

I.1.2 Irreversible processes in discrete thermodynamic systems

The first of Callen's postulates of thermostatics has two implicit corollaries, namely the existence of other states of macroscopic systems than the equilibrium ones, and the necessity to introduce new quantities besides the extensive parameters $\{\mathcal{X}_a\}$ for the description of these out-of-equilibrium states. In this subsection, these extra variables are introduced for the case of discrete systems.

I.1.2a Timescales

In the following, we shall consider composite systems made of several simple subsystems, each of which is characterized by a set of extensive parameters $\{\mathcal{X}_a^{(A)}\}$, where (A) labels the various subsystems. If the subsystems are isolated from each other, they can individually be at thermodynamic equilibrium, with definite values of the respective variables. Beginning with such a collection of equilibrium states and connecting the subsystems together, i.e. allowing them to interact with each other, the subsystems start evolving. This results in a time dependence of the extensive variables, $\{\mathcal{X}_a^{(A)}(t)\}$.

An essential assumption is that the interaction processes between macroscopic systems are slow compared to the microscopic ones within the individual subsystems, which drive each of them to its own thermodynamic equilibrium. In other terms, the characteristic timescales for macroscopic processes, i.e. for the evolution of the extensive parameters $\{\mathcal{X}_a^{(A)}(t)\}$, are much larger than the typical timescale of microscopic interactions.

Under this assumption, one can consider that the composite system undergoes a transformation across macroscopic states such that one can meaningfully define an instantaneous entropy $S(\{\mathcal{X}_a(t)\})$, with the same functional form as at thermodynamic equilibrium.

I.1.2b Affinities and fluxes in a discrete system

Consider an isolated composite system made of two simple systems A and B , with respective extensive variables $\{\mathcal{X}_a^{(A)}\}$, $\{\mathcal{X}_a^{(B)}\}$. Since the latter correspond to conserved quantities, the sum

$$\mathcal{X}_a^{(A)}(t) + \mathcal{X}_a^{(B)}(t) = \mathcal{X}_a^{\text{tot}} \quad (\text{I.4})$$

remains constant over time for every a , whether the subsystems A and B can actually exchange the quantity or not.

According to postulate III, the entropy of the composite system is

$$S^{\text{tot}}(t) = S^{(A)}(\{\mathcal{X}_a^{(A)}(t)\}) + S^{(B)}(\{\mathcal{X}_a^{(B)}(t)\}). \quad (\text{I.5})$$

Since for fixed $\mathcal{X}_a^{\text{tot}}$, $\mathcal{X}_a^{(B)}(t)$ is entirely determined by the value of $\mathcal{X}_a^{(A)}(t)$ [Eq. (I.4)], the total entropy S^{tot} is actually only a function of the latter.

At thermodynamic equilibrium, $S^{\text{tot}}(\{X_a^{(A)}\})$ is maximal (second postulate), i.e. its derivative with respect to $X_j^{(A)}$ should vanish:

$$\left. \frac{\partial S^{\text{tot}}}{\partial X_a^{(A)}} \right|_{X_a^{\text{tot}}} = 0 = \frac{\partial S^{(A)}}{\partial X_a^{(A)}} - \frac{\partial S^{(B)}}{\partial X_a^{(B)}} = \mathcal{Y}_a^{(A)} - \mathcal{Y}_a^{(B)}. \quad (\text{I.6})$$

Thus at thermodynamic equilibrium the so-called *affinity*

$$\mathcal{F}_a \equiv \mathcal{Y}_a^{(A)} - \mathcal{Y}_a^{(B)} = \left. \frac{\partial S^{\text{tot}}}{\partial X_a^{(A)}} \right|_{X_a^{\text{tot}}} \quad (\text{I.7})$$

conjugate to the extensive state variable X_a vanishes. Reciprocally, when $\mathcal{F}_a \neq 0$, the system is out of equilibrium. A process then takes place, that drives the system to equilibrium: \mathcal{F}_a thus acts as a *generalized force* (and is sometimes referred to as such).

