

Reconsidering the concept of equilibrium in classical statistical mechanics

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Abstract

In the usual procedure of deriving equilibrium thermodynamics from classical statistical mechanics, Gibbsian fine-grained entropy is taken as the analog of thermodynamical entropy. However, it is well known that the fine-grained entropy remains constant under the Hamiltonian flow. In this paper it is argued that we needn't search for alternatives for fine-grained entropy, nor do we have to give up Hamiltonian dynamics, in order to solve the problem of the constancy of fine-grained entropy and, more generally, account for the non-equilibrium part of the laws of thermodynamics. Rather, we have to weaken the requirement that equilibrium be identified with a stationary probability distribution.

1. Introduction. Consider a physical system in thermal equilibrium, which is then disturbed by outside influences. Think for example of a gas that is initially confined to a small part of a container, and at a certain time is allowed to diffuse into the whole available space when a barrier is removed. Thermodynamics predicts that there will be a new equilibrium after some time. Also, when there is no heat exchange with the environment, the entropy of the final state will be larger than that of the initial state. Can classical statistical mechanics reproduce these predictions? That is the main theme of this paper.

It is generally believed that classical statistical mechanics can reproduce all of thermodynamics, when we restrict ourselves to equilibrium properties. The way to proceed is as follows. We identify states of thermal equilibrium with probability distributions on the phase space that are constant in time. For the special cases of isolated systems and systems in thermal contact with a heat reservoir, we take the microcanonical and canonical probability distributions respectively. Further, we identify the so-called fine-grained entropy,

$$S_{fg} = -k \int \rho(x) \ln \rho(x) dx \quad (1)$$

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with the thermodynamical entropy, where $\rho(x)$ denotes the probability density on phase space, and k is Boltzmann's constant. When we introduce the expression for the (micro-)canonical distribution in (1), it turns out that the fine-grained entropy coincides with the thermodynamic entropy, up to an unimportant additive constant. It seems that we thus retrieve all thermodynamic relations by identifying S_{fg} with entropy, and the Gibbsian ensembles as states of thermal equilibrium. The entropy change in the above mentioned process of sudden expansion of a gas can now be obtained from the fine-grained entropies of the initial and the final state.

However, it is well known that the fine-grained entropy stays constant under the action of a Hamiltonian flow, as a result of Liouville's theorem. That is, if, instead of identifying the final state of thermal equilibrium with a microcanonical distribution, we calculate the final distribution by applying Hamilton's equations to each point in phase space (i.e. apply Liouville's theorem to the initial probability distribution), then a distribution results with the same entropy as the initial distribution. Therefore, the final distribution can't be the desired microcanonical one. The previously mentioned reproduction of thermodynamical results is inconsistent with the underlying dynamical evolution.

As Callender (1997) puts it:

'The ensemble at the later time should be the Hamiltonian time development of the earlier ensemble; otherwise the statement that the system is governed by Hamilton's equations is a fiction. (...) The time development of the earlier ensemble will not lead it to approach the later one in any way. This, I believe, is the real problem with fine-grained entropy, not that it doesn't increase between equilibrium states.' (Callender (1997), p. 8)

Although I fully agree that the constancy of S_{fg} under the Hamiltonian evolution needn't be as big a problem as often is claimed, the approach I will outline in this paper profits from the fact that the earlier ensemble often does approach the later one in a relevant sense, contrary to Callender's statement. In this paper I want to pay special attention to this problem of reconciling the account of equilibrium with the Hamiltonian time evolution, as a part of the more general topic of reproducing the zeroth and second law.

A popular approach to this general topic is to replace the Hamiltonian dynamics by some other evolution. Then Liouville's theorem will in general not hold, and the above inconsistency disappears. Many approaches to thermal physics do away with strict Hamiltonian dynamics: e.g. approaches based on a Markov assumption, on master equations, the subdynamics of the Brussels school, and interventionism.¹ Adopting such a strategy however immediately leads to an abandonment of the programme of reducing thermodynamics to statistical mechanics, at least when the latter theory is construed as Hamiltonian dynamics for the system of interest, supplemented with probability considerations. In this paper I want to

¹See Sklar (1993) for a discussion of these approaches, and for references

explore the possibilities of describing irreversible processes while remaining within this programme.

