

## I.2 Linear irreversible thermodynamic processes

The affinities and fluxes introduced in the previous section to describe out-of-equilibrium thermodynamic systems remain useless as long as they are not supplemented with relations that specify how the fluxes are related to the other thermodynamic parameters. In the framework of thermodynamics, these are empirical laws, involving coefficients, characteristic of each system, which have to be taken from experimental measurements.

In § I.2.1, we introduce a few physical assumptions that lead to simplifications of the functional form of these relations. The various coefficients entering the laws cannot be totally arbitrary, but are restricted by symmetry considerations as well as by relations, due to Lars Onsager,<sup>(d)</sup> which within a macroscopic approach can be considered as an additional fundamental principle (§ I.2.2). Several long known empirical laws describing the transport of various quantities are presented and recast within the general framework of irreversible thermodynamics (§ I.2.3 and I.2.4).

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<sup>(d)</sup>L. ONSAGER, 1903–1976

### 1.2.1 Linear processes in Markovian thermodynamic systems

For a given thermodynamic system, the various local intensive parameters  $\mathcal{Y}_a$ , affinities  $\mathcal{F}_a$ , and fluxes  $\mathcal{J}_a$ —where for the sake of brevity the tensorial nature of the quantities has been omitted—represent a set of variables that are not fully constrained by the assumption of local thermodynamic equilibrium, that is through the knowledge of the local equations of state alone. To close the system of equations for these variables, one needs further relations, and more precisely between the fluxes and the other parameters.

**Remark:** As implied here, the customary approach is to use the parameters  $\{\mathcal{Y}_a\}$  instead of the corresponding conjugate extensive variables  $\{\mathcal{X}_a\}$  (resp. the densities  $\{\chi_a\}$  in continuous systems). Both choices are however equivalent. Again, the intensive parameter conjugate to volume  $\mathcal{Y}_v$  drops out from the list of relevant parameters.

Most generally, a given flux  $\mathcal{J}_a(t, \vec{r})$  might conceivably depend on the values of the intensive parameters  $\mathcal{Y}_b$  and affinities  $\mathcal{F}_b$  at every instant and position allowed by causality, i.e. any time  $t' \leq t$  and position  $\vec{r}'$  satisfying  $|\vec{r} - \vec{r}'| \leq c(t - t')$ , with  $c$  the velocity of light in vacuum.

In many systems, one can however assume that the fluxes at a given time only depend on the values of the parameters  $\{\mathcal{Y}_b\}$ ,  $\{\mathcal{F}_b\}$  at the same instant—that is, automatically, at the same point. For these memoryless, “Markovian”<sup>(e)</sup> systems, one thus has

$$\mathcal{J}_a(t, \vec{r}) = \mathcal{J}_a(\{\mathcal{F}_b(t, \vec{r})\}, \{\mathcal{Y}_b(t, \vec{r})\}). \quad (\text{I.28})$$

In the remainder of this section, we shall drop the  $t$  and  $\vec{r}$  dependence of the various fields.

**Remark:** The assumption of instantaneous relationship between cause and effect automatically leaves aside hysteresis phenomena, in which the past history of the system plays an essential role, as for instance in ferromagnets.

Viewing the flux as a function of the affinities, a Taylor expansion gives

$$\mathcal{J}_a = \mathcal{J}_a^{\text{eq.}} + \sum_b' L_{ab} \mathcal{F}_b + \frac{1}{2!} \sum_{b,c}' Q_{abc} \mathcal{F}_b \mathcal{F}_c + \dots, \quad (\text{I.29a})$$

where the *kinetic coefficients*  $L_{ab}$ ,  $L_{abc}$ ,  $\dots$  are functions of the intensive parameters

$$L_{ab} = L_{ab}(\{\mathcal{Y}_d\}), \quad Q_{abc} = Q_{abc}(\{\mathcal{Y}_d\}), \dots \quad (\text{I.29b})$$

The expansion (I.29a) also includes an equilibrium current  $\mathcal{J}_a^{\text{eq.}}$ , which however does not contribute to entropy production, to account for the possible motion of the system with respect to the reference frame in which it is studied. In the presence of such a current, the relation between the entropy production rate and the affinities and fluxes becomes

$$\sigma_S = \sum_a' \mathcal{F}_a (\mathcal{J}_a - \mathcal{J}_a^{\text{eq.}}) \quad (\text{I.30})$$

instead of Eq. (I.25), which was derived in the rest frame of the system.

If the affinities and fluxes are vectors or more generally tensors of order 2 or above, the kinetic coefficients are themselves tensors. For instance, in the case of vectorial transport, the first order coefficients are tensors  $\mathbf{L}_{ab}$  of order 2, with components  $L_{ab}^{ij}$  where  $i, j = 1, 2, 3$ .