For instance, unequal temperatures result in a non-zero affinity $\mathcal{F}_E \equiv 1/T^{(A)} - 1/T^{(B)}$, and similarly one has for simple systems $\mathcal{F}_\nu \equiv \mathcal{P}^{(A)}/T^{(A)} - \mathcal{P}^{(B)}/T^{(B)}$ and for every species k (note the signs!) $\mathcal{F}_{N_k} \equiv \mu_k^{(B)}/T^{(B)} - \mu_k^{(A)}/T^{(A)}$.

The response of a system to a non-vanishing affinity \mathcal{F}_a is quite naturally a variation of the conjugate extensive quantity $X_a^{(A)}$. This response is described by a *flux*, namely the rate of change

$$\mathcal{J}_a \equiv \frac{dX_a^{(A)}}{dt}, \quad (\text{I.8})$$

which describes how much of quantity X_a is transferred from system B to system A per unit time. These fluxes are sometimes referred to as *generalized displacements*.

Remarks:

* The sign convention for the affinity is not universal: some authors define it as $\mathcal{F}_a \equiv \mathcal{Y}_j^{(B)} - \mathcal{Y}_a^{(A)}$, e.g. in Ref. [9], instead of Eq. (I.7). Accordingly, the conjugate flux is taken as the quantity transferred from system A to system B per unit time, that is the opposite of Eq. (I.8). All in all, the equation for the entropy production rate (I.9) below remains unchanged.

* In the case of discrete systems, all affinities and fluxes are scalar quantities.

1.1.2c Entropy production

The affinities and fluxes introduced above allow one to rewrite the time derivative of the instantaneous entropy in a convenient way. Thus, differentiating S^{tot} with respect to time yields the *rate of entropy production*

$$\frac{dS^{\text{tot}}}{dt} = \sum_a \frac{\partial S^{\text{tot}}}{\partial X_a^{(A)}} \frac{dX_a^{(A)}}{dt}$$

that is, using definitions (I.7) and (I.8) of the affinities and fluxes,

$$\frac{dS^{\text{tot}}}{dt} = \sum_a \mathcal{F}_a \mathcal{J}_a. \quad (\text{I.9})$$

An important property of this rate is its bilinear structure, which will remain valid in the case of a continuous medium, and also allows one to identify the affinities and fluxes in the study of non-simple systems.

I.1.3 Local thermodynamic equilibrium of continuous systems

We now turn to the description of out-of-equilibrium macroscopic systems which can be viewed as continuous media, beginning with the determination of the thermodynamic quantities suited to that case.

I.1.3a Local thermodynamic variables

The starting point when dealing with an inhomogeneous macroscopic system is to divide it in thought in small cells of fixed—yet not necessarily universal—size fulfilling two conditions:

- each cell can meaningfully be treated as a thermodynamic system, i.e. each cell must be large enough that the relative fluctuation of the usual thermodynamic quantities computed in the cell are negligible;
- the intensive thermodynamic properties vary little over the cell scale, i.e. cells cannot be too large, so that (approximate) homogeneity is restored.

Under these assumptions, one can define *local thermodynamic variables*, corresponding to the values taken in each cell—labeled by its position \vec{r} —by the extensive parameters: $U(\vec{r})$, $N_k(\vec{r})$, ... Since the size of each cell is physically irrelevant as long as it satisfies the above two conditions, there is no local variable corresponding to the volume \mathcal{V} , which only enters the game as the domain over which \vec{r} takes its values.

On the other hand, since the separation between cells is immaterial, nothing prevents matter from actually flowing from a cell to its neighbors; one thus needs additional extensive parameters to describe this motion, namely the 3 components of the total momentum $\vec{P}(\vec{r})$ of the particles in each cell. For an isolated system, total momentum is a conserved quantity, as are the energy and (in the absence of chemical reactions) the particle numbers, thus \vec{P} is on the same footing as U and the N_k .

Promoting \vec{r} to a continuous variable, these local thermodynamic parameters become *fields*. To account for their possible time dependence, the latter will collectively be denoted as $\{\mathcal{X}_a(t, \vec{r})\}$.

