

# Chapter 2

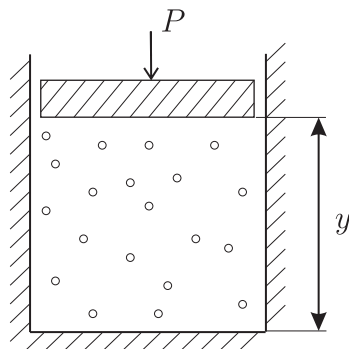
## Thermodynamics

### 2.1 Thermodynamic Description

In some cases, mechanical systems with many degrees of freedom admit a simpler description using a small number of parameters. Consider, for example, modeling of a gas in a vessel. The vessel is closed with a piston to which some force  $P$  is applied. The force compresses the gas (Fig. 2.1). The gas is envisioned as a system of a large number of rigid balls representing its molecules. The balls move inside the vessel colliding elastically with the walls and the other balls. Usually one is not interested in knowing the molecule motion. It is of interest to determine how the volume occupied by the gas depends on the applied force. This is a typical “thermodynamic” question: one is concerned with some integral characteristics of the system and the relations between them. The characteristics used for the reduced description of the system are called thermodynamic parameters. Traditionally, thermodynamics is presented as a field which is logically and conceptually independent of mechanics. In such treatments, the central notion of thermodynamics, entropy, remains vague; and achieving an understanding of thermodynamics is a similar process to that in quantum mechanics, where, by Feynman’s words, “to understand” means “to get used to and learn how to apply.” In fact, thermodynamics may be derived from mechanics. Such a derivation makes clear the notions used and provides the conditions which are necessary for the basic thermodynamical laws to be true. “The mechanical view” on thermodynamics is outlined in this chapter. We focus only on the basic ideas and skip a derivation if it is lengthy. For more details the reader is referred to [46, 50].

The reason why some universal thermodynamic relations may exist was uncovered by Boltzmann and Helmholtz: the rate of change of the thermodynamic parameters is much smaller than the rate of change of the generalized coordinates and momenta of the system. In the system of enclosed gas forced by the piston, a thermodynamic description is possible if the piston velocity is much smaller than the average molecule velocity. If the velocity of the piston is on the order of the average molecule velocity, thermodynamic description fails: the relation between the force and the gas volume becomes dependent on the details of the molecule motion.

The gas-piston system may be viewed as a mechanical system consisting of the balls and the piston. Mass of the piston is much greater than the molecule masses:

**Fig. 2.1** Gas under piston

this is the reason why the coordinate of the piston,  $y$ , changes slowly.<sup>1</sup> In case of elastic collisions, the system is Hamiltonian. One may say that the thermodynamic description of the system “gas under piston” corresponds to elimination of the fast degrees of freedom from the governing Hamiltonian equations. In fact, this situation is generic: classical thermodynamics is a theory of slow variables for a Hamiltonian system which governs micromotion.

Thermodynamics is concerned with systems possessing at least two well separated time scales and, thus, characterized by fast and slow variables. Thermodynamic theory is a theory of slow variables for such systems – this was a major Boltzmann’s insight. One can say that thermodynamic equations are the equations that are obtained by elimination of fast variables from the governing equations.

Why should macromotion obey the first and second laws of thermodynamics? Clearly, this must be caused by some special features of microdynamics. It turns out that these features are ergodicity, mixing and the Hamiltonian structure of the underlying microdynamics. The meaning of the terms ergodicity and mixing is discussed in the next section. The absence of ergodicity or Hamiltonian structure would prevent the existence at macrolevel temperature and entropy. The absence of mixing would yield the violation of the second law.<sup>2</sup>

We call the laws of thermodynamics obtained by elimination of fast degrees of freedom from Hamiltonian equations primary thermodynamics. The characteristic features of primary thermodynamics are the appearance of two new slow variables, temperature and entropy, and the dissipation of energy of slow variables (the total energy of fast and slow variables is conserved in isolated systems).

The first and the second laws of thermodynamics are the constraints which must be obeyed by any macroscopic theory. There are additional independent constraints,

<sup>1</sup> In fact, the slow change of  $y$  is accompanied by fast oscillations of small magnitude due to the collisions of the piston with the molecules. In thermodynamic description, these oscillations can be neglected. They are studied in the theory of thermodynamic fluctuations (Sect. 2.4).

<sup>2</sup> These statements will be rectified further in one respect: in fact, to have the laws of thermodynamics on macrolevel, the microequations might possess slightly more general structure than the Hamiltonian one.

which are sometimes called the third law of thermodynamics, Onsager's reciprocal relations (they are considered further in Sect. 2.6). Are there other constraints of a similar level of universality? Yes, there are. It turns out that, if dissipation is negligible, the governing equations of some slow variables must possess a Hamiltonian structure. That indicates the existence of quite peculiar "Hamiltonian reciprocities" in macrophysical interactions.

The dissipative equations of primary thermodynamics can also possess two well separated time scales. Elimination of fast degrees of freedom in primary thermodynamics yields the equations of secondary thermodynamics. If the fast variables in primary thermodynamics perform some chaotic motion then, after elimination of fast degrees of freedom and transition to the secondary thermodynamics, two new slow variables appear, "secondary entropy" and "secondary temperature." It is quite plausible that the secondary entropy possesses the features which are similar to the features of the usual thermodynamic entropy.

We touch upon all these issues in this chapter and further in Chap. 17.

## 2.2 Temperature

If a mechanical system is governed by Hamiltonian equations, and its motion is sufficiently chaotic, one can introduce the notion of temperature. First, the term "sufficiently chaotic" must be explained.

Consider a Hamiltonian system with Hamiltonian  $H(p, q)$ . Function  $H(p, q)$  does not change in the course of motion; its value is called the energy of the system. Let energy have the value  $E$ . Any trajectory of the system lies on a surface in phase space defined by the equation

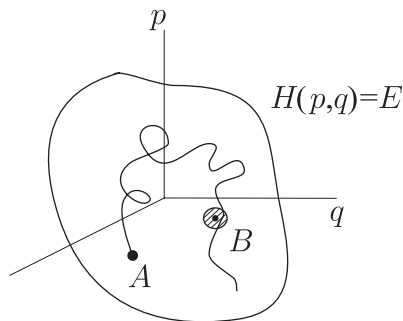
$$H(p, q) = E.$$

This surface is called an energy surface. It is assumed that energy surfaces bound finite regions in phase space.

