Non-equilibrium Thermodynamics

S. R. de Groot   P. Mazur*

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INTRODUCTION

1.1 HISTORICAL BACKGROUND OF NON-EQUILIBRIUM THERMODYNAMICS

Thermodynamic considerations were first applied to the treatment of irreversible processes by W. Thomson[1] in 1854. He analysed the various thermo-electric phenomena and established the famous two relations which bear his name. The first of these relations follows from conservation of energy. The second relation, which relates the thermoelectric potential of a thermocouple to its Peltier heat, was obtained from the two laws of thermodynamics, and an additional assumption about the so-called "reversible" contributions to the process. Later Boltzmann[2] attempted without success to justify the Thomson hypothesis. We now know that no basis exists for this hypothesis. Thomson's second relation was finally derived correctly by Onsager who showed that this relation was a consequence of the invariance of the microscopic equations of motion under time reversal. Thomson's method was applied with varying success to a number of other irreversible phenomena, but a coherent scheme for the macroscopic description of irreversible processes could not be developed in this way.

Independently of the theoretical development described above, a number of physicists undertook, at the turn of the century, to give more refined formulations of the second law of thermodynamics for non-equilibrium situations. As early as 1850, Clausius introduced the concept of "non-compensated heat" as a measure of irreversibility (in systems which need not be thermally insulated from their surroundings). Duhem, Natanson, Jaumann and Lohr and later Eckartt[3] attempted to obtain expressions for the rate of change of the local entropy in nonuniform systems by combining the second law of thermodynamics with the macroscopic laws of conservation of mass, momentum and energy. In this way they derived formulae which related irreversibility to the non-uniformity of the system. Similarly De Donder[4] was able to relate the "non-compensated heat" in a chemical reaction to the affinity, a thermodynamic variable characterizing the state of the system. The systematic discussion of irreversible processes along these lines however was not completed until much later.

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1 W. Thomson (Lord Kelvin) Proc. roy. Soc. Edinburgh 3 (1854) 225; Ibid. Trans. 21 I (1857) 123; Math. phys. Papers 1 (1882) 232.

2 L. Boltzmann, Sitz. her. Akad. Wiss. Wien, Math.-Naturw. Kl. Abt. II 96 (1887) 1258; Wiss. Abh. 3 (1909) 321.

3 P. Duhem, Energetique (2 vol.) (Gauthier-Villars, Paris, 1911).; L. Natanson, Z. phys. Chem. 21 (1896) 193.; G. Jaumann, Sitz. her. Akad. Wiss. Wien, Math.-Naturw. Kl. Abt. II A 120 (1911) 385; Denkschr. Akad. Wiss. Wien, Math.-Naturw. Kl. 95 (1918) 461.; E. Lohr, Denkschr. Akad. Wiss. Wien, Math.-Naturw. Kl. 93 (1916) 339; 99 (1924) 11, 59; Festschr. Techn. Hochsch. Brunn (1924) 176.; C. Eckart, Phys. Rev. 58 (1940) 267, 269, 919, 924.

4 Th. De'Donder, L'affinite (Gauthier-Villars, Paris, 1927).

In the meantime, in 1931, Onsager[5] established his celebrated "reciprocal relations" connecting the coefficients, which occur in the linear phenomenological laws that describe the irreversible processes. These reciprocal relations, of which Thomson's second relation is an example, reflect on the macroscopic level the time reversal invariance of the microscopic equations of motion. In 1945 Casimir[6] reformulated the reciprocal relations, so that they would be valid for a larger class of irreversible phenomena than had been previously considered by Onsager.

Finally Meixner[7] in 1941 and the following years, and somewhat later Prigogine[8], set up a consistent phenomenological theory of irreversible processes, incorporating both Onsager's reciprocity theorem and the explicit calculation for a certain number of physical situations of the so-called entropy source strength (which is in fact the noncompensated heat of Clausius). In this way a new field of "thermodynamics of irreversible processes" was born. It developed rapidly in various directions.

Coupled with the recent growing interest in the statistical mechanical theory of irreversible processes are some significant studies on the statistical basis of the thermodynamics of irreversible processes. Thus special attention is paid to the validity on one hand of thermodynamic relations outside equilibrium and, on the other hand, to the Onsager reciprocal relations. Many of these studies have employed methods and concepts borrowed from the theory of stochastic processes.

1.2   SYSTEMATIC DEVELOPMENT OF THE THEORY

The field of non-equilibrium thermodynamics provides us with a general framework for the macroscopic description of irreversible processes. As such it is a branch of macroscopic physics, which has connections with other macroscopic disciplines such as fluid dynamics and electromagnetic theory, insofar as the latter fields are also concerned with non-equilibrium situations. Thus the thermodynamics of irreversible processes should be set up from the start as a continuum theory, treating the state parameters of the theory as field variables, i.e., as continuous functions of space coordinates and time. Moreover one would like to formulate the basic equations of the theory in such a way that they only contain quantities referring to a single point in space at one time, i.e. in the form of local equations. This is also the way in which fluid dynamics and the Maxwell theory are formulated. In equilibrium thermodynamics such a local formulation is generally not needed, since the state variables are usually independent of the space coordinates.

In non-equilibrium thermodynamics the so-called balance equation for the entropy plays a central role. This equation expresses the fact that the entropy of a volume element changes with time for two reasons. First it changes because entropy flows into the volume element, second because there is an entropy source due to irreversible phenomena inside the volume element. The entropy source is always a non-negative quantity, since entropy can only be created, never destroyed. For reversible transformations the entropy source vanishes. This is the local formulation of the second law of thermodynamics. The

5 L. Onsager, Phys. Rev. 37 (1931) 405; 38 (1931) 2265.
6 H. B. G. Casimir, Rev. mod. Phys. 17 (1945) 343; or Philips Res. Rep. 1 (1945) 185.
7 J. Meixneir, Ann. Physik [5] 39 (1941) 333; 41 (1942) 409; 43 (1943) 244; Z. phys. Chem. B S3 (1943) 235.
8 I. Prigogine, Etude thennodynamique des phenomenes irreversibles (Dunod, Paris and Desoer, Liege, 1947).

main aim is to relate the entropy source explicitly to the various irreversible processes that occur in a system. To this end one needs the macroscopic conservation laws of mass, momentum and energy, in local, i.e. differential form. These conservation laws contain a number of quantities such as the diffusion flows, the heat flow and the pressure tensor, which are related to the transport of mass, energy and momentum. The entropy source may then be calculated if one makes use of the thermodynamic Gibbs relation which connects. in an isotropic multi-component fluid for instance, the rate of change of entropy in each mass element, to the rate of change of energy and the rates of change in composition. It turns out that the entropy source has a very simple appearance: it is a sum of terms each being a product of a flux characterizing an irreversible process, and a quantity, called thermodynamic force, which is related to the non-uniformity of the system (the gradient of the temperature for instance) or to the deviations of some internal state variables from their equilibrium values (the chemical affinity for instance). The entropy source strength can thus serve as a basis for the systematic description of the irreversible processes occurring in a system.

As yet the set of conservation together with the entropy balance equation and the equations of state is to a certain extent empty, since this set of equations contains the irreversible fluxes as unknown parameters and can therefore not be solved with given initial and boundary conditions for the state of the system. At this point we must therefore supplement our equations by an additional set of phenomenological equations which relate the irreversible fluxes and the thermodynamic forces appearing in the entropy source strength. In first approximation the fluxes are linear functions of the thermodynamic forces. Fick's law of diffusion, Fourier's law of heat conduction, and Ohm's law of electric conduction, for instance, belong to this class of linear phenomenological laws. It also contains in addition possible cross-effects between various phenomena, since each flux may in principle be a linear function of all the thermodynamic forces which are needed to characterize the entropy source strength. The Soret effect, which results from diffusion in a temperature gradient is an example ,of such a cross-effect. Many others exist such as the thermoelectric effects, the group of thermomagnetic and galvanomagnetic effects, and also the electrokinetic effects. Non-equilibrium thermodynamics, in its present form, is mainly restricted to the study of such linear phenomena. Very little of a sufficiently general nature is known outside this linear domain. This is not a very serious restriction however, since even in rather extreme physical situations, transport processes, for example, are still described by linear laws. Together with the phenomenological equations the original set of conservation laws may be said to be complete in the sense that one now has at one's disposal a consistent set of partial differential equations for the state parameters of a material system, which may be solved with the proper initial and boundary conditions.

Some rather important statements of a macroscopic nature may be made concerning the matrix of phenomenological coefficients which relate the fluxes and the thermodynamic forces, appearing in the entropy source strength. In the first place the Onsager-Casimir reciprocity theorem gives rise to a number of relations amongst these coefficients, thus reducing the number of independent quantities and relating distinct physical effects to each other. It is one of the aims of nonequilibrium thermodynamics to study the physical consequences of the reciprocal relations in applications of the theory to various physical situations. Apart from the reciprocity theorem, which is based on the time

reversal invariance of the microscopic equations of motion, possible spatial symmetries of a material system may further simplify the scheme of phenomenological coefficients. Thus in an isotropic fluid a scalar phenomenon like a chemical reaction cannot be coupled to a vectorial phenomenon like heat conduction. This reduction of the scheme of phenomenological coefficients, which results from invariance of the phenomenological equations under special orthogonal transformations, goes under the name of the Curie principle, but should more appropriately be called Curie's theorem.

