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Pierre Gaspard
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Thermodynamics

1.1 Generalities

Thermodynamics aims to describe many-particle systems on the macroscale, i.e., on spatial scales larger than the distances between the particles and temporal scales longer than the corresponding time intervals. Thermodynamics enunciates general principles governing the balance of physical quantities characterizing such macroscopic systems. These physical quantities are the state variables, also called macrovariables, that are defined by observing the system on the macroscale. The state variables include mechanical variables such as the energy E and the particle numbers N_k, which are defined in the framework of the underlying microscopic mechanics, as well as the nonmechanical variable called entropy S. This latter was introduced by Clausius (1865), who established its existence at the macroscale in addition to the mechanical properties, in particular, using the study of Carnot (1824) on the behavior of gases in idealized steam engines.

Basically, the system is delimited by a boundary and has a volume V. The system can be an engine, a device, a machine, a motor, or part of a larger system, such as a volume element in a continuous medium like a fluid or a solid.

The time evolution of the system may result from internal transformations and also from exchanges with its environment, as schematically represented in Figure 1.1. During the evolution of any kind (i.e., spontaneous time evolution or evolution under some external drive), some state variable X changes by some infinitesimal amount dX at every infinitesimal step of the evolution. Mathematically speaking, dX is the differential of X. This differential may have two contributions

$$dX = d_{\rm e}X + d_{\rm i}X. \tag{1.1}$$

The contribution $d_{\rm e}X$ is due to the exchanges of X with the exterior of the system (i.e., its environment) and the contribution $d_{\rm i}X$ is caused by the transformations inside the system (Prigogine, 1967). The symbols $d_{\rm e}X$ and $d_{\rm i}X$ denote contributions that are not given by the differential of some function. The notation $\cancel{d}X$ is also often used for such nondifferential contributions. If there is no environment, we have that $d_{\rm e}X = 0$ for any quantity X and the system is said to be *isolated*.

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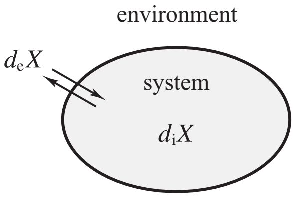

Figure 1.1 Schematic representation of a system in contact with its environment. Changes of the macrovariable X with the *exterior* of the system are denoted by $d_e X$ and $d_i X$ denotes those occurring within its *interior*.

Thermodynamics is formulated as follows with three laws, specifically concerning energy and entropy.

1.2 Energy and Other Conserved Quantities

The first law of thermodynamics is a principle of conservation.

First law: *There exists a state variable called the energy E that is conserved in every internal transformation of the system, i.e.,*

$$dE = d_e E + d_i E \qquad \text{with} \qquad d_i E = 0. \tag{1.2}$$

Energy is measured in joules (SI unit), calories, or electron-Volts (eV), depending on the context. The first law of thermodynamics expresses the conservation of energy in any form. The energy is the sum of all the forms of energy: kinetic, potential, electric, magnetic, thermal, chemical, nuclear, gravitational, etc. The first law is justified in all the mechanical theories of physics as resulting from the symmetry of the equations of motion under time translations,[1] which implies the conservation of a quantity identified as energy by the theorem of Noether (1918). We note that the first law defines energy up to a constant value that remains arbitrary.

Beside energy, there exist other quantities that are also conserved as the result of fundamental symmetries:

- linear momentum (by symmetry under spatial translations[1]);
- angular momentum (by symmetry under rotations[1]);
- electric charge (by local gauge symmetry[2]);
- leptonic number (by global symmetry[3]);
- baryonic number (by global symmetry[3]);

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[1] These fundamental symmetries of Minkowski's spacetime belong to the Poincaré group, also called the inhomogeneous Lorentz group. This group reduces to the Galilean group in the nonrelativistic limit (Weinberg, 1995).

[2] This fundamental symmetry holds at every spacetime point for the quantum fields associated with electrically charged particles (Weinberg, 1996).

[3] This other fundamental symmetry is independent of spacetime and holds for the quantum fields associated with leptonic or baryonic particles (Weinberg, 1996).

according to experimental observations (Weinberg, 1995, 1996). Every one of these quantities obeys equation (1.1) with $d_{\rm i}X = 0$, as expressed for energy by the first law.

