end at S^0 as $t \to \infty$. The entropy difference $\Delta S(t) = S(t) - S'$ is shown by the leftmost downward-pointing arrow and the cumulative reversible entropy change $\Delta_e S(t)$ by the rightmost-pointing arrow. The cumulative irreversible entropy generation $\Delta_{\rm i} S(t) > 0$ is shown by the small upward-pointing arrow.

If it happens that the entropy of the body does not explicitly depend on time, then $S(B) = S(\mathbf{X},\mathbf{I})$ must be at its *maximum* for given $\mathbf{X}$ and $\mathbf{I}$. The body, although not in equilibrium, is said to be in internal equilibrium. However, it will be in equilibrium with $\widetilde{\Sigma}_{\rm IE} \equiv \widetilde{\Sigma}(\mathbf{Y}_{\rm IE},\mathbf{A}_{\rm IE})$. In other words, there is no difference between a body in internal equilibrium at a given instant, and the same body in equilibrium with the medium $\widetilde{\Sigma}_{\rm IE}$. Accordingly, all properties of a body in equilibrium also hold for a body in internal equilibrium at each instant. For example, according to Theorem 1 established in Sec. IV, the only possible motion is a *uniform translation* and a *rigid-body rotation*. As a consequence, as discussed in Sec. IV, there is no viscous dissipation, that is, irreversible entropy generation, *within* the body at given $\mathbf{Z}_{\rm IE}$. The dissipation occurs as $\mathbf{Z}$ varies in time as discussed below; see Fig. 5. While there cannot be any relative motion between the system and $\widetilde{\Sigma}_{\rm IE}$, there may be relative motions between the system and the medium $\widetilde{\Sigma}(\mathbf{Y}_0,0)$. Of course, there can also be other nonmechanical sources of irreversible entropy generation such as due to irreversible transfer of particles. This result can be generalized to the following statement:

The only source of mechanical viscous dissipation in a collection of bodies, each in internal equilibrium, is then due to relative motions between different bodies.

We now discuss dissipation based on the current approach. Consider Σ in equilibrium with a medium $\widetilde{\Sigma}(\mathbf{Y}_0',0)$ at time $t = 0$. The corresponding macrostate is $\mathcal{M}'$ and its entropy is S'. The system is brought in contact with a medium $\widetilde{\Sigma}(\mathbf{Y}_0,0)$ at $t = 0$. The final equilibrium macrostate of entropy S^0 (which we take to be lower than S') is denoted by $\mathcal{M}^0$ as $t \to \infty$. At each instant t, the system remains in internal equilibrium; the corresponding intermediate macrostate with $\mathbf{X}$ and $\mathbf{I}$ is denoted by $\mathcal{N}(t)$. The corresponding entropy $S(t)$, and the cumulative entropy changes

$$\Delta_e S(t) \equiv \int d_e S(t), \qquad \Delta_{\rm i} S(t) \equiv \int d_{\rm i} S(t) > 0$$

in an nonequilibrium process during the interval $(0,t)$ determine $\Delta S(t) = S(t) - S' = \Delta_e S(t) + \Delta_{\rm i} S(t)$ and are shown schematically in Fig. 5. The macrostate $\mathcal{N}(t)$ with entropy $S(t)$ can be thought of as an equilibrium state of the system Σ in contact with a medium $\widetilde{\Sigma}[\mathbf{Y}_{\rm IE} = \mathbf{Y}(t),\mathbf{A}_{\rm IE} = \mathbf{A}(t)]$. If the system, instead, follows an equilibrium path so at time t, the observable of the microstate, to be denoted by $\mathcal{M}(t)$, is $\mathbf{X}$ but the affinity $\mathbf{A}(t) = 0$. In this case, its entropy will be given by $S_{\rm eq}(t)$, shown by the dotted curve. The additional entropy $S_{\rm eq}(t) - S(t) > 0$, which follows from the fact that as the internal variables relax with given fixed $\mathbf{X}_{\rm IE} = \mathbf{X}$, the entropy can only increase. We can easily extend the above discussion to the subsystems. We, thus, see that irreversible generation of entropy has been accounted for in our approach; see Eq. (86).