The system is called ergodic if (almost) any trajectory covers the entire energy surface. That means the following. Let a trajectory start at some point  $A$ . Consider a point  $B$  with some vicinity of this point  $\Delta B$ . For ergodic systems, sooner or later, the trajectory will pass through the vicinity,  $\Delta B$ , of the point  $B$  for any choice of  $B$  and  $\Delta B$  (Fig. 2.2). Since  $\Delta B$  can be chosen as small as we wish, the trajectory will be passing closer and closer to  $B$ . The time of the next passage can, however, be very large. Such a behavior is observed for almost any trajectory in the sense that the set of points  $A$  for which trajectories behave differently has zero area on the energy surface. For example, there might be periodic trajectories on the energy surface of an ergodic Hamiltonian system, but the area covered by such trajectories is zero.

Intuitively, ergodicity is a feature of chaotic motion. There is another feature of chaotic motion, mixing. To define mixing one has to view the trajectories of the Hamiltonian system on an energy surface as the trajectories of particles of some

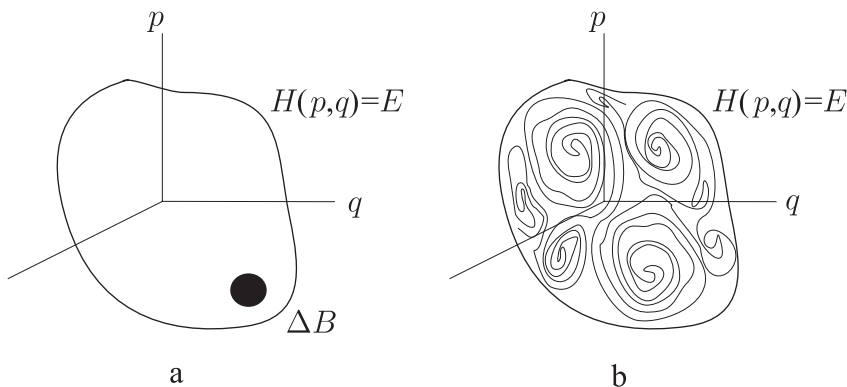
**Fig. 2.2** A sketch for the definition of ergodicity; shadowed region is  $\Delta B$



media. One can put an ink spot on the energy surface and observe its evolution in the course of motion (Fig. 2.3). If the spot tends to cover densely the entire energy surface, the system is called mixing. It turns out that every mixing system is ergodic. Ergodic systems are not necessarily mixing. Equilibrium thermodynamics discussed in Sects. 2.2–2.5 holds true for ergodic systems. In order the laws of nonequilibrium thermodynamics to be true the underlying Hamiltonian system must be also mixing. The notion of temperature and entropy is based on ergodicity only.

Consider the time average of some function,  $\varphi(p, q)$ , of generalized coordinates and momenta along a trajectory  $p(t), q(t)$ :

$$\langle \varphi \rangle = \lim_{\theta \rightarrow \infty} \frac{1}{\theta} \int_0^\theta \varphi(p(t), q(t)) dt.$$



**Fig. 2.3** A sketch for the definition of mixing: an initial small spot  $\Delta B$  is being spread by the phase flow to cover densely the entire energy surface

As was discovered by Boltzmann, for ergodic systems this time average is the same for (almost) all trajectories on the same energy surface. Moreover, this time average can be computed without knowing the particular trajectory by the formula

$$\langle \varphi \rangle = \frac{\frac{\partial}{\partial E} \int_{H(p,q) \leq E} \varphi(p, q) dp dq}{\frac{\partial}{\partial E} \int_{H(p,q) \leq E} dp dq}. \quad (2.1)$$

Here  $dp = dp_1 \dots dp_n$ ,  $dq = dq^1 \dots dq^n$ .

This formula was proven with mathematical rigor by Birkhoff and Khinchine, and is called usually the Birkhoff-Khinchine theorem.

Plugging in (2.1) various functions  $\varphi(p, q)$  and computing the integrals on the right hand side, one can find their time averages. Functions  $p_1 \frac{\partial H}{\partial p_1}, \dots, p_N \frac{\partial H}{\partial p_N}$  are of special interest: for systems with the Hamiltonian

$$H(p, q) = \frac{p_1^2}{2m_1} + \dots + \frac{p_N^2}{2m_N} + U(q) \quad (2.2)$$

they are (doubled) kinetic energies of each degree of freedom. Evaluation of the integrals from (2.1) for these functions is simple and yields the so-called equipartition law :

$$\left\langle p_1 \frac{\partial H}{\partial p_1} \right\rangle = \dots = \left\langle p_N \frac{\partial H}{\partial p_N} \right\rangle. \quad (2.3)$$

Indeed, let us find  $\left\langle p_1 \frac{\partial H}{\partial p_1} \right\rangle$ . Consider the integral,

$$\int_{H(p,q) \leq E} p_1 \frac{\partial H}{\partial p_1} dp dq.$$

Using the step function

$$\theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \quad (2.4)$$

we can write this integral as an integral over the entire phase space,

$$\int p_1 \frac{\partial H}{\partial p_1} \theta(E - H(p, q)) dp dq.$$

Therefore,

$$\frac{\partial}{\partial E} \int_{H(p,q) \leq E} p_1 \frac{\partial H}{\partial p_1} dp dq = \int p_1 \frac{\partial H}{\partial p_1} \theta'(E - H(p, q)) dp dq,$$

where  $\theta'(x)$  is the derivative of the step-function (the derivative,  $\theta'(x)$ , is equal to the  $\delta$ -function, but this is not essential at the moment). The integrand can be written as

$$\begin{aligned}
p_1 \frac{\partial H}{\partial p_1} \theta'(E - H(p, q)) &= -p_1 \frac{\partial}{\partial p_1} \theta(E - H(p, q)) \\
&= -\frac{\partial}{\partial p_1} (p_1 \theta(E - H(p, q))) + \theta(E - H(p, q)). \quad (2.5)
\end{aligned}$$

The integral of the first term in the right hand side over the entire phase space is equal to zero due to the divergence theorem and vanishing of  $\theta(E - H(p, q))$  at infinity ( $H(p, q) > E$  at infinity). Therefore,

$$\frac{\partial}{\partial E} \int_{H(p, q) \leq E} p_1 \frac{\partial H}{\partial p_1} dp dq = \int \theta(E - H(p, q)) dp dq. \quad (2.6)$$

The result (2.6) does not depend on the choice of a particular component of momenta,  $p_1, \dots, p_n$ , and the same answer we get for integrals of  $p_2 \frac{\partial H}{\partial p_2}, \dots, p_n \frac{\partial H}{\partial p_n}$ . Then the equipartition law follows from (2.1) and (2.6)

For the systems with Hamiltonians (2.2) equipartition law means that the averaged values of kinetic energies of all degrees of freedom are the same. The common value (2.3) is denoted by  $T$  and called absolute temperature. We drop the adjective and call it temperature because no other temperatures will appear in our consideration.