Among the state variables, we also have the numbers N_k of the particles of different species $k = 1, 2, \dots, c$. The particles are supposed to be identical objects that should be considered in the description of the system, such as photons, leptons, baryons, nuclei, atoms, molecules, and supramolecular entities. If some particles undergo reactions, their numbers are not conserved so that

$$dN_k = d_{\rm e}N_k + d_{\rm i}N_k \tag{1.3}$$

with $d_{\rm i}N_k \neq 0$, depending on the reaction rates and the stoichiometric coefficients of the species k in the reactions. However, if there is no reaction and the species k is conserved, we again have that $d_{\rm i}N_k = 0$ and the particle number N_k goes along the other conserved quantities.

It is also possible that the particle numbers $\{N_k\}_{k=1}^{c}$ are not conserved, but that some linear combination of them, $L_j = \sum_{k=1}^{c} \ell_{jk} N_k$, is nevertheless conserved, so that $d_{\rm i}L_j = 0$, which defines an effective conservation law. The existence of the conserved quantities L_j depends on the energy scale of the reactions taking place inside the system. For low collision energies, in the absence of chemical reactions the molecules are preserved so that $d_{\rm i}N_k = 0$, where k denotes a molecular species. At higher collision energies, though still below the energy of the strongest chemical bonds, some parts of molecules called moieties (Nelson and Cox, 2017) may be preserved by the reactions, in which case the numbers L_j of these moieties are conserved. At collision energies higher than the energy of the chemical bonds, the molecules break up into atoms so that only the numbers A_j of atoms are conserved. If ionization occurs, the numbers of electrons and ions become the relevant state variables, as in electrolytes or plasmas. Moreover, different isotopes may be distinguished by their mass m_j. The numbers of isotopes are conserved as long as there is no radioactivity. Within the nonrelativistic description, the law of mass conservation holds, which is expressed as $dM = d_{\rm e}M + d_{\rm i}M$ with $d_{\rm i}M = 0$, where $M = \sum_j m_j A_j$ is the total mass of the system. For still higher energies at the scale of MeV or higher, radioactivity and nuclear reactions break the conservation laws of the mass and the numbers of atomic nuclei, so that systems should be described in terms of nucleons and possibly other particles such as photons, electrons, positrons, and neutrinos. At energies above about 100 MeV, further particles should be included in the description (Weinberg, 1995, 1996).

We note that entities much larger than atoms or molecules may also be counted, such as atomic or molecular clusters, colloidal particles, crystalline particles, or biological entities such as viruses, organelles, or cells. In every case, an issue is to assess the relevance of the thermodynamic description adopted.

A system is said to be *closed* if only energy is exchanged with its environment, i.e., if $d_{\rm e}E \neq 0$ but $d_{\rm e}N_k = 0$. A system is said to be *open* if energy and matter are exchanged with its environment, i.e., if $d_{\rm e}E \neq 0$ and $d_{\rm e}N_k \neq 0$.

The environment is often supposed to be much larger than the system, in which case it plays the role of energy or particle reservoir. The environment may also be composed of several such reservoirs in contact with the system.

1.3 Entropy

In addition to the mechanical state variables, there is a nonmechanical variable that obeys the

Second law: *There exists a state variable called entropy S such that*

$$dS = d_{\mathrm{e}}S + d_{\mathrm{i}}S \qquad \textit{with} \qquad d_{\mathrm{i}}S \geq 0. \tag{1.4}$$

The entropy production $d_{\mathrm{i}}S$ is thus always nonnegative. The evolution or transformation undergone by the system is said to be *reversible* if $d_{\mathrm{i}}S = 0$ and *irreversible* if $d_{\mathrm{i}}S > 0$. The system remains at *thermodynamic equilibrium* if $d_{\mathrm{i}}S = 0$ and it is *out of equilibrium* if $d_{\mathrm{i}}S > 0$. In this latter case, there is a time asymmetry in the macroscopic description of the system. We note that $d_{\mathrm{e}}S$ may be positive, negative, or zero, depending on the exchanges between the system and its environment.