The reciprocal relations have transformation properties which have been studied extensively. Thus Meixner showed that the Onsager relations are invariant under certain transformations of the fluxes and the thermodynamic forces. There exist a number of other general theorems, which are of use in non-equilibrium thermodynamics: one can show that at mechanical equilibrium the entropy production has some additional invariance properties. It can also be shown that stationary non-equilibrium states are characterized by a minimum property: under certain restrictive conditions the entropy production has, in the stationary state, a minimum value compatible with given boundary conditions. Both of these theorems have first been obtained by Prigogine.

Just as the principles of equilibrium thermodynamics must be justified by means of statistical mechanical methods, so the principles of thermodynamics of irreversible processes require a discussion of their microscopic basis. In the present state of theoretical development a microscopic discussion of irreversibility itself from first principles would lie outside the scope of this treatise. However, even if the irreversible behaviour of macroscopic systems is taken for granted, one still has the problem of discussing the remaining foundations of the theory. On these premises Onsager's reciprocity theorem can indeed be derived from microscopic properties of a mechanical many-particle system. Concepts of fluctuation theory and the theory of stochastic processes play an essential role in such a discussion of the foundations, to which Onsager and Machlup have contributed by using a Brownian motion type model for the regression of fluctuations. Such a model can also serve for a justification of the use of thermodynamic relations outside equilibrium. Furthermore the methods of the theory of stochastic processes are used in relating the spontaneous fluctuations in equilibrium to the macroscopic response of a system under external driving forces. The relation thus obtained is known as the fluctuation-dissipation theorem and is due to Callen, Greene and Welton. It represents in fact a generalization of the famous Nyquist formula in the theory of electric noise.

The problem of justifying the principles of non-equilibrium thermodynamics can alternatively be approached from the viewpoint of the kinetic theory of gases. Such a method is more limited since it only applies to gaseous systems at low density, however it permits one to express those macroscopic quantities which pertain to irreversible processes in terms of molecular parameters. The irreversibility itself is already contained in the fundamental equation of the kinetic theory of gases, the Boltzmann integro-differential equation. One may then justify the use of thermodynamic relations for gases outside equilibrium (as was first done by Prigogine), and derive the Onsager reciprocal relations.

The theory of non-equilibrium thermodynamics has found a great variety of applications in physics and chemistry. For a systematic classification of these applications one may group the various irreversible phenomena according to their "tensorial character". First one has "scalar phenomena". These include chemical reactions and structural

relaxation phenomena. Onsager relations are of help in this case in solving the set of ordinary differential equations which describe the simultaneous relaxation of a great number of internal variables.

A second group of phenomena is formed by "vectorial processes" such as diffusion, heat conduction, and their cross-effects. Viscous phenomena can be considered as a third group to which methods of non-equilibrium thermodynamics have been applied. In particular the theory of acoustical relaxation has been consistently developed within this framework by Meixner.

Altogether new aspects arise when an electromagnetic field acts on a material system. Then the continuity laws for electromagnetic energy and momentum which follow from the Maxwell equations must also be taken into account. One must therefore reformulate the theory to suit the need of this case with its numerous applications to both polarized and unpolarized media.

Part I

GENERAL THEORY

2

CONSERVATION LAWS

2.1 INTRODUCTION

Thermodynamics is based on two fundamental laws: the first law of thermodynamics or law of conservation of energy, and the second law of thermodynamics or entropy law. A systematic macroscopic scheme for the description of non-equilibrium processes (i.e. the scheme of thermodynamics of irreversible processes) must also be built upon these two laws. However, it is necessary to formulate these laws in a way suitable for the purpose at hand. In this chapter we shall be concerned with the first law of thermodynamics. Since we wish to develop a theory applicable to systems of which the properties are continuous functions of space coordinates and time, we shall give a local formulation of the law of conservation of energy. As the local momentum and mass densities may change in time, we shall also need local formulations of the laws of conservation of momentum and mass. In the following sections these conservation laws will be written down for a multi-component system in which chemical reactions may occur and on which conservative external forces are exerted. It may be remarked that the macroscopic conservation laws of matter, momentum and energy are, from a microscopic point of view, consequences of the mechanical laws governing the motions of the constituent particles of the system.

2.2 CONSERVATION OF MASS

Let us consider a system consisting of n components amongst which r chemical reactions are possible. The rate of change of the mass of component k within a given volume V is

$$\frac{d}{dt} \int^V \rho_k dV = \int^V \frac{\partial \rho_k}{\partial t} dV \tag{1}$$

where ρ_k is the density (mass per unit volume) of k. This quantity is equal to the sum of the material flow of component k into the volume V through its surface Ω and the total production of k in chemical reactions which occur inside V

$$\int^V \frac{\partial \rho_k}{\partial t} dV = - \int^\Omega \rho_k v_k \cdot d\Omega + \sum_{j=1}^r \int^V \nu_{kj} J_j dV \tag{2}$$

where $d\Omega$ is a vector with magnitude $d\Omega$ normal to the surface and counted positive from the inside to the outside. Furthermore v_k is the velocity of k, and $\nu_{kj} J_j$ the production of k per unit volume in the jth chemical reaction. The quantity ν_{kj} divided by the molecular mass M_k of component k is proportional to the stoichiometric coefficient with which

k appears in the chemical reaction j. The coefficients v_{kj} are counted positive when components k appear in the second, negative when they appear in the first member of the reaction equation. The quantity J_j is called the chemical reaction rate of reaction j. It represents a mass per unit volume and unit time. The quantities ρ_k, v_k and J_j occurring in (2) are all functions of time and of space coordinates. Applying Gauss' theorem to the surface integral occurring in (2), we obtain

$$\frac{\partial \rho_k}{\partial t} = -\text{div } \rho_k v_k + \sum_{j=1}^{r} v_{kj} J_j \tag{3}$$

since (2) is valid for an arbitrary volume V. This equation has the form of a so-called balance equation: the local change of the left-hand side is equal to the negative divergence of the flow of k and a source term giving the production (or destruction) of substance k. Since mass is conserved in each separate chemical reaction we have

$$\sum_{k=1}^{n} v_{kj} = 0 \tag{4}$$

Summing equation (3) over all substances k one obtains then the law of conservation of mass:

$$\frac{\partial \rho}{\partial t} = -\text{div } \rho v \tag{5}$$

where ρ the total density

$$\rho = \sum_{k=1}^{n} \rho_k \tag{6}$$

and v the centre of mass ("barycentric") velocity

$$v = \sum_{k=1}^{n} = \rho_k v_k / \rho \tag{7}$$

Equation (5) expresses the fact that the total mass is conserved, i.e. that the total mass in any volume element of the system can only change if matter flows into (or out of) the volume element. The mass equations can be written in an alternative form by introducing the (barycentric) substantial time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v \cdot \text{grad} \tag{8}$$

and the "diffusion flow" of substance k defined with respect to the barycentric motion

$$J_k = \rho_k \left(v_k - v \right) \tag{9}$$

With the help of (8) and (9), equations (3) become

$$\frac{d\rho_k}{dt} = -\rho_k \text{div } v - \text{div } J_k + \sum_{j=1}^{r} v_{kj} J_j \tag{10}$$

and equation (5)

$$\frac{d\rho}{dt} = -\rho \text{div } v \tag{11}$$

If mass fractions c_k:

$$c_k = \rho_k / \rho \tag{12}$$

are employed, equations (10) take the simple form

$$\rho \frac{dc_k}{dt} = -\text{div } J_k + \sum_{j=1}^{r} v_{kj} J_j \tag{13}$$

where (11) has been used also.

With the specific volume $v = p^{-1}$ formula (11) may also be written as

$$\rho \frac{dv}{dt} = \text{div } v \tag{14}$$

We note that it follows from (7) and (9) that

$$\sum_{k=1}^{n} J_k = 0 \tag{15}$$

which means that only $n-1$ of the n diffusion flows are independent. Similarly only $n-1$ of the n equations (13) are independent. In fact by summing (13) over all k, both members vanish identically as a result of (4), (12) and (15). The nth independent equation describing the change of mass density within the system is now equation (14). We note finally that the following relation, valid for an arbitrary local property a, (which may be a scalar or a component of a vector or tensor, etc.):

$$\rho \frac{da}{dt} = \frac{\partial a\rho}{\partial t} + \text{div } a\rho v \tag{16}$$

is a consequence of the mass equation (5) and of (8).

2.3 THE EQUATION OF MOTION

The equation of motion of the system is

$$\rho \frac{dv_\alpha}{dt} = -\sum_{\beta=1}^{3} \frac{\partial}{\partial x_\beta} P_{\beta\alpha} + \sum_{k=1}^{n} \rho_k F_{k\alpha} \tag{17}$$

where v_α ($\alpha = 1,2,3$) is a Cartesian component of v, and where x_α ($\alpha = 1,2,3$) are the Cartesian coordinates. The derivative dv_α / dt is a component of the acceleration of the centre of gravity motion.