C. Thermodynamic potentials

Under the mildest possible assumption that the medium is in internal equilibrium [so $\widetilde{\mathbf{w}} = \mathbf{w}_0$ are defined via Eq. (61)], but the system itself is, or its subsystems are, not necessarily in internal equilibrium, we are able to identify the thermodynamic potential. It is obvious that the product $\mathbf{w}_0 \cdot \mathbf{Z} \equiv \mathbf{y}_0 \cdot \mathbf{X}$ is dimensionless because the entropy is dimensionless. Accordingly, $\widetilde{S}(\widetilde{\mathbf{Z}})$ can be expressed in terms of $\mathbf{y}_0 \cdot \mathbf{X}$; see, for example, the form of $G(t)$ or $\Omega(t)$. It follows, then, that the thermodynamic potentials will contain $\mathbf{y}_0$ and not $\mathbf{y}(t)$; the latter are defined only when the body is in internal equilibrium. This is surprising since one knows that, in equilibrium thermodynamics, the thermodynamic potentials are state quantities so they contain quantities related to the system. But this is not true when the system is not in equilibrium. These potentials have the required thermodynamic property that they will *never increase* in any spontaneous process, as seen from Eq. (63) or (65). In contrast, functions obtained from thermodynamic potentials by replacing medium's fields by the body's field, does not have this required thermodynamic property.

We now generalize Eq. (18) for $T(t) = \partial E/\partial S$, $P(t) = T(t)\partial S/\partial V$, and so on. We consider the $\mathcal{L}$ frame. Let us, first, consider the temperature. Introducing $r_k(t) \equiv \partial e_k/\partial E$ $[\sum r_k(t) = 1]$, we have

$$\beta(t) \equiv \partial S/\partial E = \sum_k \beta_k(t) r_k(t).$$

Similarly, we have

$$\beta(t)P(t) = \sum_k \beta_k(t) r_k^{\rm v}(t) P_k(t),$$

where $r_k^{\rm v}(t) \equiv \partial v_k/\partial V$, $\sum_k r_k^{\rm v}(t) = 1$. In general,

$$\mathbf{w}(t) \equiv \beta(t)\mathbf{W}(t) = \sum_k \beta_k(t) r_k^l(t) \mathbf{W}_k(t)$$

in terms of the field $\mathbf{W}_k$ of the k-th subsystem; here $r_k^l(t) \equiv \partial z_{lk}/\partial Z_l$, $\sum_k r_k^l(t) = 1$.

D. Contrast with local nonequilibrium thermodynamics

Our approach differs from the traditional local nonequilibrium thermodynamics due to de Groot [13–16], briefly discussed in Sec. II, in four important ways.

(1) The first one relates to the principle of additivity of energy. The energy in the local nonequilibrium thermodynamics is not the sum of the energies of its various part due to

the presence of the mutual interaction energies expressed by $\psi(\mathbf{r})dV$ as seen from Eq. (3). Thus, the local nonequilibrium thermodynamics takes the additivity of entropy as a postulate even though the energy is not additive.

(2) Because the volume element dV is treated infinitesimal in the local theory, all thermodynamic quantities are also treated as continuous in space, while this continuity is not a prerequisite in our approach.

(3) The thermodynamic potentials differ in the two theories. For example, the Gibbs free energy of the volume element dV is taken to be $\widehat{g}(t)dV$.

(4) In our approach, the reversible entropy change and the irreversible entropy generation in each subsystem also depends on the equilibrium state of the system. The irreversible entropy generation in the local theory depends only on the current local properties.