1.3.1 Equilibrium Macrostates

If the system is at equilibrium, i.e., if $d_{\mathrm{i}}S/dt = 0$, its (absolute) *temperature* is defined by differentiating the energy with respect to the entropy,

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,\{N_k\}_{k=1}^{c}}, \tag{1.5}$$

where all the other variables remain constant. The SI unit of temperature is the kelvin (K), which is related to the SI unit of energy by Boltzmann's constant $k_{\mathrm{B}} = 1.380649 \times 10^{-23}$ J/K. Accordingly, the entropy has the units of joule per kelvin (J/K). At equilibrium again, the (hydrostatic) *pressure* is defined as

$$p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,\{N_k\}_{k=1}^{c}}, \tag{1.6}$$

and the *chemical potential* of species k as

$$\mu_k \equiv \left(\frac{\partial E}{\partial N_k}\right)_{V,S,\{N_j\}_{j(\neq k)=1}^{c}}. \tag{1.7}$$

As a consequence, the energy of an equilibrium macrostate varies according to the *Gibbs relation*

$$dE = T\,dS - p\,dV + \sum_{k=1}^{c} \mu_k\,dN_k, \tag{1.8}$$

when changing its entropy, its volume, and particle numbers. In equation (1.8), ${\mathchar'26\mkern-12mu d}Q = T\,dS$ corresponds to the change of heat under the transformation. We note that other contributions may be included for instance from electromagnetism

$$dE\big|_{\mathrm{em}} = \int_V (\boldsymbol{\mathcal{E}} \cdot d\boldsymbol{\mathcal{D}} + \boldsymbol{\mathcal{H}} \cdot d\boldsymbol{\mathcal{B}})\, d^3r, \tag{1.9}$$

where $\boldsymbol{\mathcal{E}}$ is the electric field, $\boldsymbol{\mathcal{D}}$ the electric displacement, $\boldsymbol{\mathcal{H}}$ the magnetizing field, $\boldsymbol{\mathcal{B}}$ the magnetic field, and d^3r the volume element (Landau and Lifshitz, 1984); or from the interface between two bulk phases

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$$dE\big|_{\text{surf}} = \gamma\, d\Sigma, \tag{1.10}$$

where γ is the surface tension and $d\Sigma$ some change of the interfacial surface area Σ. Between three bulk phases, a further contribution from line tension should be added (Rowlinson and Widom, 1989).

Since energy, entropy, and particle numbers are *extensive variables* proportional to the volume, the thermodynamically conjugated variables, which are temperature, pressure, and chemical potentials, are *intensive variables* independent of the volume at the macroscale. Further intensive variables can be defined by dividing the extensive variables, for instance, with the volume to get the *densities*.

An important consequence of the second law is that the entropy should be maximal at equilibrium. In turn, the Gibbs relation (1.8) implies that the temperature, the pressure, and the chemical potentials must be uniform across an equilibrium system, as shown in Appendix A. This fundamental property of equilibrium macrostates does not preclude the existence of equilibrium spatial structures since thermodynamically conjugated variables, i.e., the entropy, mass, and particle densities, are left unconstrained. In particular, crystals are equilibrium spatially periodic structures classified by the 230 space groups in three dimensions (Ashcroft and Mermin, 1976). Vortex lattices in type-II superconductivity are other examples of equilibrium spatial structures. In any case, equilibrium macrostates are stationary at the macroscale (although dynamical at the microscale).

Since the second law is formulated in terms of a differential, the entropy is only defined up to a constant, as in the case of energy. Nevertheless, the constant of entropy can be determined with the

Third law: *If the system has a unique microstate of minimal energy, the entropy vanishes at absolute zero temperature:*

$$\lim_{T\to 0} S = 0. \tag{1.11}$$

Accordingly, the absolute value of the entropy can be defined with the third law on the basis of an assumption about the microstates of minimal energy (Pauling, 1970).

Another consequence of the Gibbs relation (1.8) is that the energy E is a state variable that depends on the entropy S, the volume V, and the particle numbers $\{N_k\}_{k=1}^c$. The energy therefore plays the role of thermodynamic potential $E(S, V, \{N_k\}_{k=1}^c)$ for a system with independently fixed values of these variables. However, another set of independent variables may be required if the entropy, the volume, and the particle numbers are not fixed in the system of interest. We are thus led to define other thermodynamic potentials by performing Legendre transforms, substituting one variable by the thermodynamically conjugated variable that is fixed, as explained in Appendix A. This leads to the definition of the enthalpy describing systems where the pressure is fixed instead of volume, the Helmholtz free energy for systems where the temperature is fixed instead of entropy, the Gibbs free energy (or free enthalpy) if the temperature and the pressure are fixed instead of entropy and volume, or the grand thermodynamic potential if the temperature and the chemical potentials are fixed instead of entropy and particle numbers. Various thermodynamic potentials can thus be introduced depending on the experimental conditions imposed on the system of interest. Moreover, inverting equation (1.8), we obtain an expression for the change of entropy

