... the laws of macroscopic bodies are quite different from those of mechanics or electromagnetic theory. They do not afford a complete microscopic description of a system. They provide certain macroscopic observable quantities, such as pressure or temperature. These represent averages over microscopic properties.

— F. Mandl [1]

Abstract According to Chap. 5 a quantity, which may meaningfully be termed “pressure,” is required to exist, at least in equilibrium. This variable relies on a process, in which some extensive quantity changes while entropy remains invariant (adiabatic processes). Here a definition of pressure based on the quantum microstate is given. On the basis of this definition the above-mentioned behavior is demonstrated for various standard processes. It is shown that the adiabatic process may even be stabilized by the influence of the environment.

It appears as if one could introduce pressure within classical statistical mechanics as an observable, i.e., as a function of the microstate. The momentary change of the momenta of all particles that occurs due to the interaction with some wall has to equal the force exerted onto that wall and could thus be interpreted as pressure. And indeed, there are simple models of ideal gases which can account for some of their properties in this way [2, 3]. In general, however, this is not the way pressure is calculated within statistical mechanics. No ensemble average over such a “pressure observable” is taken. Instead one calculates the internal energy $U$ as a function of entropy $S$ and volume $V$. The derivative of the internal energy with respect to volume, while keeping entropy constant, is then identified with negative pressure (cf. (3.18))

$$\left(\frac{\partial U}{\partial V}\right)_{S=\text{const.}} := -P.$$  (14.1)

This amounts to identifying the pertinent force with the change of energy per change of length, which appears quite convincing, but the claim is that the change appears in such a way that entropy does not change. The internal energy of the system could, in principle, change in many ways but it is assumed that a process is selected that
keeps entropy constant. Without this assumption the above definition (14.1) would be meaningless.

In this way pressure is defined by an infinitesimal step of an adiabatic process. It has to be examined if, and under what conditions, adiabatic processes occur at all. In the case of temperature it is rather obvious that processes exist during which entropy changes while the volume is kept constant; in this case, however, it is far from obvious that processes exist during which the volume changes while entropy remains constant.

14.1 On the Concept of Adiabatic Processes

At first sight, isentropic processes may appear almost trivial: If the influence of the environment on the system under consideration, S, would be described by means of a time-dependent change of some parameter \( a(t) \) entering the Hamiltonian of the system S, i.e., if the environment could be reduced to a changing “effective potential,” a classical control by \( \hat{H}^S(a(t)) \) would result. Irrespective of \( a(t) \), the von Neumann entropy of S would necessarily remain constant.

However, in the context of the present theory, such a reduction is considered “unphysical.” The environment, regardless of whether or not it gives rise to a changing Hamiltonian for the considered system, will always become correlated with the considered system, thus causing the local entropy of the latter to increase (see Sect. 10.2.2). To understand the combined effect of an “adiabatic process inducing” environment onto the system, we divide the continuous evolution into steps alternating between two different mechanisms: during one step type the effect of the environment is modeled only by the changing parameter in the local Hamiltonian, \( a(t) \), and during the other only by the inevitable relaxation into the microcanonical equilibrium as described in Chap. 6 and Sect. 10.2.2. Letting the step duration go to zero should result in the true combined effect. Since the relaxation to microcanonical equilibrium makes the off-diagonal elements (in energy representation) of the local density operator, \( \hat{\rho}^S \), vanish, the remaining entropy is controlled by the energy occupation probabilities. Thus, if those change during the “parameter changing steps,” entropy changes inevitably as well under the full evolution. Therefore, adiabatic processes are not trivial at all in a true physical process. The invariance of entropy, however, can be guaranteed if the occupation numbers do not change during the parameter changing steps. (They will obviously not be changed during the “relaxation steps,” for we assume microcanonical conditions.) In quantum mechanics such a behavior can be found within the scheme of adiabatic following.

Under the conditions of adiabatic following not only the entropy, but all occupation numbers of states remain constant. Similar to the classical picture, for adiabatic following to work, the speed of change must be low enough. This is shortly explained in the following.

The adiabatic approximation (see [4–6] and for the classical version remember Sect. 4.5) is a method of solving the time-dependent Schrödinger equation with a