ACKNOWLEDGMENTS

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APPENDIX A: RELATION BETWEEN LAB AND BODY FRAMES

Let us consider a particle of mass m in the laboratory frame $\mathcal{L}$, where it has a velocity $\mathbf{v}_{\mathcal{L}}$ and the potential energy U. The Lagrangian $L_{\mathcal{L}}$ in this frame is given by

$$L_{\mathcal{L}} = (1/2)m\mathbf{v}_{\mathcal{L}}^2 - U.$$

Let us transform to a rotating frame $\mathcal{C}$ which is moving with a velocity $\mathbf{V}$ and rotating with an angular velocity $\mathbf{\Omega}$. The velocity of the particle in $\mathcal{C}$ is given by $\mathbf{v}_{\mathcal{C}}$ and is related to $\mathbf{v}_{\mathcal{L}}$ according to

$$\mathbf{v}_{\mathcal{L}} = \mathbf{v}_{\mathcal{C}} + \mathbf{V} + \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}}, \tag{A1}$$

where $\mathbf{r}_{\mathcal{C}}$ is the coordinate of the particle in the $\mathcal{C}$ frame and is related to the coordinate $\mathbf{r}_{\mathcal{L}}$ of the particle in the laboratory frame $\mathcal{L}$ by

$$\mathbf{r}_{\mathcal{L}} \equiv \mathbf{R} + \mathbf{r}_{\mathcal{C}}.$$

In the following, it would also be convenient to consider a nonrotating frame $\mathcal{I}$, which is only moving with the velocity $\mathbf{V}$ with respect to the laboratory frame, but whose origin coincides with that of $\mathcal{C}$. The Lagrangian in the frame $\mathcal{C}$ is given by

$$\begin{aligned} L_{\mathcal{C}} &= (1/2)m(\mathbf{v}_{\mathcal{C}} + \mathbf{V} + \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}})^2 - U \\ &= (1/2)m\mathbf{v}_{\mathcal{C}}^2 + (1/2)m(\mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}})^2 + m\mathbf{v}_{\mathcal{C}} \cdot \mathbf{V} \\ &\quad + m\mathbf{v}_{\mathcal{C}} \cdot \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}} + m\mathbf{V} \cdot \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}} - U, \end{aligned} \tag{A2}$$

in which we have omitted $(1/2)m\mathbf{V}^2$, which is a total time derivative.

The canonical momentum is obtained as

$$\mathbf{p}_{\mathcal{C}} = \partial L_{\mathcal{C}}/\partial \mathbf{v}_{\mathcal{C}} = m(\mathbf{v}_{\mathcal{C}} + \mathbf{V} + \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}}),$$

so the energy of the particle becomes

$$\begin{aligned} E_{\mathcal{C}} = \mathbf{p}_{\mathcal{C}} \cdot \mathbf{v}_{\mathcal{C}} - L_{\mathcal{C}} &= (1/2)m\mathbf{v}_{\mathcal{C}}^2 - (1/2)m(\mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}})^2 \\ &\quad - m\mathbf{V} \cdot \mathbf{\Omega} \times \mathbf{r}_{\mathcal{C}} + U. \end{aligned} \tag{A3}$$

Expressing $\mathbf{v}_{\mathcal{C}}$ in terms of $\mathbf{v}_{\mathcal{L}}$ from Eq. (A1), we find that

$$\begin{aligned} E_{\mathcal{C}} &= E_{\mathcal{L}} + (1/2)m\mathbf{V}^2 - \mathbf{p}_{\mathcal{L}} \cdot \mathbf{V} - m\mathbf{r}_{\mathcal{C}} \times \mathbf{v}_{\mathcal{L}} \cdot \mathbf{\Omega} \\ &= E_{\mathcal{L}} + (1/2)m\mathbf{V}^2 - \mathbf{p}_{\mathcal{L}} \cdot \mathbf{V} - \mathbf{m} \cdot \mathbf{\Omega}, \end{aligned} \tag{A4}$$

where

$$E_{\mathcal{L}} = (1/2)m\mathbf{v}_{\mathcal{L}}^2 + U, \quad \mathbf{p}_{\mathcal{L}} = m\mathbf{v}_{\mathcal{L}}, \quad \mathbf{m} = m\mathbf{r}_{\mathcal{C}} \times \mathbf{v}_{\mathcal{L}}. \tag{A5}$$

Incidentally, we also note that

$$\mathbf{p}_{\mathcal{C}} = p_{\mathcal{L}}.$$

Thus,

$$\mathbf{m} = \mathbf{r}_{\mathcal{C}} \times \mathbf{p}_{\mathcal{L}} = \mathbf{r}_{\mathcal{C}} \times \mathbf{p}_{\mathcal{C}},$$

which explains why there is no need to use $\mathcal{L}$ or $\mathcal{C}$ as a subscript in $\mathbf{m}$.

