

Part IV

Entropy in statistical mechanics

Chapter 11

Introduction to Part IV

11.1 Entropy in statistical mechanics

Part III of this dissertation was concerned with the question of why the algorithm of calculating microcanonical averages works for predicting the values of thermodynamic quantities. This algorithm is geared to quantities that are functions of the positions and momenta of the constituents of the system, i.e. to phase functions. However, not all quantities within SM are generally thought of as phase functions. Notorious exceptions are temperature, entropy and chemical potential, which are usually treated either as a parameter in a probability distribution, or as some other function of the probability distribution. This Part is concerned with the statistical mechanical treatment of such quantities, and above all with entropy.

Two simple thermodynamic phenomena will suffice to illustrate the problems one encounters in giving a statistical mechanical account of entropy and the thermal phenomena which are described using this concept. The phenomena in question, to which I will repeatedly refer in the remainder of this Part, are quasistatic adiabatic expansion, and free adiabatic expansion of a gas respectively. Consider a gas which is initially in (phenomenological) equilibrium. Next, the volume of the container is increased, and the gas expands adiabatically. Here “adiabatic” means that the container is thermally isolated: No heat is exchanged between the gas and its environment. For quasistatic adiabatic expansion, the volume is increased so slowly that the gas can be taken to be in equilibrium continuously during the process. The gas performs work, at the expense of its internal energy. For free adiabatic expansion on the other hand, the volume is increased suddenly, and the gas will undergo a non-equilibrium process. During this process it will perform no work, and its internal

energy remains constant. Finally, it will settle into a new equilibrium state.

The second law of thermodynamics, when applied to adiabatic processes, says that entropy either remains constant or increases, but it can never decrease. The two above processes serve to illustrate these two cases. During the quasistatic adiabatic expansion the entropy will remain constant. In the free adiabatic expansion the entropy of the final equilibrium state will be larger than that of the initial equilibrium state. The question with which we will be mainly concerned in this chapter is how statistical mechanics can account for these thermodynamic facts.

The Gibbsian approach offers an account of the mentioned phenomena along the following lines. The state of the gas is represented by a probability distribution, and the entropy of the gas is given by the Gibbs entropy, which is a functional on this probability distribution. At the stages of the process at which the gas is in equilibrium (in the initial and final state of the free expansion, and during the entire quasistatic expansion) the state of the gas is given by a microcanonical distribution, since the gas is thermally isolated. Note that at different stages of the process the state will be a different microcanonical distribution, namely the one with the appropriate value of the volume and energy. During the free expansion the gas will undergo some non-equilibrium process, represented by a sequence of non-stationary probability distributions. The entropy change can readily be calculated from the Gibbs entropies of initial and final state, i.e. of the initial and final microcanonical distributions. If the appropriate values of volume, energy and particle number are substituted in the expression for the Gibbs entropy, the thermodynamic predictions can be reproduced.

However, a truly statistical mechanical account would not simply posit that the final state after the expansion is again a microcanonical distribution, but calculate the time evolution of the state of the system on the basis of the mechanical laws. Here the above Gibbsian account fails, and it fails rather dramatically. This is because the Gibbs entropy of any state will necessarily remain constant under the Hamiltonian laws of motion. Similarly, an evolution from one microcanonical distribution to another is dynamically impossible. It follows that the above account of the expansion processes is incompatible with the underlying Hamiltonian evolution.

These problems that are faced by the Gibbs ensemble approach are related not only to the second law, but also to the approach to equilibrium, as we have already seen in chapter 3. Thermodynamics predicts that any system, if left to itself, will eventually reach a state of equilibrium. But in the above-outlined Gibbsian approach, such a state of equilibrium is represented by a stationary probability distribution (in the above case, this is a microcanonical distribution). Such a state,

however, can never be reached by a Hamiltonian evolution from a non-stationary distribution. Thus, in the case of the free adiabatic expansion of a gas, there are two thermodynamic regularities that the Gibbsian approach to statistical mechanics cannot account for in a way that is compatible with the underlying Hamiltonian dynamics. First, the fact that the gas will sooner or later reach a state of equilibrium; secondly, the fact that its entropy in the final state will be larger than in the initial state.

In chapter 3 the first of these problems has been discussed at length. I have argued there that the standard account of equilibrium as a stationary probability distribution is too strict. But the weaker notion of ϵ -equilibrium captures the thermodynamic notion of equilibrium, and an ϵ -equilibrium state can be reached from a non-equilibrium state by a Hamiltonian evolution. This implies that the final state, corresponding to thermal equilibrium, may approximate a (micro)canonical distribution, but it will not equal such a distribution. In this Part, I will use a similar strategy to handle the second problem, and argue that a quasistatic process is not exactly equal to a curve consisting of (micro)canonical distributions, but is only approximated by it.