The integral in the right hand side of (2.6) is called the phase volume,

$$\Gamma(E) = \int \theta(E - H(p, q)) dp dq = \int_{H(p, q) \leq E} dp dq.$$

The denominator in (2.1) is the derivative of the phase volume,  $d\Gamma(E)/dE$ , which will also be denoted for brevity  $\Gamma_E(E)$ .

Finally, temperature can be expressed explicitly in terms of the phase volume  $\Gamma(E)$ :

$$T = \frac{\Gamma(E)}{d\Gamma(E)/dE}. \quad (2.7)$$

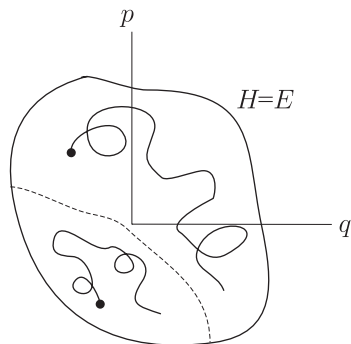
As follows from (2.7), temperature has the dimension of energy. Traditionally, temperature is measured in degrees. The two numbers are linked by Boltzmann's constant  $k$ : if  $T^\circ$  is the value of temperature in degrees Kelvin, then

$$T = k T^\circ.$$

The constant  $k$  is very small:

$$k = 1.38 \times 10^{-16} \text{ erg/deg}.$$

**Fig. 2.4** A sketch of energy surface for a two-temperature system



i.e. one degree Kelvin corresponds to energy of about  $10^{-16}$  g cm<sup>2</sup>/s<sup>2</sup>. Temperature becomes on the order of unity if measured in electron-volts. (1 eV is the energy which an electron gains accelerating between the points with the difference of electric potential equal to 1 V; this energy is very small due to the small mass of an electron). Room temperature corresponds to about 1/40 eV. Energy units for temperature are convenient in all theoretical treatments and will be used here; Boltzmann's constant appears only at the stage of comparing theory and experiments.

Ergodicity is necessary to introduce temperature. If the system is not ergodic, temperature may not exist. For example, consider the system for which the energy surface contains two parts such that trajectory started in one part always remains in that part (see Fig. 2.4). For such systems, formula (2.1) does not hold, and the equipartition law is not true. Under some additional conditions, one may say that the system has two temperatures corresponding to each part of the energy surface, but such a situation is beyond the scope of classical thermodynamics.

Ergodicity yields immediately irreversibility of macromotion. This is seen from the equipartition law. Consider, for example, the gas-piston system. Let the piston be given some initial velocity. After some time, the equipartition of energy sets up in the system. This means that the average kinetic energy of the piston is equal to the average kinetic energy of a molecule. Since the mass of the piston is much larger than the mass of molecules, the velocity of the piston becomes very small, i.e. the piston comes to rest. This clearly demonstrates the irreversible character of piston's motion in spite of reversibility of the underlying microdynamics.

## 2.3 Entropy

Entropy is a characteristic of slow processes in ergodic Hamiltonian systems.<sup>3</sup>

<sup>3</sup> The term "entropy" is widely explored now in many different senses. What we mean here by entropy is, precisely, the thermodynamic entropy introduced by Clausius. The meaning of Clausius' entropy for ergodic Hamiltonian systems was determined by J.W. Gibbs and P. Hertz.

To explain what entropy is, consider first the gas-piston system. Let the position of the piston,  $y$ , be changed slowly by some “hard device.” This means that we prescribe the function,  $y(t)$ . Changing  $y$  we do some work. Therefore energy of the system changes. To find the dependence of energy on time we note that Hamiltonian of the system,

$$H(p, q, y) = \frac{p_1^2}{2m} + \dots + \frac{p_n^2}{2m} + U(q_1, \dots, q_n, y), \quad (2.8)$$

depends explicitly on time through the dependence of potential energy on  $y$ . The energy rate is

$$\frac{dE}{dt} = \frac{dH(p, q, y)}{dt} = \frac{\partial H}{\partial p_i} \frac{dp_i}{dt} + \frac{\partial H}{\partial q^i} \frac{dq^i}{dt} + \frac{\partial H}{\partial y} \frac{dy}{dt} = \frac{\partial H(p, q, y)}{\partial y} \frac{dy}{dt}. \quad (2.9)$$

The two terms in (2.9) are canceled due to Hamiltonian equations (1.63). The derivative  $\partial H/\partial y$  has the meaning of force which one has to apply in order to make the piston move along the path  $y(t)$ .<sup>4</sup>

If we know the trajectory of the systems,  $p(t)$ ,  $q(t)$ , we could find the energy at time  $t$  by integrating (2.9):

$$E(t) - E(t_0) = \int_{t_0}^t \frac{\partial H(p(\tau), q(\tau), y(\tau))}{\partial y(\tau)} \frac{dy(\tau)}{d\tau} d\tau. \quad (2.10)$$

In principle, one obtains different values of energy at time  $t$  for different trajectories  $p(\tau)$ ,  $q(\tau)$  and different piston paths  $y(\tau)$ . Remarkably, for ergodic Hamiltonian systems and a slow change of the parameter  $y$ , the final value of energy depends only on the final value of the parameter  $y$ , the initial values of energy,  $E_0 = E(t_0)$  and the initial value of the parameter  $y$ ,  $y_0 = y(t_0)$ , and depends neither on the trajectories,  $p(\tau)$ ,  $q(\tau)$ , nor on the path,  $y(\tau)$ :

$$E(t) = \text{function}(y(t), y_0, E_0). \quad (2.11)$$

Moreover, the dependence of the final value of energy,  $E(t)$ , on  $y_0$  and  $E_0$  is “degenerated”: the parameters  $y_0$  and  $E_0$  enter (2.11) only through a combination  $S(E_0, y_0)$ , where  $S(E, y)$  is some function which is determined uniquely by Hamilton function  $H(p, q, y)$ :

$$E(t) = E(y(t), S_0(E_0, y_0)). \quad (2.12)$$

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<sup>4</sup> For the gas-piston system the factor  $\partial H(p, q, y)/\partial y$  does not depend on  $p$  due to (2.8), but this is not essential in our reasoning and we proceed in a more general setting.