APPENDIX B: A ROTATING AND TRANSLATING SYSTEM

Let us now extend the previous calculation for a single particle to a system of particles of total mass M at a given instant t. The system is also characterized by the number of particles and its volume. For specificity, we use N and $V(t)$ to denote these quantities. The notation should not mean that we are only considering the system Σ here. The system we have in mind is any generic system. We assume that this system is translating with a velocity $\mathbf{V}(t)$ and rotating with an angular velocity $\mathbf{\Omega}(t)$ as a whole, both of which can change in time. For notational simplicity, we will suppress the explicit t dependence of various quantities here. We focus on one particular instant t. We take the center of mass of this system to coincide with the origin of $\mathcal{C}$, so $\mathcal{C}$ is fixed to the body and rotating with it. In this case, $\mathcal{C}$ represents the *center-of-mass frame*. We now sum Eq. (A4) over all particles, with the result that it is replaced by

$$E_{\mathcal{C}} = E_{\mathcal{L}} + \mathbf{P}^2/2M - \mathbf{P}_{\mathcal{L}} \cdot \mathbf{V} - \mathbf{M} \cdot \mathbf{\Omega}, \tag{B1}$$

where we have introduced

$$\mathbf{P} = M\mathbf{V}, \quad \mathbf{P}_{\mathcal{L}} = \sum m\mathbf{v}_{\mathcal{L}}, \quad \mathbf{M} \equiv \sum \mathbf{r}_{\mathcal{C}} \times \mathbf{p}_{\mathcal{L}} \equiv \sum \mathbf{r}_{\mathcal{C}} \times \mathbf{p}_{\mathcal{C}}. \tag{B2}$$

Here, $\mathbf{M}_{\mathcal{C}}$ is the *intrinsic* angular momentum of the system of particles in the $\mathcal{C}$ frame. The summation in the above formulas, which are also applicable to nonuniform rotation and translation of the center-of-mass frame $\mathcal{C}$, is a sum over all the particles in the system. The value of $E_{\mathcal{C}}$ in the $\mathcal{C}$ frame represents the internal energy E^{i} of the system. Equation (B1) generalizes the result given by Landau and Lifshitz [[30], see their Eq. (39.13)] to the case when $\mathbf{V} \neq 0$. The present generalization is not limited to constant rotation and translation.

We can express $\mathbf{M}$ as follows:

$$\begin{aligned}\mathbf{M} &= \sum m\mathbf{r}_{\mathcal{C}} \times (\mathbf{v}_{\mathcal{C}} + \mathbf{V} + \boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}})\\ &= \sum m\mathbf{r}_{\mathcal{C}} \times \mathbf{v}_{\mathcal{C}} + \left(\sum m\mathbf{r}_{\mathcal{C}}\right) \times \mathbf{V} + \sum m\mathbf{r}_{\mathcal{C}} \times (\boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}}),\end{aligned}$$

in which the second sum on the right vanishes for $\mathcal{C}$, the center-of-mass frame. For the same reason, the third term in the second equation in Eq. (A3) does not contribute to the energy of the system. Thus, we find

$$\mathbf{M} = \sum m\mathbf{r}_{\mathcal{C}} \times \mathbf{v}_{\mathcal{C}} + \sum m\mathbf{r}_{\mathcal{C}} \times (\boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}}), \tag{B3a}$$

$$E_{\mathcal{C}} = (1/2)\sum m\mathbf{v}_{\mathcal{C}}^2 - (1/2)m(\boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}})^2 + U. \tag{B3b}$$

We see that

$$\mathbf{M} \cdot \boldsymbol{\Omega} = \sum m\mathbf{r}_{\mathcal{C}} \cdot (\mathbf{v}_{\mathcal{C}} \times \boldsymbol{\Omega}) + \sum m(\boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}})^2. \tag{B4}$$

The first term vanishes when the motion is radial. Thus, it is the contribution to the energy from the relative transverse motion in the $\mathcal{C}$ frame and will vanish if the system is stationary in the this frame. The latter condition is met when the system is in internal equilibrium in accordance with Theorem 1.