Remarks:

* The actual values of $\vec{P}(t, \vec{r})$ obviously depend on the reference frame chosen for describing the system.

* As always in field theory, one relies on a so-called *Eulerian*^(c) description, in which one studies the changes in the thermodynamic variables with time at a given position, irrespective of the fact that the microscopic particles in a given cell do not remain the same over time, but constantly move from one cell to the other.

Rather than relying on the local thermodynamic variables, which depend on the arbitrary size of the cells, it is more meaningful to introduce their densities, i.e. the amounts of the quantities per unit volume: internal energy density $e(t, \vec{r})$, particle number densities $n_k(t, \vec{r})$, momentum density $\vec{p}(t, \vec{r})$... Except for the internal energy (see footnote 3), these densities will be denoted by the corresponding lowercase letter, and thus collectively referred to as $\{\chi_a(t, \vec{r})\}$.

Alternatively, one can also consider the quantities per unit mass⁽⁵⁾ which will be denoted in lowercase with a subscript m— $e_m(t, \vec{r})$, $n_{k,m}(t, \vec{r})$, ... , and collectively $\{\chi_{a,m}(t, \vec{r})\}$ —, with the exception of the momentum per unit mass, which is called *flow velocity* and will be denoted by $\vec{v}(t, \vec{r})$. Representing the mass density at time t at position \vec{r} by $\rho(t, \vec{r})$, one trivially has the identity

$$\chi_a(t, \vec{r}) = \rho(t, \vec{r}) \chi_{a,m}(t, \vec{r}) \quad (\text{I.10})$$

for every extensive parameter \mathcal{X}_a .

⁽⁵⁾The use of these so-called specific quantities is for example favoured by Landau & Lifshitz.

^(c)L. EULER, 1707–1783

1.1.3b Local entropy

Since it is assumed that each small cell is at every instant t in a state of thermodynamic equilibrium, one can meaningfully associate to it a *local entropy* $S(t, \vec{r})$. From there, one can define the *local entropy density* $s(t, \vec{r})$ and the specific entropy $s_m(t, \vec{r})$.

The important *local equilibrium assumption* amounts to postulating that the dependence of $s(t, \vec{r})$ on the thermodynamic densities $\chi_a(t, \vec{r})$ —which momentarily include a “local volume density” $\chi_{\mathcal{V}}$ identically equal to 1—is given by the same fundamental equation as between the entropy S and its extensive parameters $\{\mathcal{X}_a\}$ in a system at thermodynamic equilibrium.

In differential form, this hypothesis leads to the total differential [cf. Eq. (I.1)]

$$ds(t, \vec{r}) = \sum'_a \mathcal{Y}_a(t, \vec{r}) d\chi_a(t, \vec{r}). \quad (\text{I.11})$$

Since the differential $d\chi_{\mathcal{V}}$ is actually identically zero, the intensive parameter $\mathcal{Y}_{\mathcal{V}}$ conjugate to volume actually drops out from the sum, which is indicated by the primed sum sign.

Considering instead the integral form of the fundamental equation, and after summing over cells—i.e., effectively, integrating over the volume of the system—, the total entropy of the continuous medium reads

$$S^{\text{tot}}(t) = \sum_a \int_{\mathcal{V}} \mathcal{Y}_a(t, \vec{r}) \chi_a(t, \vec{r}) d^3\vec{r}. \quad (\text{I.12})$$

Equations (I.11) and (I.12) yield for the local intensive variables

$$\mathcal{Y}_a(t, \vec{r}) = \frac{\partial s(t, \vec{r})}{\partial \chi_a(t, \vec{r})} = \frac{\delta S^{\text{tot}}(t)}{\delta \chi_a(t, \vec{r})}, \quad (\text{I.13})$$

i.e. $\mathcal{Y}_a(t, \vec{r})$ can be seen either as a partial derivative of the local entropy density, or as a functional derivative of the total entropy. The relations

$$\mathcal{Y}_a(t, \vec{r}) = \mathcal{Y}_a(\{\chi_b(t, \vec{r})\}) \quad (\text{I.14})$$

for the various $\mathcal{Y}_a(t, \vec{r})$ are the *local equations of state* of the system. One easily checks that the local equilibrium hypothesis amounts to assuming that the local equations of state have the same form as the equations of state of a system in *global* thermodynamic equilibrium.

