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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

$$dX = d_e X + d_i X. \quad (1.1)$$

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

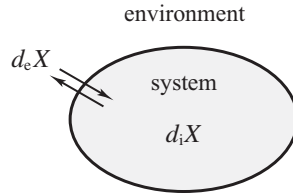


Figure 1.1 Schematic representation of a system in contact with its environment. Changes of the macrovariable X with the *exterior* of the system are denoted by $d_e X$ and $d_i X$ denotes those occurring within its *interior*.

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.,*

$$dE = d_e E + d_i E \quad \text{with} \quad d_i E = 0. \quad (1.2)$$

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 translations¹);
- angular momentum (by symmetry under rotations¹);
- electric charge (by local gauge symmetry²);
- leptonic number (by global symmetry³);
- baryonic number (by global symmetry³);

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 $d_i X = 0$, 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

$$dN_k = d_e N_k + d_i N_k \quad (1.3)$$

with $d_i N_k \neq 0$, 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 $d_i N_k = 0$ 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, $L_j = \sum_{k=1}^c l_{jk} N_k$, is nevertheless conserved, so that $d_i L_j = 0$, 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 $d_i N_k = 0$, 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 $dM = d_e M + d_i M$ with $d_i M = 0$, 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 $d_e E \neq 0$ but $d_e N_k = 0$. A system is said to be *open* if energy and matter are exchanged with its environment, i.e., if $d_e E \neq 0$ and $d_e N_k \neq 0$.

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*

$$dS = d_e S + d_i S \quad \text{with} \quad d_i S \geq 0. \quad (1.4)$$

The entropy production $d_i S$ is thus always nonnegative. The evolution or transformation undergone by the system is said to be *reversible* if $d_i S = 0$ and *irreversible* if $d_i S > 0$. The system remains at *thermodynamic equilibrium* if $d_i S = 0$ and it is *out of equilibrium* if $d_i S > 0$. In this latter case, there is a time asymmetry in the macroscopic description of the system. We note that $d_e S$ 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 $d_i S/dt = 0$, its (absolute) *temperature* is defined by differentiating the energy with respect to the entropy,

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

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 $k_B = 1.380649 \times 10^{-23}$ J/K. Accordingly, the entropy has the units of joule per kelvin (J/K). At equilibrium again, the (hydrostatic) *pressure* is defined as

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

and the *chemical potential* of species k as

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

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

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

when changing its entropy, its volume, and particle numbers. In equation (1.8), $dQ = T dS$ corresponds to the change of heat under the transformation. We note that other contributions may be included for instance from electromagnetism

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

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

$$dE|_{\text{surf}} = \gamma d\Sigma, \quad (1.10)$$

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:*

$$\lim_{T \rightarrow 0} S = 0. \quad (1.11)$$

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

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

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 $d_i S/dt > 0$.

Isolated Systems

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

$$\frac{dS}{dt} = \frac{d_i S}{dt} \geq 0. \quad (1.13)$$

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

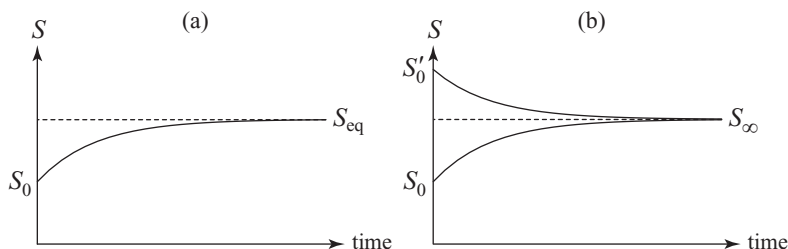


Figure 1.2 Possible time evolutions of the entropy towards an asymptotic stationary value in (a) an isolated system and (b) a nonisolated system.

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 $S_{\text{univ}} = S_{\text{sys}} + S_{\text{env}}$, 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 $dS_{\text{univ}}/dt = d_i S_{\text{univ}}/dt \geq 0$ 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 $dS_{\text{sys}}/dt = d_e S_{\text{sys}}/dt + d_i S_{\text{sys}}/dt$ and $dS_{\text{env}}/dt = d_e S_{\text{env}}/dt + d_i S_{\text{env}}/dt$. Moreover, the amounts of entropy exchanged between the system and its environment and *vice versa* are opposite to each other: $d_e S_{\text{sys}}/dt = -d_e S_{\text{env}}/dt$. Therefore, the sum of the entropies produced inside the system and its environment is equal to the one produced in the universe: $d_i S_{\text{univ}}/dt = d_i S_{\text{sys}}/dt + d_i S_{\text{env}}/dt \geq 0$. We note that the system of interest is often significantly smaller than the universe, in which case $d_i S_{\text{univ}}/dt \gg d_i S_{\text{sys}}/dt \geq 0$.

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

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad (1.14)$$

with some entropy exchange rate $d_e S/dt$. 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 $\lim_{t \rightarrow \infty} S = S_\infty$. Since equilibrium is global in this stationary macrostate, there is no entropy exchange between the system and its environment, $\lim_{t \rightarrow \infty} d_e S/dt = 0$. Therefore, the entropy production rate also vanishes in this limit, $\lim_{t \rightarrow \infty} d_i S/dt = 0$, 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 $S_\infty = S_{\text{eq}}$.

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

$$\frac{d_i S}{dt} = -\frac{d_e S}{dt} > 0 \quad (1.15)$$

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

$$\partial_t x + \nabla \cdot \mathbf{J}_x = \sigma_x, \quad (1.16)$$

where \mathbf{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

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

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

$$X \equiv \int_V x d^3r. \quad (1.17)$$

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

$$\frac{dX}{dt} = \frac{d_e X}{dt} + \frac{d_i X}{dt}, \quad (1.18)$$

where

$$\frac{d_e X}{dt} = - \int_{\partial V} \mathbf{J}_x \cdot d\boldsymbol{\Sigma} \quad (1.19)$$

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

$$\frac{d_i X}{dt} = \int_V \sigma_x d^3r \quad (1.20)$$

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 \mathbf{J}_x associated with the density x according to

$$\mathbf{J}_x = x\mathbf{v} + \mathcal{J}_x, \quad (1.21)$$

where \mathcal{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 \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 $\sum_k m_k \mathcal{J}_k = 0$, 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 \mathcal{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, v_{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, \mathbf{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 $\mathbf{\Pi} \equiv \mathcal{J}_g$.*

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

pressure tensor is symmetric $\mathbf{P} = \mathbf{P}^T$, 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

⁶ Because of the local conservation of linear momentum $\partial_t \mathbf{g} + \nabla \cdot \mathbf{J}_g = 0$, the angular momentum density $\boldsymbol{\ell} = \mathbf{r} \times \mathbf{g}$ obeys the balance equation $\partial_t \boldsymbol{\ell} + \nabla \cdot \mathbf{J}_\ell = \boldsymbol{\sigma}_\ell$ with the angular momentum current density $\mathbf{J}_\ell = \mathbf{r} \times \mathbf{J}_g$ and the source density with components $(\boldsymbol{\sigma}_\ell)_i = -\sum_{jk} \epsilon_{ijk} P_{jk}$ 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).

Table 1.2. *The irreversible processes in normal fluids, their affinity \mathcal{A}_α , their associated diffusive current density \mathcal{J}_α , their space character, and the time-reversal parity of their affinity (Prigogine, 1967; Nicolis, 1979; de Groot and Mazur, 1984). The symmetrized gradient of the velocity field is denoted by $(\nabla \mathbf{v})^S = (\nabla \mathbf{v} + \nabla \mathbf{v}^T)/2$ and $\overset{\circ}{\Pi} = \Pi - p \mathbf{1}$ denotes the traceless part of the viscous pressure tensor $\Pi = \mathbf{P} - p \mathbf{1}$ with $\Pi = (\text{tr } \Pi)/3$, T the temperature, μ_k the chemical potential of the species k , and ν_{kr} the stoichiometric coefficient of the species k in the reaction r of rate w_r .*

Irreversible Process	\mathcal{A}_α	\mathcal{J}_α	Space	Time
Shear viscosity	$\overset{\circ}{\mathbf{A}}_{\mathbf{g}} = -\left[(\nabla \mathbf{v})^S - \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1}\right]/T$	$\overset{\circ}{\mathbf{J}}_{\mathbf{g}} = \overset{\circ}{\Pi}$	Tensor	Odd
Dilational viscosity	$\mathcal{A}_{\mathbf{g}} = -(\nabla \cdot \mathbf{v})/T$	$\mathcal{J}_{\mathbf{g}} = \Pi$	Scalar	Odd
Reaction r	$\mathcal{A}_r = -\sum_k \mu_k \nu_{kr}/T$	$\mathcal{J}_r = w_r$	Scalar	Even
Heat conductivity	$\mathcal{A}_q = \nabla(1/T)$	\mathcal{J}_q	Vector	Even
Diffusion of species k	$\mathcal{A}_k = \nabla(-\mu_k/T)$	\mathcal{J}_k	Vector	Even

$$ds = \frac{1}{T} de - \sum_{k=1}^c \frac{\mu_k}{T} dn_k, \tag{1.22}$$

as shown in Appendix A. Accordingly, the entropy density is given by the equilibrium function $s = s(e, \{n_k\}_{k=1}^c)$ locally defined at every point and every time in the fluid. Therefore, the hypothesis of local thermodynamic equilibrium assumes that the entropy density depends on the densities of the quantities relevant to the continuous medium, $s(\{x\})$. However, this hypothesis may have to be extended to include the gradients of some densities, e.g., taking $s(\{x\}, \{\nabla x\})$, for inhomogeneous fluids (Penrose and Fife, 1990; Wang et al., 1993), or some systems with chemical reactions (Mátyás and Gaspard, 2005). The inclusion of gradients leads in particular to the Ginzburg–Landau theory of the free-energy functional density (Landau and Lifshitz, 1980a,b; Evans, 1979).

According to equation (1.22), which is based on the hypothesis of local thermodynamic equilibrium in normal fluids, the balance equations (1.16) for the particle and energy densities allow us to deduce the balance equation for the entropy density, as shown in Appendix A. This equation has the form of equation (1.16) with $x = s$, with the diffusive current density of entropy given by

$$\mathcal{J}_s = \frac{1}{T} \mathcal{J}_q - \sum_{k=1}^c \frac{\mu_k}{T} \mathcal{J}_k \tag{1.23}$$

in terms of the heat current density and the diffusive current densities of the particles, and the entropy production rate density

$$\sigma_s = \sum_{\alpha} \mathcal{A}_{\alpha} \mathcal{J}_{\alpha} \geq 0 \tag{1.24}$$

expressed with the affinities \mathcal{A}_{α} and current densities \mathcal{J}_{α} of the irreversible processes taking place in the system. These latter quantities are given in Table 1.2 for normal fluids. The entropy production rate density (1.24) should always be nonnegative in accordance with

the second law. Integrating the balance equation of the entropy density s recovers the global balance equation (1.14) with the entropy exchange and production rates given by equations (1.19) and (1.20) for $X = S$ and $x = s$. Entropy is conserved if the irreversible processes are negligible.

We note that the diffusive current densities of particle species should satisfy the mass conservation condition $\sum_{k=1}^c m_k \mathcal{J}_k = 0$. Consequently, one of these current densities can be related to the other ones:

$$\mathcal{J}_c = - \sum_{k=1}^{c-1} \frac{m_k}{m_c} \mathcal{J}_k. \quad (1.25)$$

The species c is often taken as the solvent and the other ones as the solutes. The total contribution of diffusion to the entropy production rate density (1.24) can thus be expressed in terms of the mutual diffusion of the solute species in the solvent as

$$\sum_{k=1}^c \mathcal{A}_k \mathcal{J}_k = \sum_{k=1}^{c-1} \mathcal{A}'_k \mathcal{J}_k, \quad (1.26)$$

by redefining the affinities according to

$$\mathcal{A}'_k \equiv \nabla \left(-\frac{\mu'_k}{T} \right) \quad \text{with} \quad \mu'_k \equiv \mu_k - \frac{m_k}{m_c} \mu_c. \quad (1.27)$$

These affinities are the thermodynamic forces of mutual diffusion of the solute species k with respect to the solvent c . Since these redefinitions are linear, they can be performed every time the constraint of mass conservation is met.