For the center-of-mass frame $\mathcal{C}$, $\mathbf{P} = \mathbf{P}_{\mathcal{L}}$, so the energy of the system in the frame $\mathcal{C}$ is given by

$$E_{\mathcal{C}} = E_{\mathcal{L}} - \mathbf{P}^2/2M - \mathbf{M} \cdot \boldsymbol{\Omega}, \tag{B5}$$

which can be rewritten as

$$E_{\mathcal{L}} = E_{\mathcal{C}} + \mathbf{P}^2/2M + \mathbf{M} \cdot \boldsymbol{\Omega}. \tag{B6}$$

Using Eq. (B3b), we find that

$$\begin{aligned}E_{\mathcal{L}} = E_{\mathcal{C}} &+ \mathbf{P}^2/2M + (1/2)\sum m(\boldsymbol{\Omega} \times \mathbf{r}_{\mathcal{C}})^2\\ &+ \sum m\mathbf{r}_{\mathcal{C}} \cdot (\mathbf{v}_{\mathcal{C}} \times \Omega),\end{aligned} \tag{B7}$$

in which the last term is the contribution of the transverse motion.

The energy of the system in the $\mathcal{I}$ frame, in which the system has only rotation, is given by

$$E_{\mathcal{I}} = E_{\mathcal{L}} - \mathbf{P}^2/2M. \tag{B8}$$

It is obvious that $E_{\mathcal{I}}$ does not depend on the velocity $\mathbf{V}$. Thus,

$$E_{\mathcal{C}} = E_{\mathcal{I}} - \mathbf{M} \cdot \boldsymbol{\Omega}$$

does not depend explicitly on $\mathbf{V}$. We can take $E_{\mathcal{C}}$ as a function of $E_{\mathcal{I}}$ and Ω, from which it follows that

$$(\partial E_{\mathcal{C}}/\partial \mathbf{V})|_{E_{\mathcal{I}},V,N,\boldsymbol{\Omega}} = 0, \tag{B9}$$

$$(\partial E_{\mathcal{C}}/\partial \boldsymbol{\Omega})|_{E_{\mathcal{I}},V,N} = -\mathbf{M}. \tag{B10}$$

All the above results are for a particular microstate of the system undergoing a Hamiltonian dynamics. To obtain thermodynamics of the system, we need to average the above equations over all allowed microstates using their probabilities, which is taken up in Sec. VIII. The averaging takes into account the stochastic nature of the dynamics, which has not been considered in either Appendix.

[1] P. D. Gujrati, Phys. Rev. E **81**, 051130 (2010); P. D. Gujrati, e-print arXiv:0910.0026.

[2] E. Bouchbinder and J. S. Langer, Phys. Rev. E **80**, 031131 (2009); **80**, 031132 (2009); **80**, 031133 (2009).

[3] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, Oxford, 1982).

[4] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 3rd ed. (Pergamon Press, Oxford, 1986).

[5] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **121**, 2852 (2004).

[6] H. C. Öttinger, Phys. Rev. E **74**, 011113 (2006); see also H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, NJ, 2005).

[7] Y. Oono and M. Paniconi, Prog. Theor. Phys. Suppl. **130**, 29 (1998).

[8] S.-I. Sasa and H. Tasaki, J. Stat. Phys. **125**, 125 (2006).

[9] M. A. Biot, J. Appl. Phys. **25**, 1385 (1954).

[10] J. C. Keck and D. Gillespie, Combust. Flame **17**, 237 (1971); J. C. Keck, Prog. Energy Combust. Sci. **16**, 125 (1990).