The quantities $P_{\alpha\beta}$ ($\alpha, \beta = 1,2,3$) and $F_{k\alpha}$ ($\alpha = 1,2,3$) are the Cartesian components of the pressure (or stress) tensor P of the medium and of the force per unit mass F_k exerted on the chemical component k respectively. We shall assume here[1] that the pressure tensor P is symmetric,

$$P_{\alpha\beta} = P_{\beta\alpha} \tag{18}$$

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[1] This assumption is usually made in hydrodynamics, but is rigorously only justified for systems consisting of spherical molecules or at very low densities. For other systems however the pressure tensor may contain an antisymmetric part.

In tensor notation equations ([17]) are written as

$$\rho \frac{dv_\alpha}{dt} = \text{Div } \boldsymbol{P} + \sum_k \rho_k \boldsymbol{F}_k \tag{19}$$

From a microscopic point of view one can say that the pressure tensor $\boldsymbol{P}$ results from the short-range interactions between the particles of the system, whereas $\boldsymbol{F}_k$ contains the external forces as well as a possible contribution from long-range interactions in the system.

For the moment we shall restrict the discussion to the consideration of conservative forces which can be derived from a potential ψ_k independent of time

$$\boldsymbol{F}_k = -\text{grad } \psi_k \,, \quad \frac{\partial \psi_k}{\partial t} = 0 \tag{20}$$

Using relation ([16]), the equation of motion ([19]) can also be written as

$$\frac{\partial \rho \boldsymbol{v}}{dt} = -\text{Div } (\rho \boldsymbol{vv} + \boldsymbol{P}) + \sum_k \rho_k \boldsymbol{F}_k \tag{21}$$

where $\boldsymbol{vv}$ is an ordered (dyadic) product, (cf. Appendix I on matrix and tensor notation). This equation has the form of a balance equation for the momentum density $\rho \boldsymbol{v}$. In fact it is seen that one can interpret the quantity $\rho \boldsymbol{vv} + \boldsymbol{P}$ as a momentum flow, with a convective part $\rho \boldsymbol{vv}$, and the quantity $\sum_k \rho_k \boldsymbol{F}_k$ as a source of momentum.

It is possible to derive from ([17]) a balance equation for the kinetic energy of the centre of gravity motion by multiplying both members with the component v_α of the barycentric velocity and summing over α

$$\rho \frac{d \frac{1}{2} v^2}{dt} = -\sum_{\alpha\beta} \frac{\partial}{\partial x_\beta} P_{\beta\alpha} v_\alpha + \sum_{\alpha\beta} P_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_\alpha + \sum_{k=1}^n \rho_k F_{k\alpha} v_\alpha \tag{22}$$

or, in tensor notation,

$$\rho \frac{d \frac{1}{2} v^2}{dt} = -\text{div } (\boldsymbol{P} \cdot \boldsymbol{v}) + \boldsymbol{P} : \text{Grad } \boldsymbol{v} + \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v} \tag{23}$$

where

$$\boldsymbol{P} : \text{Grad } \boldsymbol{v} = \sum_{\alpha\beta} P_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_\alpha \tag{24}$$

With the help of ([16]), equation ([23]) becomes

$$\frac{\partial \frac{1}{2} \rho v^2}{\partial t} = -\text{div } \left(\frac{1}{2} \rho v^2 \boldsymbol{v} + \boldsymbol{P} \cdot \boldsymbol{v} \right) + \boldsymbol{P} : \text{Grad } \boldsymbol{v} + \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v} \tag{25}$$

We wish to establish now an equation for the rate of change of the potential energy density $\rho \psi = \sum_k \rho_k \psi_k$. In fact it follows from ([3]), ([9]) and ([20]) that

$$\frac{\partial \rho \psi}{\partial t} = -\text{div } \left(\rho \psi \boldsymbol{v} + \sum_{k=1}^n \psi_k \boldsymbol{J}_k \right) - \sum_{k=1}^n \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v} - \sum_{k=1}^n \boldsymbol{J}_k \cdot \boldsymbol{F}_k + \sum_{k=1}^n \sum_{j=1}^r \psi_k \nu_{kj} J_j \tag{26}$$

The last term vanishes if the potential energy is conserved in a chemical reaction

$$\sum_k \rho_k \nu_{kj} = 0 \tag{27}$$

This is the case if the property of the particles, which is responsible for the interaction with a field of force, is itself conserved. Examples for this case are the mass in a gravitational field and the charge in an electric field. Equation (26) then reduces to

$$\frac{\partial \rho \psi}{\partial t} = -\mathrm{div}\ \left(\rho \psi v + \sum_k \psi_k J_k \right) - \sum_k \rho_k F_k \cdot v - \sum_k J_k \cdot F_k \tag{28}$$

Let us now add the two equations (25) and (28) for the rate of change of the kinetic energy $\frac{1}{2}\rho v^2$ and the potential energy $\rho \psi$:

$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \psi \right)}{\partial t} = -\mathrm{div}\ \left(\rho \left(\frac{1}{2} v^2 + \psi \right) v + P \cdot v + \sum_k \psi_k J_k \right) + P : \mathrm{Grad}\ v - \sum_k J_k \cdot F_k \tag{29}$$

This equation shows that the sum of kinetic and potential energy is not conserved, since a source term appears at the right-hand side.

2.4 CONSERVATION OF ENERGY

According to the principle of conservation of energy the total energy content within an arbitrary volume V in the system can only change if energy flows into (or out of) the volume considered through its boundary Ω

$$\frac{d}{dt} \int^V \rho e\, dV = \int^V \frac{\partial \rho e}{\partial t} dV = -\int^{\Omega} J_e \cdot d\Omega \tag{30}$$

Here e is the energy per unit mass, and J_e the energy flux per unit surface and unit time. We shall refer to e as the total specific energy, because it includes all forms of energy in the system. Similarly we shall call J_e the total energy flux. With the help of Gauss' theorem we obtain the differential or local form of the law of conservation of energy

$$\frac{\partial \rho e}{\partial t} = -\mathrm{div}\ J_e \tag{31}$$

In order to relate this equation to the previously obtained result (29) for the kinetic and potential energy, we must specify which are the various contributions to the energy e and the flux J_e.

The total specific energy e includes the specific kinetic energy $\frac{1}{2}v^2$, the specific potential energy ψ, and the specific internal energy u:

$$e = \frac{1}{2}v^2 + \psi + u \tag{32}$$

From a macroscopic point of view this relation can be considered as the definition of internal energy u. From a microscopic point of view u represents the energy of thermal agitation as well as the energy due to the short-range molecular interactions. Similarly the total energy flux includes a convective term $\rho e v$, an energy flux $P \cdot v$ due to the

mechanical work performed on the system, a potential energy flux $\sum_k \psi_k J_k$ due to the diffusion of the various components in the field of force, and finally a "heat flow" J_q:

$$J_e = \rho e v + P \cdot v + \sum_k \psi_k J_k + J_q \tag{33}$$

This relation may be considered as defining the heat flow J_q. If we subtract equation (29) from equation (31), we obtain, using also (32) and (33), the balance equation for the internal energy u:

$$\frac{\partial \rho u}{\partial t} = -\text{div} \ (\rho u v + J_q) - P : \text{grad } v + \sum_k J_k \cdot F_k \tag{34}$$

It is apparent from this equation that the internal energy u is not conserved. In fact a source terms appears, which is equal but of opposite sign to the source term of the balance equation (29) for kinetic and potential energy.

The equation (34) may be written in an alternative form. We can split the total pressure tensor into a scalar[2] hydrostatic part p and a tensor Π:

$$P = pU + \Pi \tag{35}$$

where U is the unit matrix with elements $\delta_{\alpha\beta}$ ($\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$). With this relation and (16), equation (34) becomes

$$\rho \frac{du}{dt} = \rho \frac{dq}{dt} - p\text{div } v - \Pi : \text{Grad } v + \sum_k J_k \cdot F_k \tag{36}$$

where use has been made of the equality

$$U : \text{Grad } v = \text{div } v \tag{37}$$

and where

$$\rho \frac{dq}{dt} = -\text{div } J_q \tag{38}$$

defines dq, the "heat" added per unit of mass.

With (14) equation (36), the "first law of thermodynamics", can finally be written in the form

$$\frac{du}{dt} = \frac{dq}{dt} - p\frac{dv}{dt} - v\Pi : \text{Grad } v + v \sum_k J_k \cdot F_k \tag{39}$$

where $v = \rho^{-1}$ is the specific volume.

As stated in the preceding section we have restricted ourselves in this chapter to the consideration of conservative forces F_k of the type (20). The more general case, which arises for instance when electromagnetic forces are considered, will be treated in Chapter XIII.

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2 In assuming that the equilibrium part of the total tensor is a scalar we restrict the discussion to non-elastic :fluids. For an elastic medium the equilibrium "pressure" tensor is the elastic stress tensor.

3

ENTROPY LAW AND ENTROPY BALANCE

3.1 THE SECOND LAW OF THERMODYNAMICS

According to the principles of thermodynamics one can introduce for any macroscopic system a state function S, the entropy of the system, which has the following properties.