1.4.3 Equilibrium and Nonequilibrium Constitutive Relations

Closing the partial differential equations of the fluid first requires the knowledge of two equilibrium equations of state, one for the pressure $p(T, \{n_k\}_{k=1}^c)$ and another one for the internal energy $e(T, \{n_k\}_{k=1}^c)$. These equations of state are the equilibrium properties for the material composing the system.

Besides this, we also need the nonequilibrium properties given by some relations between the affinities and the current densities in Table 1.2. These nonequilibrium constitutive relations should satisfy the symmetries of the continuous medium. For this purpose, we use the Curie symmetry principle (Curie, 1894; Prigogine, 1967). Since normal fluids are isotropic, their properties are symmetric under continuous spatial rotations, so that the tensorial character of the affinities \mathcal{A}_α and current densities \mathcal{J}_α should be respected. In crystals, the space group of the lattice should determine the relations between the affinities and the current densities. Moreover, the underlying microscopic mechanics is symmetric under time reversal according to electrodynamics. Therefore, the relations between the affinities and the current densities should also satisfy the consequences of this discrete symmetry called *microreversibility*.

The nonequilibrium constitutive relations may be linear or nonlinear.

Linear Relations

Typically, the relations are linear if the gradients of the macrofields extend over distances $\|(\nabla x)/x\|^{-1}$ larger than the mean free path of the particles in the fluid. This is usually the case for transport properties such as viscosity, heat conduction, and particle diffusion. Under such circumstances, the current densities are linearly related to the affinities as

$$\mathcal{J}_\alpha = \sum_{\beta} \mathcal{L}_{\alpha,\beta} \mathcal{A}_\beta \quad (1.28)$$

with some linear response coefficients $\mathcal{L}_{\alpha,\beta}$ characterizing the nonequilibrium properties of the fluid. In order to satisfy the Curie symmetry principle, such relations may only exist between current densities and affinities of the same tensorial character.

Since there is only one quantity given by a tensor, the traceless part of the viscous pressure is related to the corresponding affinity by $\overset{\circ}{\Pi} = \overset{\circ}{\mathcal{L}}_{\mathbf{g},\mathbf{g}} \overset{\circ}{\mathbf{A}}_{\mathbf{g}}$ where the linear response coefficient is proportional to the coefficient η of shear viscosity by $\overset{\circ}{\mathcal{L}}_{\mathbf{g},\mathbf{g}} = 2T\eta$. Among the scalar quantities, the direct linear relation $\Pi = \mathcal{L}_{\mathbf{g},\mathbf{g}} \mathcal{A}_{\mathbf{g}}$ holds in the absence of chemical reactions, which defines the dilational or bulk viscosity $\zeta \equiv \mathcal{L}_{\mathbf{g},\mathbf{g}}/T$. Consequently, the viscous part of the pressure tensor is given by

$$\Pi = -\eta \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T - \frac{2}{3} \nabla \cdot \mathbf{v} \mathbf{1} \right) - \zeta \nabla \cdot \mathbf{v} \mathbf{1}. \quad (1.29)$$

For the vectorial quantities, the direct relations $\mathcal{J}_q = \mathcal{L}_{q,q} \mathcal{A}_q$ and $\mathcal{J}_k = \mathcal{L}_{k,k} \mathcal{A}_k$ give, respectively,

$$\text{Fourier's law:} \quad \mathcal{J}_q = -\kappa \nabla T \quad (1.30)$$

with the coefficient of heat conductivity $\kappa \equiv \mathcal{L}_{q,q}/T^2$, and

$$\text{Fick's law:} \quad \mathcal{J}_k = -\mathcal{D}_k \nabla n_k \quad (1.31)$$

with the coefficient of diffusion $\mathcal{D}_k \equiv (\mathcal{L}_{k,k}/T)(\partial \mu_k / \partial n_k)_T$.

Beyond the direct effects described by the coefficients $\mathcal{L}_{\alpha,\alpha}$, there also exists the possibility of thermodiffusive coupling between heat conduction and particle transport with the Soret effect relating \mathcal{J}_k to \mathcal{A}_q and the reciprocal Dufour effect relating \mathcal{J}_q to \mathcal{A}_k , as well as possible cross-diffusion expressed by linear relations between \mathcal{J}_k and \mathcal{A}_l with $k \neq l$ (de Groot and Mazur, 1984; Haase, 1969). These effects are described by the coefficients $\mathcal{L}_{\alpha,\beta}$ with $\alpha \neq \beta$, coupling together the affinity and the current density of different processes. These couplings often play essential roles because they make possible the driving of a process by the thermodynamic force of another process, as in thermoelectric and mechanochemical effects. They may thus induce energy transduction of different kinds. For such couplings between different transport processes, microreversibility leads to the Onsager–Casimir reciprocal relations, as discussed in the following chapters.

With the linear relations (1.28), the entropy production rate density (1.24) is given by the quadratic form

$$\sigma_s = \sum_{\alpha\beta} \mathcal{L}_{\alpha,\beta}^S \mathcal{A}_\alpha \mathcal{A}_\beta \geq 0, \quad \text{where} \quad \mathcal{L}_{\alpha,\beta}^S \equiv \frac{1}{2}(\mathcal{L}_{\alpha,\beta} + \mathcal{L}_{\beta,\alpha}) \quad (1.32)$$

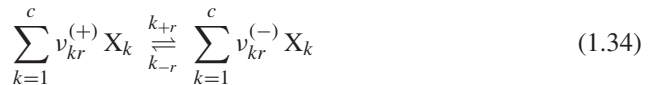
forms the symmetrized matrix of linear response coefficients. According to the second law, this matrix should be nonnegative, i.e., $(\mathcal{L}_{\alpha,\beta}^S) \geq 0$. Therefore, the transport coefficients such as the shear and dilational viscosities, the heat conductivity, and the diffusion coefficients should be nonnegative: $\eta \geq 0$, $\zeta \geq 0$, $\kappa \geq 0$, and $\mathcal{D}_k \geq 0$. In the case of coupling between two processes $\alpha, \beta = 1, 2$, the symmetrized linear response coefficients should satisfy the condition $\mathcal{L}_{1,1}^S \mathcal{L}_{2,2}^S \geq (\mathcal{L}_{1,2}^S)^2$ in order for the entropy production to be always nonnegative.

Nonlinear Relations

However, if the macrofields rapidly vary over distances comparable to or smaller than the mean free path of the particles, the constitutive relations are nonlinear and of the general form

$$\mathcal{J}_\alpha = \sum_{\beta} \mathcal{L}_{\alpha,\beta} \mathcal{A}_\beta + \frac{1}{2} \sum_{\beta\gamma} \mathcal{M}_{\alpha,\beta\gamma} \mathcal{A}_\beta \mathcal{A}_\gamma + \frac{1}{6} \sum_{\beta\gamma\delta} \mathcal{N}_{\alpha,\beta\gamma\delta} \mathcal{A}_\beta \mathcal{A}_\gamma \mathcal{A}_\delta + \dots \quad (1.33)$$

with nonlinear response coefficients $\mathcal{M}_{\alpha,\beta\gamma}$, $\mathcal{N}_{\alpha,\beta\gamma\delta}$, ... This is the case, in particular, for chemical reactions because their reactants and products are separated by molecular distances corresponding to the rearrangement of atoms in the reaction. Therefore, the relations between the reaction rates w_r and the associated affinities \mathcal{A}_r are typically nonlinear. In dilute solutions, the rates of elementary chemical reactions⁷ are proportional to the densities of all the species incoming the reactive events, which is the basis of the so-called *mass action law* (Pauling, 1970; Moore, 1972; Berry et al., 1980; Kondepudi and Prigogine, 1998). Accordingly, the elementary chemical reaction



between the molecular species $\{X_k\}_{k=1}^c$ has the net rate density

$$w_r = w_{+r} - w_{-r} = k_{+r} \prod_{k=1}^c \left(\frac{n_k}{n^0}\right)^{v_{kr}^{(+)}} - k_{-r} \prod_{k=1}^c \left(\frac{n_k}{n^0}\right)^{v_{kr}^{(-)}} \quad (1.35)$$

expressed in terms of the rate constants $k_{\pm r}$ and the numbers $v_{kr}^{(\pm)}$ of molecules of species k respectively incoming the forward and reverse reactions, as well as the standard density n^0

⁷ An elementary reaction is associated with a single barrier or transition state separating reactants from products, as opposed to a reaction that goes through several barriers or transition states. Every barrier or transition state forms a bottleneck where the process is slowed down and the transition rate is lower than the pace of dynamics in the potential wells of reactants and products. The crossing of the barrier may result from thermal activation or quantum tunneling. An overall reaction or reaction network should be decomposed into elementary reactions before evaluating the entropy production.

equal to one mole per liter. We note that the stoichiometric coefficient of the species k in the reaction (1.34) is given by $v_{kr} = v_{kr}^{(-)} - v_{kr}^{(+)}$. Since the chemical potential of a solute in a dilute solution is given by

$$\mu_k = \mu_k^0 + k_B T \ln \frac{n_k}{n^0}, \quad (1.36)$$

where k_B is Boltzmann's constant, the net rate density depends on the affinity $\mathcal{A}_r = k_B \ln(w_{+r}/w_{-r})$ of the reaction according to the nonlinear relations

$$w_r = w_{+r} \left(1 - e^{-\mathcal{A}_r/k_B}\right) = w_{-r} \left(e^{\mathcal{A}_r/k_B} - 1\right). \quad (1.37)$$

The contribution of the elementary reaction r to the entropy production rate density is given by

$$\sigma_{s,r} = \mathcal{A}_r w_r = k_B (w_{+r} - w_{-r}) \ln \frac{w_{+r}}{w_{-r}} \geq 0, \quad (1.38)$$

which is always nonnegative since the rate constants $k_{\pm r}$ and the rate densities $w_{\pm r}$ are nonnegative. At chemical equilibrium, the rate vanishes together with the affinity because there is *detailed balance* for every reaction r , resulting in equality between the rates of the forward and reversed reactions, $w_{+r} = w_{-r}$ (Wegscheider, 1901; Fowler, 1929). As a consequence, the net reaction rate (1.35) is equal to zero at equilibrium, which implies that the equilibrium densities of the reacting species should satisfy the Guldberg–Waage condition

$$\prod_{k=1}^c \left(\frac{n_k}{n^0}\right)_{\text{eq}}^{v_{kr}} = K_r \quad (1.39)$$

with the equilibrium constant $K_r \equiv k_{+r}/k_{-r}$ (Guldberg and Waage, 1879; Moore, 1972). Since the affinity of the reaction is equal to zero at equilibrium $\mathcal{A}_r = 0$, the equilibrium values of the chemical potentials should obey the identity $\sum_{k=1}^c \mu_{k,\text{eq}} v_{kr} = 0$. We note that, close to chemical equilibrium, the reaction rate is approximately proportional to the affinity, $w_r \simeq \mathcal{L}_{r,r} \mathcal{A}_r$, which defines the linear response coefficient $\mathcal{L}_{r,r} = w_{+r}/k_B$. Beyond, i.e., for larger values of the affinity, we should include nonlinear terms, obtained with the Taylor expansion (1.33) for equation (1.37). Similar nonlinear relations also exist in diodes and transistors where electron and hole densities sharply vary across the junctions at the core of these nonlinear electric devices. We also note that, in virtue of Curie's symmetry principle, the divergence of the velocity field may contribute to the reaction rates and, reciprocally, the chemical reactions may contribute to the scalar component of the viscous pressure tensor (de Groot and Mazur, 1984; Haase, 1969).

Using these equilibrium and nonequilibrium constitutive relations, the balance equations can be closed and the fluid macrofields may be obtained by solving their partial differential equations with the boundary conditions applied to the system. The balance equation for linear momentum leads to the Navier–Stokes equations, while the balance equation for energy leads to the heat equation for the temperature. Several paradigmatic examples will be presented below. Beyond normal fluids, similar considerations are known for the different bulk phases of matter (Martin et al., 1972; Fleming and Cohen, 1976), as well as for active

matter (Jülicher et al., 2018). Moreover, nonequilibrium thermodynamics can be extended to systems with two bulk phases separated by an interface, as shown in Section A.9.