Derivation of (2.12) is quite simple. First, we note that on the right hand side of (2.10)  $dy/d\tau$  changes slowly. Therefore,  $\partial H/\partial y$  may be substituted by its average over the energy surface  $H(p, q, y(\tau)) = E(\tau)$ ,

$$E(t) - E(t_0) = \int_{t_0}^t \left\langle \frac{\partial H}{\partial y} \right\rangle \frac{dy}{d\tau} d\tau,$$

or, after differentiation with respect to  $t$ ,

$$\frac{dE}{dt} = \left\langle \frac{\partial H}{\partial y} \right\rangle \frac{dy}{dt}. \quad (2.13)$$

The average value  $\langle \partial H/\partial y \rangle$  can be computed using the Birkhoff-Khinchine theorem (2.1) as

$$\left\langle \frac{\partial H}{\partial y} \right\rangle = \frac{\frac{\partial}{\partial E} \int_{H(p,q,y) \leq E} \frac{\partial H}{\partial y} dpdq}{\frac{\partial}{\partial E} \int_{H(p,q,y) \leq E} dpdq}. \quad (2.14)$$

Introducing the phase volume bounded by the energy surface  $H(p, q, y) = E$ ,

$$\Gamma(E, y) = \int_{H(p,q,y) \leq E} dpdq = \int \theta(E - H(p, q, y)) dpdq, \quad (2.15)$$

and differentiating (2.15) with respect to  $y$  we find

$$\begin{aligned} \frac{\partial \Gamma(E, y)}{\partial y} &= - \int \theta'(E - H(p, q, y)) \frac{\partial H(p, q, y)}{\partial y} dpdq \\ &= - \frac{\partial}{\partial E} \int \theta(E - H(p, q, y)) \frac{\partial H(p, q, y)}{\partial y} dpdq \\ &= - \frac{\partial}{\partial E} \int_{H(p,q,y) \leq E} \frac{\partial H(p, q, y)}{\partial y} dpdq. \end{aligned} \quad (2.16)$$

From (2.14) and (2.16)

$$\left\langle \frac{\partial H}{\partial y} \right\rangle = - \frac{\partial \Gamma(E, y)/\partial y}{\partial \Gamma(E, y)/\partial E}. \quad (2.17)$$

Plugging (2.17) into (2.13) we obtain

$$\frac{\partial \Gamma(E, y)}{\partial E} \frac{dE}{dt} + \frac{\partial \Gamma(E, y)}{\partial y} \frac{dy}{dt} = 0. \quad (2.18)$$

Hence, the phase volume does not change in time, which is also true of any function of the phase volume,  $S(\Gamma)$ .

Let us specify function  $S(\Gamma)$  by the condition that

$$\frac{\partial S(\Gamma(E, y))}{\partial E} = \frac{1}{T}. \quad (2.19)$$

Since

$$\frac{\partial S(\Gamma(E, y))}{\partial E} = \frac{dS}{d\Gamma} \frac{\partial \Gamma}{\partial E},$$

and according to (2.7),  $T = \Gamma(\partial \Gamma / \partial E)^{-1}$ , we obtain for  $S(\Gamma)$  the differential equation

$$\frac{dS}{d\Gamma} = \frac{1}{\Gamma},$$

the only solution of which is

$$S(E, y) = \ln \Gamma(E, y) + \text{const}. \quad (2.20)$$

This function is called thermodynamic entropy.

Entropy does not change in the process under consideration. Hence,

$$S(E, y) = S_0, \quad S_0 = S(E_0, y_0). \quad (2.21)$$

If  $T > 0$ , then  $\partial S / \partial E > 0$  and we can solve (2.21) with respect to  $E$ . We see that energy is determined by the current value of  $y$ , while the initial values of energy and  $y$  enter in this dependence only through the combination  $S_0 = S_0(E_0, y_0)$ , i.e. we arrive at (2.12).

In terms of entropy, equation (2.17) for the force,  $\langle \partial H / \partial y \rangle$ , takes the form

$$\left\langle \frac{\partial H}{\partial y} \right\rangle = -T \frac{\partial S(E, y)}{\partial y}. \quad (2.22)$$

Obviously, our derivation remains valid if the system has a number of slow parameters,  $y^1, \dots, y^m$ . In this case,  $y$  in all previous equations denotes the set  $y = (y^1, \dots, y^m)$  while (2.22) is replaced by the equation

$$\left\langle \frac{\partial H}{\partial y^\mu} \right\rangle = -T \frac{\partial S(E, y)}{\partial y^\mu}, \quad (2.23)$$

where  $\mu$  runs through values  $1, \dots, m$ .

Equations (2.19) and (2.23) link temperature,  $T$ , and generalized forces,  $\langle \partial H / \partial y^\mu \rangle$ , with the slow characteristics of the system,  $E$  and  $y^\mu$ . They are called

constitutive equations. The constitutive equations are specified as soon as entropy is known as a function of  $E$  and  $y^\mu$ . For a given Hamiltonian of the system,  $H(p, q, y)$ , one can determine the phase volume computing the integral (2.15), and then find entropy  $S(E, y)$  from (2.20).

Constitutive equations (2.19) and (2.23) take a simpler form in the terms of function  $E(y, S)$ :

$$T = \frac{\partial E(y, S)}{\partial S}, \quad \left\langle \frac{\partial H}{\partial y^\mu} \right\rangle = \frac{\partial E(y, S)}{\partial y^\mu}. \quad (2.24)$$

Indeed, the equation

$$S(E(S, y), y) = S \quad (2.25)$$

must be an identity for all values of parameters  $S$  and  $y$ . Differentiating (2.25) with respect to  $S$  and  $y^\mu$ , we obtain

$$\frac{\partial S}{\partial E} \frac{\partial E(S, y)}{\partial S} = 1, \quad \frac{\partial S}{\partial E} \frac{\partial E(S, y)}{\partial y^\mu} + \frac{\partial S}{\partial y^\mu} = 0. \quad (2.26)$$

Equations (2.24) follow from (2.19), (2.23) and (2.26).