In the example of a simple system in mechanical equilibrium—so that $\vec{v}(t, \vec{r})$ vanishes at each point—, Eq. (I.11) reads [cf. Eq. (I.2a)]

$$ds(t, \vec{r}) = \frac{1}{T(t, \vec{r})} de(t, \vec{r}) - \sum_k \frac{\mu_k(t, \vec{r})}{T(t, \vec{r})} dn_k(t, \vec{r}), \quad (\text{I.15})$$

which defines the local temperature $T(t, \vec{r})$ and chemical potentials $\mu_k(t, \vec{r})$.

Remark: Throughout, “local” actually means “at each place at a given instant”. A more accurate denomination would be to refer to “local and instantaneous” thermodynamic variables, which is however never done.

1.1.4 Affinities and fluxes in a continuous medium

We can now define the affinities and fluxes inside a continuous thermodynamic system. For that purpose, we first introduce the local formulation of balance equations in such a system, which relies on flux densities (§ I.1.4 a). Building on these, we consider the specific case of entropy balance (§ I.1.4 b), and deduce from it the form of the affinities (§ I.1.4 c). Throughout this section, the system is studied within its own rest frame, i.e. it is globally at rest.

1.1.4a Balance equations

Consider a fixed geometrical volume \mathcal{V} inside a continuous medium, delimited by an immaterial surface $\partial\mathcal{V}$. Let $G(t)$ be the amount of a given extensive thermodynamic quantity within this

volume. For the sake of simplicity, we consider here only the case of a scalar quantity. The corresponding density and amount per unit mass are respectively denoted by $g(t, \vec{r})$ and $g_m(t, \vec{r})$.

Introducing the local mass density $\rho(t, \vec{r})$, one has [see Eq. (I.10)]

$$G(t) = \int_{\mathcal{V}} g(t, \vec{r}) d^3\vec{r} = \int_{\mathcal{V}} \rho(t, \vec{r}) g_m(t, \vec{r}) d^3\vec{r}. \quad (\text{I.16})$$

At each point \vec{r} of the surface $\partial\mathcal{V}$, the amount of quantity G flowing through an infinitesimal surface element $d^2\mathcal{S}$ in the time interval $[t, t + dt]$ is given by

$$\vec{J}_G(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2\mathcal{S} dt,$$

where $\vec{e}_n(\vec{r})$ denotes the unit normal vector to the surface, oriented towards the exterior of \mathcal{V} , while $\vec{J}_G(t, \vec{r})$ is the *current density* or *flux density* (often referred to as *flux*) of G .

The integral *balance equation* for G reads

$$\frac{dG(t)}{dt} + \int_{\partial\mathcal{V}} \vec{J}_G(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2\mathcal{S} = \int_{\mathcal{V}} \sigma_G(t, \vec{r}) d^3\vec{r}. \quad (\text{I.17})$$

$\sigma_G(t, \vec{r})$ is a *source density*⁽⁶⁾ which describes the rate at which the quantity G is created per unit volume—in the case of a conserved quantity, the corresponding source density σ_G vanishes. In words, Eq. (I.17) states that the net rate of change of G inside volume \mathcal{V} and the flux of G exiting through the surface $\partial\mathcal{V}$ per unit time add up to the amount of G created per unit time in the volume.

In the first term of the balance equation, $G(t)$ can be replaced by a volume integral using Eq. (I.16), and the time derivation and volume integration can then be exchanged. In turn, the second term on the right-hand side of Eq (I.17) can be transformed with the help of the divergence theorem, leading to

$$\int_{\mathcal{V}} \frac{\partial g(t, \vec{r})}{\partial t} d^3\vec{r} + \int_{\mathcal{V}} \vec{\nabla} \cdot \vec{J}_G(t, \vec{r}) d^3\vec{r} = \int_{\mathcal{V}} \sigma_G(t, \vec{r}) d^3\vec{r}.$$