Another approach to non-equilibrium theory is coarse graining. Here one takes the so-called coarse-grained entropy rather than the fine-grained entropy as the analog of the thermodynamical entropy. I will argue (section 4) that this approach cannot take away the afore-mentioned inconsistency. Also, I question the need for replacing the fine-grained entropy. I then go on to propose a new approach, in which the conditions for equilibrium are relaxed, and the fine-grained entropy is retained as analog of thermodynamical entropy. This approach circumvents the inconsistency (section 5). Finally, I will discuss whether the more general goal of reproducing the zeroth and second laws of thermodynamics can be achieved in my new approach (section 6). But before going into non-equilibrium theory, I begin by taking a closer look at the theory of thermodynamics itself (section 2), and the successful reproduction by statistical mechanics in case of equilibrium (section 3).

2. The Zeroth and Second Law of Thermodynamics. In thermodynamics a system is said to be in equilibrium if all its observable characteristics are constant in time, when the system is left to itself. The orthodox theory of thermodynamics deals mainly with such equilibrium situations. Still, at two major points in the theory a general statement about non-equilibrium processes is introduced, namely both in the zeroth and the second law. The former says that every isolated system will eventually reach an equilibrium state. The latter, in the form of Kelvin's principle, says that it is impossible to extract heat from a single heat reservoir and perform an equivalent amount of work in *any* cyclic process, without further effect. From this principle the law of increase of entropy is derived.

The central problem of this paper relates to both the approach to equilibrium and the increase of entropy. Remember our paradigm example of a gas that is suddenly allowed to diffuse into a container. The two claims were that a new equilibrium will settle in, and that the entropy will increase.

Entropy in thermodynamics is a state function, i.e. a function of the macroscopic quantities that define the thermodynamic state of the system. It is formally introduced as the total differential $\delta S_{TD} = \delta Q/T$ where δQ is to be evaluated along quasistatic processes, that is, processes that are so slow that the system can be considered to be in equilibrium all the time. Only these processes can be described by paths in state space.

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. If these endpoints can also be connected by a quasistatic process, this entropy change obeys

$$\Delta S_{TD} \geq \int \delta Q/T. \quad (2)$$

For adiabatic processes ($\delta Q = 0$) this reduces to the more familiar statement that the entropy of a thermally isolated system can never decrease.

For our discussion two points need to be stressed. First, we have seen 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. Second, note that in order to get an increase of entropy, some outside influence is necessary. A system in equilibrium will always remain in equilibrium, unless it is perturbed from the outside.

3. Retrieving equilibrium results in statistical mechanics.

We now turn to a discussion of the well-known procedure of deriving equilibrium thermodynamics from statistical mechanics, that, as noted before, will eventually lead to an inconsistency with the underlying dynamics. In order to make the connection between the two theories, identifications are made between thermodynamical and statistical mechanical concepts.

First of all, thermodynamic states are identified, not with points in phase space, but with probability distributions over them. An important special case is formed by the equilibrium states, which are identified with stationary probability distributions, the Gibbsian probability distributions (or ensembles) being the most important examples.

Second, thermodynamic quantities (like energy and pressure) are identified with ensemble averages of phase functions. It is with the justification of these identifications that ergodic theory is concerned, by trying to show that ensemble averages coincide with time averages, and therefore may be used for calculating actual measurement results. For thermodynamic quantities like entropy and temperature the situation is more complicated. They are generally construed as properties of the probability distribution, but there are also expressions available for these quantities as phase functions. We will meet an example of that later on, for the temperature of microcanonically distributed systems.