The problem that the Gibbs approach as outlined above cannot account for the approach to equilibrium or for the increase of entropy is well-known, and was in fact already discussed by Gibbs himself in his 1902 book (Gibbs 1902, Ch. XII). In principle, there are several possibilities for a remedy. First, one could adopt different definitions of entropy and of equilibrium, in such a way that Hamiltonian dynamics does not exclude entropy changes or an approach to equilibrium. The approach I will propose is of this kind. Secondly, one could escape the consequences of Liouville's theorem by considering other dynamical laws that do allow increases of entropy, and transitions from one microcanonical distribution to another.

Gibbs himself offered a solution of the first kind with his method of coarse graining. Starting point of this method is the observation that due to measurement imprecision no actual measurement can reveal the exact microstate of a system. This is taken to imply that it is sufficient to describe the state of a system in a coarse-grained way, by a 'smeared out' distribution ρ_{cg} which does not discriminate between microstates that cannot be told apart by any actual measurement. The Gibbs entropy of ρ_{cg} (known as the coarse-grained entropy) can indeed change in time; despite the fact that its time evolution is determined by the Hamiltonian time evolution of the phase points (and the particular coarse graining used), it does not itself obey the Liouville equation. Also, systems can reach an equilibrium state in a coarse-grained sense. i.e. a distribution which is uniformly spread over all cells, but

which is not uniform within the cells.

Also the (neo-)Boltzmannian approach to SM gives an account of the approach to equilibrium and of the increase of entropy which features both Hamiltonian dynamics, and notions of equilibrium and entropy that differ from the fine-grained Gibbs quantities. Therefore the mentioned problems do not arise in this approach. Recall from chapter 3 that according to Boltzmann a state of equilibrium corresponds to that macrostate which occupies the largest volume in phase space. The Boltzmann entropy of a macrostate is related to its volume W in phase space according to $S_{\mathbf{B}} = k \ln W$. The key idea is that systems will evolve into the equilibrium state, simply because it takes up an immensely larger volume in phase space than other states and is therefore much more probable. And because entropy is directly related to the volume, it will have increased. It is clear that in this approach, and contrary to the Gibbs approach, there are no dynamical constraints that make impossible an approach to equilibrium, or an increase of entropy. But this is not to say that it manages to give an unproblematic account of irreversible processes in terms of the dynamics. Indeed, serious weaknesses of the Boltzmannian approach lie just there, since it oversimplifies the role of the dynamics, when assuming rather than proving that systems will evolve into the macrostate of largest volume. However, a discussion of Boltzmann's approach to SM falls outside the scope of this dissertation. I refer to (Ridderbos 2000) for a detailed critical exposition of this approach.

The constancy of the Gibbs entropy is a consequence of the Liouville equation, which gives the time evolution of a probability distribution under the Hamiltonian dynamics. By considering different dynamical laws the limitations imposed by Liouville's theorem can be escaped, and in fact many approaches to SM do just that (approaches based on a Markov assumption, on master equations, the subdynamics of the Brussels school, interventionism). Most of these approaches replace the precise dynamical laws by some probabilistic assumption. The question whether these assumptions follow from, or are even consistent with, the internal dynamics is set aside. Therefore they do not satisfy the goal of this dissertation, which is to understand thermal phenomena in terms of the dynamics of the microconstituents. An exception is interventionism, since this approach preserves the fine-grained quantities in its account of the dynamics. The Hamiltonian evolution of the system is supplemented with non-Hamiltonian interactions with the surroundings. For the mentioned reason I will only discuss interventionism.

This Part is organised as follows. In the next section I will state the thermodynamic account of entropy and the laws of TD, especially the second law. In chapter 12 the fine-grained Gibbs approach and its problems to reconcile its account of

thermal phenomena with the microdynamics will be discussed in detail. Laying the finger on the problems of the Gibbs approach is a first step for an alternative account of entropy in statistical mechanics, which I will present in chapter 13. This account will be tested against the criteria of section 1.2 for a satisfactory account of thermal phenomena. Finally, in chapter 14 I will compare my proposal with the mentioned alternatives, coarse graining and interventionism.

The upshot of the analysis in this Part is that there is a way of meeting the objections to the fine-grained Gibbs approach that does not lead far away from that approach – and consequently manages to keep the advantages and successes of it.

11.2 Entropy and the laws of thermodynamics

If one's goal is to reproduce thermodynamic predictions within SM, it is of course important to have a good feel for what TD itself has to say. In this section I will give a brief survey of the theory of TD, its basic Laws, and especially the place of entropy within this framework.