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \sum_{k=1}^{c} \frac{\mu_k}{T}\,dN_k, \tag{1.12}$$

showing that the entropy can also play the role of thermodynamic potential given by the function $S(E, V, \{N_k\}_{k=1}^{c})$.

The thermodynamic properties of chemical substances have been measured experimentally and they are known, in particular, under standard conditions ($T^0 = 298.15$ K, $p^0 = 100$ kPa). The values of the standard molar enthalpy and the Gibbs free energy of formation, as well as the standard molar entropy, are tabulated for many chemical substances (Lide, 2000). Since the values of the state variables do not depend on the pathway followed to reach some equilibrium macrostate, the thermodynamic properties can be determined in mixtures on the basis of their composition.

1.3.2 Nonequilibrium Macrostates

The system is out of equilibrium if entropy is produced inside the system, i.e., if $d_{\rm i}S/dt > 0$.

Isolated Systems

If the system is isolated, there is no environment, which implies that $d_{\rm e}S/dt = 0$. In this case, the time derivative of the entropy is only determined by the entropy production rate according to

$$\frac{dS}{dt} = \frac{d_{\rm i}S}{dt} \geq 0. \tag{1.13}$$

Therefore, the entropy increases in the system up to its maximal value corresponding to the equilibrium macrostate, as shown in Figure 1.2(a).[4] The second law thus conveys the

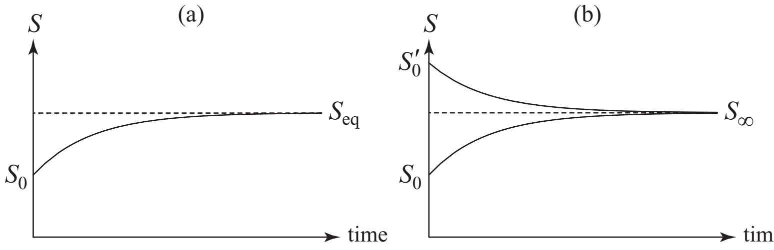

Figure 1.2 Possible time evolutions of the entropy towards an asymptotic stationary value in (a) an isolated system and (b) a nonisolated system.

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[4] Clausius (1865) expressed the first and second laws for the universe. If the entropy state variable was known everywhere in the universe, the entropy of the universe could be decomposed as $S_{\rm univ} = S_{\rm sys} + S_{\rm env}$, i.e., into the entropies of the system and its environment shown in Figure 1.1. Since the universe contains everything, it is isolated, so that $dS_{\rm univ}/dt = d_{\rm i}S_{\rm univ}/dt \geq 0$ by equation (1.13), which is the statement of Clausius (1865). Neither the system nor its environment being isolated, the second law (1.4) gives $dS_{\rm sys}/dt = d_{\rm e}S_{\rm sys}/dt + d_{\rm i}S_{\rm sys}/dt$ and $dS_{\rm env}/dt = d_{\rm e}S_{\rm env}/dt + d_{\rm i}S_{\rm env}/dt$. Moreover, the amounts of entropy exchanged between the system and its environment and *vice versa* are opposite to each other: $d_{\rm e}S_{\rm sys}/dt = -d_{\rm e}S_{\rm env}/dt$. Therefore, the sum of the entropies produced inside the system and its environment is equal to the one produced in the universe: $d_{\rm i}S_{\rm univ}/dt = d_{\rm i}S_{\rm sys}/dt + d_{\rm i}S_{\rm env}/dt \geq 0$. We note that the system of interest is often significantly smaller than the universe, in which case $d_{\rm i}S_{\rm univ}/dt \gg d_{\rm i}S_{\rm sys}/dt \geq 0$.

observation that, during some nonequilibrium transients, an isolated macroscopic system undergoes a relaxation towards the macrostate of thermodynamic equilibrium and that energy is dissipated in the sense that the macroscopic movements in the system come to rest when the equilibrium macrostate is reached. This time asymmetry is a characteristic feature of nonequilibrium systems at the macroscale.