The variation of the entropy dS may be written as the sum of two terms

$$dS = d_e S + d_i S \qquad (40)$$

where $d_e S$ is the entropy supplied to the system by its surroundings, and $d_i S$ the entropy produced inside the system. The second law of thermodynamics states that $d_i S$ must be zero for reversible (or equilibrium) transformations and positive for irreversible transformations of the system:

$$d_i S \geq 0 \qquad (41)$$

The entropy supplied, $d_e S$, on the other hand may be positive, zero or negative, depending on the interaction of the system with its surroundings. Thus for an adiabatically insulated system (i.e. a system which can exchange neither heat nor matter with its surroundings) $d_e S$ is equal to zero, and it follows from (40) and (41) that

$$dS \geq 0 \text{ for an adiabatically insulated system} \qquad (42)$$

This is a well-known form of the second law of thermodynamics.

For a so-called closed system, which may only exchange heat with its surroundings, we have according to the theorem of Carnot-Clausius:

$$d_e S = \frac{\delta Q}{T} \qquad (43)$$

where δQ is the heat supplied to the system by its surroundings and T the absolute temperature at which heat is received by the system.

From (1) and (2) it follows for this case that

$$dS \geq \frac{dQ}{T} \text{ for a closed system} \qquad (44)$$

which is also a well-known form of the second law of thermodynamics. For open systems, i.e. systems which may exchange heat as well as matter with their surroundings $d_e S$ contains also a term connected with the transfer of matter (cf. also section 2 of this chapter). The theorem of Carnot-Clausius, which is contained in formulae (40), (41) and (43), does not apply to such systems. However the very general statements contained in (40) and (41) alone remain valid.

We may remark at this point that thermodynamics in the customary sense is concerned with the study of the reversible transformations for which the equality in (41) holds. In thermodynamics of irreversible processes, however, one of the important objectives is to relate the quantity d_iS, the entropy production, to the various irreversible phenomena which may occur inside the system. Before calculating the entropy production in terms of the quantities which characterize the irreversible phenomena, we shall rewrite (40) and (41) in a form which is more suitable for the description of systems in which the densities of the extensive properties (such as mass and energy, considered in the previous chapter) are continuous functions of space coordinates. Let us write

$$S = \int^V \rho s dV \tag{45}$$

$$\frac{d_eS}{dt} = -\int^\Omega \boldsymbol{J}_{s,tot} \cdot d\boldsymbol{\Omega} \tag{46}$$

$$\frac{d_iS}{dt} = \int^V \sigma dV \tag{47}$$

where s is the entropy per unit mass, $\boldsymbol{J}_{s,tot}$ the total entropy flow per unit area and unit time, and σ the entropy source strength or entropy production per unit volume and unit time. With (45), (46) and (47), formula (40) may be rewritten, using also Gauss' theorem, in the form

$$\int^V \left(\frac{\partial \rho s}{\partial t} + \text{div } \boldsymbol{J}_{s,tot} - \sigma \right) dV = 0 \tag{48}$$

From this relation it follows, since (40) and (41) must hold for an arbitrary volume V, that

$$\frac{\partial \rho s}{\partial t} = -\text{div } \boldsymbol{J}_{s,tot} + \sigma \tag{49}$$

$$\sigma \geq 0 \tag{50}$$

These two formulae are the local forms of (40) and (41), i.e. the local mathematical expression for the second law of thermodynamics. Equation (49) is formally a balance equation for the entropy density ρs, with a source term σ which satisfies the important inequality (50). With the help of relation (16), equation (49) can be rewritten in a slightly different form,

$$\rho \frac{ds}{dt} = -\text{div } \boldsymbol{J}_s + \sigma \tag{51}$$

where the entropy flux $\boldsymbol{J}_s$ is the difference between the total entropy flux $\boldsymbol{J}_{s,tot}$ and a convective term $\rho s \boldsymbol{v}$

$$\boldsymbol{J}_s = \boldsymbol{J}_{s,tot} - \rho s \boldsymbol{v} \tag{52}$$

In obtaining (49) and (50) we have assumed that the statements (40) and (41) also hold for infinitesimally small parts of the system, or in other words, that the laws which are valid for macroscopic systems remain valid for infinitesimally small parts of it. This is in agreement with the point of view currently adopted in a macroscopic description of a continuous system. It implies, on a microscopic model, that the local macroscopic measurements performed on the system, are really measurements of the properties of small parts of the system, which still contain a large number of the constituting particles. Such small parts of the system one might call physically infinitesimal. With this in mind it still makes sense to speak about the local values of such fundamentally macroscopic concepts as entropy and entropy production.

3.2   THE ENTROPY BALANCE EQUATION

We must now relate the variations in the properties of systems studied in Chapter II to the rate of change of the entropy. This will enable us to obtain more explicit expressions for the entropy flux ls and the entropy source strength σ which appear in (51). From thermodynamics we know that the entropy per unit mass s is, for a system in equilibrium, a well-defined function of the various parameters which are necessary to define the macroscopic state of the system completely. For the systems considered in Chapter II these are the internal energy u, the specific volume v, and the mass fractions c_k:

$$s = s(u, v, c_k) \tag{53}$$

This is also expressed by the fact that, in equilibrium, the total differential of s is given by the Gibbs relation (cf. Appendix II):

$$T ds = du + p dv - \sum_{k=1}^{n} \mu_k dc_k \tag{54}$$

where p is the equilibrium pressure, and μ_k the thermodynamic or chemical potential of component k (partial specific Gibbs function). It will now be assumed that, although the total system is not in equilibrium, there exists within small mass elements a state of "local" equilibrium, for which the local entropy s is the same function (53) of u, v and c_k as in real equilibrium. In particular we assume that formula (54) remains valid for a mass element followed along its centre of gravity motion:

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_{k=1}^{n} \mu_k \frac{dc_k}{dt} \tag{55}$$

where the time derivatives are given by (8). This hypothesis of "local" equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it. For special microscopic models it can indeed be shown that the relation (55) is valid for deviations from equilibrium which are not "too large". Criteria specifying how far from equilibrium (55) can be used may also be derived from these microscopic considerations. We shall come back to this point in Chapters VII and IX. It may already be stated here that for most familiar transport phenomena the use of (55) is justified.

In order to find the explicit form of the entropy balance equation (51) we have to insert the expressions (39), with (38), for du/dt and (13) for dc_k/dt into formula (55). This gives

$$\rho \frac{ds}{dt} = -\frac{\operatorname{div} \boldsymbol{J}_q}{T} - \frac{1}{T} \boldsymbol{\Pi} : \operatorname{Grad} \boldsymbol{v} + \frac{1}{T} \sum_{k=1}^{n} \boldsymbol{J}_k \cdot \boldsymbol{F}_k + \frac{1}{T} \sum_{k=1}^{n} \mu_k \operatorname{div} \boldsymbol{J}_k - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \tag{56}$$

where we have introduced the so-called chemical affinities of the reactions $j\,(=1, 2, \ldots, r)$ defined by

$$A_j = \sum_{k=1}^{n} \nu_{kj} \mu_k \tag{57}$$

It is easy to cast equation (56) into the form (51) of a balance equation:

$$\rho \frac{ds}{dt} = - \operatorname{div} \left(\frac{\boldsymbol{J}_q - \sum_k \mu_k \boldsymbol{J}_k}{T} \right) - \frac{1}{T^2} \boldsymbol{J}_q \cdot \operatorname{grad} T$$
$$- \frac{1}{T} \sum_{k=1}^{n} \boldsymbol{J}_k \cdot \left(T \operatorname{grad} \frac{\mu_k}{T} - \boldsymbol{F}_k \right) - \frac{1}{T} \boldsymbol{\Pi} : \operatorname{Grad} \boldsymbol{v} - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \tag{58}$$

From comparison with (51) it follows that the expressions for the entropy flux and the entropy production are given by

$$\boldsymbol{J}_s = \frac{1}{T} \left(\boldsymbol{J}_q - \sum_k \mu_k \boldsymbol{J}_k \right) \tag{59}$$

$$\sigma = - \frac{1}{T^2} \boldsymbol{J}_q \cdot \operatorname{grad} T - \frac{1}{T} \sum_{k=1}^{n} \boldsymbol{J}_k \cdot \left(T \operatorname{grad} \frac{\mu_k}{T} - \boldsymbol{F}_k \right) - \frac{1}{T} \boldsymbol{\Pi} : \operatorname{Grad} \boldsymbol{v} - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \tag{60}$$

The way in which the separation of the right-hand side of (56) into the divergence of a flux and a source tern1 has been achieved may at first sight seem to be to some extent arbitrary. The two parts of (58) must, however, satisfy a number of requirements which determine this separation. uniquely. Thus we know that the entropy source strength σ must be zero if the thermodynamic equilibrium conditions are satisfied within the system. Another requirement which (60) must satisfy is that it be invariant under a Galilei transformation, since the notions of reversible and irreversible behaviour must be invariant under such a transformation. It is seen that (60) satisfies automatically this requirement.

Finally it may be noted that by integrating (58) over the volume V of a closed system one obtains, with the inequality of (60),

$$\frac{dS}{dt} \geq - \int^{\Omega} \frac{\boldsymbol{J}_q}{T} \cdot d\boldsymbol{\Omega} \tag{61}$$

which is equivalent with the Carnot-Clausius theorem (44) as it should be.

Let us consider in more detail the expressions (59) and (60) for the entropy flow $\boldsymbol{J}_s$ and the entropy production σ. The first formula shows that for open systems the entropy flow consists of two parts: one is the "reduced" heat flow $\boldsymbol{J}_q/T$, the other is connected with the diffusion flows of matter $\boldsymbol{J}_k$. The second formula demonstrates that the entropy production contains four different contributions. The first term at the right-hand side of (60) arises from heat conduction, the second from diffusion, the third is connected to the gradients of the velocity field, giving rise to viscous flow, and the fourth is due to chemical reactions.