[11] G. P. Beretta and E. P. Gyftopoulos, J. Chem. Phys. **121**, 2718 (2004).

[12] D. Bedeaux, S. Kjelstrup, L. Zhu, and G. J. M. Koper, Phys. Chem. Chem. Phys. **8**, 5421 (2006).

[13] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, 1st ed. (Dover, New York, 1984).

[14] Th. de Donder and P. van Rysselberghe, *Thermodynamic Theory of Affinity* (Stanford University, Stanford, 1936).

[15] D. Kondepudi and I. Prigogine, *Modern Thermodynamics* (John Wiley & Sons, West Sussex, 1998).

[16] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, 3rd ed. (Interscience, New York, 1967).

[17] W. Muschik, S. Gümbel, M. Kröger, and H. C. Öttinger, Physica A **285**, 448 (2000).

[18] Y. Demirel, *Nonequilibrium Thermodynamics* (Elsevier, Amsterdam, 2007).

[19] P. D. Gujrati, Symmetry **2**, 1201 (2010).

[20] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part I, 3rd ed. (Pergamon Press, Oxford, 1986).

[21] M. Merolle, J. P. Garrahan, and D. Chandler, Proc. Natl. Acad. Sci. USA **102**, 10837 (2005).

[22] P. G. Wolynes, Proc. Natl. Acad. Sci. USA **106**, 1353 (2009).

[23] L. Hong, P. D. Gujrati, V. N. Novikov, and A. P. Sokolov, J. Chem. Phys. **131**, 194511 (2009).

[24] R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953).

[25] P. D. Gujrati, in *Modeling and Simulation in Polymers*, edited by P. D. Gujrati and A. I. Leonov (Wiley-VCH, Weinheim, 2010).

[26] S. V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State* (CRC Press, Boca Raton, FL, 1995).

[27] I. Gutzow and J. W. P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology and Crystallization* (Springer, Berlin, 1995).

[28] A. Sommerfeld, *Mechanics of Deformable Bodies* (Academic Press, New York, 1950).

[29] G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, Cambridge, 1967).

[30] L. D. Landau and E. M. Lifshitz, *Mechanics*, 3rd ed. (Pergamon Press, Oxford, 1982).

[31] P. D. Gujrati, e-print arXiv:1101.0429.

[32] J. Lebowitz, Rev. Mod. Phys. **71**, S346 (1999).

[33] D. Ruelle, J. Stat. Phys. **85**, 1 (1996).

[34] G. D. C. Kuiken, *Thermodynamics of Irreversible Processes* (John Wiley & Sons, Chichester, 1994).

[35] P. D. Gujrati and P. P. Aung, Phys. Rev. E **85**, 041129 (2012).

[36] P. D. Gujrati, Phys. Rev. E **51**, 957 (1995); J. Chem. Phys. **108**, 5089 (1998); **108**, 5104 (1998).

[37] M. Mosayebi, E. Del Gado, P. Ilg, and H. C. Ottinger, Phys. Rev. Lett. **104**, 205704 (2010).

[38] J. H. Keenan, *Thermodynamics* (MIT Press, Cambridge, 1941).

[39] J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).

[40] P. D. Gujrati, Recent Res. Devel. Chem. Phys. **4**, 243 (2003).

[41] P. D. Gujrati, S. S. Rane, and A. Corsi, Phys. Rev. E **67**, 052501 (2003).

[42] G. A. Maugin, *The Thermomechanics of Nonlinear Irreversible Behaviors: An Introduction* (World Scientific, Singapore, 1999).

[43] L. I. Mandelstam and M. A. Leontovich, Zh. Eksp. Teor. Fiz. **7**, 438 (1937).

[44] V. N. Pokrovski, Eur. J. Phys. **26**, 769 (2005).

[45] I. Prigogine and P. Mazur, Physica **19**, 241 (1953).

[46] B. D. Coleman and M. E. Gurtin, J. Chem. Phys. **47**, 597 (1967).