1.5 Hydrodynamics and Chemohydrodynamics

1.5.1 Hydrodynamics in One-Component Fluids

In one-component fluids, the local conservation of mass leads to the continuity equation

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (1.40)$$

According to Tables 1.1 and 1.2, the balance equation (1.16) for linear momentum combined with the continuity equation (1.40) and the viscous pressure tensor (1.29) gives the Navier–Stokes equations for fluid mechanics,

$$\rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \eta \nabla^2 \mathbf{v} + \left(\zeta + \frac{\eta}{3} \right) \nabla (\nabla \cdot \mathbf{v}), \quad (1.41)$$

assuming that the viscosity coefficients do not depend on the densities so that $\nabla \eta = \nabla \zeta = 0$.

If the viscosity coefficients are equal to zero ($\eta = \zeta = 0$), we recover the Euler equations of hydrodynamics where fluid entropy is conserved and which thus describe a fluid without dissipation. If the fluid is incompressible, its mass density is constant in time and the continuity equation reduces to the constraint $\nabla \cdot \mathbf{v} = 0$, so that the property of dilational viscosity ζ does not exist in an incompressible fluid.

Furthermore, the continuity and Navier–Stokes equations should be coupled to the heat equation for the temperature field (see Appendix A).

1.5.2 Chemohydrodynamics in Multicomponent Fluids

Reactions may occur in multicomponent fluids. If the heat of reactions is negligible, the fluid may be supposed to be isothermal. Moreover, if the fluid is at rest, the velocity field \mathbf{v} is equal to zero, the Navier–Stokes equations are satisfied, and the continuity equation implies that the mass density is constant in time. Therefore, the quantities evolving in such systems are the particle densities or concentrations of the different species reacting in the system. Since the different particle species $\{k\}$ composing the system may be transported by diffusion and transformed by the reactions $\{r\}$, the evolution is ruled by diffusion–reaction equations

$$\partial_t n_k = \mathcal{D}_k \nabla^2 n_k + \sum_r v_{kr} w_r (\{n_l\}_{l=1}^c) \quad (1.42)$$

under the assumptions that the diffusion coefficients have a negligible dependence on the densities such that $\nabla \mathcal{D}_k = 0$ and cross-diffusion can also be neglected.

As an example, we have the following diffusion–reaction equation for the density $n = n_X$ of the species X generated by the autocatalytic reaction

$$X \stackrel{k_+}{\rightleftharpoons} 2X: \quad \partial_t n = D \nabla^2 n + k_+ n - k_- n^2, \tag{1.43}$$

which is nonlinear because of the autocatalytic character of the reaction. This equation describes the Verhulst model of population dynamics (Nicolis, 1995).

If the reactions are exothermic or endothermic, the diffusion–reaction equations should be coupled to the heat equation (see Appendix A).

1.6 Hydrodynamic Modes of Relaxation to Equilibrium

1.6.1 Hydrodynamic Modes in One-Component Fluids

As previously mentioned, the second law of thermodynamics predicts the relaxation towards equilibrium in an isolated system. This system can be considered as a one-component fluid of infinite extension in space. The equilibrium macrostate corresponds to a fluid at rest with zero velocity, uniform temperature T , uniform pressure p , and thus uniform mass density ρ . The hydrodynamic modes are the solutions of the fluid equations of motion corresponding to small deviations from equilibrium. Linearizing the continuity equation, the Navier–Stokes equations, and the balance equation of entropy around equilibrium given in Appendix A, we obtain the following set of partial differential equations for the deviations in the mass density $\delta\rho$, the entropy per unit mass $\delta s = \delta(s/\rho)$, and the fluid velocity $\delta\mathbf{v}$:

$$\partial_t \delta\rho = -\rho \nabla \cdot \delta\mathbf{v}, \tag{1.44}$$

$$\partial_t \delta s = \frac{\kappa}{\rho T} \nabla^2 \delta T, \tag{1.45}$$

$$\partial_t \delta\mathbf{v} = -\frac{1}{\rho} \nabla \delta p + \frac{\eta}{\rho} \nabla^2 \delta\mathbf{v} + \frac{1}{\rho} \left(\zeta + \frac{\eta}{3} \right) \nabla(\nabla \cdot \delta\mathbf{v}). \tag{1.46}$$

The hydrodynamic modes of relaxation to equilibrium are spatially periodic solutions with an exponential dependence on time of the form $\delta\rho, \delta s, \delta\mathbf{v} \sim \exp(i \mathbf{q} \cdot \mathbf{r} + zt)$ with $i = \sqrt{-1}$. The dispersion relations of these modes give the dependence of their exponential rate z on their wave number $q = \|\mathbf{q}\|$ and they are obtained by solving equations (1.44)–(1.46) (Balescu, 1975; Résibois and De Leener, 1977). As shown in Appendix A, the dispersion relations of the hydrodynamic modes are given by

$$2 \text{ shear modes: } z = -\frac{\eta}{\rho} q^2, \tag{1.47}$$

$$1 \text{ heat mode: } z = -\frac{\kappa}{\rho c_p} q^2 + O(q^3), \tag{1.48}$$

$$2 \text{ sound modes: } z = \mp i v_1 q - \frac{1}{2\rho} \left[\zeta + \frac{4}{3} \eta + \kappa \left(\frac{1}{c_v} - \frac{1}{c_p} \right) \right] q^2 + O(q^3), \tag{1.49}$$

in terms of the sound velocity,

$$v_1 \equiv \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_s}, \tag{1.50}$$

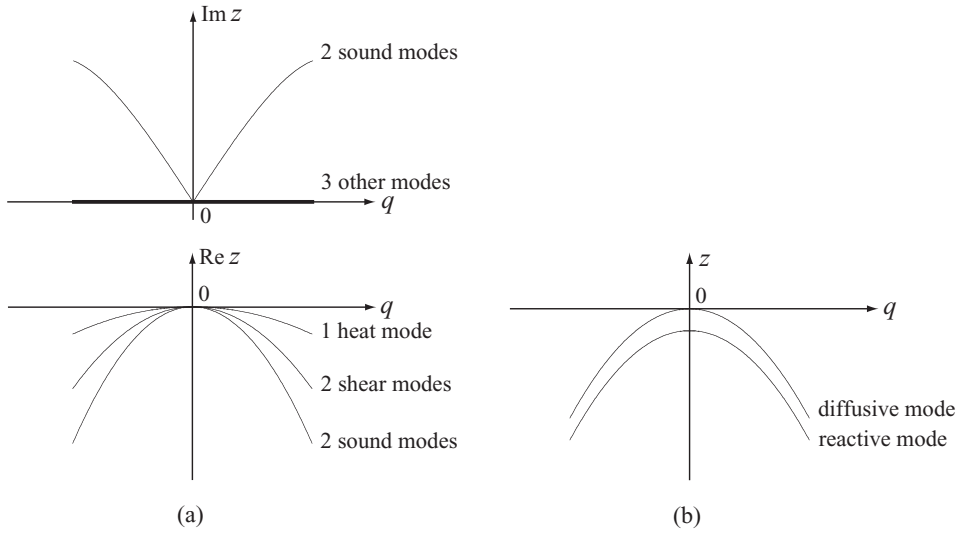


Figure 1.3 (a) Imaginary and real parts of the dispersion relations (1.47)–(1.49) for the five hydrodynamic modes in a normal fluid with one component. (b) Dispersion relations of the diffusive and reactive modes (1.54)–(1.55) for the reaction of isomerization $A \rightleftharpoons B$ taking place in an isothermal fluid at rest.

the heat capacities per unit mass at constant volume and pressure,

$$c_v \equiv T \left(\frac{\partial T}{\partial \mathfrak{s}} \right)_\rho^{-1} \quad \text{and} \quad c_p \equiv T \left(\frac{\partial T}{\partial \mathfrak{s}} \right)_p^{-1}, \quad (1.51)$$

and the transport coefficients η , ζ , and κ . The shear modes are transverse to the wave vector \mathbf{q} , while the heat and sound modes are longitudinal.⁸

The dispersion relations of the five modes are shown in Figure 1.3(a). All of them are vanishing with the wave number q since the five modes are associated with the five conserved quantities, namely, mass, energy, and the three components of linear momentum. The two shear modes and the heat mode are diffusive, while the two sound modes are propagating. They are all damped because the transport properties, i.e., the viscosities and the heat conductivity, dissipate energy. Consequently, the deviations given by the linear superpositions of these five modes undergo relaxation towards equilibrium. We note that this relaxation is here expressed in terms of the transport coefficients. If the latter are equal to zero, there is no energy dissipation and the fluid flow is isoentropic.

⁸ These results hold if the wavelength, $\lambda = 2\pi/q$, of the deviations is larger than the mean free path, under which circumstances the particles are interacting. Nevertheless, the ideal gas law may still be used (after expressing the pressure in terms of the entropy per unit mass) as long as the mean free path is larger than the range of interaction between the particles. In this regard, the sound velocity (1.50) is the feature of interacting particles.

1.6.2 The Relaxation Modes in Diffusion–Reaction Systems

In fluids with several components but no reaction, there exist extra hydrodynamic modes associated with the mutual diffusion between the different species. There are as many extra modes as there are solutes in the solvent. The dispersion relations of these extra modes are also vanishing with the wave number q because of the conservation of species in the absence of chemical reactions.

However, this is no longer the case in the presence of reactions, as shown by the following example. We consider the isothermic reaction of isomerization, $A \xrightleftharpoons[k_-]{k_+} B$, between two solute species A and B. The molecules A and B are diffusing in a solvent of inert molecules, the whole fluid being at rest. This system is a ternary mixture in which we expect five standard hydrodynamic modes plus two modes of mutual diffusion in the absence of reaction. For simplicity, the fluid is assumed to be at rest with a uniform temperature. If cross-diffusion is neglected, the system can be modeled by the two coupled diffusion–reaction equations:

$$\partial_t n_A = \mathcal{D}_A \nabla^2 n_A - k_+ n_A + k_- n_B, \quad (1.52)$$

$$\partial_t n_B = \mathcal{D}_B \nabla^2 n_B + k_+ n_A - k_- n_B. \quad (1.53)$$

Supposing that the deviations with respect to uniform densities behave as $\delta n_A, \delta n_B \sim \exp(i \mathbf{q} \cdot \mathbf{r} + zt)$, we obtain two dispersion relations:

$$1 \text{ diffusive mode: } z = -\mathcal{D} q^2 + O(q^4), \quad (1.54)$$

$$1 \text{ reactive mode: } z = -k_+ - k_- - \mathcal{D}_r q^2 + O(q^4), \quad (1.55)$$

with the diffusion coefficients

$$\mathcal{D} \equiv \frac{k_+ \mathcal{D}_B + k_- \mathcal{D}_A}{k_+ + k_-} \quad \text{and} \quad \mathcal{D}_r \equiv \frac{k_+ \mathcal{D}_A + k_- \mathcal{D}_B}{k_+ + k_-}. \quad (1.56)$$

These dispersion relations are depicted in Figure 1.3(b).

The dispersion relation of the diffusive mode is vanishing with the wave number q , because of the conservation of the total number of molecules A and B. However, the dispersion relation of the reactive mode is not vanishing because the reaction breaks the separate conservations of the molecule numbers of the two species. We notice that the dispersion relation (1.55) of the reactive mode satisfies $z(q = 0) = 0$ if the reaction rates vanish, i.e., $k_+ = k_- = 0$, in which case the ternary mixture has two diffusive modes in addition to its five standard hydrodynamic modes, as expected. Accordingly, we conclude that some hydrodynamic diffusive modes become kinetic modes with $z(q = 0) \neq 0$ in reacting systems. These reactive modes may evolve over timescales ranging from femtoseconds (for the fastest chemical reactions) to eons.

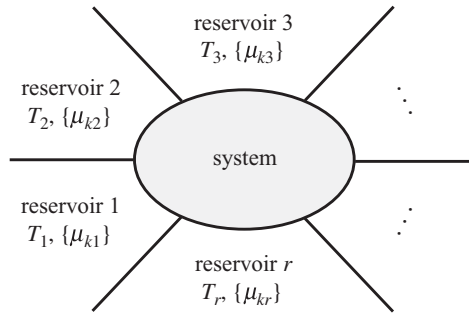


Figure 1.4 Schematic representation of a system in contact with r reservoirs at fixed temperatures T_j and chemical potentials $\{\mu_{kj}\}$.