Systems in Contact with One Reservoir

If the system is not isolated, its environment may form an energy or particle reservoir. Now, the system is closed or open due to the exchanges of energy or particles with the environment, so that

$$\frac{dS}{dt} = \frac{d_{\rm e}S}{dt} + \frac{d_{\rm i}S}{dt} \tag{1.14}$$

with some entropy exchange rate $d_{\rm e}S/dt$. If these conditions hold, the system will undergo a relaxation towards a macrostate of global equilibrium with its environment. In the long-time limit, the entropy of the system will reach a stationary value, as schematically represented in Figure 1.2(b) with $\lim_{t\to\infty} S = S_\infty$. Since equilibrium is global in this stationary macrostate, there is no entropy exchange between the system and its environment, $\lim_{t\to\infty} d_{\rm e}S/dt = 0$. Therefore, the entropy production rate also vanishes in this limit, $\lim_{t\to\infty} d_{\rm i}S/dt = 0$, and the stationary macrostate reached after the nonequilibrium transients is the equilibrium macrostate corresponding to the temperature, pressure, and chemical potentials of the environment. Since the system is not isolated, the entropy does not have to increase with time and the initial value of the entropy may be smaller or larger than its asymptotic value, as shown in Figure 1.2(b). For instance, the system may initially be hotter than its environment, in which case there will be a heat flux outgoing the system during the nonequilibrium transients, the system will thus cool, and its entropy will decrease from S'_0 to $S_\infty = S_{\rm eq}$.

Systems in Contact with Several Reservoirs

If the environment is composed of several energy or particle reservoirs at different fixed values of their temperature, pressure, and chemical potentials, the system in contact with these reservoirs cannot reach an equilibrium macrostate as long as these differences persist. Since arbitrarily large reservoirs keep their temperature, pressure, and chemical potentials, the system can be maintained in macrostates with persistent exchanges of energy or particles between the system and the different reservoirs. Remarkably, several types of macrostates are possible under nonequilibrium conditions. After some possible transitory relaxation, stationarity can be reached in the system. Again, since the system is not isolated, the initial value of the entropy may be smaller or larger than its asymptotic value S_∞, as depicted in Figure 1.2(b). In such a stationary macrostate, the entropy of the system remains stationary so that $dS/dt = 0$. Therefore, the second law and equation (1.14) imply that

$$\frac{d_{\rm i}S}{dt} = -\frac{d_{\rm e}S}{dt} > 0 \tag{1.15}$$

in the stationary macrostate. Consequently, the entropy produced inside the system is evacuated to the environment, thus keeping invariant the system entropy. Such macrostates are called *nonequilibrium steady states*. Since entropy is continuously produced, energy should be supplied in order to compensate energy dissipation and maintain these steady states.

In addition, there also exist macrostates that are nonstationary even after transients. Such macrostates may be oscillatory with periodic, quasiperiodic, or chaotic dynamical behavior. The latter is nonperiodic, manifesting sensitivity to initial conditions and dynamical randomness over long timescales, as in turbulence. In these regimes, the macrostates evolve with time towards attractors in the space of macrovariables because of dissipation. These attractors are limit cycles, tori, or fractals, whether the dynamical behavior is periodic, quasiperiodic, or chaotic (Bergé et al., 1984; Eckmann and Ruelle, 1985; Strogatz, 1994; Nicolis, 1995).

Systems with Time-Dependent Driving

Systems may also be driven out of equilibrium by time-dependent external forces. Examples are systems heated by electromagnetic waves or driven by the periodic motion of pistons. In such circumstances, the system cannot reach a stationary macrostate and its state variables remain time dependent.

1.4 Thermodynamics in Continuous Media

1.4.1 Balance Equations

In continuous media, the principles of thermodynamics are applied to every volume element d^3r of the macrosystem, which is here assumed to be nonrelativistic. This latter is described in terms of densities associated with the slowest observable quantities, which include the locally conserved quantities such as mass, energy, linear momentum, and possibly other variables such as particle numbers or order parameters. The set of these quantities depends on the continuous medium whether it is a fluid with one or several compounds, a liquid crystal, a crystal, a superfluid, a plasma, or something else. Since these systems differ by their compositions, the relevant variables will be different, but the breaking of continuous symmetries, for instance in liquid crystal, crystals, and superfluids, may introduce order parameters and extra slow modes called the Nambu–Goldstone modes that arise from the fast kinetic modes of normal fluids at phase transitions (Forster, 1975).