It is worthing emphasize that, if the system were not ergodic or the parameters  $y$  were not slow, then the energy at time  $t$  computed from differential equation (2.9) depends on the initial values of the generalized coordinates and momenta  $p_0, q_0$ , and the entire trajectory  $y(\tau)$ ,  $\tau < t$ . Therefore, the constitutive equations obtained do not make sense.

Formulas (2.12), (2.19), (2.21), (2.23) and (2.24) are valid for any ergodic Hamiltonian system no matter how many degrees of freedom it has. For example, one can speak of entropy and temperature of a pendulum, which has just one degree of freedom. In this case the energy surfaces are closed curves in the phase space (for sufficiently small  $E$ ). Each trajectory covers the entire energy surface, thus the system is ergodic. Assuming for definiteness that the length of the pendulum is a slow parameter, one can find entropy of the pendulum from (1.68): in the limit of small energies,  $S = \ln(E\sqrt{l/g}) + \text{const.}$

*Example.* Let us find entropy of a gas occupying volume  $V$ . We model the gas by a Hamiltonian system of  $N$  rigid spheres of radii  $a$  and of equal masses  $m$ . Each ball has three translational degrees of freedom, so the total number of degrees of freedom,  $n$ , is  $3N$ . Hamilton function is a sum of kinetic energy  $K$  and particle-particle and particle-wall interaction energy  $U$ :

$$H = K + U, \\ K = \frac{p_1^2}{2m} + \dots + \frac{p_n^2}{2m}, \quad U = U(q_1, \dots, q_n). \quad (2.27)$$

Interaction energy is zero if particles do not overlap with each other and the wall, otherwise it is equal to infinity. The question of ergodicity of such a system is not elementary. We proceed assuming that the system is ergodic. We have to find

$$\Gamma = \int_{H(p,q,y) \leq E} dp dq.$$

Since  $H = +\infty$  if any two particles overlap or a particle overlaps with the wall and, otherwise,  $H = K$  and does not depend on  $q$ , the phase volume is the product of two integrals:

$$\Gamma = \Gamma_p \Gamma_q, \quad \Gamma_p = \int_{H(p) \leq E} dp, \quad \Gamma_q = \int_{\text{admissible } q} dq. \quad (2.28)$$

The integral,  $\Gamma_p$ , is the volume of the sphere of the radius  $\sqrt{2mE}$  in  $n$ -dimensional space. If  $R$  is the radius of a sphere in  $n$ -dimensional space, its volume is

$$V_n(R) = c_n R^n, \quad c_n = \frac{\pi^{n/2}}{\frac{n}{2} \Gamma(\frac{n}{2})},$$

$\Gamma(s)$  being the  $\Gamma$ -function. For an integer  $s$ ,  $\Gamma(s) = (s-1)!$  So,

$$\Gamma_p = c_n (2mE)^{n/2}. \quad (2.29)$$

The integral,  $\Gamma_q$ , can easily be found in the limit when the ball radius tends to zero. In this limit one may neglect overlapping of the balls and take into account only the positions of the balls inside the volume  $V$ . Then

$$\Gamma_q = V^N. \quad (2.30)$$

Dropping additive constants we obtain for entropy from (2.20), (2.28), (2.29) and (2.30):

$$S = \ln(E^{3N/2} V^N) = N \left( \frac{3}{2} \ln E + \ln V \right). \quad (2.31)$$

One can find temperature from (2.19) and (2.31) as

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \frac{N}{E}. \quad (2.32)$$

Determining energy in terms of temperature from (2.32), we arrive at the familiar constitutive equation of the perfect gas:

$$E = \frac{3}{2}NT. \quad (2.33)$$

An important consequence of formula (2.31) is an unbounded growth of entropy when the gas volume increases. Such a behavior of entropy changes if a force,  $P$ , acts on the piston. Then the Hamiltonian of the system acquires an additional term:<sup>5</sup>

$$H = K + U + Py. \quad (2.34)$$

Calculation of entropy of the system (2.34) is reduced to the previous one for the system (2.27) by changing  $E$  to  $E - Py$  :

$$S = N \left( \frac{3}{2} \ln(E - Py) + \ln V \right).$$

Taking into account that  $V$  is a linear function of  $y$ :  $V = y\Omega$ ,  $\Omega$  being the area of the piston, and dropping unessential constants, we obtain

$$\begin{aligned} S(E, y) &= N \ln \left[ \frac{3}{2} \ln(E - Py) + \ln(y\Omega) \right] \\ &= N \ln \left[ \frac{Py}{E} \left( 1 - \frac{Py}{E} \right)^{3/2} \right] + const. \end{aligned}$$

A graph of the entropy per particle,  $S/N$ , as a function of the dimensionless distance  $y^* = Py/E$  is shown in Fig. 2.5.

The remarkable feature of this graph is that entropy reaches its maximum value. The point where entropy is maximum corresponds to the equilibrium state of the system the reader is invited to check this fact. It turns out that this property of entropy, reaching its maximum value at equilibrium, is generic. The physical origin of this property is explained in Sect. 2.5.

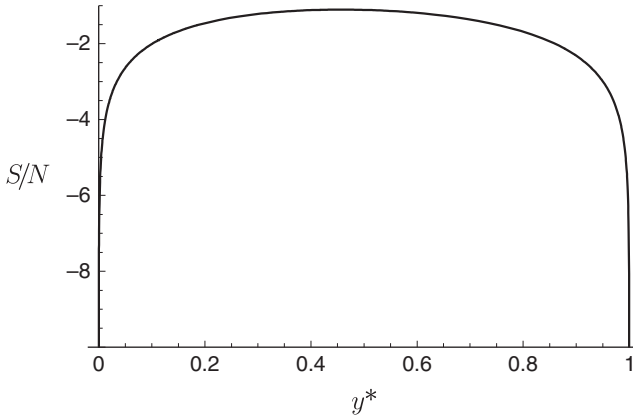
So far we have considered the case when all external forces act only on slow variables as is seen from the energy equation (2.9). Such processes are called adiabatic. If there are some external forces,  $F_i$ , acting on the fast coordinates,  $q_i$ , then the energy equation gets the additional term

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<sup>5</sup> Formula (2.34) becomes obvious if one writes first the energy of the entire system “gas+piston” endowing the piston with some mass  $M$  :

$$H = K + U + Py + \frac{Y^2}{2M},$$

where  $Y$  is the momentum of the piston. In (2.34) we dropped the kinetic energy of the piston which is negligible because, due to the equipartition of energy over all degrees of freedom, near equilibrium it is on the order of kinetic energy of one molecule,  $K/N$ . The sign + at  $Py$  corresponds to the negative direction of the force acting on the piston for  $P \geq 0$  (indeed, the Lagrange function of the piston corresponding to the Hamilton function chosen is  $L = \frac{1}{2}M\dot{y}^2 - Py$ , thus  $M\ddot{y} = -P$ ).