1.7 Nonequilibrium Steady States

1.7.1 From Local to Global Affinities

Let us consider an open system formed by a solution at rest ($\mathbf{v} = 0$) and surrounded by an environment composed of several heat or particle reservoirs $j = 1, 2, \dots, r$ at fixed temperatures T_j and chemical potentials $\{\mu_{kj}\}_{k=1}^c$, as shown in Figure 1.4.

We suppose that there is no reaction going on in the system and its environment. If the reservoirs have different temperatures and chemical potentials, the equilibrium conditions are not satisfied, so the system is out of equilibrium and crossed by fluxes of energy and/or matter. After some time, the system evolves towards a nonequilibrium steady state where the macrovariables take invariant values, in particular, $\partial_t T = 0$ and $\partial_t n_k = 0$. Accordingly, the balance equations for energy and particle numbers reduce to $\nabla \cdot \mathcal{J}_q = 0$ and $\nabla \cdot \mathcal{J}_k = 0$ in the nonequilibrium steady state. The entropy production rate is thus given by

$$\frac{d_i S}{dt} = \int_V \left(\mathcal{A}_q \cdot \mathcal{J}_q + \sum_{k=1}^c \mathcal{A}_k \cdot \mathcal{J}_k \right) d^3 r \geq 0, \tag{1.57}$$

in terms of the local affinities $\mathcal{A}_q = \nabla(1/T)$ and $\mathcal{A}_k = \nabla(-\mu_k/T)$. Substituting these expressions back into equation (1.57) and integrating by parts, the entropy production rate becomes

$$\frac{d_i S}{dt} = \int_V \left[\nabla \cdot \left(\frac{1}{T} \mathcal{J}_q \right) - \underbrace{\frac{1}{T} \nabla \cdot \mathcal{J}_q}_{=0} - \sum_{k=1}^c \nabla \cdot \left(\frac{\mu_k}{T} \mathcal{J}_k \right) + \sum_{k=1}^c \frac{\mu_k}{T} \underbrace{\nabla \cdot \mathcal{J}_k}_{=0} \right] d^3 r \geq 0. \tag{1.58}$$

Using the conditions of stationarity and the divergence theorem, the volume integral is reduced to a surface integral over the boundary ∂V of the system

$$\frac{d_i S}{dt} = \int_{\partial V} \left(\frac{1}{T} \mathcal{J}_q - \sum_{k=1}^c \frac{\mu_k}{T} \mathcal{J}_k \right) \cdot d\boldsymbol{\Sigma} \geq 0, \tag{1.59}$$

where $d\boldsymbol{\Sigma}$ is a vector surface element pointing towards the exterior of the volume V . Now, we notice that the boundary is composed of several parts, $\partial V = \cup_{j=1}^r \partial_j V$, each one in

contact with one reservoir. On the part $\partial_j V$ of the boundary, the temperature and the chemical potentials are, respectively, fixed at the values T_j and $\{\mu_{kj}\}_{k=1}^c$ of the corresponding reservoir. Therefore, equation (1.59) can be written as

$$\frac{d_i S}{dt} = \sum_{j=1}^r \left(-\frac{1}{T_j} J_{qj} + \sum_{k=1}^c \frac{\mu_{kj}}{T_j} J_{kj} \right) \geq 0 \tag{1.60}$$

in terms of the surface integrals of the heat and particle current densities that are *incoming* the system from the reservoir j :

$$J_{qj} \equiv - \int_{\partial_j V} \mathcal{J}_q \cdot d\Sigma \quad \text{and} \quad J_{kj} \equiv - \int_{\partial_j V} \mathcal{J}_k \cdot d\Sigma. \tag{1.61}$$

These quantities are the current intensities or, more simply, the currents. By conservation of energy and particle numbers (since there is no reaction), we have that

$$\sum_{j=1}^r J_{qj} = 0 \quad \text{and} \quad \sum_{j=1}^r J_{kj} = 0. \tag{1.62}$$

Accordingly, the current from one reservoir is determined by the currents from all the other reservoirs. Taking the reservoir $j = r$ as reference, the expression (1.60) finally becomes

$$\frac{1}{k_B} \frac{d_i S}{dt} = \sum_{j=1}^{r-1} \left(A_{qj} J_{qj} + \sum_{k=1}^c A_{kj} J_{kj} \right) \geq 0 \tag{1.63}$$

in terms of the global affinities respectively defined as

$$\text{thermal affinity:} \quad A_{qj} \equiv \frac{1}{k_B T_r} - \frac{1}{k_B T_j}, \tag{1.64}$$

$$\text{chemical affinity:} \quad A_{kj} \equiv \frac{\mu_{kj}}{k_B T_j} - \frac{\mu_{kr}}{k_B T_r}, \tag{1.65}$$

for the different reservoirs $j = 1, 2, \dots, r - 1$ (except the reference one) and the different particle species $k = 1, 2, \dots, c$. The global affinities are here introduced by dividing the entropy production rate with Boltzmann’s constant k_B , so that the thermal affinities have the units of J^{-1} and the chemical affinities are dimensionless. These global affinities are the direct control parameters of the nonequilibrium drives because they are fixed in the reservoirs at the boundaries of the system, where the conditions are supposed to be under experimental control. If all these global affinities are equal to zero, the temperatures and chemical potentials are all equal in the reservoirs and the stationary macrostate becomes the equilibrium macrostate where the currents are equal to zero, together with the entropy production rate.

We note that similar considerations apply to nonequilibrium systems with fluid flow where the affinities are determined by the boundary conditions on the velocity field, as in Couette–Taylor or Poiseuille flows. Mechanical affinities may also be introduced in systems where external forces or torques perform work driving the system out of equilibrium, as ions driven by an electric field.

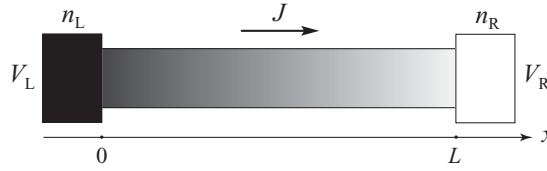


Figure 1.5 Schematic representation of a nonequilibrium steady state in the transport process of diffusion between two reservoirs with particle densities n_L and n_R and separated by the distance L .

1.7.2 Diffusion

As an example, let us consider the diffusion of a single solute species in an isothermal dilute solution in contact with two reservoirs located at $x = 0$ and $x = L$ and, respectively, having the densities n_L and n_R , as schematically depicted in Figure 1.5. The velocity of the solution is assumed to be equal to zero. This transport process is ruled by Fick's law $J = \mathcal{J} = -\mathcal{D}(n)\nabla n$ with a diffusion coefficient $\mathcal{D}(n)$ *a priori* depending on the density n . The diffusion equation is thus given by

$$\partial_t n = \nabla \cdot [\mathcal{D}(n)\nabla n] \quad (1.66)$$

in the three-dimensional physical space (x, y, z) . Taking the boundary conditions $n(0, y, z, t) = n_L$ and $n(L, y, z, t) = n_R$ for all times, the time evolution of the density will undergo a relaxation towards a stationary state $n(x)$ obeying

$$\frac{d}{dx} \left[\mathcal{D}(n) \frac{dn}{dx} \right] = 0. \quad (1.67)$$

Accordingly, the current density should take the uniform value $J = -\mathcal{D}(n)dn/dx$ across the system, so that the density profile is given by solving the ordinary differential equation $dn/dx = -J/\mathcal{D}(n)$, which can be integrated to obtain the current flowing across the sectional area Σ as

$$J \equiv \Sigma J = \frac{\Sigma}{L} \int_{n_R}^{n_L} \mathcal{D}(n) dn. \quad (1.68)$$

If the diffusion coefficient is independent of the density, the profile is linear,

$$n(x) = n_L - \frac{n_L - n_R}{L} x, \quad (1.69)$$

and Fick's law is recovered at the global scale in the form,

$$J = \Sigma \frac{\mathcal{D}}{L} (n_L - n_R). \quad (1.70)$$

Otherwise, Fick's law only holds locally. The global affinity is here given by

$$A = \frac{1}{k_B T} (\mu_L - \mu_R) = \ln \frac{n_L}{n_R}. \quad (1.71)$$

Taking the left or right reservoir as reference, the current (1.70) can be expressed in terms of the global affinity, respectively, as

$$J(A) = \Sigma \frac{D}{L} n_L (1 - e^{-A}) \quad \text{or} \quad J(A) = \Sigma \frac{D}{L} n_R (e^A - 1). \quad (1.72)$$

In general, the current (1.68) is a function $J(A)$ of the global affinity and the other properties of the macrostate. The entropy production rate is thus given by

$$\frac{1}{k_B} \frac{d_i S}{dt} = A J(A) \geq 0. \quad (1.73)$$

We note that, although we use a linear local relation between the current density and the local affinity with Fick’s law, we find a nonlinear relation between the current and the global affinity for the nonequilibrium steady state driven by boundary conditions on the system.

If both reservoirs have the same density $n_L = n_R$, the global affinity together with the current and the entropy production rate (1.73) are equal to zero.

If we suppose that the reservoirs on the left and right sides of the conductive medium have finite volumes larger than the volume of the open system, i.e., $V_L, V_R \gg V_s = \Sigma L$, there will be a slow evolution of their particle numbers $N_L = V_L n_L$ and $N_R = V_R n_R$ ruled by $dN_L/dt \simeq -J$ and $dN_R/dt \simeq +J$ with the current given by equation (1.68) or (1.70). In the simple diffusive case (1.70), there will thus be an exponential equilibration of the particle densities in the reservoirs according to

$$\frac{d}{dt} (n_L - n_R) \simeq -\Gamma (n_L - n_R) \quad \text{with the rate} \quad \Gamma = \frac{D}{L^2} \left(\frac{V_s}{V_L} + \frac{V_s}{V_R} \right). \quad (1.74)$$

The equilibration time, $t_{\text{equil}} = 1/\Gamma$, should be compared with the relaxation time, $t_{\text{relax}} \sim L^2/D$, taken to reach the nonequilibrium steady state in the diffusive medium of length L . We thus find that

$$\frac{t_{\text{relax}}}{t_{\text{equil}}} \sim \frac{V_s}{V_L} + \frac{V_s}{V_R} \ll 1, \quad (1.75)$$

i.e., the relaxation towards the nonequilibrium steady state is faster than the time taken by the reservoirs to reach a global equilibrium across the whole system if the reservoirs are much larger than the open system, i.e., $V_L, V_R \gg V_s$. Accordingly, the reservoirs should be arbitrarily large in order to maintain a nonequilibrium steady state in an open system in contact with them.

Analogous considerations apply to heat conduction ruled by Fourier’s law in terms of the temperature instead of the particle density.

1.7.3 Ohm’s Law for Electric Resistance

If we consider the transport of electric charges in a conductor, we need to include the effects of the electric field $\mathcal{E} = -\nabla\Phi$, or, equivalently, the electric potential Φ . For simplicity, we consider positive charge carriers moving in a conductor such as a resistor or an electrolytic solution. The electric charge density is thus given by $\rho_e = e(n - n_0)$ where $e = |e|$ is

the elementary electric charge, n the density of positively charged particles, and n_0 the uniform and invariant density of negatively charged particles forming a background, which is called the jellium model. The associated electric current density can be expressed as $\mathbf{J}_e = e\mathbf{J} = e\mathcal{J}$ in terms of the diffusive current density of the mobile particles

$$\mathcal{J} = -\mathcal{D}\nabla n + \beta e\mathcal{D}n\mathcal{E} = -\mathcal{D}e^{-\beta e\Phi}\nabla(e^{\beta e\Phi}n), \quad (1.76)$$

where \mathcal{D} is their diffusion coefficient and $\beta = (k_B T)^{-1}$ is the inverse temperature, which is known as the Nernst–Planck equation (Probstein, 2003). Since the electric charge is locally conserved, the continuity equation

$$\partial_t \rho_e + \nabla \cdot \mathbf{J}_e = 0 \quad (1.77)$$

is satisfied. Moreover, the electric field obeys Gauss' law

$$\nabla \cdot \mathcal{E} = \frac{\rho_e}{\epsilon}, \quad (1.78)$$

where ϵ is the dielectric coefficient of the material. The coupled equations (1.76), (1.77), and (1.78) define the so-called Nernst–Planck–Poisson problem.