Since the equality should hold for arbitrary volume \mathcal{V} , one obtains the *local balance equation*

$$\frac{\partial g(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_G(t, \vec{r}) = \sigma_G(t, \vec{r}), \quad (\text{I.18a})$$

or equivalently

$$\frac{\partial}{\partial t} [\rho(t, \vec{r}) g_m(t, \vec{r})] + \vec{\nabla} \cdot \vec{J}_G(t, \vec{r}) = \sigma_G(t, \vec{r}). \quad (\text{I.18b})$$

When the source density vanishes, that is for conserved quantities G , these local balance equations reduce to so-called *continuity equations*.

I.1.4 b Entropy production

In the case of the entropy, which is not a conserved quantity, the general balance equation (I.17) becomes

$$\frac{dS(t)}{dt} = - \int_{\partial\mathcal{V}} \vec{J}_S(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2\mathcal{S} + \int_{\mathcal{V}} \sigma_S(t, \vec{r}) d^3\vec{r} \equiv \frac{dS_{\text{ext.}}(t)}{dt} + \frac{dS_{\text{int.}}(t)}{dt}, \quad (\text{I.19})$$

with \vec{J}_S the entropy flux density and σ_S the entropy source density, which is necessarily non-negative. The first term in the right member of the equation arises from the exchanges with the exterior of the volume \mathcal{V} under consideration. If \mathcal{V} corresponds to the whole volume of an isolated system, then this term vanishes, since by definition the system does not exchange anything with its environment.

⁽⁶⁾ ... or “sink density”, in case the quantity G is destroyed.

The second term on the right-hand side of the balance equation (I.19) corresponds to the creation of entropy due to internal changes in the bulk of \mathcal{V} , and can be non-vanishing even for isolated systems. This contribution is called *entropy production rate*, or often more briefly *entropy production* or even *dissipation*.

The corresponding local balance equation for entropy reads [cf. Eq. (I.18a)]

$$\frac{\partial s(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_S(t, \vec{r}) = \sigma_S(t, \vec{r}). \quad (\text{I.20})$$

This equation will now be exploited to define, in analogy with the case of a discrete system of § I.1.2, the affinities conjugate to the extensive thermodynamic variables.

I.1.4c Affinities and fluxes

The local equilibrium assumption, according to which the local entropy $S(t, \vec{r})$ has the same functional dependence on the local thermodynamic variables $\mathcal{X}_a(t, \vec{r})$ as given by Gibbs' fundamental equation in equilibrium, leads on the one hand to Eq. (I.11), from which follows

$$\frac{\partial s(t, \vec{r})}{\partial t} = \sum'_a \mathcal{Y}_a(t, \vec{r}) \frac{\partial \mathcal{X}_a(t, \vec{r})}{\partial t}. \quad (\text{I.21})$$

On the other hand, the same hypothesis suggests for the entropy flux density \vec{J}_S the expression

$$\vec{J}_S(t, \vec{r}) = \sum'_a \mathcal{Y}_a(t, \vec{r}) \vec{J}_a(t, \vec{r}), \quad (\text{I.22})$$

with \vec{J}_a the flux density for the quantity \mathcal{X}_a . Taking the divergence of this identity yields

$$\vec{\nabla} \cdot \vec{J}_S(t, \vec{r}) = \sum'_a \left[\vec{\nabla} \mathcal{Y}_a(t, \vec{r}) \cdot \vec{J}_a(t, \vec{r}) + \mathcal{Y}_a(t, \vec{r}) \vec{\nabla} \cdot \vec{J}_a(t, \vec{r}) \right].$$

Inserting this divergence together with the time derivative (I.21) in the local balance equation for the entropy (I.20) gives the entropy production rate

$$\sigma_S(t, \vec{r}) = \sum'_a \left\{ \vec{\nabla} \mathcal{Y}_a(t, \vec{r}) \cdot \vec{J}_a(t, \vec{r}) + \mathcal{Y}_a(t, \vec{r}) \left[\vec{\nabla} \cdot \vec{J}_a(t, \vec{r}) + \frac{\partial \mathcal{X}_a(t, \vec{r})}{\partial t} \right] \right\},$$

i.e., after taking into account the continuity equations for the conserved thermodynamic quantities,

$$\sigma_S(t, \vec{r}) = \sum'_a \vec{\nabla} \mathcal{Y}_a(t, \vec{r}) \cdot \vec{J}_a(t, \vec{r}). \quad (\text{I.23})$$