The justification of all these identifications or analogies, and of the choice of the Gibbsian ensembles, is largely beyond the scope of this paper. A discussion of this rich field can for instance be found in Sklar's (1993) review of the field. A discussion of the role ergodic theory can play is Earman and Rédei (1996). In the following, I will take all analogies mentioned above for granted, except for those of equilibrium and of entropy. I will now turn to the standard approach to the latter.

It is well known that the fine-grained entropy (1) of the standard Gibbs ensembles displays the appropriate thermodynamical relation. For instance, when we introduce the canonical distribution function for the ideal gas in (1), we arrive at

$$S_{fg}(T, V) = Nk \left(\ln V + \frac{3}{2} \ln(2\pi mkT) \right) + \text{const.} \quad (3)$$

which is familiar from thermodynamics. In general, the entropy will be a function of the external parameters (like the volume V) and the parameters characterizing the ensemble (like the temperature T in the canonical ensemble), and it will be the same function of those quantities as S_{TD} is.

We can make the connection with thermodynamics even tighter, by not only noticing the similarity of S_{fg} to S_{TD} , but also mimicking its

derivation (see Uhlenbeck and Ford (1963), pp. 21-24). That is, we can introduce entropy, just like in thermodynamics, as the total differential belonging to heat, which is defined as

$$T\delta S = \delta Q \equiv \delta E - \delta W. \quad (4)$$

Here the quantities on the right hand side are calculated as ensemble averages: energy (E) as that of the Hamiltonian, and work (δW) as

$$\delta W = \sum_k \left\langle \frac{\partial H}{\partial a_k} \right\rangle \delta a_k \quad (5)$$

where the a_k denote the external parameters. The temperature is connected to the parameter in the distribution function in the usual way, $T = 1/(k\beta)$. Remember that in thermodynamics the left equation in (4) holds only for quasistatic processes. The crucial point is that these are now construed as processes in which the system is always considered to be canonically distributed. That is, it is assumed that after small changes in temperature or in the external parameters the system will again be member of a canonical ensemble, albeit a different one. In this respect the system is in equilibrium all the time during quasistatic processes.

Following these lines, we find an entropy of (grand-)canonically distributed systems which equals the fine-grained entropy of these ensembles. For such ensembles, this completes the standard account of equilibrium theory.

For the microcanonical ensemble the situation is a bit more difficult, since temperature is not a parameter of this distribution. However, after adding an appropriate definition of β as a phase function, e.g. as the structure function $\omega(E, V, \dots)$ divided by the integrated structure function $\Omega(E, V, \dots)$, similar results apply here also².

So far we have arrived at only part of the second law. To proceed towards the part that concerns non-equilibrium, the inequality (2), we could of course invoke Kelvin's principle at this stage. But that would mean a retreat to one of the cornerstones of the theory of thermodynamics itself, instead of a reduction of the latter to statistical mechanics. Much progress would be achieved if we could explain the second law from statistical mechanics alone. Unfortunately, Uhlenbeck and Ford give us no clue in that direction. They write:

‘I will omit a more detailed discussion about the question in which precise sense the entropy $S(\dots)$ has also the property (\dots) of increasing in any spontaneous transition from one equilibrium state to another. Since we have explained the zeroth law the reader will believe that this part of the second law, which is a more precise expression of the irreversible behaviour

²This definition comes down to choosing one of the sets of analogies already proposed by Gibbs (1902, p. 170). It seems that we put in the desired result by hand. But note that we at least gain the description of quasistatic processes, something that Gibbs himself does not offer. Also, our construction assures the thermodynamical relationship between entropy, temperature and energy; a change in the definition of temperature leading to a change in entropy. Some arbitrariness pertains, but that is also the case in thermodynamics itself.

of macroscopic systems, can be “explained” in a similar way.’
(Uhlenbeck and Ford (1963), p. 23)

Their explanation of the zeroth law, however, only makes it plausible that equilibrium (construed in Boltzmann’s manner, as the most probable state) will be reached in the course of time, but doesn’t contain any reference to the entropy of these final equilibrium states. A rigorous explanation of the second law is therefore still lacking.