The structure of the expression for σ is that of a bilinear form: it consists of a sum of products of two factors. One of these factors in each term is a flow quantity (heat flow $\boldsymbol{J}_q$, diffusion flow $\boldsymbol{J}_k$, momentum flows or viscous pressure tensor $\boldsymbol{Pi}$, and chemical reaction rate J_j) already introduced in the conservation laws of Chapter II. The other factor in each term is related to a gradient of an intensive state variable (gradients of ten1perature, chemical potential and velocity) and may contain the external force $\boldsymbol{F}_k$; it can also be a difference of thermodynamic state variables, viz. the chemical affinity A_j. These quantities which multiply the fluxes in the expression for the entropy production are called "thermodynamic forces" or "affinities".

3.3 ALTERNATIVE EXPRESSIONS FOR THE ENTROPY PRODUCTION; ON DIFFERENT DEFINITIONS OF THE HEAT FLOW

It is convenient for a number of applications to write the entropy production (60) in a different form. The thermodynamic force which multiplies the diffusion flow J_k includes a part which is proportional to the gradient of the temperature. By using the thermodynamic relation

$$T d \left(\frac{\mu_k}{T} \right) = (d\mu_k)_T - \frac{h_k}{T} dT \tag{62}$$

where the index T indicates that the differential has to be taken at constant temperature, and where h_k is the partial specific enthalpy of component k, and by introducing a new flux, defined as

$$J_q' = J_q - \sum_{k=1}^{n} h_k J_k \tag{63}$$

the entropy production (60) can be written as

$$\sigma = -\frac{1}{T^2} J_q' \cdot \operatorname{grad} T - \frac{1}{T} \sum_{k=1}^{n} J_k \cdot (\operatorname{grad} (\mu_k)_T - F_k) - \frac{1}{T} \Pi : \operatorname{Grad} v - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \tag{64}$$

In this way the thermodynamic force conjugate to the diffusion flow J_k does not contain a term in grad T. However, the flow which is conjugate to the temperature gradient is now J_q' of formula (63) instead of J_q. From (63) it is clear that the difference between J_q and J_q' represents a transfer of heat due to diffusion. Therefore the quantity J_q' also represents an irreversible heat flow. In fact in diffusing mixtures the concept of heat flow can be defined in different ways. Obviously a different definition of the notion of heat flux leaves all physical results unchanged. But to any particular choice corresponds a special form of the entropy production σ. It is a matter of expediency which choice is the most suitable in a particular application of the theory. The freedom of defining the heat flow in various ways, of which the possibility was indicated here in the framework of a macroscopic treatment, exists also in the microscopic theories of transport phenomena in mixtures.

With the definition (63) the entropy flow gets the form

$$J_s = \frac{1}{T} J_q' + \sum_{k=1}^{n} s_k J_k \tag{65}$$

where $s_k = -(\mu_k - h_k)/T$ is the partial specific entropy of component k. Written in this way the entropy flux contains the heat flow J_q'; and a transport of partial entropies with respect to the barycentric velocity v.

Still a different form of the entropy production can be obtained by using the equality

$$T \operatorname{grad} \left(\frac{\mu_k}{T} \right) = \operatorname{grad} \mu_k - \left(\frac{\mu_k}{T} \right) \operatorname{grad} T \tag{66}$$

and the definition (59) of the entropy flow:

$$T\sigma = -J_s \cdot \operatorname{grad} T - \sum_{k=1}^{n} J_k \cdot (\operatorname{grad} \mu_k - F_k) - \Pi : \operatorname{Grad} v - \sum_{j=1}^{r} J_j A_j \tag{67}$$

It is seen that in this way the force conjugate to the diffusion flow J_k contains simply a gradient of the chemical potential μ_k. Since [cf. (20)]

$$\mathbf{F}_k = -\text{grad } \psi_k \tag{68}$$

we may write, by introducing the quantity

$$\tilde{\mu}_k = \mu_k + \psi_k \tag{69}$$

instead of (28)

$$T\sigma = -\mathbf{J}_s \cdot \text{grad } T - \sum_{k=1}^{n} \mathbf{J}_k \cdot \text{grad } \tilde{\mu}_k - \mathbf{\Pi} : \text{Grad } \mathbf{v} - \sum_{j=1}^{r} J_j A_j \tag{70}$$

In the case of an electrostatic potential energy, ψ_k is equal to $z_k \phi$ with z_k the charge per unit mass of component k, and ϕ the electrostatic potential, and $\tilde{\mu}_k$ is then the electrochemical potential. Quite in general it can be said that in the form (67) of the entropy production σ, where the entropy flow $\mathbf{J}_s$ is employed, the thermodynamic force conjugate to the diffusion flow can be written as the gradient of a single quantity, if the force $\mathbf{F}_k$ is conservative (e.g. an electrostatic or a gravitational force). This is the reason why the form (67) is of special advantage in applications, dealing with electric processes.

3.4   KINETIC ENERGY OF DIFFUSION

In Chapter II, Section 4, we have defined the internal energy u by equation (32), i.e. by subtracting from the total energy e the potential energies of all components $\psi = \sum_k c_k \psi_k$ and the barycentric kinetic energy $\frac{1}{2}v^2$. This means that the internal energy u still contains the macroscopic kinetic energy of the components with respect to the centre of gravity motion. It is possible to define a different internal energy per unit mass u^*, by subtracting from the total energy e, the potential energies and the kinetic energies of all components

$$u^* = e - \sum_k c_k \psi_k - \sum_k \frac{1}{2} c_k v_k^2 = u - \sum_k \frac{1}{2} c_k (v_k - v)^2 \tag{71}$$

where (7) and (32) have been used. Since the internal energy should only contain contributions from the thermal agitation and the short-range molecular interactions, the quantity u^* has perhaps more right to this name than the quantity u. In equilibrium the Gibbs relation (54) is in fact a relation between the entropy s and the quantities u^*, v and c_k, since in equilibrium diffusion fluxes must vanish. Therefore (54) should read

$$Tds = du^* + pdv - \sum_{k=1}^{n} \mu_k^* dc_k \tag{72}$$

where we have introduced the chemical potential μ_k^* related to u^* by

$$\sum_k c_k \mu_k^* = u^* - Ts + pv \tag{73}$$

In agreement with the hypothesis of local equilibrium one should therefore assume (72) to hold outside equilibrium in the form

$$T\frac{ds}{dt} = \frac{du^*}{dt} + p\frac{dv}{dt} - \sum_{k=1}^{n} \mu_k^* \frac{dc_k}{dt} \tag{74}$$

instead of (55).

Introducing into this equation the relation (71), one obtains, with (9)

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - \sum_{k=1}^{n} \mu_k \frac{dc_k}{dt} - \rho^{-1} \sum_{k=1}^{n} J_k \cdot \frac{d(v_k - v)}{dt} \tag{75}$$

where μ_k is related to μ_k^* by

$$\mu_k = \mu_k^* + \frac{1}{2}(v_k - v)^2 \tag{76}$$

and to u by the relation analogous to (73)

$$\sum_k c_k \mu_k = u - Ts + pv \tag{77}$$

It is seen that (75) and (55) are identical if $d(v_k - v)/dt$ vanishes, i.e. if the substantial time derivative of the velocities of the various components with respect to the barycentric motion may be neglected. We shall see later that frequently this may indeed be done. The use of (55) is then justified. From (75) one obtains, using (39), (38) and (13), the entropy balance equation, which reads now

$$\rho\frac{ds}{dt} = - \operatorname{div} \left(\frac{J_q - \sum_k \mu_k J_k}{T} \right) - \frac{1}{T^2} J_q \cdot \operatorname{grad} T$$
$$- \frac{1}{T} \sum_k J_k \cdot \left(T\operatorname{grad} \frac{\mu_k}{T} - F_k + \frac{d(v_k - v)}{dT} \right) - \frac{1}{T}\mathbf{\Pi} : \operatorname{Grad} v - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \tag{78}$$

This equation is identical with (58) except for the inclusion of an "inertia term" in the thermodynamic force of diffusion. Examples in which such "inertia terms" must be retained will be considered later.

4

THE PHENOMENOLOGICAL EQUATIONS

4.1 THE LINEAR LAWS

In the preceding chapter it has already been mentioned that the expression for the entropy production σ vanishes, when the thermodynamic equilibrium conditions are satisfied, i.e. when the (independent) thermodynamic forces are zero. In conformity with the concept of equilibrium we also require that all fluxes in u vanish simultaneously with the thermodynamic forces.

It is known empirically that for a large class of irreversible phenomena and under a wide range of experimental conditions, the irreversible flows are linear functions of the thermodynamic forces, as expressed by the phenomenological laws which are introduced ad hoc in the purely phenomenological theories of irreversible processes. Thus, e.g. Fourier's law for heat conduction expresses that the components of the heat flow are linear functions of the components of the temperature gradient, and Fick's law establishes a linear relation between the diffusion flow of matter and the concentration gradient. Also included in this kind of description are the laws for such cross-phenomena as thermal diffusion, in which the diffusion flow depends linearly on both the concentration and temperature gradients. If we restrict ourselves to this linear region we may write quite generally

$$J_i = \sum_k L_{ik} X_k \tag{79}$$

where J_i and X_i are any of the Cartesian components of the independent fluxes and thermodynamic forces appearing in the expression for the entropy production [cf. e.g. (III.21)], which is of the form $\sigma = \sum_i J_i X_i$.