Defining now *affinities* as

$$\vec{\mathcal{F}}_a(t, \vec{r}) \equiv \vec{\nabla} \mathcal{Y}_a(t, \vec{r}) \quad (\text{I.24})$$

the entropy production rate (I.23) can be rewritten as

$$\sigma_S(t, \vec{r}) = \sum'_a \vec{\mathcal{F}}_a(t, \vec{r}) \cdot \vec{J}_a(t, \vec{r}). \quad (\text{I.25})$$

The entropy production rate in a continuous medium thus has the same bilinear structure in the affinities and fluxes as in a discrete thermodynamic system. This remains true when one considers not only the exchange of scalar quantities (like energy or particle number), but also when exchanging vector quantities (like momentum) or when allowing for chemical reactions.

One should however note several differences:

- σ_S is the rate of entropy production per unit volume, while dS^{tot}/dt is for the whole volume of the system;

- the “fluxes” $\vec{\mathcal{J}}_a$ are actually flux densities, in contrast to the discrete fluxes \mathcal{J}_a , which are rates of change;
- the affinities conjugate to scalar extensive quantities in a continuous medium are the gradients of the intensive parameters, while in the discrete case they are differences.

Since the intensive variable conjugate to a vectorial extensive parameter is itself a vector, as exemplified by Eq. (I.3) for momentum, one easily finds that the corresponding affinity is a tensor of order 2. In that case, the flux density is also a tensor of order 2.

Eventually, chemical reactions in a continuous medium can be accounted for by splitting it in thought in a discrete set of continuous media, corresponding to the various chemical components. The affinities and fluxes describing the exchanges between these discrete systems then follows the discussion in § I.1.2

The transport of scalar quantities like internal energy or particle number is thus a vectorial process (the $\vec{\mathcal{J}}_a$ are vectors), while the transport of momentum is a tensorial process (of order 2), and chemical reactions are scalar processes.

As an example of the considerations in this paragraph, consider a chemically inert simple continuous medium in local mechanical equilibrium—i.e. $\vec{\nabla}(\vec{r}) = \vec{0}$ everywhere. The entropy production rate (I.23) reads (for the sake of brevity the dependence on time and position is omitted)

$$\sigma_S = \vec{\nabla} \left(\frac{1}{T} \right) \cdot \vec{\mathcal{J}}_E - \sum_k \vec{\nabla} \left(\frac{\mu_k}{T} \right) \cdot \vec{\mathcal{J}}_{N_k}, \quad (\text{I.26})$$

with $\vec{\mathcal{J}}_E$ the flux density of internal energy and $\vec{\mathcal{J}}_{N_k}$ the particle flux density for species k . This entropy production rate can be rewritten using the entropy flux density, which according to formula (I.22) is given by

$$\vec{\mathcal{J}}_S = \frac{1}{T} \vec{\mathcal{J}}_E - \sum_k \frac{\mu_k}{T} \vec{\mathcal{J}}_{N_k}, \quad (\text{I.27a})$$

so that

$$\sigma_S = -\frac{1}{T} \vec{\mathcal{J}}_S \cdot \vec{\nabla} T - \sum_k \frac{1}{T} \vec{\mathcal{J}}_{N_k} \cdot \vec{\nabla} \mu_k. \quad (\text{I.27b})$$

According to this expression, the affinities conjugate to the flux densities $\vec{\mathcal{J}}_S$ and $\vec{\mathcal{J}}_{N_k}$ —which are the “natural” fluxes in the *energy representation*, where the variables are S and the $\{N_k\}$, rather than U and the $\{N_k\}$ in the *entropy representation*—are respectively $-(1/T)\vec{\nabla}T$ and $-(1/T)\vec{\nabla}\mu_k$.