When the affinities are small, one may approximate the flux (I.29a) by the constant and first order terms in the expansion only, while neglecting the higher order terms. Such a *linear process* thus obeys the general relationship

$$\mathcal{J}_a = \mathcal{J}_a^{\text{eq.}} + \sum_b' L_{ab} \mathcal{F}_b. \quad (\text{I.31})$$

<sup>(e)</sup>A. A. MARKOV, 1859–1922

**Remarks:**

\* The kinetic coefficients  $L_{ab}$ , as well as the various related transport coefficients ( $\kappa$ ,  $D$ ,  $\sigma_{\text{el}}$ ,  $\epsilon_S$ ,  $\Pi$ ,  $\eta$ ,  $\zeta$ ...) introduced in § I.2.3–I.2.4 below, are conventionally defined for *stationary* flux densities. As we shall see in Chapter ??, these coefficients are in fact the low-frequency, long-wavelength limits of respective response functions relating time- and position-dependent affinities and fluxes.

\* The relations (I.31)—or more generally (I.29a)—between fluxes and affinities are sometimes called *constitutive equations*.

\* Restricting the discussion to that of linear processes, as we shall from now on do, amounts to restricting the class of out-of-equilibrium states under consideration: among the vast number of possible macroscopic states of a system, we actually only consider those that are relatively close to equilibrium, i.e. in which the affinities are “small”. This smallness of the gradients  $\vec{\nabla}\mathcal{Y}_a$  means that the typical associated length scale  $(|\vec{\nabla}\mathcal{Y}_a|/\mathcal{Y}_a)^{-1}$  should be “large” compared to the size of the mesoscopic scale on which the medium can be subdivided into small cells.

In the case of linear processes, the rate of entropy production (I.30) becomes

$$\sigma_S = \sum'_{a,b} L_{ab} \mathcal{F}_a \mathcal{F}_b. \quad (\text{I.32})$$

Since the product  $\mathcal{F}_a \mathcal{F}_b$  is symmetric under the exchange of quantities  $a$  and  $b$ , only the symmetric part  $\frac{1}{2}(L_{ab} + L_{ba})$  contributes to the entropy production (I.32), while the antisymmetric part does not contribute.

The requirement that  $\sigma_S \geq 0$  implies  $L_{aa} \geq 0$  for every  $a$ , as well as  $L_{aa}L_{bb} - \frac{1}{4}(L_{ab} + L_{ba})^2 \geq 0$  for every  $a$  and  $b$ .<sup>(7)</sup>

**Specific case of discrete systems**

In a discrete system, the fluxes are the rates of change of the basic extensive quantities  $\{\mathcal{X}_a(t)\}$ , see Eq. (I.8). By working in the system rest frame, one can ensure the absence of equilibrium fluxes.

Instead of the parameters  $\{\mathcal{X}_a(t)\}$ , let us consider their departures  $\{\Delta\mathcal{X}_a(t)\}$  from their respective equilibrium values,  $\Delta\mathcal{X}_a(t) \equiv \mathcal{X}_a(t) - \mathcal{X}_a^{\text{eq}}$ . Obviously the flux  $\mathcal{J}_a(t)$  is also the rate of change of  $\Delta\mathcal{X}_a(t)$ :

$$\mathcal{J}_a(t) = \frac{d\Delta\mathcal{X}_a(t)}{dt}.$$

The entropy  $S(t)$  is a function of the variables  $\{\mathcal{X}_a(t)\}$ , or equivalently of the  $\{\Delta\mathcal{X}_a(t)\}$ . In turn, each affinity  $\mathcal{F}_b(t)$ , which is a derivative of the entropy, is a function of the  $\{\Delta\mathcal{X}_a(t)\}$ . For small departures from equilibrium, i.e. small values of the  $\{\Delta\mathcal{X}_a(t)\}$ , this dependence can be linearized.<sup>(8)</sup>

$$\mathcal{F}_b = - \sum_c \beta_{bc} \Delta\mathcal{X}_c.$$

Defining then  $\lambda_{ac} \equiv \sum_b L_{ab} \beta_{bc}$ , and using the expressions for the flux  $\mathcal{J}_a$  resp. the affinities  $\mathcal{F}_b$  as given by the previous two equations, the constitutive linear relation (I.31) becomes

$$\frac{d\Delta\mathcal{X}_a(t)}{dt} = - \sum_c \lambda_{ac} \Delta\mathcal{X}_c(t). \quad (\text{I.33})$$

That is, we find coupled first-order differential equations for the departures from equilibrium  $\Delta\mathcal{X}_a(t)$ . These equations should describe the relaxation of each individual  $\Delta\mathcal{X}_a(t)$  to 0 at equilibrium—which amounts to the relaxation of  $\mathcal{X}_a(t)$  to its equilibrium value  $\mathcal{X}_a^{\text{eq}}$ : the eigenvalues of the matrix with coefficients  $\lambda_{ac}$  should thus all be positive.