We consider electric conduction in a piece of length L and cross-sectional area Σ in contact with two reservoirs, as shown in Figure 1.5. Here, the reservoirs have fixed values for the particle density and the electric potential: $n(0) = n_L$ with $\Phi(0) = \Phi_L$, and $n(L) = n_R$ with $\Phi(L) = \Phi_R$. In the presence of electric potential, the chemical potential should be replaced by the electrochemical potential, $\tilde{\mu} = \mu + e\Phi$. The global affinity (1.71) is thus given by $A = \beta(\tilde{\mu}_L - \tilde{\mu}_R) = \beta eV$, where

$$V = \Phi_L - \Phi_R + \frac{1}{\beta e} \ln \frac{n_L}{n_R} \quad (1.79)$$

is the applied voltage difference with respect to the Nernst potential with the assumption that the charge carriers are dilute in the conductor. The voltage (1.79) is equal to zero at equilibrium.

In the stationary macrostate, the current density $\mathbf{J} = (J, 0, 0)$ is invariant and uniform because of the continuity equation (1.77) and the stationary condition $\partial_t n = 0$. Moreover, the electric field $\mathcal{E} = (\mathcal{E}, 0, 0)$ is determined by Gauss' law. Consequently, the stationary profiles of the particle density and the electric field are obtained by solving the coupled equations

$$\frac{dn}{dx} = \beta en\mathcal{E} - \frac{J}{\mathcal{D}} \quad \text{and} \quad \frac{d\mathcal{E}}{dx} = \frac{e}{\epsilon}(n - n_0). \quad (1.80)$$

These latter admit the uniform solution with $n = n_0$ (electroneutrality) and $J = \beta e\mathcal{D}n_0\mathcal{E}$, corresponding to *Ohm's law*, $j_e = \sigma\mathcal{E}$ with the electric conductivity $\sigma = \beta e^2\mathcal{D}n_0$. In this case, the uniform charge density requires the boundary conditions $n_L = n_R = n_0$. Moreover, integrating the uniform electric field over the length L of the conductor, we obtain the potential difference $\mathcal{E} = (\Phi_L - \Phi_R)/L$, so that the voltage (1.79) is related to the electric field by $V = \mathcal{E}L$, as expected. In the stationary state, the electric current is given by $I = eJ = e\Sigma J$. Therefore, we find Ohm's law $V = RI$ with the resistance $R = L/(\sigma\Sigma)$.

For general boundary conditions, there are deviations with respect to electroneutrality near the contacts with the reservoirs and a uniform electric field. These deviations typically extend over a distance of the size of Debye’s screening length

$$\ell_D = \sqrt{\frac{\epsilon k_B T}{e^2 n_0}} \tag{1.81}$$

if the electric field is moderate, i.e., $|\mathcal{E}| \ll \sqrt{k_B T n_0 / \epsilon}$. Since Debye’s screening length is usually much smaller than the size of the conductor, $\ell_D \ll L$, the assumption of uniform electric field and electroneutrality is well satisfied.

Otherwise, the x -component of the second expression of the current density in equation (1.76) gives

$$\frac{d}{dx} (e^{\beta e \Phi} n) = -\frac{J}{\mathcal{D}} e^{\beta e \Phi}, \tag{1.82}$$

which can be integrated from $x = 0$ to $x = L$ to obtain (Andrieux and Gaspard, 2009)

$$J = \Sigma J = \Sigma \mathcal{D} \frac{n_L e^{\beta e \Phi_L} - n_R e^{\beta e \Phi_R}}{\int_0^L e^{\beta e \Phi(x)} dx}. \tag{1.83}$$

This expression is equal to zero at equilibrium where the applied voltage (1.79) is equal to zero. Again, if the density is uniform with $n_L = n_R = n_0$ and the electric field uniform with $\Phi(x) = \Phi_L - \mathcal{E}x$, the integral in the denominator can be performed and we recover the current density $J = \beta e \mathcal{D} n_0 \mathcal{E}$, giving Ohm’s law.

In the presence of an electric field, the entropy production rate is given by (de Groot and Mazur, 1984)

$$\frac{1}{k_B} \frac{d_i S}{dt} = \int_V \frac{\mathcal{D}}{n} (\nabla n - \beta e n \mathcal{E})^2 d^3 r \geq 0. \tag{1.84}$$

If the charge and current densities are uniform so that Ohm’s law holds, this entropy production rate becomes

$$\frac{1}{k_B} \frac{d_i S}{dt} = \frac{VI}{k_B T} = \frac{P}{k_B T} \geq 0, \tag{1.85}$$

where $P = VI = RI^2$ is the power dissipated by the electric current flowing in the resistor according to *Joule’s law*.

1.7.4 Electric Circuits

Electric components can be wired together to form circuits. Figure 1.6 shows common examples of such components. Electric generators such as batteries are characterized by their electromotive force $\mathcal{E} = V$. Capacitors, inductors, and resistors are components with a linear relation between the voltage V and, respectively, the electric charges $\pm Q$ on the capacitor plates, the time derivative dI/dt of the current I , and the current itself. In this regard, these components are linear. However, there are also nonlinear components such as diodes and transistors. For instance, the current–voltage relation of diodes can be

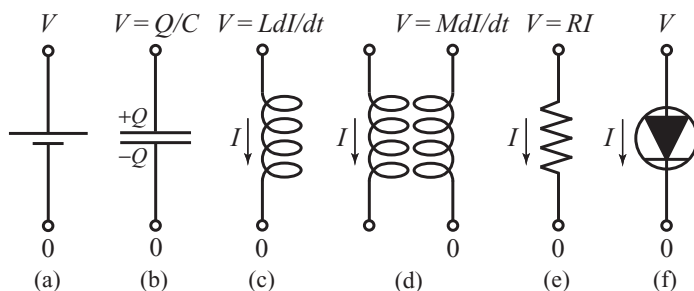


Figure 1.6 Various components of electric circuits: (a) battery of electromotive force $\mathcal{E} = V$, (b) capacitor of capacitance C , (c) inductor of inductance L , (d) two coupled inductors with mutual inductance M , (e) resistor of resistance R , (f) diode.

approximated by the expression $I = I_s (e^{\beta eV} - 1)$ with the saturation current I_s , as will be further discussed in Section 10.6.2.

Electric circuits are networks with nodes connected by edges. As long as the electromagnetic radiation of the circuit is negligible, the electric currents and potentials can be determined in the circuit using the current–voltage relations characterizing every component and the laws of Kirchhoff (1847):

1. The sum of electric currents in all the edges arriving at any node in the circuit is zero.
2. The sum of the electric potential differences along any loop in the circuit is zero.

Kirchhoff's first law, or current law, results from the local conservation of electric charge and the assumption that conduction is large enough so that electroneutrality is maintained in the wires connected together at any node. Kirchhoff's second law, or voltage law, is the consequence of Faraday's law of electromagnetism, provided that the magnetic field is localized inside the inductors (Reitz and Milford, 1967). Accordingly, the circulation of the electric field around any loop is equal to zero, i.e., $\oint_{\text{loop}} \mathcal{E} \cdot d\mathbf{r} = \sum_{i \rightarrow j} V_{i \rightarrow j} = 0$, where the sum extends over all the oriented edges $i \rightarrow j$ in the loop and $V_{i \rightarrow j} = \Phi_i - \Phi_j$ in terms of the electric potentials $\{\Phi_i\}$ at the nodes $\{i\}$. In Kirchhoff's second law, the contribution of every electromotive element is equal to minus its electromotive force, this latter driving the circuit out of equilibrium.

Energy is supplied by the electromotive forces of batteries. Capacitors and inductors conserve energy. Inside capacitors, energy is stored in the electric field between oppositely charged plates. Inside inductors, energy is stored in the magnetic field generated by the electric current. Other components dissipate energy and produce entropy, which is the case for resistors, diodes, and transistors. The entropy production rate in an electric circuit at temperature T can be evaluated as $d_i S/dt = P_{\text{diss}}/T \geq 0$ in terms of the power P_{diss} that is dissipated in all the components.

1.8 Reaction Networks

Reaction networks are envisaged in different fields of science. Nuclear reaction networks are considered for primordial or stellar nucleosynthesis to explain the abundance

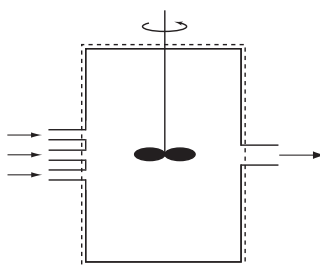


Figure 1.7 Schematic representation of a continuous-flow stirred tank reactor (CSTR). The open system itself is delimited by the dashed line. Reactants are continuously pumped into the reactor by several pipes shown on its left-hand side. The outflow of products is carried out by the large pipe on its right-hand side. The solution inside the reactor is mechanically stirred by the rotating blades of an impeller.

of isotopes in the universe. Moreover, the chemical elements may combine to form millions of known chemical compounds (Pauling, 1970). These compounds are transformed in chemical or biochemical reaction networks (Nelson and Cox, 2017). There exist networks of different sizes depending on the number of relevant species included in the description. A famous example is the Belousov–Zhabotinsky reaction, which involves about fourteen species, but can be described by the Oregonator model with only three variables (Nicolis and Prigogine, 1977; Bergé et al., 1984; Scott, 1991; Nicolis, 1995; Epstein and Pojman, 1998). Complex reaction networks are considered in astrochemistry, atmospheric chemistry, petrochemistry, studies in prebiotic chemistry, and combustion theory. Biochemical reaction networks are also known in enzyme kinetics, metabolic pathways, signal transduction pathways, cellular rhythms, and gene regulation (Segel, 1975; Hill, 1989; Nicolis and Prigogine, 1977; Goldbeter, 1996; Qian and Beard, 2005; Michal and Schomburg, 2012; Wachtel et al., 2018).

Chemical or biochemical reactions can be controlled in reactors of different types. Batch reactors are closed systems at controlled temperature where reactants are initially poured in a stirred solution, yielding products until chemical equilibrium is reached. In contrast, continuous-flow stirred tank reactors are open systems continuously fed by reactants, the products exiting by an outflow. These reactors are equipped with a stirrer to guarantee the quasi-uniformity of the reacting mixture.

1.8.1 Flow Reactors

A flow reactor called a continuous-flow stirred tank reactor (CSTR) is schematically represented in Figure 1.7 with the inflow of reactants and the outflow of the solution in excess, also containing products (Aris, 1989; Nicolis, 1995; Epstein and Pojman, 1998; Blokhuis et al., 2018). The stirrer induces hydrodynamic mixing, so that the concentrations of reactants and products are made uniform inside the reactor.

Kinetics

In the flow reactor, the reactant and product densities $\{n_k\}_{k=1}^c$ are ruled by the balance equations

$$\partial_t n_k + \nabla \cdot (n_k \mathbf{v} + \mathcal{J}_k) = \sum_r v_{kr} w_r, \quad (1.86)$$

where \mathbf{v} is the fluid velocity, $\mathcal{J}_k = -\mathcal{D}_k \nabla n_k$ the diffusive current density, and v_{kr} the stoichiometric coefficient of species k in the reaction r of rate w_r .