**Fig. 2.5**  $S/N$ , as a function of the dimensionless distance between the piston and the bottom,  $y^* = P y/E$

$$\frac{dE}{dt} = \frac{\partial H}{\partial y^\mu} \frac{dy^\mu}{dt} + \frac{\partial H}{\partial q^i} F^i.$$

Averaging over time and taking into account that  $E$  and  $y$  change slowly, we have

$$\frac{dE}{dt} = \left\langle \frac{\partial H}{\partial y^\mu} \right\rangle \frac{dy^\mu}{dt} + \frac{dQ}{dt}, \quad \frac{dQ}{dt} = \left\langle \frac{\partial H}{\partial q^i} F^i \right\rangle. \quad (2.35)$$

The additional work of external forces denoted by  $dQ$  is called heat supply. Heat supply causes entropy to change. The process is called quasi-equilibrium, if the constitutive equations (2.28) remain valid for  $dQ \neq 0$ . Then, we have from energy equation (2.35)

$$\frac{\partial E(y, S)}{\partial y^\mu} \frac{dy^\mu}{dt} + \frac{\partial E(y, S)}{\partial S} \frac{dS}{dt} = \left\langle \frac{\partial H}{\partial y^\mu} \right\rangle \frac{dy^\mu}{dt} + \frac{dQ}{dt}. \quad (2.36)$$

The first terms on both sides of (2.36) cancel out due to (2.24), and (2.36) becomes a link between entropy, temperature and heat supply:

$$\frac{dQ}{dt} = T \frac{dS}{dt}. \quad (2.37)$$

If  $dQ \neq 0$ , entropy may either increase or decrease depending on whether energy is pumped to the system ( $dQ > 0$ ) or taken from the system ( $dQ < 0$ ).

Comparing the two characteristics of the system, energy and entropy, one may say that energy is a more fundamental one: energy makes sense for any system while entropy can be introduced only for slow processes in ergodic systems.

We have seen that the Hamiltonian structure of the equations of micromechanics yields the laws of equilibrium thermodynamics. One may wonder how important

it is that the equations of micromechanics are Hamiltonian. In other words: could non-Hamiltonian equations of microdynamics yield the equations of classical equilibrium thermodynamics? It turns out that the class of such equations is indeed slightly wider than the class of Hamiltonian equations (see Appendix E).

## 2.4 Entropy and Probability

Slow parameters  $y$  fluctuate near the equilibrium values. For example, in the system “gas under piston” the distance between the piston and the bottom,  $y$ , varies slightly due to the collisions of the piston with the molecules. One may wonder what is the probability density of  $y$ ,  $f(y)$ ? The answer was found by Einstein: the probability density of slow variables fluctuating near the equilibrium values is determined only by the equilibrium properties of the system, namely, by the function  $S(E, y)$ , and is given by the formula

$$f(y) = \text{const } e^{S(E,y)}. \quad (2.38)$$

Formula (2.38) has an asymptotic nature and holds for systems with a very large number of fast degrees of freedom,  $n$ . There is a generalization of this formula for systems with any finite  $n$  [43, 46].

According to (2.38), the most probable values of  $y$  are the values for which entropy takes its maximum value. Since entropy is usually proportional to the number of fast degrees of freedom (for a gas this is seen from (2.31)) which is large, maximum is very sharp and, in fact, the slow variables just fluctuate slightly around the equilibrium values.

## 2.5 Gibbs Principles

Gibbs suggested use of the maximum property of entropy as the first principle in any modeling of thermodynamic equilibrium.

**The first Gibbs principle.** *In a state of thermodynamic equilibrium, the entropy  $S$  of an isolated system attains its maximum on all possible states of the system with a given energy  $E$ .*

The Gibbs principle differs considerably from the variational principles of analytical mechanics. In mechanics, only the particle positions are subject to change, but in the Gibbs principles virtually all characteristics of equilibrium are varied. In the consideration of phase equilibrium, for example, the interphase surface and the masses of both phases are subject to change. An example of the application of the Gibbs principles to the equilibrium of elastic media will be given in Sect. 7.4. Consider here another example.

Let us show that temperatures of two contacting systems are equal if the systems are in thermodynamical equilibrium and isolated from the environment. Denote

entropies and energies of the systems by  $E_1, S_1$ , and  $E_2, S_2$ . Thermodynamical properties of the systems are determined by the functions  $S_1(E_1)$  and  $S_2(E_2)$ . The total entropy of the two systems, by our assumption, is

$$S(E_1, E_2) = S_1(E_1) + S_2(E_2). \quad (2.39)$$

Systems are in contact and may exchange energies: heat may flow from one system to another. The total energy must not change in such a process because the systems are isolated from the environment:

$$E_1 + E_2 = E. \quad (2.40)$$

The total energy  $E$  is supposed to be given. In equilibrium, the entropy (2.39) must be maximum on the set of all possible values  $E_1, E_2$  obeying the constraint (2.40). The condition of thermodynamical equilibrium may be obtained, for example, by eliminating the variable  $E_2$ ,

$$S = S_1(E_1) + S_2(E - E_1),$$

and differentiating entropy with respect to  $E_1$ . We get

$$\left. \frac{dS_1(E_1)}{dE_1} - \frac{dS_2(E_2)}{dE_2} \right|_{E_2=E-E_1} = 0$$

or

$$\frac{1}{T_1} = \frac{1}{T_2}$$

as claimed. Similar result holds for many systems in contact. The first Gibbs principle can be put in another form which is often used:

**The second Gibbs principle.** *In the state of thermodynamic equilibrium, the energy  $E(y, S)$  of an isolated system attains its minimum on all states of the system with a given value of entropy  $S$ .*

The two Gibbs principles are equivalent except in some degenerate cases.

## 2.6 Nonequilibrium Processes

Consider an isolated system characterized by a number of slow variables,  $y^1, \dots, y^n$ . There are some equilibrium values of  $y$ ; the system remains in the state with such values of  $y$  indefinitely. If the initial values of  $y$  differ from the equilibrium values, the slow variables evolve approaching the equilibrium values. The theory of nonequilibrium processes aims to establish equations describing this evolution. In



this section we discuss the situation when the governing equations of the evolution to equilibrium are ordinary differential equations.