The quantities L_{ik} are called the phenomenological coefficients and the relations (79) will be referred to as the phenomenological equations. It is clear that this scheme includes the examples mentioned above.

If one introduces the phenomenological equations into the expression for the entropy production σ, one gets a quadratic expression in the thermodynamic forces of the form $\sum_{i,k} L_{ik} X_i X_k$ which, since one has $\sigma \geq 0$, must be positive definite or at least non-negative definite. A sufficient condition for this is that all principal co-factors of the symmetric matrix with elements $L_{ik} + L_{ki}$ are positive (or at least non-negative). This implies that all diagonal elements are positive whereas the off-diagonal elements must satisfy, for instance, conditions of the form $L_{ii} L_{kk} \geq 0.25(L_{ik} + L_{ki})^2$.

With the help of the relations (79) it is now possible, using the conservation laws and balance equations of Chapters II and III, to determine in principle the evolution in time of all local thermodynamic state variables of the system. This is one of the advantages of

the systematic formulation of thermodynamics of irreversible processes. On the other hand this formulation will also enable us to derive some important relationships which exist between the phenomenological coefficients (cf. Section 3).

It is very well possible that some irreversible processes must be described by non-linear phenomenological laws. Such processes lie outside the scope of the present theory. However, even for such processes one may assume the linear relations to be valid within a very limited range close to equilibrium. Thus ordinary transport phenomena like heat conduction and electric conduction are linear even under rather extreme experimental conditions, whereas chemical reactions must nearly always be described by non-linear laws.

In the following sections the linear laws (79) will be given in explicit form for the systems studied in the preceding chapters, and the general properties of the matrix L_{ik} of phenomenological coefficients will be studied.

4.2   INFLUENCE OF SYMMETRY PROPERTIES OF MATTER ON THE LINEAR LAWS: CURIE PRINCIPLE

Before stating in this section the influence of the symmetry properties of matter on the phenomenological equations (79), we wish to write the entropy production (60), (64) or (70) in a slightly different form.

Let us split up the symmetric viscous pressure tensor P and the tensor Grad v in the following way[1]

$$P = p\boldsymbol{U} + \boldsymbol{\Pi} \tag{80}$$

$$\text{Grad } \boldsymbol{v} = \frac{1}{3}(\text{div } \boldsymbol{v})\boldsymbol{U} + \overset{\circ}{\text{Grad}}\ \boldsymbol{v} \tag{81}$$

where the quantity p is given by

$$p = \frac{1}{3}\boldsymbol{P} : \boldsymbol{U} \tag{82}$$

that is, as one third of the trace of the viscous pressure tensor. Similarly div v the trace of Grad v [cf. (11.37)]:

$$\text{div } \boldsymbol{v} = (\text{Grad } \boldsymbol{v}) : \boldsymbol{U} \tag{83}$$

The tensors $\boldsymbol{\Pi}$ and $\overset{\circ}{\text{Grad}}\ v$ defined by (80) and (81) have zero trace according to (82) and (83):

$$\boldsymbol{\Pi} : \boldsymbol{U} = 0 \tag{84}$$

$$\overset{\circ}{\text{Grad}}\ \boldsymbol{v} : \boldsymbol{U} = 0 \tag{85}$$

For the scalar product of (80) and (81), one finds with the help of (84) and (85)

$$\boldsymbol{P} : \text{Grad } \boldsymbol{v} = \boldsymbol{\Pi} : \overset{\circ}{\text{Grad}}\ \boldsymbol{v} + p\,\text{div } \boldsymbol{v} \tag{86}$$

The tensor $\overset{\circ}{\text{Grad}}\ v$ can be split into a symmetric and an antisymmetric part

$$\overset{\circ}{\text{Grad}}\ \boldsymbol{v} = (\overset{\circ}{\text{Grad}}\ \boldsymbol{v})^s + (\overset{\circ}{\text{Grad}}\ \boldsymbol{v})^a \tag{87}$$

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1 The original symbology in this section is at odds with Chapter 3. Here I replace the odd symbology with that of Chapter 3.

with

$$(\overset{\circ}{\mathrm{Grad}}\ \boldsymbol{v})^s = \frac{1}{2}\left(\frac{\partial v_\beta}{\partial x_\alpha} + \frac{\partial v_\alpha}{\partial x_\beta}\right) - \frac{1}{3}\delta_{\alpha\beta}\sum_\gamma \frac{\partial v_\gamma}{\partial x_\gamma} \tag{88}$$

$$(\overset{\circ}{\mathrm{Grad}}\ \boldsymbol{v})^a = \frac{1}{2}\left(\frac{\partial v_\beta}{\partial x_\alpha} - \frac{\partial v_\alpha}{\partial x_\beta}\right) \tag{89}$$

Using (87) the result (86) becomes

$$\boldsymbol{P} : \mathrm{Grad}\ \boldsymbol{v} = \boldsymbol{\Pi} : (\overset{\circ}{\mathrm{Grad}}\ \boldsymbol{v})^s + p\,\mathrm{div}\ \boldsymbol{v} \tag{90}$$

since the doubly contracted product of a symmetric and an antisymmetric tensor vanishes.

If one introduces (90) into the form (64) of the entropy production and eliminates J_n with the help of (15), one obtains

$$
\begin{aligned}
\sigma = & -\frac{1}{T^2}\boldsymbol{J}_q' \cdot \mathrm{grad}\ T - \frac{1}{T}\sum_{k=1}^{n-1} \boldsymbol{J}_k \cdot \left((\mathrm{grad}\ (\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n\right) \\
& -\frac{1}{T}\boldsymbol{\Pi} : (\overset{\circ}{\mathrm{Grad}}\ \boldsymbol{v})^s - \frac{1}{T}p\,\mathrm{div}\ \boldsymbol{v} - \frac{1}{T}\sum_{j=1}^{r} J_j A_j \geq 0
\end{aligned}
\tag{91}
$$

The total contribution of viscous phenomena to the entropy production has thus been split up into two parts. The second part, $-(1/T)p\,\mathrm{div}\ \boldsymbol{v}$, is related to the rate of change of specific volume. This is the part which is due to bulk viscosity.

We shall now establish the phenomenological equations (79) between the independent fluxes and thermodynamic forces of this expression. In principle any Cartesian component of a flux can be a linear function of the Cartesian components of all thermodynamic forces. We note, however, that the fluxes and the thermodynamic forces of (91) do not all have the same tensorial character: some are scalars, some are vectors and one is a tensor (of second rank). This means that under rotations and reflections the Cartesian components of these quantities transform in different ways. As a consequence symmetry properties of the material system considered may have the effect that the components of the fluxes do not depend on all components of the thermodynamic forces. This fact is often referred to as the Curie symmetry principle. Thus, in particular for an isotropic system (i.e. a system of which the properties at equilibrium ate the same in all directions) it can be shown that fluxes and thermodynamic forces of different tensorial character do not couple. The proof of this statement will be given in Chapter VI, where we shall study in a more formal way the influence of symmetry elements on the coupling of fluxes. and thermodynamic forces. For an isotropic system the phenomenological equations read

$$\boldsymbol{J}_q' = -L_{qq}(\mathrm{grad}\ T)/T^2 - \sum_{k=1}^{n-1} L_{qk}((\mathrm{grad}\ (\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n)/T \tag{92}$$

$$\boldsymbol{J}_i = -L_{iq}(\mathrm{grad}\ T)/T^2 - \sum_{k=1}^{n-1} L_{ik}((\mathrm{grad}\ (\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n)/T \tag{93}$$

$$\Pi_{\alpha\beta} = -\frac{L}{T}(\overset{\circ}{\mathrm{Grad}}\ \boldsymbol{v})^s_{\alpha\beta} \tag{94}$$

$$p = -l_{vv}(\mathrm{div}\ \boldsymbol{v})/T - \sum_{m=1}^{r} l_{vm} A_m/T \tag{95}$$

$$J_j = -l_{jv}(\text{div } \boldsymbol{v})/T - \sum_{m=1}^{r} l_{jm} A_m/T \qquad (96)$$

Equations (92) and (93) describe the vectorial phenomena of heat conduction, diffusion and their cross-effects. The coefficients L_{qq}, L_{qk}, L_{iq} and L_{ik} (i, k = 1,2, ... , n) are scalar quantities. This is also a consequence of the isotropy of the system. Equations (94) relate the Cartesian components of the pressure tensor $\boldsymbol{\tau}$ to the components of the symmetric tensor $\dot{\varepsilon}$. Due to the isotropy of the system only corresponding tensor components α, β are linearly related with each other by means of the same coefficient L. Finally equations (95) and (96) describe the scalar processes of bulk viscosity and chemistry and their possible cross-phenomena.