The theory of thermodynamics as developed by its founding fathers Kelvin, Clausius and Planck is based on a small number of empirical principles. In broad lines the structure of the theory is as follows. Each empirical principle leads to the introduction of a new concept into the theory (for example, the principle of the impossibility of perpetual motion leads to the introduction of energy), and to the formulation of one of the Laws (in the mentioned case the first law, expressing the conservation of energy). It should be noted that this transparent structure of the theory is a bit deceitful. A quick search in thermodynamic textbooks would reveal a surprising variety in the formulation of the basic laws of the theory. Also, a critical study of the derivations of the laws from the empirical principles would reveal many weak spots in the argumentation, that often have to be fixed by including additional assumptions. For such critical studies into the foundations of TD the reader is referred to (Ehrenfest-Afanassjewa 1956) and (for a detailed study of the history and foundations of the second law) to (Uffink 2001). But setting aside the exact way in which the theory is set up, I take the Laws as formulated below to be the undisputed content of TD.

Connected with the zeroth law are two different empirical principles. The first one deals with the approach to equilibrium, and I will call it the equilibrium principle:

Equilibrium Principle: *All isolated systems, if left to themselves, will eventually reach a state of equilibrium.*

Now consider two separate systems A and B , each of which is in equilibrium, that are brought into thermal contact. It is an empirical fact that often the combined system will not be in equilibrium. But since the combined system is now itself a thermally isolated system, it will undergo changes in its state parameters until it reaches a new equilibrium state. Then A and B are said to be in equilibrium *with each other*. For such situations the following law is formulated, again based on empirical experience:

Zeroth Law of Thermodynamics: *Thermal equilibrium is transitive: If A is in thermal equilibrium with B and B is in thermal equilibrium with C , then A is in thermal equilibrium with C .*

From the equilibrium principle and the zeroth law one concludes that there is a function of the state of the system which has the property that it takes the same value for systems in equilibrium with each other. This function is called the empirical temperature θ , and for simple systems it is a function of pressure and volume alone. However, the scale of θ is not yet fixed, so that in fact many different functions exist that can characterise a state of thermal equilibrium.

The first law of thermodynamics is ‘nothing more than the principle of the conservation of energy applied to phenomena involving the production or absorption of heat’ (Planck 1927). The law is connected with the principle of the impossibility of perpetual motion, which, again in Planck’s words, says that

‘it is in no way possible, either by mechanical, thermal, chemical, or other devices, to obtain perpetual motion, i.e. it is impossible to construct an engine which will work in a cycle and produce continuous work, or kinetic energy, from nothing.’ (Planck 1927)

The first law expresses the conservation of energy, together with the empirical finding that heat and work are equivalent, i.e. can be transformed into each other:

First Law of Thermodynamics: *The change in energy of a system is equal to the amount of heat absorbed by the system, minus the amount of work done by the system: $\Delta E = Q - W$, or in infinitesimal form: $dE = \delta Q - \delta W$.*

However, it is not true (as is sometimes claimed) that the first law can be derived from the impossibility of perpetual motion; the obsolete theory of Carnot (in which perpetual motion is impossible, but the first law as formulated above does not hold) is evidence of this. But the converse, i.e. that the first law excludes perpetual motion, does hold.

The notation δ means that heat and work are not state parameters, of which δQ and δW are infinitesimal variations; rather, these quantities denote infinitesimal amounts of heat and work. Thus, the amount of heat absorbed by a system (or work performed by the system) in a process from A to B is not a function of the states A and B , but may differ dependent on the process. In general, a differential dF that is a variation of a state function is called an exact differential, and a differential δF is called an inexact differential.

The work done by the system can also be expressed as

$$\delta W = \sum_k A_k da_k, \quad (11.1)$$

where A_k are the so-called thermodynamic forces (such as pressure), and a_k the corresponding external parameters (such as the volume). The external parameters are external both in the sense that they take into account circumstances external to the system of interest such as field strengths or moving pistons, and in the sense that they are external to the theory TD.

Also the second law is based on an empirical principle that denies the possibility of certain phenomena. This principle has two classic formulations:

Clausius' principle: *It is impossible to perform a cyclic process which has no other result than that heat is absorbed from a reservoir with a low temperature and emitted into a reservoir with a higher temperature.*

Kelvin's Principle: *It is impossible to perform a cyclic process which has no other result than that heat is absorbed from a reservoir, and work is performed.*

For most applications of thermodynamics the two principles are equivalent. However, when negative temperatures are allowed, such as in spin systems, the two above formulations cease to be equivalent. In such cases a reservoir of higher energy than another reservoir may have lower temperature. Thus, heat may flow from low to high temperature without other effect, and Clausius' principle as formulated above does not hold.

The above principles serve as a starting point for the introduction of two important thermodynamic quantities: absolute (as opposed to empirical) temperature, and entropy. The absolute temperature, unlike the empirical temperature, has a fixed scale. It is introduced with reference to a Carnot cycle, which makes use of two heat reservoirs of different temperature, and consists of two isothermal processes and two adiabatic processes. In the isothermal process at the lower temperature θ_1

the system surrenders an amount of heat Q_1 to the reservoir, while in the isothermal process at the higher temperature θ_2 the system absorbs an amount of heat Q_2 . It can be shown that a function T of the empirical temperature exists that obeys

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (11.2)$$

and this is taken to define the absolute temperature scale.