Clausius found from phenomenological reasoning that entropy of an isolated system may not decrease in the path to equilibrium. This is the so-called second law of thermodynamics. For Hamiltonian systems this feature of entropy was established by Kubo [163]. Hamiltonian systems possess such a feature if the phase flow is mixing. In summary, the first and the second laws of thermodynamics are observed only for one reason: the equations governing micromotion are Hamiltonian and mixing.<sup>6</sup> If micromotion is not Hamiltonian or mixing, one can construct examples showing that the first and/or the second laws are violated.

The governing equations of nonequilibrium thermodynamics are purely phenomenological. They must obey the constraint of the second law: if the system is isolated, its entropy may not decrease. To construct the evolution equations one usually chooses as the main idea that entropy has a maximum value at equilibrium. Then the simplest system of equations warranting the approach to equilibrium is

$$\frac{dy^\mu}{dt} = D^{\mu\nu}(y) \frac{\partial S(E, y)}{\partial y^\nu}, \quad (2.41)$$

where  $D^{\mu\nu}(y)$  is some positive semi-definite matrix. Indeed, entropy of the system grows along each trajectory  $y(t)$  of the system (2.41):

$$\frac{dS(E, y(t))}{dt} = \frac{\partial S(E, y)}{\partial y^\mu} D^{\mu\nu}(y) \frac{\partial S(E, y)}{\partial y^\nu} \geq 0. \quad (2.42)$$

We assumed here that the system is isolated, so the energy remains constant. According to (2.42),  $D^{\mu\nu}(y)$  have the meaning of dissipation coefficients, i.e. the coefficients controlling the entropy growth.

If  $y(t)$  are close to the equilibrium values, one can use a linearized version of (2.41). To write down the linearized equations (2.41) we accept that the equilibrium corresponds to the zero values of  $y$ . Then, expanding  $S$  in a Taylor series with respect to  $y$  in vicinity of equilibrium, we have

$$S = \text{const} - \frac{1}{2} a_{\mu\nu} y^\mu y^\nu,$$

where  $a_{\mu\nu}$  is a non-negative symmetric matrix. In linear approximation the coefficients  $D^{\mu\nu}$  are some constants,  $D^{\mu\nu} = D^{\mu\nu}(0)$ . The governing equations take the form a system of linear differential equations,

$$\frac{dy^\mu}{dt} = -D^{\mu\nu}(0) a_{\lambda\nu} y^\lambda. \quad (2.43)$$

---

<sup>6</sup> Up to some refinements of this statement like that made at the end of Sect. 2.3, which, most probably, are of little physical significance.

Equations (2.41) are more a concept than a “Law of Nature”: in modeling the evolution to equilibrium, one may try equations of the form (2.41), but, in fact, the physically adequate dynamical equations may have a different form: all one must not violate is the evolution of entropy to its maximum value.

Are there other constraints to the governing equations, which are additional to the first and the second laws of thermodynamics? Yes, there are. They are caused by the Hamiltonian structure of microdynamics. The first such constraint was discovered by Onsager [236]: the dissipative coefficients,  $D^{\mu\nu}(0)$ , are not arbitrary. They must obey the reciprocal relations

$$D^{\mu\nu}(0) = D^{\nu\mu}(0). \quad (2.44)$$

Onsager’s reciprocal relations follow from reversibility of micromotion. The latter takes place if Hamilton function is an even function of momenta,  $p$ . There are systems for which Hamilton function is not an even function, like, for example, the systems under action of external constant magnetic field,  $B$ : Hamilton function contains the terms of the form,  $pB$ , which change the sign if time is reversed. For systems in a magnetic field, the coefficients  $D^{\mu\nu}$  may also depend on the magnetic field, and Onsager’s reciprocal relations are replaced by

$$D^{\mu\nu}(0, B) = D^{\nu\mu}(0, -B).$$

Note that the coefficients of the linear differential equations (2.43), the product of two symmetric matrices, are not necessarily symmetric.

Onsager’s reciprocal relations are independent of the first and the second laws of thermodynamics. They are sometimes called the third law of thermodynamics.

There are also other constraints [44, 50]: if the slow variables are the coordinates and momenta of the underlying Hamiltonian microdynamics, and the dissipation is negligibly small, the equations of slow evolution must possess a Hamiltonian structure with some effective Hamilton function,  $H_{\text{eff}}(y, S)$ ,

$$\frac{dy^\mu}{dt} = \omega^{\mu\nu} \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\nu}. \quad (2.45)$$

Here  $\omega^{\mu\nu}$  is the constant tensor defining the Hamiltonian structure

$$\omega^{\mu\nu} = \begin{cases} 1 & \mu \geq n+1, \nu = \mu \\ -1 & \mu \leq n, \nu = n+\mu \\ 0 & \text{otherwise} \end{cases}.$$

The effective Hamilton function,  $H_{\text{eff}}(y, S)$ , can be calculated explicitly in terms of the phase volume of the Hamiltonian system. This calculation shows that it has the meaning of the total energy of the system. Entropy in (2.45) is a given constant. In many models of continuum mechanics, the kinematic variables can be viewed as the slow variables of the underlying Hamiltonian system. Therefore, if the dissipation is

neglected, the governing dynamics is Hamiltonian, and the corresponding principle of least action must exist.<sup>7</sup> This implies that only quite special interactions with specific “variational reciprocal relations” are possible in continuum mechanics. Most considerations in this book are based on that point.

In general, if the dissipative terms are taken into account, then the slow evolution is governed by the equations

$$\begin{aligned} \frac{dy^\mu}{dt} &= \omega^{\mu\nu} \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\nu} - \frac{1}{T} D^{\mu\nu}(y, S) \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\nu} \\ \frac{dS}{dt} &= \frac{1}{T^2} D^{\mu\nu}(y, S) \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\mu} \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\nu}, \quad T = \frac{\partial H_{\text{eff}}(y, S)}{\partial S}. \end{aligned} \quad (2.46)$$

In these equations, the dissipative processes are characterized by the dissipative coefficients,  $D^{\mu\nu}(y, S)$ . The dissipative coefficients must be symmetric:

$$D^{\mu\nu}(y, S) = D^{\nu\mu}(y, S). \quad (2.47)$$

Equation (2.47) may be viewed as an extension of Onsager’s relations to the non-linear case.