A continuous medium is described in terms of fields $x(\mathbf{r}, t)$ defined at any position $\mathbf{r} \in \mathbb{R}^3$ inside the system and any time $t \in \mathbb{R}$. The time evolution of some density x is ruled by the balance equation

$$\partial_t x + \nabla \cdot \boldsymbol{J}_x = \sigma_x, \tag{1.16}$$

where $\boldsymbol{J}_x$ is the associated current density and σ_x the corresponding production rate density. The current density has the units of the density x multiplied by a velocity or, equivalently, the units of the transported quantity X per unit surface and unit time.[5] Integrating the density x

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[5] Current densities are also called flows (Balescu, 1975; de Groot and Mazur, 1984).

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over some volume V that is assumed to be fixed in space, we obtain the amount of this quantity in this volume

$$X \equiv \int_V x \, d^3 r . \tag{1.17}$$

Carrying out the same integration for the balance equation (1.16), we get the time derivative of this quantity as

$$\frac{dX}{dt} = \frac{d_{\rm e}X}{dt} + \frac{d_{\rm i}X}{dt}, \tag{1.18}$$

where

$$\frac{d_{\rm e}X}{dt} = -\int_{\partial V} \boldsymbol{J}_x \cdot d\boldsymbol{\Sigma} \tag{1.19}$$

is the contribution due to the exchanges of the quantity X at the boundary ∂V of the system with the exterior ($d\boldsymbol{\Sigma}$ being the vector surface element) and where

$$\frac{d_{\rm i}X}{dt} = \int_V \sigma_x \, d^3 r \tag{1.20}$$

is the production rate of X inside the system. We thus recover the global form (1.1) at the basis of the formulation of thermodynamics.

If the quantity x is locally conserved, the production rate density is equal to zero, i.e., $\sigma_x = 0$.

In normal fluids, the fluid elements are advected by the motion of the fluid described by the velocity field $\mathbf{v}$. In every element of the fluid, the velocity is defined as the velocity of the center of mass of the element. Denoting $d\mathbf{P}$ to be the linear momentum in the fluid element of volume d^3r and mass dM, the velocity is thus defined as $\mathbf{v} \equiv d\mathbf{P}/dM$. Introducing the mass density $\rho \equiv dM/d^3r$ and the linear momentum density $\mathbf{g} \equiv d\mathbf{P}/d^3r$, the velocity is thus given by $\mathbf{v} = \mathbf{g}/\rho$. The advection contributes to the current density $\boldsymbol{J}_x$ associated with the density x according to

$$\boldsymbol{J}_x = x\mathbf{v} + \boldsymbol{\mathscr{J}}_x, \tag{1.21}$$

where $\boldsymbol{\mathscr{J}}_x$ is the rest of the current density due to the flow of x with respect to the center of mass of the fluid element, which is either identical or related to the corresponding diffusive or dissipative current density $\boldsymbol{\mathcal{J}}_x$.

Table 1.1 gives the different quantities that are relevant in normal fluids with chemical reactions (Prigogine, 1967; de Groot and Mazur, 1984). Every quantity with $\sigma_x = 0$ is locally conserved. This is the case in particular for mass, which thus obeys the well-known continuity equation. The local conservation of mass results from the balance equations of the different molecular species k because the diffusive current densities are defined with respect to the center of mass of every fluid element, so that $\sum_k m_k \boldsymbol{\mathcal{J}}_k = 0$, and because every chemical reaction conserves mass, $\sum_k m_k \nu_{kr} = 0$, where m_k is the mass of the molecules of species k and ν_{kr} the stoichiometric coefficient of species k in the reaction r of rate density w_r. We note that the local conservation of angular momentum implies that the