Up till now we have treated processes without even mentioning Hamilton’s equations which govern the motion of points in phase space. In including these equations in our scheme, a first requirement to meet is of course consistency, and we have seen before that already this cannot be fulfilled. When the time evolution of the fine-grained entropy is calculated by applying Hamilton’s equations to every point x in phase space, i.e.

$$S_{fg}(t) = -k \int \rho(T_t x) \ln \rho(T_t x) dx. \quad (6)$$

then the entropy remains constant. This shows that an evolution from one canonical distribution to another is dynamically forbidden, and our account of equilibrium as stationary, Gibbsian ensembles is inconsistent with the Hamiltonian formalism. For quasistatic processes the accusation of inconsistency only becomes more painful, since it applies to every infinitesimal step of them.

4. Coarse-grained entropy. Advocates of the coarse graining approach argue that fine-grained entropy is not the correct candidate for the analog of thermodynamic entropy, precisely because it remains constant under the Hamiltonian flow. They propose an alternative called coarse-grained entropy S_{cg} which is obtained as follows. First divide the phase space into a large number of small, but finite-sized regions R_i . Take an average of the probability distribution ρ_t over each of these regions:

$$\bar{\rho}_t(i) = \frac{1}{\mu(R_i)} \int_{R_i} \rho_t(x) dx \quad (7)$$

and attribute this value of the distribution to all $x \in R_i$. The coarse-grained entropy is then obtained by substituting the distribution in (1). If the fine-grained distribution ρ_t is uniform over each cell R_i , then S_{cg} and S_{fg} coincide; otherwise the coarse-grained entropy is larger.

A major task for proponents of the coarse graining approach is the justification of the choice of the partition. The size of the cells is usually chosen in correspondence with the limited precision with which points in phase space can be discriminated by means of macroscopic observables. According to Van Kampen (1962, p. 183), the question how to choose this set is the main problem in statistical mechanics of irreversible processes. Indeed, the exact choice of partition is of great importance in the coarse-graining approach. Not only the value of S_{fg} depends on the chosen partition of phase space. Grünbaum (1973, Ch. 19) gives an example showing that even the direction of entropy change can depend on the partition.

The philosophical debate on the adequacy of S_{cg} as analog of S_{TD} often concentrates on whether the coarse graining procedure is subjective.³ Opponents of the coarse graining approach argue, that since the existence of thermodynamic behaviour cannot be due to lack of human capabilities to perform accurate measurements, this account of irreversible processes is unacceptable.

Although its time evolution is induced by that of ρ_t , the coarse-grained distribution doesn't itself obey Liouville's equation. Accordingly, S_{cg} may vary in time. For example, the above properties of S_{cg} show that if the initial state is given by a distribution that is uniform over the R_i , as in our paradigm example of the expanding gas, the coarse-grained entropy will have increased at any later time. A notorious problem is however to demonstrate the appropriate time behaviour for states in between. Only in special cases monotonic increase can be demonstrated, namely when a Markovian postulate is added (see Van Kampen (1962), and Sklar (1993, pp. 212-215)). It remains however an open problem whether this assumption is even consistent with the deterministic evolution of the points in phase space, let alone whether it can be derived from the Hamiltonian evolution for actual systems.

Although proponents of the coarse-graining procedure often try to prove monotonic increase of entropy, this isn't necessary in order to reproduce thermodynamical second law. What has to be shown, is that the value of S_{cg} in equilibrium coincides with that of the thermodynamical entropy. Again, in our paradigm example, the initial state is uniform, so its entropy equals S_{fg} and therefore S_{TD} as well. We know however that after removal of the barrier, the distribution can't evolve to a uniform one in the fine-grained sense. Therefore, we cannot by the same reasoning conclude that the final entropy equals its thermodynamical counterpart.