Equations (2.46) form a system of ordinary differential equations for unknown functions  $y^\mu(t)$  and  $S(t)$ . The model is specified by the effective Hamiltonian,  $H_{\text{eff}}(y, S)$ , and the dissipative coefficients,  $D^{\mu\nu}(y, S)$ . The effective Hamiltonian is determined by the equilibrium properties of the system since it can be expressed in terms of its phase volume. In contrast, the dissipative coefficients are the characteristics of the nonequilibrium behavior; they describe the mixing properties of the underlying Hamiltonian system. The dissipative coefficients are independent of equilibrium properties: one may envision the systems with the same equilibrium properties but different laws of evolution to equilibrium.

Energy of the system,  $H_{\text{eff}}(y, S)$ , is conserved in the course of evolution to equilibrium:

$$H_{\text{eff}}(y, S) = E = \text{const}, \quad (2.48)$$

as it must be for an isolated system. Indeed,

$$\frac{dH_{\text{eff}}(y, S)}{dt} = \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\mu} \frac{dy^\mu}{dt} + \frac{\partial H_{\text{eff}}(y, S)}{\partial S} \frac{dS}{dt}, \quad (2.49)$$

and the right hand side of (2.49) vanishes due to (2.46).

The energy conservation allows us to reduce the order of the system. The resulting equations take a simple form if expressed in terms of the function,  $S(E, y)$ ,

---

<sup>7</sup> The fact that (2.45) holds for isolated systems is not a constraint in consideration of continuum media: the isolation requirement just specifies the boundary conditions and does not affect the differential equations.

which is the solution of (2.48) with respect to  $S$  for a given  $E$ . For this function, similarly to (2.26),

$$\frac{1}{T} = \frac{\partial S(E, y)}{\partial E}, \quad \frac{\partial S(E, y)}{\partial y^\mu} = -\frac{1}{T} \frac{\partial H_{\text{eff}}(y, S)}{\partial y^\mu}.$$

Therefore, the governing differential equations become a system of  $m$  differential equations of the first order:

$$\begin{aligned} \frac{dy^\mu}{dt} = & -\omega^{\mu\nu} \frac{1}{\partial S(E, y)/\partial E} \frac{\partial S(E, y)}{\partial y^\nu} \\ & + D^{\mu\nu}(y, S(E, y)) \frac{1}{\partial S(E, y)/\partial E} \frac{\partial S(E, y)}{\partial y^\nu}. \end{aligned} \quad (2.50)$$

This system is determined by the functions,  $S(E, y)$  and  $D^{\mu\nu}(y, S)$ , while  $E$  is considered as a given parameter.

An important process which is not covered by (2.46) or (2.50) is heat conduction. In this case, the slow variables,  $y^\mu$ , are the energies of small parts of the body; they are not the coordinates or momenta of the underlying Hamiltonian system. The equations of heat conduction also possess a special structure; the reader is referred to [50] for consideration of this case and for further details regarding the derivation of (2.46) and (2.50).

## 2.7 Secondary Thermodynamics and Higher Order Thermodynamics

The special structure of thermodynamic equations, comprised of the existence of energy and entropy, the equations of state and the constitutive equations and the special form of equations of nonequilibrium thermodynamics, pertains only to the equations governing the evolution of slow variables of a Hamiltonian system. Such a theory may be called primary thermodynamics. It might happen that the equations of primary thermodynamics also admit two well-separated time scales. One may wonder what are the governing equations for the slow variables of the primary thermodynamics or, in other words, which equations do we get after the elimination of the fast variables in the equations of primary thermodynamics. We call the corresponding theory of slow variables of primary thermodynamics secondary thermodynamics. There are two important examples of secondary thermodynamics: plasticity theory and turbulence theory. Plasticity of crystalline bodies is caused by motion of defects of crystal lattice, such as dislocations. The crystal lattice may be viewed as a Hamiltonian system. The defects are the slow variables of this Hamiltonian system. Therefore the governing dynamical equations for defects are the subject of primary thermodynamics. Accordingly, macroscopic plastic behavior of crystals and polycrystals is the subject of secondary thermodynamics. Another example: turbulence theory. Equations describing fluid motion are the equations

of primary thermodynamics. In the case of a chaotic fluid motion, turbulence, the motion is characterized by fast and slow variables. Elimination of fast variables and construction of the equations governing the slow variables is the major goal of turbulence theory. For both examples of secondary thermodynamics, the development of a theory of slow variables has not been completed yet. In particular, it is not known whether the equations of secondary thermodynamics must possess a special structure, as do the equations of primary thermodynamics. Most probably, there are no statements of the same level of generality as for primary thermodynamics. In particular, in turbulence theory different flow geometries may yield quite different systems of equations for slow variables. One feature of secondary thermodynamics can be quite general though. If the equations of primary thermodynamics exhibit chaotic behavior, then a new entropy can enter the theory. As in primary thermodynamics, its meaning is two fold: the new entropy characterizes fluctuations of the slow variables and the information on the system lost in the elimination of fast degrees of freedom. In the case of materials with random microstructures, this new characteristic called entropy of microstructure is introduced and studied in Sect. 18.5–18.8. In contrast to thermodynamic entropy, entropy of microstructure should decrease in an isolated system.<sup>8</sup> This feature is caused by the appearance of attractors in the phase space: the phase volume shrinks when the system approaches the equilibrium state.

One may envision the situations when a secondary thermodynamics model possesses two well-separated time scales. Then the elimination of the fast variables yields the equations of tertiary thermodynamics, etc. What will be common for all levels of thermodynamics is the existence of energy and entropy equations as long as energy and entropy remain slow variables. Besides, thermodynamic entropy, once appeared, will remain an increasing function for closed systems.

The existence of entropy is intimately related to the Hamiltonian structure of microdynamics. Such a structure is guaranteed by the classical approximation in quantum mechanics. However, if the quantum mechanics problem has two well-separated time scales, the elimination of the fast variables may yield the dissipative equations already at the level of the quantum mechanics description. On the next level, the classical mechanics description, one would have a system that is not Hamiltonian but instead a system with dissipation. Presumably, entropy can still be introduced, but such a consideration seems not have been pursued yet. The continuum mechanics level of description will then correspond at least to secondary thermodynamics.

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<sup>8</sup> An exception is the case of unstable systems. For such systems entropy of microstructure can be generated without external actions.



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