Table 1.1. *Normal fluids with chemical reactions: The relevant quantities, their density* x*, the rest* $\mathscr{J}_x$ *of the current density, and production rate density* σ_x*. Here,* $n_k \equiv dN_k/d^3r$ *denotes of the density of species* k *(also called concentration),* $\mathcal{J}_k$ *the corresponding diffusive current density,* ν_{kr} *the stoichiometric coefficient of species* k *in the reaction* r *of rate density* w_r*,* ρ *the mass density,* m_k *the mass of the particles of species* k*,* $\mathbf{g}$ *the linear momentum density,* $\mathbf{v}$ *the fluid velocity field,* P *the pressure tensor,* ϵ *the total energy density,* e *the internal energy density,* $\mathcal{J}_q$ *the heat current density,* s *the entropy density, and* $\mathcal{J}_s$ *the diffusive current density of entropy. The pressure tensor is composed of the hydrostatic pressure* p *multiplied by the* 3×3 *identity matrix* $\mathbf{1}$*, and its viscous part* $\mathbf{\Pi} \equiv \mathcal{J}_{\mathbf{g}}$.

Quantity	x	$\mathscr{J}_x \equiv \boldsymbol{J}_x - x\mathbf{v}$	σ_x
Number of particles k	n_k	$\mathcal{J}_k$	$\sum_r \nu_{kr} w_r$
Mass	$\rho = \sum_k m_k n_k$	0	0
Momentum	$\mathbf{g} = \rho\mathbf{v}$	$\mathsf{P} = p\,\mathbf{1} + \mathbf{\Pi}$	0
Energy	$\epsilon = \frac{\rho}{2}\mathbf{v}^2 + e$	$\mathsf{P} \cdot \mathbf{v} + \mathcal{J}_q$	0
Entropy	s	$\mathcal{J}_s$	$\sigma_s \geq 0$

pressure tensor is symmetric $\mathsf{P} = \mathsf{P}^{\mathrm{T}}$, where the superscript T denotes the transpose.[6] In the presence of external force fields, the balance equations of linear momentum and energy have nonvanishing source terms σ_x describing the force and work exerted by the resulting external force on the fluid element (de Groot and Mazur, 1984).

At every time t, the macrostate of a normal fluid with c components is determined by their densities $\{n_k(\mathbf{r},t)\}_{k=1}^{c}$, the velocity field $\mathbf{v}(\mathbf{r},t)$, and the temperature field $T(\mathbf{r},t)$, at every point $\mathbf{r}$ of the system. An alternative set of fields is given by the mass density $\rho(\mathbf{r},t)$, the fluid velocity, the temperature, and the mass fractions of the solute species because the mass fraction of the solvent can be deduced from them and the mass density. Since the temperature determines the internal energy, the time evolution of the fluid macrostate is ruled by $c + 4$ partial differential equations given by the balance equations for the particle densities, the linear momentum, and the energy. However, these balance equations do not yet form a closed set of partial differential equations because knowledge of the fluid properties is still missing.

1.4.2 Local Thermodynamic Equilibrium and Consequences

In order to determine the still missing properties in accordance with the second law, the hypothesis of local thermodynamic equilibrium is supposed to hold in every fluid element. Using the entropy density as thermodynamic potential, its variations satisfy the Gibbs relation

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[6] Because of the local conservation of linear momentum $\partial_t \mathbf{g} + \nabla \cdot \boldsymbol{J}_{\mathbf{g}} = 0$, the angular momentum density $\boldsymbol{\ell} = \mathbf{r} \times \mathbf{g}$ obeys the balance equation $\partial_t \boldsymbol{\ell} + \nabla \cdot \boldsymbol{J}_{\boldsymbol{\ell}} = \boldsymbol{\sigma}_{\boldsymbol{\ell}}$ with the angular momentum current density $\boldsymbol{J}_{\boldsymbol{\ell}} = \mathbf{r} \times \boldsymbol{J}_{\mathbf{g}}$ and the source density with components $(\boldsymbol{\sigma}_{\boldsymbol{\ell}})_i = -\sum_{jk} \epsilon_{ijk} P_{jk}$ expressed in terms of the Levi-Civita totally antisymmetric tensor such that $\epsilon_{ijk} = \epsilon_{jki} = -\epsilon_{ikj}$ and $\epsilon_{xyz} = +1$. Accordingly, the source density is equal to zero if the pressure tensor is symmetric, $P_{jk} = P_{kj}$. The assumption here is that there is no intrinsic angular momentum (spin), which should otherwise be included in the balance equation, leading to a possible antisymmetric part for the pressure tensor (de Groot and Mazur, 1984).