Another consequence of the fact that in isotropic media fluxes and thermodynamic forces of different tensorial character do not interfere, is that the entropy production (91) falls apart into three contributions, which are separately positive definite

$$\sigma_0 = -\frac{1}{T} p \text{div } \boldsymbol{v} - \frac{1}{T} \sum_{j=1}^{r} J_j A_j \geq 0 \qquad (97)$$

$$\sigma_1 = -\frac{1}{T^2} \boldsymbol{J}_q' \cdot \text{grad } T - \frac{1}{T} \sum_{k=1}^{n-1} \boldsymbol{J}_k \cdot (((\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n) \geq 0 \qquad (98)$$

$$\sigma_2 = -\frac{1}{T} \boldsymbol{\Pi} : (\overset{\circ}{\text{Grad }} \boldsymbol{v})^s \geq 0 \qquad (99)$$

This can be concluded when the phenomenological equations (92)-(96) are substituted into (91).

We shall also write down the general form of the phenomenological equations in anisotropic crystals in which no chemical reactions occur. Since in such systems no viscous flows exist, we are left with the phenomena of heat conduction, diffusion and their cross-effects. The phenomenological equations corresponding to this case are

$$\boldsymbol{J}_q' = -\boldsymbol{L}_{qq} \cdot (\text{grad } T)/T^2 - \sum_{k=1}^{n-1} \boldsymbol{L}_{qk} \cdot ((\text{grad } (\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n)/T \qquad (100)$$

$$\boldsymbol{J}_i = -\boldsymbol{L}_{iq} \cdot (\text{grad } T)/T^2 - \sum_{k=1}^{n-1} \boldsymbol{L}_{ik} \cdot ((\text{grad } (\mu_k - \mu_n))_T - \boldsymbol{F}_k + \boldsymbol{F}_n)/T \qquad (101)$$

The quantities $\boldsymbol{L}_{qq}$, $\boldsymbol{L}_{qk}$, $\boldsymbol{L}_{iq}$ and $\boldsymbol{L}_{ik}$ are tensors. For instance $\boldsymbol{L}_{qq}$ is related to the heat conduction tensor. The form of these tensors depends on the symmetry elements of the system. We have seen above that in isotropic - media all tensors in (100) and (101) reduce to scalar multiples of the unit tensor. This is also the case in crystals with cubic symmetry. Since the isotropic fluid and the anisotropic crystal are in actual physical applications the two most frequently encountered types of systems, we have confined the discussion of the influence of symmetry properties of matter on the phenomenological laws to these two cases.

4.3   THE ONSAGER RECIPROCAL RELATIONS

In the preceding section we have considered the influence of spatial symmetry on the phenomenological equations. In this section we shall discuss the influence of the property

of "time reversal invariance" of the equations of motion of the individual particles, of which the system consists, on the phenomenological equations. This property of "time reversal invariance" expresses the fact that the mechanical equations of motion (classical as well as quantum mechanical) of the particles are symmetric with respect to the time. It implies that the particles retrace their former paths if all velocities are reversed.

From this microscopic property one may conclude to a macroscopic theorem, due to Onsager. In this section we shall state the content of this theorem. In Chapter VII the derivation of this theorem is discussed.

Let us consider an adiabatically insulated system. We shall first take the case that no external magnetic field acts on the system. The state of the system can be described by a number of independent parameters.

These parameters may be of two types. Some of these are even functions of the particle velocities (one may think, for instance, of local energies, concentrations, etc.). These are denoted by A_1, A_2, ..., A_n. The other parameters are odd functions of the particle velocities (e.g. momentum densities), and are denoted by B_1, B_2, ..., B_m. The equilibrium values of these variables are A_1^0, A_2^0, ..., A_n^0 and B_1^0, B_2^0, ..., B_m^0. The deviations of all these parameters from their equilibrium values are given by

$$\alpha_i = A_i - A_i^0 \tag{102}$$

$$\beta_i = B_i - B_i^0 \tag{103}$$

At equilibrium the entropy has a maximum, and the state variables α_1, α_2, ..., α_n and β_1, β_2, ..., β_m are zero by definition; this means that for a non-equilibrium state one can write for the deviation ΔS of the entropy from its equilibrium value, as a first approximation, a quadratic expression in the state variables α_1, α_2, ..., α_n and β_1, β_2, ..., β_m:

$$\Delta S = -\frac{1}{2} \sum_{i,k}^{n} g_{ik} \alpha_k \alpha_i - \frac{1}{2} \sum_{i,k}^{m} h_{ik} \beta_k \beta_i \tag{104}$$

where g_{ik} (i, k = 1, 2, ... , n) and h_{ik} (i, k = 1, 2, ... , m), the second derivatives of ΔS with respect to the α and β-variables, are positive definite matrices. In the absence of an external magnetic field no cross-terms between α- and β-type variables occur in (104) since ΔS must be an even function of the particle velocities.

It is assumed that the time behaviour of the state parameters can be described by linear phenomenological equations of the type

$$\frac{d\alpha_i}{dt} = -\sum_{k=1}^{n} M_{ik}^{(\alpha\alpha)} \alpha_k - \sum_{k=1}^{m} M_{ik}^{(\alpha\beta)} \beta_k \tag{105}$$

$$\frac{d\beta_i}{dt} = -\sum_{k=1}^{n} M_{ik}^{(\beta\alpha)} \alpha_k - \sum_{k=1}^{m} M_{ik}^{(\beta\beta)} \beta_k \tag{106}$$

where the $M_{ik}^{\alpha\alpha}$, $M_{ik}^{\alpha\beta}$, $M_{ik}^{\beta\alpha}$, $M_{ik}^{\beta\beta}$ are the phenomenological coefficients. Onsager's theorem establishes a number of relations between these coefficients, viz.,

$$\sum_{k=1}^{n} M_{ik}^{(\alpha\alpha)} g_{kj}^{-1} = \sum_{k=1}^{n} M_{jk}^{(\alpha\alpha)} g_{ki}^{-1} \tag{107}$$

$$\sum_{k=1}^{n} M_{ik}^{(\alpha\beta)} g_{kj}^{-1} = - \sum_{k=1}^{n} M_{jk}^{(\beta\alpha)} g_{ki}^{-1} \tag{108}$$

$$\sum_{k=1}^{n} M_{ik}^{(\beta\beta)} g_{kj}^{-1} = \sum_{k=1}^{n} M_{jk}^{(\beta\beta)} g_{ki}^{-1} \tag{109}$$

where the g_{ik}^{-1} and h_{ik}^{-1} are the reciprocal matrices of the g_{ik} and h_{ik}. These relations, which express the content of Onsager's theorem, can be written in a somewhat more transparent form, by writing the phenomenological equations (105) and (106) in a different fashion. To this purpose let us introduce the following linear combinations of the state parameters

$$X_i = \frac{\partial \Delta S}{\partial \alpha_i} = - \sum_{k=1}^{n} g_{ik} \alpha_k \tag{110}$$

$$Y_i = \frac{\partial \Delta S}{\partial \beta_i} = - \sum_{k=1}^{m} h_{ik} \beta_k \tag{111}$$

Solving for the α_i and β_i we obtain

$$\alpha_i = - \sum_{k=1}^{n} g_{ik}^{-1} X_k \tag{112}$$

$$\beta_i = - \sum_{k=1}^{m} h_{ik}^{-1} Y_k \tag{113}$$

Introducing (112) and (113) into (105) and (106), these relations become

$$\frac{d\alpha_i}{dt} = \sum_{k=1}^{n} L_{ik}^{(\alpha\alpha)} X_k + \sum_{k=1}^{m} L_{ik}^{(\alpha\beta)} Y_k \tag{114}$$

$$\frac{d\beta_i}{dt} = \sum_{k=1}^{n} L_{ik}^{(\beta\alpha)} X_k + \sum_{k=1}^{m} L_{ik}^{(\beta\beta)} Y_k \tag{115}$$

where the coefficients are given by

$$L_{ik}^{(\alpha\alpha)} = \sum_{j=1}^{n} M_{ij}^{(\alpha\alpha)} g_{jk}^{-1} \tag{116}$$

$$L_{ik}^{(\alpha\beta)} = \sum_{j=1}^{m} M_{ij}^{(\alpha\beta)} h_{jk}^{-1} \tag{117}$$

$$L_{ik}^{(\beta\alpha)} = \sum_{j=1}^{n} M_{ij}^{(\beta\alpha)} g_{jk}^{-1} \tag{118}$$

$$L_{ik}^{(\beta\beta)} = \sum_{j=1}^{m} M_{ij}^{(\beta\beta)} h_{jk}^{-1} \tag{119}$$

With the help of these quantities, the Onsager relations (107)-(109) become

$$L_{ik}^{(\alpha\alpha)} = L_{ki}^{(\alpha\alpha)} \tag{120}$$

$$L_{ik}^{(\alpha\beta)} = -L_{ki}^{(\beta\alpha)} \tag{121}$$

$$L_{ik}^{(\beta\beta)} = L_{ki}^{(\beta\beta)} \tag{122}$$

In this simple form they are usually referred to as Onsager's reciprocal relations.