The number of the molecules of species k inside the volume V delimited by the dashed line in Figure 1.7 is defined by $N_k = \int_V n_k d^3r$. This number evolves in time according to

$$\frac{dN_k}{dt} = \frac{d_e N_k}{dt} + \frac{d_i N_k}{dt}, \quad (1.87)$$

which has a form reminiscent of equation (1.3) with the contribution $d_e N_k/dt$ due to the exchanges of molecules at the boundaries of the volume where inflow and outflow are controlled, and the internal contribution $d_i N_k/dt$ due to the reactions taking place inside the system. By the divergence theorem, the exchanges with the exterior contribute according to

$$\frac{d_e N_k}{dt} = - \int_{\partial V} (n_k \mathbf{v} + \mathcal{J}_k) \cdot d\mathbf{\Sigma}, \quad (1.88)$$

where ∂V is the boundary of the volume V . Since the solution is well stirred by the mixer, the density n_k is practically uniform inside the reactor, so that $N_k \simeq V n_k$ and $\mathcal{J}_k = -\mathcal{D}_k \nabla n_k \simeq 0$. Moreover, exchanges only happen where the fluid velocity is not equal to zero in the direction transverse to the boundary ∂V , i.e., at the portions of the boundary, $\partial_{k,\text{in}} V$ and $\partial_{\text{out}} V$, respectively, corresponding to the inflow of species k and the outflow of the solution in excess. Consequently, we have that

$$\frac{d_e N_k}{dt} \simeq - \int_{\partial_{k,\text{in}} V} n_k \mathbf{v} \cdot d\mathbf{\Sigma} - \int_{\partial_{\text{out}} V} n_k \mathbf{v} \cdot d\mathbf{\Sigma} = \phi_{k,\text{in}} n_{k,\text{in}} - \phi_{\text{out}} n_k \quad (1.89)$$

in terms of the density $n_{k,\text{in}}$ inside the inlet pipe of species k , the ingoing flux $\phi_{k,\text{in}} = - \int_{\partial_{k,\text{in}} V} \mathbf{v} \cdot d\mathbf{\Sigma}$, and the outgoing flux $\phi_{\text{out}} = \int_{\partial_{\text{out}} V} \mathbf{v} \cdot d\mathbf{\Sigma}$. We note that $\phi_{\text{out}} = \sum_k \phi_{k,\text{in}}$ because of the fluid incompressibility, $\nabla \cdot \mathbf{v} = 0$. In addition, the reactions inside the system contribute to

$$\frac{d_i N_k}{dt} = \int_V \sum_r v_{kr} w_r d^3r \simeq V \sum_r v_{kr} w_r, \quad (1.90)$$

since the solution is well stirred and the densities are thus uniform inside the reactor. Substituting these results back into equation (1.87), we find that the density of species k is ruled by

$$\frac{dn_k}{dt} = \sum_r v_{kr} w_r + \frac{1}{\tau} (n_{k0} - n_k) \quad \text{with} \quad n_{k0} \equiv \frac{\phi_{k,\text{in}}}{\phi_{\text{out}}} n_{k,\text{in}}, \quad (1.91)$$

where $\tau \equiv V/\phi_{\text{out}}$ is the mean residence time of the species inside the reactor. The macrostate inside the open system is thus determined by the control parameters τ and n_{k0} . We note that the conservation of the total mass, $M = V \sum_k m_k n_k$, implies that $d_i M/dt = 0$, so that $dM/dt = d_e M/dt = (M_0 - M)/\tau$, and $M = M_0$ in steady regimes.

If the fluxes are equal to zero, the residence time is infinite ($\tau = \infty$), and the system is closed, corresponding to a batch reactor. However, the system is open and out of equilibrium

if the residence time is finite and some reactants are injected inside the reactor. In the limit of a vanishingly small residence time ($\tau = 0$), the densities converge towards their injection values $\lim_{t \rightarrow \infty} n_k(t) = n_{k0}$.

Thermodynamics

The thermodynamics of the reactions can be investigated using the Gibbs free energy as thermodynamic potential if the temperature and the pressure are supposed to be uniform inside the system. The Gibbs free energy density is given by

$$g = \sum_k \mu_k n_k, \quad (1.92)$$

where μ_k is the chemical potential of species k . For this quantity, Gibbs' relation has the form

$$dg = -s dT + dp + \sum_k \mu_k dn_k. \quad (1.93)$$

Under isothermal and isobaric conditions, $dT = 0$ and $dp = 0$, the time evolution of the Gibbs free energy density is thus ruled by the changes of densities according to equation (1.91), so that

$$\frac{dg}{dt} = \sum_k \mu_k \frac{dn_k}{dt} = \sum_{kr} \mu_k \nu_{kr} w_r + \frac{1}{\tau} \sum_k \mu_k (n_{k0} - n_k), \quad (1.94)$$

which can be written in the equivalent form

$$\frac{dg}{dt} = -T \sigma_{s, \text{react}} + \frac{1}{\tau} (g_0 - g), \quad (1.95)$$

in terms of $g_0 = \sum_k \mu_k n_{k0}$ and the entropy production rate density $\sigma_{s, \text{react}}$ due to the reactions. If the solution is dilute and the kinetics obeys the mass action law, the chemical potentials of the reacting solute species are given by equation (1.36) and the entropy production rate density reads as

$$\sigma_{s, \text{react}} = -\frac{1}{T} \sum_{kr} \mu_k \nu_{kr} w_r = k_B \sum_r (w_{+r} - w_{-r}) \ln \frac{w_{+r}}{w_{-r}} \geq 0. \quad (1.96)$$

If the residence time is infinite ($\tau = \infty$), there is no exchange with the exterior of the reactor. Therefore, the system is closed and evolves from an initial macrostate with a high content of Gibbs free energy, towards the equilibrium macrostate where Gibbs free energy is minimal and the entropy maximal, as required. Accordingly, the solution undergoes relaxation towards chemical equilibrium where the conditions of detailed balance are satisfied for all the reactions, $w_{+r} = w_{-r}$, corresponding to the minimum of Gibbs free energy in the reactor. For dilute solutions, the Gibbs free energy (1.92) can be written as

$$g = g_{\text{eq}} + k_B T \sum_{k=1}^{c-1} \left[n_k \ln \frac{n_k}{n_{k, \text{eq}}} - (n_k - n_{k, \text{eq}}) \right], \quad (1.97)$$

where $n_{k,eq}$ are the equilibrium densities of the solute species in the closed reactor, corresponding to the free energy minimum given the constraints coming from the initial densities and the reactions. Since $g \geq g_{eq}$ and $dg/dt \leq 0$ in a closed reactor, the function (1.97) plays the role of Lyapunov function, implying that the equilibrium macrostate is the unique attractor in the closed reactor (Shear, 1967; Horn and Jackson, 1972; Rao and Esposito, 2016).

However, if the reactor is open the condition $dg/dt \leq 0$ is no longer always satisfied because equation (1.95) has the extra term $(g_0 - g)/\tau$ due to the exchanges of the reactor with the exterior. Accordingly, the function (1.97) is no longer a Lyapunov function and the existence and uniqueness of a stationary macrostate no longer hold. Actually, complex dynamics with multistability, as well as periodic, or chaotic oscillations become possible for flow reactors driven far from equilibrium, i.e., beyond some instability threshold for the stationary macrostate issued from equilibrium by increasing the nonequilibrium constraints (Bergé et al., 1984; Scott, 1991; Nicolis, 1995; Epstein and Pojman, 1998). In the limit where the residence time is vanishingly small ($\tau = 0$), the free energy density becomes equal to its injection value $g = g_0$.

We note that, if the system is closed (as in a batch reactor) and large enough pools of some species are maintained during long time intervals, these species are practically chemostatted and their densities can be assumed to remain invariant. During such lapses of time, the system can be maintained far enough from equilibrium to sustain dynamical behaviors similar to those observed in flow reactors.

1.8.2 Stoichiometric Analysis of Reaction Networks

The theory of chemical reaction networks has been developed since the 1960s on the basis of the stoichiometric matrix and in close relation with thermodynamics (Poletini and Esposito, 2014; Rao and Esposito, 2016; Feinberg, 2019).

The densities of all the species in the reaction network are ruled by the closed set of ordinary differential equations (1.91), defining a so-called *dynamical system*. These equations can be written in the vectorial form

$$\frac{d\mathbf{n}}{dt} = \mathbf{v} \cdot \mathbf{w} + \frac{1}{\tau}(\mathbf{n}_0 - \mathbf{n}), \quad (1.98)$$

ruling the time evolution for the c -dimensional vector $\mathbf{n} \in \mathbb{R}^c$ of the reactant and product densities. The control parameters are the components of the invariant vector $\mathbf{n}_0 \in \mathbb{R}^c$ and the residence time τ . The reaction rates form the m -dimensional vector $\mathbf{w} = (w_r)_{r=1}^m$ and the stoichiometric coefficients the $c \times m$ matrix $\mathbf{v} = (v_{kr})$ with $k = 1, 2, \dots, c$ and $r = 1, 2, \dots, m$. The time evolution generates trajectories $\mathbf{n}(t)$ in the *phase space* $\{\mathbf{n} \in \mathbb{R}^c\}$ of the dynamical system (1.98) (Bergé et al., 1984; Nicolis, 1995).

Closed Reactors

Let us first assume that the reactor is closed ($\tau = \infty$). On the one hand, the left null eigenvectors $\mathbf{l} \in \mathbb{R}^c$ of the stoichiometric matrix are defined by

$$\mathbf{l}^T \cdot \mathbf{v} = 0. \quad (1.99)$$

Since the solution is uniform in the volume V of the system because of stirring, we may introduce the quantities

$$L \equiv V \mathbf{l}^T \cdot \mathbf{n} \quad (1.100)$$

that are conserved by the reaction network and are thus constants of motion for the set of ordinary differential equations, $dL/dt = 0$. These *conserved quantities* include, in particular, the total mass and the moieties that are preserved by the reaction network (Haraldsdóttir and Fleming, 2016). The number l of these conserved quantities is given by the dimension of the null space of the transpose of the stoichiometric matrix, also called the cokernel: $l = \dim \text{coker } \mathbf{v}$. On the other hand, the right null eigenvectors $\mathbf{e} \in \mathbb{R}^m$ of the stoichiometric matrix such that

$$\mathbf{v} \cdot \mathbf{e} = 0 \quad (1.101)$$

define the so-called *stoichiometric cycles* of the network,⁹ forming cyclic reaction pathways in the network. The number, o , of cycles is given by the dimension of the null space of the stoichiometric matrix, also called the kernel: $o = \dim \ker \mathbf{v}$. A general property of linear algebra shows that the rank of the stoichiometric matrix is given by

$$\text{rank } \mathbf{v} = c - l = m - o. \quad (1.102)$$

Open Reactors

Next, the reactor is supposed to be open with a finite residence time ($\tau < \infty$). In this case, the contribution $d_e \mathbf{n}/dt = (\mathbf{n}_0 - \mathbf{n})/\tau$ due to the exchanges should be added to the internal contribution $d_i \mathbf{n}/dt = \mathbf{v} \cdot \mathbf{w}$. Consequently, the quantities L are no longer constants of motion, but instead they obey

$$\frac{dL}{dt} = \frac{1}{\tau}(L_0 - L) \quad (1.103)$$

with $L_0 \equiv V \mathbf{l}^T \cdot \mathbf{n}_0$, because of the inflow and outflow generating exchanges with the exterior. Consequently, the quantities L evolve in time according to

$$L(t) = L(0)e^{-t/\tau} + L_0(1 - e^{-t/\tau}). \quad (1.104)$$

Nevertheless, these quantities reach constant values L_0 fixed by the inflow over a timescale longer than the residence time: $L(t) \simeq L_0$ for $t \gg \tau$. We notice that in a closed reactor, these quantities take the constant values $L(t) = L(0)$ fixed by their initial conditions, $L(0)$, that may differ from the constant values L_0 fixed by the inflow in an open reactor. A general remark is that the quantities L continue to obey conservation laws if the system is open. Indeed, equation (1.103) can be written in the form $dL/dt = d_e L/dt + d_i L/dt$ with $d_e L/dt = (L_0 - L)/\tau$ and $d_i L/dt = 0$, showing that these quantities get their time dependence because of the exchanges with the exterior.

⁹ The stoichiometric cycles of the network should not be confused with the limit cycles of the dynamical system, which are periodic trajectories for the dynamics.