<sup>(7)</sup>More generally, every minor of the symmetric matrix with elements  $\frac{1}{2}(L_{ab} + L_{ba})$  is non-negative.

<sup>(8)</sup>We denote the coefficients as  $-\beta_{bc}$  to parallel the notation in Landau & Lifshitz [3], §120], who use the opposite sign convention for affinities and fluxes as adopted in these notes, see the remark following Eq. (I.8).

## 1.2.2 Curie principle and Onsager relations

In the relation (I.31) [or more generally Eq. (I.29a)] between flux and affinities, it is assumed that a given flux  $\mathcal{J}_a$  depends not only on the conjugate affinity  $\mathcal{F}_a$ , but also on the other affinities  $\mathcal{F}_b$  with  $b \neq a$ . We now discuss general principles that restrict the possible values of kinetic coefficients  $L_{ab}$  (and more generally  $Q_{abc\dots}$ ), that go beyond the already mentioned positivity of the symmetric matrix with elements  $\frac{1}{2}(L_{ab} + L_{ba})$ .

### 1.2.2a Curie symmetry principle

A first principle is that, going back to Pierre Curie<sup>(f)</sup> (1894), according to which the effects—here, the fluxes—should have the same symmetry elements as their causes—here, the affinities.

**Remark:** Strictly speaking, this principle holds when considering *all* possible effects of a given cause, i.e. when all realizations of some possible spontaneous symmetry breaking—which does not occur here—are taken into account.

Restricting ourselves to locally isotropic continuous media, which are symmetric under arbitrary spatial rotations and under space parity, two consequences of this principle can be listed:

- In the transport of scalar quantities, for which fluxes and affinities are vectors, the tensors  $\mathbf{L}_{ab}$  are actually proportional to the identity, i.e. involve a single number:  $\mathbf{L}_{ab} = L_{ab} \mathbf{1}_3$ , with  $\mathbf{1}_3$  the unit order-two tensor on three-dimensional space; in terms of (Cartesian) components  $L_{ab}^{ij} = L_{ab} \delta^{ij}$ , with  $\delta^{ij}$  the Kronecker symbol.
- Fluxes and affinities whose tensorial orders are of different parities cannot be coupled together. Such a pair, for instance a vector (order 1) and a tensor of order 2, would involve a tensorial kinetic coefficient of odd order, in the example of order 1 or 3, which does not stay invariant under rotations or space parity.

### 1.2.2b Onsager reciprocal relations

Another symmetry principle—which was first found experimentally in various systems and then formalized in 1931 by Lars Onsager [10, 11] within statistical mechanics—regards the cross-coefficients  $L_{ab}$  with  $a \neq b$ .<sup>(9)</sup>

The latter describe “indirect” transport, as e.g. when energy is transported not only because of a temperature gradient [or more accurately, a non-vanishing  $\mathcal{F}_E = \vec{\nabla}(1/T)$ ]—which amounts to transfer through *conduction*—, but also due to a gradient in particle density (within the formalism, a gradient in  $\mathcal{Y}_N = -\mu/T$ ) or in velocity—which is energy transfer due to *convection*.

In the simplest case where both extensive quantities  $X_a$  and  $X_b$  behave similarly under time reversal—as is for instance the case of internal energy  $U$  and any particle number  $N$ , which all remain unchanged when  $t$  is changed to  $-t$  in the equations of motion—then the associated cross-coefficients are equal

$$L_{ab} = L_{ba}. \quad (\text{I.34})$$

Thus when a gradient in  $\mathcal{Y}_b$  causes a change in  $X_a$ , then a gradient in  $\mathcal{Y}_a$  induces a change in  $X_b$  of the same relative size.

These relations were generalized by Casimir<sup>(g)</sup> [13] to relations between the kinetic coefficients for thermodynamic parameters that behave differently under time reversal. Let  $\epsilon_a = \pm 1$  denote the parity (or *signature*) of  $X_a$ , or equivalently the density  $\chi_a$ , under the substitution  $t \rightarrow -t$ . Internal energy  $U$ , particle numbers  $N_k$ , position  $\vec{r}$  have parity  $+1$ , while momentum  $\vec{P}$  or velocity  $\vec{v}$  have

<sup>(9)</sup>A review of (older) experimental results supporting the Onsager reciprocal relations can be found in Ref. [12].

<sup>(f)</sup>P. CURIE, 1859–1906    <sup>(g)</sup>H. CASIMIR, 1909–2000

parity  $-1$ . Under consideration of these signatures, the Onsager–Casimir relations in the absence of external magnetic field and of global rotation read

$$L_{ab} = \epsilon_a \epsilon_b L_{ba}. \quad (\text{I.35})$$

The relations express the symmetry or antisymmetry of the kinetic coefficients.