To summarize the results it can be said that the Onsager relations (122)-(120) are valid for the coefficients of the phenomenological equations, if the independent "fluxes" J_i and I_i

$$J_i = \frac{d\alpha_i}{dt} \tag{123}$$

$$I_i = \frac{d\beta_i}{dt} \tag{124}$$

are written as linear functions of the independent "thermodynamic forces" X_i and Y_i which are the derivatives of the entropy with respect to α_i and β_i respectively

$$X_i = \frac{\partial\Delta S}{\partial\alpha_i} \tag{125}$$

$$Y_i = \frac{\partial\Delta S}{\partial\beta_i} \tag{126}$$

The Onsager relations hold in the form (120)-(122) if no external magnetic field B is present. In the presence of an external magnetic field the property of "time reversal invariance" implies that the particles retrace their former paths only if both the particle velocities and the magnetic field are reversed. This follows from the form of the expression for the Lorentz force, which is proportional to the vector product of the particle velocity and the magnetic field. A similar situation arises in rotating systems. Then the particles retrace their former paths if both their velocities and the angular velocity were reversed, since the particles are then subjected to the so-called Coriolis force which is proportional to the vector product of the particle velocity and the angular velocity. As a consequence the Onsager relations (120)-(122) must be modified to read[2]:

$$L_{ik}^{(\alpha\alpha)}(\boldsymbol{B},\boldsymbol{\omega}) = L_{ki}^{(\alpha\alpha)}(-\boldsymbol{B},-\boldsymbol{\omega}) \tag{127}$$

$$L_{ik}^{(\alpha\beta)}(\boldsymbol{B},\boldsymbol{\omega}) = -L_{ki}^{(\beta\alpha)}(-\boldsymbol{B},-\boldsymbol{\omega}) \tag{128}$$

$$L_{ik}^{(\beta\beta)}(\boldsymbol{B},\boldsymbol{\omega}) = L_{ki}^{(\beta\beta)}(-\boldsymbol{B},-\boldsymbol{\omega}) \tag{129}$$

It is interesting to write down the time derivative of the entropy (104), i.e. the entropy production, due to the irreversible processes occurring in the system:

$$\frac{d\Delta S}{dt} = -\sum_{i,k} g_{ik}\alpha_k\frac{d\alpha_i}{dt} - \sum_{i,k} h_{ik}\beta_k\frac{d\beta_i}{dt} \tag{130}$$

and therefore with (110), (111) and (123), (124):

$$\frac{d\Delta S}{dt} = \sum_{i=1}^{n} J_i X_i + \sum_{i=1}^{m} I_i Y_i \tag{131}$$

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2 It should be noted that in the presence of a magnetic field the thermodynamic forces (125) and (126) are not given by the last members of (110) and (111) since the entropy as may then contain cross-terms between α- and β-variables (the entropy must be invariant for a reversal of both the particle velocities and the magnetic field, cf. Chapter VII).

The entropy production is therefore a bilinear expression in the fluxes and thermodynamic forces appearing in the phenomenological equations for which the Onsager relations hold. The calculations of the entropy production therefore affords a means of finding the proper "conjugate" irreversible fluxes and thermodynamic forces necessary for the establishment of phenomenological equations of which the coefficients obey the Onsager relations (120)-(122) or (127)-(129).

Although the fluxes in the local entropy production σ, calculated in the preceding chapter and used in section 2 of this chapter, are not necessarily time derivatives of state variables as the fluxes (123) and (124) in (131), or in other words, although the local entropy production σ is not a total time derivative such as (130) is, it can be shown that the phenomenological coefficients appearing in the linear laws established between fluxes and thermodynamic forces of the local entropy production also obey the reciprocal relations (120)-(122) or (127)-(129). The formal proof of this statement will be given in Chapter VI.

Thus the following relations exist amongst the coefficients of the phenomenological laws (92)-(96) of the isotropic fluid (in the absence of a magnetic field)

$$L_{qi} = L_{iq} \tag{132}$$

$$L_{ik} = L_{ki} \tag{133}$$

$$l_{vj} = -l_{jv} \tag{134}$$

$$l_{jm} = l_{mj} \tag{135}$$

Relation (134) is an example of (121) since it describes a cross-effect between an α- and a β-type variable; the chemical affinity A and the divergence of the velocity v respectively. The symmetry relations (132)-(135) establish a number of connections between otherwise independent irreversible processes. One of the objectives of non-equilibrium thermodynamics is to study the physical consequences of such relations (see part B).

For the coefficients of the phenomenological laws (100) and (101) of the anisotropic crystal the reciprocal relations, in the presence of a magnetic field, are

$$L_{qq}(\boldsymbol{B}) = \tilde{L}_{qq}(-\boldsymbol{B}) \tag{136}$$

$$L_{qi}(\boldsymbol{B}) = \tilde{L}_{iq}(-\boldsymbol{B}) \tag{137}$$

$$L_{ik}(\boldsymbol{B}) = \tilde{L}_{ki}(-\boldsymbol{B}) \tag{138}$$

where the tildas mean transposing of Cartesian components μ and ν of a tensor, for instance

$$\tilde{L}_{iq,\mu\nu}(\boldsymbol{B}) = L_{iq,\nu\mu}(\boldsymbol{B}) \tag{139}$$

We note that for the anisotropic case, the Onsager relations, in the absence of a magnetic field ($\boldsymbol{B} = 0$), have as a consequence that the tensors L_{qq} and L_{ii} ($i = 1, 2, \ldots, n - l$) are symmetric. In the presence of a magnetic field the relations (136)-(138) yield also some information about the parity of certain coefficients with respect to reversal of the magnetic field.

The Onsager relations have been written down here for the phenomenological equations involving the fluxes and thermodynamic forces occurring in the form (91) of the entropy

production. Any of the alternative forms of the entropy production derived in Chapter III involving other fluxes and thermodynamic forces would have led to phenomenological laws with other coefficients for which, however, reciprocal relations still hold. In fact it can easily be seen that the transformations of Chapter III, from the description with one set of fluxes and thermodynamic forces to another, preserve the validity of the Onsager relations (cf. also Chapter VI, Section 5).

4.4 THE DIFFERENTIAL EQUATIONS

If one substitutes the phenomenological equations (92)-(96) into the conservation laws for matter (13), the momentum equation (19) and the balance equation of internal energy (36), one obtains with (5) a set of $n + 4$ partial differential equations for the $n + 4$ independent variables: the density p, the $n - 1$ concentrations $c_1, c_2, \ldots, c_{n-1}$, the three Cartesian components v_x, v_y, and v_z of the velocity v, and the temperature T. The equations of state of the system allow to express the energy u, the equilibrium pressure p and the chemical potentials μ_k, occurring in the partial differential equations, in terms of those independent variables.

For a one-component isotropic fluid these partial differential equations are (in the absence of external forces):

$$\frac{\partial \rho}{\partial t} = -\operatorname{div} \rho v \tag{140}$$

$$\rho \frac{dv}{dt} = -\operatorname{grad} p + \eta \Delta v + \left(\frac{1}{3}\eta + \eta_v \right) \operatorname{grad} \operatorname{div} v \tag{141}$$

$$\rho \frac{du}{dt} = \lambda \Delta T - p \operatorname{div} v + 2\eta (\overset{\circ}{\operatorname{Grad}} v)^s : (\overset{\circ}{\operatorname{Grad}} v)^s + \eta_v (\operatorname{div} v)^2 \tag{142}$$

The first of these equations is simply the equation of conservation of mass (5). The second is found by substituting (80), (94) and (95) (without chemical terms) into (9) with (35). The coefficients η and η_v defined as $\eta = L/2T$ and $\eta_v = l_{vv}/T$, are called the shear viscosity and the bulk viscosity respectively. It has been assumed here that the viscosity coefficients are constants. The third equation follows from (36) with (92) (without diffusion terms), (94) and (95). The coefficient λ, defined as L_{qq}/T^2, is called the heat conductivity, and has also been assumed to be a constant. The symbol Δ stands for the Laplace operator. These equations must be supplemented by the equations of state

$$p = p(\rho, T) \tag{143}$$

$$u = u(\rho, T) \tag{144}$$

Equations (140)-(144) describe completely the time behaviour of the one component isotropic fluid for specified initial and boundary conditions.

It is customary to limit the field of hydrodynamics to equations (140), (141) and (143) alone, by assuming that either isothermal or isentropic conditions are fulfilled. In both cases pressure is a function of density only, so that the hydrodynamic behaviour is completely described by (140) and (141). In the more general case the complete set of equations (140)-(144) is necessary to describe the behaviour of the system. One might call the theory based on this complete set of equations "thermohydrodynamics" which is

thus found to be part of the more general theory of non-equilibrium thermodynamics. On the other hand the theory of heat conduction is also contained in these equations.

We note that (141) is the well-known Navier-Stokes equation. The last two terms of (142) represent the Rayleigh dissipation function. Equation (142) becomes Fourier's differential equation for heat conduction

$$\rho c_v \frac{\partial T}{\partial t} = \lambda \Delta T \tag{145}$$

for a medium in which the velocity v is zero; ($c_v = (\partial u / \partial T)_v$ is the specific heat at constant volume per unit mass).

For more general cases, for instance in a multi-component system where diffusion occurs, the set of simultaneous differential equations becomes more complicated. It may be said that non-equilibrium thermodynamics has the purpose to study various irreversible processes as heat conduction, diffusion and viscous flow from a single point of view. It englobes a number of phenomenological theories such as the hydrodynamics of viscous fluids, the theory of diffusion and the theory of heat conduction.

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