In a flow reactor, the contributions $d_c \mathbf{n}/dt = (\mathbf{n}_0 - \mathbf{n})/\tau$ due to transport between the system and the exterior can be handled in the same way as for reactions, writing equation (1.98) in the equivalent form

$$\frac{d\mathbf{n}}{dt} = \mathbf{v}' \cdot \mathbf{w}' \quad \text{with} \quad \mathbf{v}' = (\mathbf{v}, \mathbf{1}), \quad (1.105)$$

by extending the stoichiometric matrix \mathbf{v} with the $c \times c$ identity matrix $\mathbf{1}$, and the vector of reaction rates into $\mathbf{w}' = (\mathbf{w}, \tilde{\mathbf{w}})^T$, where $\mathbf{w} \in \mathbb{R}^m$ is the previous one and $\tilde{\mathbf{w}} = (\mathbf{n}_0 - \mathbf{n})/\tau \in \mathbb{R}^c$. The new stoichiometric matrix \mathbf{v}' thus has dimensions $c \times m'$ with $m' = m + c$. Instead of equation (1.102), here we have the relation, $\text{rank } \mathbf{v}' = m' - o' = c - l'$, with $l' = 0$, since there is no longer any constant of motion as a consequence of equation (1.103). Therefore, the number of cycles is equal to $o' = m' - c = m$ in the flow reactor, instead of $o = m - c + l \leq m$ in the closed one. There are thus new cycles in the open reactor due to the exchanges with the exterior, which are called external cycles. A general cycle can be split as $\mathbf{e}' = (\mathbf{e}, \tilde{\mathbf{e}})^T$, such that $\mathbf{v}' \cdot \mathbf{e}' = \mathbf{v} \cdot \mathbf{e} + \tilde{\mathbf{e}} = 0$. Here, a distinction can be made between the previously identified internal cycles \mathbf{e}'_γ with $\mathbf{v} \cdot \mathbf{e}_\gamma = 0$ and $\tilde{\mathbf{e}}_\gamma = 0$ for $\gamma = 1, 2, \dots, o$, and the external cycles \mathbf{e}'_α such that $\tilde{\mathbf{e}}_\alpha = -\mathbf{v} \cdot \mathbf{e}_\alpha \neq 0$ for $\alpha = 1, 2, \dots, m - o$ (Blokhuis et al., 2018). These external cycles have a pathway involving transport from or to the exterior of the flow reactor.

Thermodynamics in Open Reactors

Noting that Gibbs free energy density can be expressed as $g = \boldsymbol{\mu}^T \cdot \mathbf{n}$ in terms of the c -dimensional vector of chemical potentials $\boldsymbol{\mu} = \{\mu_k\}_{k=1}^c$, equation (1.94) can be written as

$$\frac{dg}{dt} = \boldsymbol{\mu}^T \cdot \mathbf{v}' \cdot \mathbf{w}'. \quad (1.106)$$

In a stationary macrostate, the relation $\mathbf{v}' \cdot \mathbf{w}' = 0$ holds, so that the vector of reaction rates can be decomposed in the basis of the right null eigenvectors as $\mathbf{w}' = \sum_{\gamma=1}^o w_\gamma \mathbf{e}'_\gamma + \sum_{\alpha=1}^{m-o} w_\alpha \mathbf{e}'_\alpha$. If these conditions are satisfied, the entropy production rate density (1.96) simplifies to

$$\sigma_{s, \text{react}}|_{\text{st}} = -\frac{1}{T} \boldsymbol{\mu}^T \cdot \mathbf{v} \cdot \mathbf{w} + \frac{1}{T} \sum_{\alpha=1}^{m-o} w_\alpha \boldsymbol{\mu}^T \cdot \tilde{\mathbf{e}}_\alpha \geq 0, \quad (1.107)$$

because $\mathbf{v} \cdot \mathbf{e}_\gamma = 0$ for internal cycles and $\mathbf{v} \cdot \mathbf{e}_\alpha = -\tilde{\mathbf{e}}_\alpha$ for external cycles. The entropy production rate can thus be written in the form

$$\frac{d_i S}{dt} \Big|_{\text{st}} = V \sigma_{s, \text{react}}|_{\text{st}} = k_B \sum_{\alpha=1}^{m-o} A_\alpha J_\alpha \geq 0 \quad (1.108)$$

in terms of the global affinities $A_\alpha \equiv \boldsymbol{\mu}^T \cdot \tilde{\mathbf{e}}_\alpha / (k_B T)$ and the currents $J_\alpha = V w_\alpha$ associated with the external cycles $\alpha = 1, 2, \dots, m - o$.¹⁰ The consequence is that, in stationary

¹⁰ We note that the currents associated with the reactions are proportional to the volume, although the currents (1.68) or (1.70) associated with transport between reservoirs are proportional to the surface area of the interfaces with the reservoirs. The reason is that the reaction currents – also called reaction fluxes – are microscopic, since the bottlenecks of the reactions have submolecular sizes (Moore, 1972; Berry et al., 1980).

macrostates, the entropy production is only determined by the external cycles able to drive the open system away from equilibrium (Blokhuis et al., 2018). The entropy produced inside the system is evacuated to the exterior by the flow term. At equilibrium where detailed balance is satisfied, the reaction rates are equal to zero, i.e., $w_r = w_{+r} - w_{-r} = 0$, together with the entropy production rate.

If the solution $\mathbf{n}(t)$ of equation (1.98) depends on time, we may consider the time average

$$\bar{X} \equiv \lim_{\mathcal{T} \rightarrow \infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} X(t) dt \quad (1.109)$$

for any quantity X of interest. Taking the time average of equation (1.105), we find that $\bar{\mathbf{w}}$ is still a right null eigenvector of the stoichiometric matrix introduced in equation (1.105), $\mathbf{v}' \cdot \bar{\mathbf{w}} = 0$, which can again be decomposed in the basis of the right null eigenvectors to give

$$\bar{\mathbf{n}} = \mathbf{n}_0 + \tau \mathbf{v} \cdot \bar{\mathbf{w}} = \mathbf{n}_0 - \tau \sum_{\alpha=1}^{m-o} \bar{w}_\alpha \tilde{\mathbf{e}}_\alpha. \quad (1.110)$$

Therefore, the deviations of the mean densities with respect to the effective injected densities \mathbf{n}_0 are given in terms of the external cycles of the network. The time average can also be applied to the balance equation (1.95) for the Gibbs free energy. In this way, we obtain the time average of the entropy production rate

$$\overline{\frac{d_i S}{dt}} = V \bar{\sigma}_{s, \text{react}} = \frac{V}{T\tau} (\bar{g}_0 - \bar{g}) \geq 0, \quad (1.111)$$

giving the mean value of the Gibbs free energy density as

$$\bar{g} = \bar{g}_0 - T\tau \bar{\sigma}_{s, \text{react}} \leq \bar{g}_0. \quad (1.112)$$

This result shows that the mean value of the Gibbs free energy inside the reactor is always lower than or equal to its mean injection value \bar{g}_0 .

1.9 Dissipative Dynamics and Structures

Systems are driven out of equilibrium by control parameters such as the global affinities or the reactant inflow rates for reactors. If these control parameters are switched on, some fluxes of energy or matter are generated inside the system, and the equilibrium macrostate of the undriven system turns into a nonequilibrium steady state for the driven system. Since the perturbations with respect to this macrostate are damped by dissipation, the nonequilibrium steady state is a stationary attractor for the time evolution of the system, as is the case at equilibrium. When the control parameters are increased, a critical threshold may be reached where the nonequilibrium steady state becomes unstable and the system undergoes a transition, called bifurcation, leading to the emergence of new attractors.

These emerging attractors may be stationary or dynamical. In the latter case, they can manifest periodic, quasiperiodic, or chaotic oscillations (see Appendix B). The attractors of

periodic oscillations are called *limit cycles*, in reference to the convergence in the long-time limit towards a cyclic time evolution. Quasiperiodic oscillations have tori as attractors in the phase space of macrovariables. The dimension of the attractor is a quantitative characterization of the effective number of macrovariables that are dynamically active in the system. Steady states and limit cycles have their dimensions equal to zero and one, respectively. For tori, the dimension gives the number of incommensurable frequencies in the quasiperiodicity they represent. Chaotic oscillations are characterized by the property of sensitivity to initial conditions, generating aperiodicity over long timescales. The attractors of chaotic oscillations typically form fractals in the phase space (Bergé et al., 1984; Eckmann and Ruelle, 1985; Strogatz, 1994; Nicolis, 1995).

In spatially extended systems, the attractor may correspond to stationary patterns or spatiotemporal structures, referred to as *dissipative structures* (Prigogine, 1967; Glansdorff and Prigogine, 1971; Kondepudi and Prigogine, 1998). The formation of these macroscopic structures is possible because the system is open and the entropy produced by dissipation inside the system is evacuated to the exterior, allowing self-organization to happen far from equilibrium at the macroscale (Nicolis and Prigogine, 1977).

These nonequilibrium phenomena manifest themselves in different physicochemical systems.

In hydrodynamics, the Rayleigh–Bénard instability in a fluid layer subjected to gravity and a temperature gradient induces the formation of stationary convective rolls (Mareschal and Kestemont, 1987). This dissipative structure may undergo further instabilities, leading to turbulence, which is a chaotic behavior of high dimension in the phase space (Bergé et al., 1984; Nicolis, 1995).

Nonequilibrium phenomena are also a feature of reactions with nonlinear mechanisms caused by autocatalysis or cross-catalysis (Nicolis and Prigogine, 1977; Scott, 1991; Epstein and Pojman, 1998). The so-called chemical clocks are periodic oscillations observed in the Belousov–Zhabotinsky reaction and other reactions. Quasiperiodic and chaotic oscillations have also been observed in these reactions. Here, the time evolution takes place in the phase space of the chemical concentrations (i.e., the densities). In spatially extended systems where the reactions are coupled to the diffusion of the reacting species, stationary dissipative structures called *Turing patterns* may emerge, as well as spatiotemporal structures forming circular or spiral waves, which may become turbulent if the system is driven far enough from equilibrium.

In addition, similar phenomena are observed in lasers, nonlinear optics, electronics, and other areas (Haken, 1975; Lugatio and Lefever, 1987; Schöll, 2001).

Dissipative structures often emerge through symmetry breaking at the macroscale. For instance, the symmetry under temporal translations is broken at the onset of oscillations, while the symmetry under spatial translations is broken in the Rayleigh–Bénard instability or the formation of Turing patterns in reaction–diffusion systems (Prigogine and Nicolis, 1967; Prigogine and Lefever, 1968).

The transitions, called bifurcations, occurring between the different nonequilibrium regimes have been classified (Strogatz, 1994; Nicolis, 1995). They include the pitchfork bifurcation shown in Figure 1.8(a), where two new stable steady states emerge from

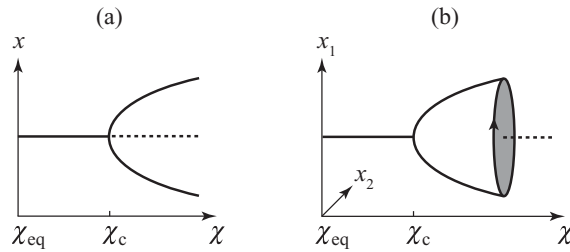


Figure 1.8 Schematic representation of bifurcations in the phase space of the dynamical variables versus the control parameter χ : (a) Pitchfork bifurcation with the emergence of two new stable steady states in the variable x ; (b) Hopf bifurcation with the emergence of a limit cycle in the phase space of the variables (x_1, x_2) . In both cases, the equilibrium macrostate is located at the value χ_{eq} of the control parameter, and the bifurcation happens at the critical threshold χ_c . The solid lines depict the stable solutions and the dashed lines the unstable ones.

the instability of a previously existing steady state, leading to multistability. Another important nonequilibrium transition is the Hopf bifurcation shown in Figure 1.8(b), where a limit cycle emerges from the instability of a steady state, leading to rhythmic behavior. Successive bifurcations may lead to chaotic regimes, such as the cascade of period-doubling bifurcations.

In time-dependent regimes, the attractor can be characterized by the time average (1.109) for the different quantities of interest. Indeed, in dissipative dynamical systems, every attractor is typically surrounded by a basin of attraction where all the time evolutions converge towards the attractor. Therefore, the time averages (1.109) of any time evolution starting in the basin of attraction will have values associated with the same attractor (Eckmann and Ruelle, 1985).

1.10 Engines

Heat engines such as steam engines or internal combustion engines are mechanical devices that convert heat into work. More generally, engines and motors achieve the transduction of heat, chemical energy, or electric energy into work, i.e., mechanical energy. Many engines function in such a way that gases undergo a cycle of transformations, including compression and expansion, heating and cooling, and/or inflow and outflow. Engines may have an autonomous periodic motion, which can be represented as the limit cycle of a dissipative dynamical system. In general, engines should be described as piecewise continuous media in terms of hydrodynamics and transport theory. Otherwise, the cycle of an engine can be idealized as the succession of several transformations driven by time-dependent external forcing, as conceived by Carnot (1824) for heat engines. Moreover, there also exist engines that function under isothermal conditions using a difference of pressure or chemical potential to power their motion. Such idealized engines can be directly analyzed in terms of the first and second laws of thermodynamics in order to determine their efficiencies, as discussed below.