Taking now into account the possible presence of an external magnetic field  $\vec{\mathcal{B}}$  and/or of a global rotation of the system with angular velocity  $\vec{\Omega}$  — which are both odd under time reversal —, the generalized Onsager–Casimir relations become

$$L_{ab}(\vec{\mathcal{B}}, \vec{\Omega}) = \epsilon_a \epsilon_b L_{ba}(-\vec{\mathcal{B}}, -\vec{\Omega}). \quad (\text{I.36})$$

Note that the latter relations actually relate *different* systems, with opposite values of the parameters  $\vec{\mathcal{B}}, \vec{\Omega}$ .

**Remarks:**

- \* The Onsager(–Casimir) relations are sometimes considered as the “4th law of thermodynamics”, which complements the three classical laws recalled at the end of § I.1.1
- \* The Onsager relations will be derived from general principles in Chapter ??.

### I.2.3 First examples of linear transport phenomena

Following the example set by Onsager in his original articles [10, 11], we now enumerate several empirical linear transport laws formulated in the 19th century and re-express them in terms of relations between fluxes and affinities as formalized in section I.2.1

We shall begin with a few “direct” transport phenomena—for heat, particle number, or electric charges. Next, we turn to a case in which indirect transport plays a role, namely that of thermoelectric effects. These first examples will be studied in the respective rest frames of the systems under study, so that the equilibrium fluxes  $\mathcal{J}_j^{\text{eq}}$  will vanish. Eventually, we describe the various transport phenomena in a simple fluid, which will allow us to derive the classical laws of hydrodynamics.

In most of this section, we shall for the sake of brevity drop the  $(t, \vec{r})$ -dependence of the various physical quantities under consideration.

#### I.2.3a Heat transport

In an insulating solid with a temperature gradient, heat is transported through the vibrations of the underlying crystalline structure—whose quantum mechanical description relies on phonons—rather than through particle transport.

Traditionally, this transport of energy is expressed in the form of *Fourier’s*<sup>(h)</sup> law (1822)

$$\vec{\mathcal{J}}_E = -\kappa \vec{\nabla} T, \quad (\text{I.37a})$$

with  $\kappa$  the *heat conductivity* of the insulator.

Using the general formalism of linear irreversible thermodynamic processes, the relationship between the energy flux density and the conjugate affinity, in the case when there is no gradient of the ratio  $\mu/T$ ,<sup>(10)</sup> reads in the linear regime

$$\vec{\mathcal{J}}_E = \mathbf{L}_{EE} \cdot \vec{\nabla} \left( \frac{1}{T} \right), \quad (\text{I.37b})$$

with  $\mathbf{L}_{EE}$  a tensor of order 2 of (first-order) kinetic coefficients. If the insulating medium under

<sup>(10)</sup> Phonons are massless and carry no conserved quantum number, so that their chemical potential vanishes everywhere.

<sup>(h)</sup> J. FOURIER, 1768–1830

consideration is isotropic.<sup>(11)</sup> this tensor is for symmetry reasons proportional to the identity

$$\mathbf{L}_{EE} = L_{EE} \mathbf{1}_3.$$

The comparison between Eqs. (I.37a) and (I.37b) then gives the identification

$$\kappa = \frac{1}{T^2} L_{EE}. \quad (\text{I.37c})$$

Since  $L_{EE} \geq 0$  to ensure the positivity of the entropy production rate,  $\kappa$  is also non-negative. The flux (I.37a) thus transports energy from the regions of higher temperatures to the colder ones.

Combining Fourier's law (I.37a) with the continuity equation (I.18a) applied to the energy density  $e$  yields

$$\frac{\partial e}{\partial t} = -\vec{\nabla} \cdot \vec{J}_E = \vec{\nabla} \cdot (\kappa \vec{\nabla} T)$$

Assuming that the heat conductivity is uniform in the medium under study,  $\kappa$  can be factorized out of the divergence, so that the right-hand side becomes  $\kappa \Delta T$ , with  $\Delta$  the Laplacian. According to a well known thermodynamic relation, at fixed volume the change in the internal energy equals the product of the change in temperature with the heat capacity at constant volume  $c_V$ , which results in  $de = c_V dT$ . If the heat capacity is independent of temperature, one readily obtains the evolution equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{c_V} \Delta T. \quad (\text{I.38})$$

This is the generic form of a diffusion equation [see Eq. (I.40) below], with diffusion coefficient  $\kappa/c_V$ .

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<sup>(11)</sup>... which is strictly speaking never the case at the microscopic level in a crystal, since the lattice structure is incompatible with local invariance under the whole set of three-dimensional rotations. Nevertheless, for lattices with a cubic elementary mesh, isotropy holds, yet at the mesoscopic level.