For any cyclic process one now derives, from the first law and Kelvin's principle, the following inequality: (see for example (Fermi 1936, pp. 46–48))

$$\oint \frac{\delta Q}{T} \leq 0. \quad (11.3)$$

In the derivation of this relation it is assumed that the system of interest interacts with a number of heat reservoirs at different temperatures, and exchanges heat with those reservoirs. The temperature T denotes the temperature of those reservoirs.

The relation (11.3) holds for any type of cyclic process. A special case arises if the cycle is quasistatic, i.e. if it is so slow that the system can be considered in equilibrium at all stages. Since the system has enough time to relax to equilibrium continuously, its temperature will be equal to that of its surroundings, which implies that T in the above expression now applies not only to the reservoir, but also to the system itself. Another important special property of quasistatic cycles is that the equality sign holds:

$$\oint \frac{\delta Q}{T} = 0. \quad (11.4)$$

It follows from this relation that the integral $\int_A^B \delta Q/T$, when evaluated along a quasistatic path, is independent of the exact path between A and B ; or in other words, that $\delta Q/T$ is the exact differential of a state function. This fact is used to define entropy as this exact differential $dS = \delta Q/T$. Here δQ is to be evaluated along quasistatic processes. (Note that since only its differential is fixed, entropy is hereby defined up to an additive integration constant.) Substituting this relation into the first law, we have

$$TdS = dE + \delta W \quad (11.5)$$

again for quasistatic processes only. I will refer to this equation as the “fundamental equation”. Note that T may be interpreted here as the temperature of the system itself.

Outside equilibrium entropy is not defined. Still, it is possible to derive a general statement (the second law) about the change of entropy in all processes beginning

and ending in equilibrium states. Suppose that a cycle consists of an arbitrary (generally non-quasistatic) part (nq) from state A to B and a quasistatic part (q) from B back to A . Then, since the integration along (q) simply yields the entropy difference between the two states, we have the following:

$$\begin{aligned} 0 &\geq \oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T} \Big|_{(nq)} + \int_B^A \frac{\delta Q}{T} \Big|_{(q)} \\ &= \int_A^B \frac{\delta Q}{T} \Big|_{(nq)} + S_A - S_B \end{aligned} \quad (11.6)$$

from which follows that

$$\Delta S = S_B - S_A \geq \int_A^B \frac{\delta Q}{T} \Big|_{(nq)} \quad (11.7)$$

for arbitrary processes from A to B . For adiabatic processes ($\delta Q = 0$) this reduces to the more familiar statement that the entropy of a thermally isolated system can never decrease. Thus we have:

Second Law of Thermodynamics: *The entropy of a thermally isolated system can never decrease. More generally, $\Delta S \geq \int \delta Q/T$, where the equality sign applies to quasistatic processes.*

Note that thermodynamic entropy is only defined for equilibrium states. From this it follows immediately that the second law of thermodynamics does not, as is sometimes claimed, say that entropy increases monotonically during the approach to equilibrium. The only processes during which the entropy is defined all the time, are the quasistatic processes. Rather, the second law compares the value of the entropy in the initial and final state of a process, where both states have to be equilibrium states. This also implies that in order to get an increase of entropy, some outside influence is necessary, because a system in equilibrium will always remain in equilibrium, unless it is perturbed from the outside.

Since quasistatic processes play such a key role in the definition of entropy, it is good to reflect on their exact characterisation. A quasistatic process is an “infinitely slow” process. It is so slow, that at each instant the system can be considered to be in equilibrium. Still, in the long run changes do take place. This means that there must be an external device (such as a machine slowly pushing a piston) which causes these changes, since if the system were left to itself it would stay in equilibrium. But the external influences are so slow that the system has enough time to settle down to equilibrium constantly.

Ehrenfest-Afanassjewa introduces a useful distinction between quasistatic processes and quasi processes (Ehrenfest-Afanassjewa 1956). A quasi process is a curve in state space, consisting of a succession of equilibrium states. It is not a real process, but an idealised mathematical representation of a process. A quasistatic process is a process in the real world, that comes closest to the representation as a curve in state space. This means that the external device must operate “infinitely slowly”. In this sense also a quasistatic process is idealised. Ehrenfest-Afanassjewa assumes that for any two points on a curve in state space (i.e. in a quasi process), no matter how close they are, a quasistatic process can be performed between the two points by operating the external device ever more slowly.

The relation $TdS = \delta Q$ holds both for quasi processes and for quasistatic processes, and the same is true for the equality sign in (11.5) and (11.7).