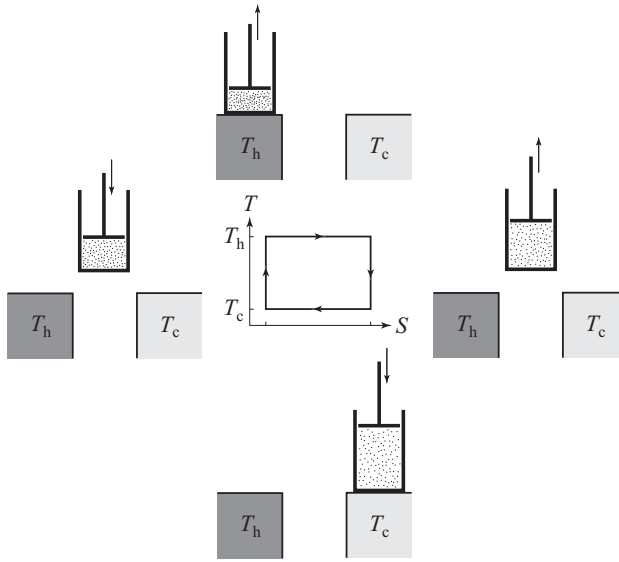


Figure 1.9 The cycle of the Carnot heat engine in the plane of the entropy S and the temperature T . The piston is filled with gas and alternately put in contact with the hot heat reservoir at the temperature T_h and the cold heat reservoir at the temperature T_c , or held isolated from them.

1.10.1 Carnot Heat Engine

This famous engine is composed of a piston containing a dilute gas and two heat reservoirs at the temperatures T_h and T_c . The piston forms a closed system where the number of molecules does not change.

The cycle of this engine is shown in Figure 1.9. First, the piston is put in contact with the hot reservoir, which generates the isothermal expansion of the gas and the heat transfer $Q_h > 0$ from the reservoir to the gas. Next, the piston is isolated from the reservoirs and the gas is subjected to an adiabatic (i.e., isentropic) expansion, cooling the gas. When the temperature T_c is reached, the piston is placed in contact with the cold reservoir. Now, the isothermal compression of the gas can be carried out, releasing some heat $|Q_c|$ (with $Q_c = -|Q_c|$) towards that reservoir. Finally, the piston is again isolated from the reservoirs and the gas is compressed adiabatically, increasing its temperature back to the one of the hot reservoir. When this cycle is completed, the state variables of the gas have recovered their initial values, which is the case, in particular, for the energy E and the entropy S of the gas. Consequently, the integrals of their changes over the cycle are equal to zero: $\oint dE = 0$ and $\oint dS = 0$.

Integrating the first law (1.2) over the cycle and using the conservation of molecules in the closed system ($dN = 0$), we get

$$0 = \oint dE = \oint d_e E = \oint (dQ - p dV), \quad (1.113)$$

where

$$\oint dQ = |Q_h| - |Q_c| \quad \text{and} \quad \mathcal{W} \equiv \oint p dV \quad (1.114)$$

are, respectively, the heat exchanged with the reservoirs during the isothermal transformations and the work performed by the piston on the exterior during the cycle. Thus, energy conservation implies that

$$\mathcal{W} = |Q_h| - |Q_c|. \quad (1.115)$$

Next, integrating the second law (1.4) over the cycle gives

$$0 = \oint dS = \oint d_e S + \oint d_i S \quad (1.116)$$

with $\oint d_i S \geq 0$. Since $d_e S = dQ/T$, we have that

$$0 \geq \oint d_e S = \oint \frac{dQ}{T} = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}. \quad (1.117)$$

The efficiency is defined as the ratio between the work performed by the engine and the heat supplied by the hot source. According to the first and second laws, the efficiency is bounded as

$$\eta \equiv \frac{\mathcal{W}}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \leq \eta_C = 1 - \frac{T_c}{T_h} \quad (1.118)$$

by the Carnot efficiency η_C reached in the absence of entropy production during the cycle, i.e., if $\oint d_i S = 0$. In any case, the efficiency is equal to zero if both reservoirs are in equilibrium (i.e., if $T_h = T_c$).

Most often, engines are running at speeds that maximize their power, which has the effect of reducing efficiency, as compared to arbitrarily slow regimes aiming at the optimization of efficiency. Using linear relations between currents and global affinities, the efficiency at maximum power is estimated to reach the value

$$\eta_{\text{max power}} = 1 - \sqrt{\frac{T_c}{T_h}}, \quad (1.119)$$

which is thus smaller than the Carnot efficiency of a reversible cycle (Curzon and Ahlborn, 1975; Van den Broeck, 2005; Esposito et al., 2010).

1.10.2 Isothermal Engines Working on Potential Differences

There also exist isothermal engines, which use a difference of pressure or chemical potential to perform work. An example is the pneumatic engine schematically depicted in Figure 1.10. This engine is composed of a piston connected with two reservoirs by two valves, which are successively open or closed, allowing some dilute gas to be transferred from each reservoir to the piston and vice versa. The piston thus forms an open system, where the number of molecules changes along the cycle. The gas pressure has the high value p_h in the left

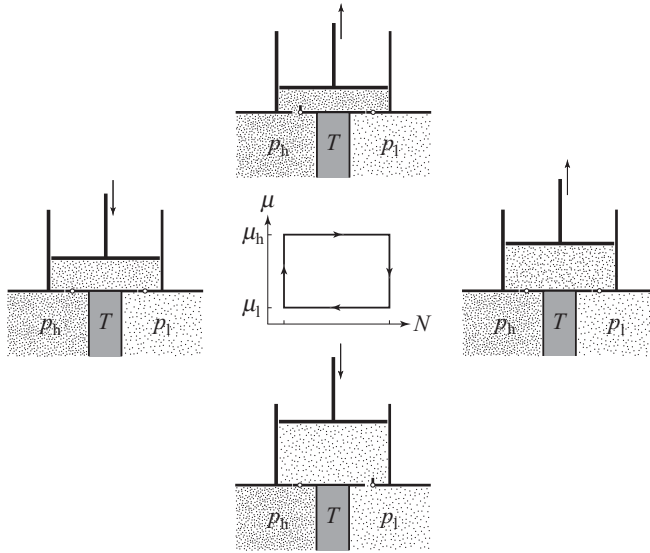


Figure 1.10 The cycle of the isothermal pneumatic engine in the plane of the particle number N and the chemical potential μ . The piston can be filled with gas or emptied via two valves opening to the left reservoir at the high pressure p_h and the right one at the low pressure p_l . The system is kept isothermal at the temperature T by the heat reservoir in contact with the piston and both gas reservoirs.

reservoir and the low value p_l in the right reservoir. Moreover, there is a heat reservoir in contact with the piston and the two gas reservoirs, keeping the temperature uniform at the value T . Since the gas is dilute, its chemical potential is related to its pressure by $\mu(p, T) = \mu^0(T) + k_B T \ln(p/p^0)$, where p^0 is the standard pressure.

The cycle of this engine starts when both valves are closed and the gas pressure in the piston has the high value p_h . The pressures in the piston and the high pressure reservoir being equal, the valve between them can be slowly opened without causing dissipation by viscosity or friction. The piston can thus move up with an inflow of ΔN gas molecules at the high pressure p_h . Next, the valve is closed and the gas in the piston undergoes an isothermal expansion, decreasing the pressure to the low value p_l . The valve with the low pressure reservoir may now be opened and the piston moved down, releasing ΔN gas molecules into that reservoir. After closing the valve on the right-hand side, the gas is isothermally compressed, increasing its pressure back to the high value p_h . In this cycle, the number N of molecules in the piston, the energy E , and the entropy S recover their initial values since they are state variables, so that $\oint dN = 0$, $\oint dE = 0$, and $\oint dS = 0$.

Here, the first law (1.2) gives

$$0 = \oint dE = \oint d_e E = \oint (dQ - p dV + \mu dN), \tag{1.120}$$

where $\oint dQ$ is the heat exchanged with the reservoirs, $\mathcal{W} \equiv \oint p dV$ the work performed by the piston during the cycle, and

$$\Delta\mathcal{G} \equiv \oint \mu dN = (\mu_h - \mu_l)\Delta N \quad (1.121)$$

the free energy used by the engine. Since $d_e S = dQ/T$ and the cyclic process is isothermal, the second law (1.4) implies that

$$0 \geq \oint d_e S = \oint \frac{dQ}{T} = \frac{1}{T} \left(\underbrace{\oint dE}_{=0} + \underbrace{\oint p dV}_{=\mathcal{W}} - \underbrace{\oint \mu dN}_{=\Delta\mathcal{G}} \right). \quad (1.122)$$

Consequently, the work $\mathcal{W} > 0$ performed by the engine satisfies $\mathcal{W} \leq \Delta\mathcal{G}$. Here, we may introduce the thermodynamic efficiency

$$\eta_{\text{th}} \equiv \frac{\mathcal{W}}{\Delta\mathcal{G}} \leq 1, \quad (1.123)$$

which may never exceed the unit value because of the second law. We note that the thermodynamic efficiency (1.123) is defined using the net free energy $\Delta\mathcal{G} > 0$ consumed to drive the engine, while the usual efficiency (1.118) involves the heat $|Q_h|$ supplied by one reservoir, which explains the difference between their upper bounds.

If we consider the reverse process where the work $W \equiv -\mathcal{W} > 0$ is performed by the exterior onto the system in order to store the free energy $\Delta G \equiv -\Delta\mathcal{G} > 0$ inside the system, we obtain the so-called *Clausius inequality*

$$W \geq \Delta G. \quad (1.124)$$

Therefore, the thermodynamic efficiency of free-energy storage should satisfy the following inequality

$$\eta'_{\text{th}} \equiv \frac{1}{\eta_{\text{th}}} = \frac{\Delta G}{W} \leq 1, \quad (1.125)$$

according to the second law. The same results hold for multicomponent mixtures with $\Delta\mathcal{G} = \oint \sum_{k=1}^c \mu_k dN_k = -\Delta G$.

Electric motors working with the electric potential difference supplied by a battery obey similar relations with the high and low electrochemical potentials $\mu_h = e\Phi_h$ and $\mu_l = e\Phi_l$, and the total electric charge $e\Delta N$ transferred during the cycle. If the cycle has the period \mathcal{T} , the mechanical power of the electric motor is given by $P_{\text{mech}} \equiv \mathcal{W}/\mathcal{T} \leq \Delta\mathcal{G}/\mathcal{T} = VI$ with the voltage $V = \Phi_h - \Phi_l$ and the electric current $I = e\Delta N/\mathcal{T}$. The difference $P_{\text{diss}} = VI - P_{\text{mech}}$ represents the power dissipated by the irreversible processes.

Isothermal engines working on potential differences constitute an important class of engines from the macroscale down to the nanoscale, e.g., for molecular motors running at ambient temperature using chemical energy.

1.11 Open Issues

This chapter has been devoted to thermodynamics, which provides a general framework to identify the equilibrium and nonequilibrium properties in relation to the conservation laws of energy and particle numbers within the macroscopic description of matter. In this regard, thermodynamics plays a fundamental role in the energetics of various dissipative phenomena.

As already understood by Maxwell (1871), the domain of validity of thermodynamics is the macroscopic world. Since the discovery of the atomic structure of matter and the development of the molecular kinetic theory of heat, thermodynamics has been confronted with the microscopic description of matter in terms of atoms and molecules moving according to the laws of classical or quantum mechanics on the basis of electrodynamics.

At the microscale, the particles undergo collisions that conserve energy and their dynamics are symmetric under time reversal, which is the property of microreversibility. This is in contrast with the time asymmetry observed at the macroscale in processes dissipating energy and producing entropy, in particular, during relaxation towards thermodynamic equilibrium. Such irreversible phenomena manifest a loss of memory of their initial conditions, which should be understood in terms of the microscopic dynamics of atoms and molecules.

If thermodynamics provides the framework to consistently formulate the equilibrium and nonequilibrium constitutive relations, these latter remain unknown in theory without using the microscopic dynamics. Furthermore, microreversibility has consequences for the coupling between the currents and affinities of different irreversible processes, and thus for the description of energy transduction down to the nanoscale.

These open issues will be addressed in the following chapters.