In conclusion, there are many disadvantages and open problems connected to the coarse-grained entropy, while not even the nice properties of fine-grained entropy are kept. In the next two sections I will argue that we needn't throw the fine-grained entropy away, as long as we restrict its applicability to states of equilibrium. It is however the latter concept, equilibrium, that needs reconsideration.

We have seen that there is an annoying inconsistency at the heart of the standard account of equilibrium theory. Moreover, this inconsistency can be formulated without even mentioning entropy, and therefore its resolution cannot be expected from changing to an entropy function that may increase under the influence of the Hamiltonian evolution. With the new concept of equilibrium to be presented in the next section, we can get a Hamiltonian evolution from one state of equilibrium to another, thereby solving the problem of inconsistency. It is only then that we can start thinking what entropy to attribute to these new style equilibrium states.

³Grünbaum (1973) argues that coarse-grained entropy is not an anthropomorphism. According to Sklar (1993), a 'relativity of coarse-grained entropy value and behavior to a coarse-graining chosen is no mark whatever of "subjectivity"' (p. 358). Redhead (1995) on the other hand, who discusses the coarse graining procedure in his Tarnier Lecture titled 'Science and Subjectivity', calls it 'one of the most deceitful artifices I have ever come across in theoretical physics' (p. 31).

5. What is equilibrium? In the previous section we were led to the suggestion that the identification of thermal equilibrium with stationary distributions may be too strict. The time evolution of an arbitrary time-dependent probability distribution will, strictly speaking, never lead to a stationary distribution. It might however be expected to approximate a stationary distribution, in some relevant sense. I therefore propose to relax this condition, and allow also approximately stationary distributions to represent equilibrium.

To be more specific, let's consider a class Ω of macroscopically relevant quantities and define the system to be in Ω -equilibrium if its distribution belongs to the set

$$\{\rho_t | \forall f \in \Omega : |\langle f \rangle_{\rho_t} - \langle f \rangle_{\mu}| \leq \epsilon_f\} \quad (8)$$

where μ is a given stationary distribution. That is, a system is in equilibrium when the ensemble averages of phase functions in some class Ω are time-independent, or may fluctuate in time at most within some small, fixed intervals ϵ_f . An advantage of this definition is that the reference to macroscopic quantities makes it close to the thermodynamical definition.

Of course this definition has to be made more precise. Some numbers ϵ_f have to be fixed, the most obvious proposal being small fractions of the limiting values of the ensemble averages. Also it has to be specified what the relevant macroscopic quantities are. A straightforward choice is to take just the quantities that are used in the thermodynamical description of the phenomenon, but various other options are conceivable.

The main point I wish to argue is that it is possible to give a characterization of equilibrium along these lines that is compatible with a Hamiltonian evolution between equilibrium states. Indeed, irrespective of the exact choice of the class Ω and of ϵ_f dynamical evolution from one equilibrium state to another is now possible. The previous argument showing the inconsistency is invalidated, even for systems for which we cannot actually prove they will approach equilibrium. Moreover, I would claim that in weakening the conditions for equilibrium we haven't lost any desired property of equilibrium. On the contrary, due to the reference to macroscopic quantities we have come closer to the thermodynamical concept.

An important result that is relevant for this proposal applies to so-called mixing systems, i.e. dynamical systems obeying

$$\lim_{t \rightarrow \infty} \mu(T_t A \cap B) = \mu(A)\mu(B) \quad \forall A, B \subset \Gamma \quad (9)$$

where $T_t A$ denotes the time evolution of the set A and μ stands for the microcanonical measure. Suppose that such a system is described by an arbitrary, time-dependent probability distribution ρ_t which is however required to be absolutely continuous (a.c.) with respect to the microcanonical (Lebesgue) measure. Then all ensemble averages will, in the infinite time limit, coincide with the microcanonical averages:

$$\lim_{t \rightarrow \infty} \langle f \rangle_{\rho_t} = \langle f \rangle_{\mu} \quad (10)$$

for every bounded, measurable function f .⁴ In this sense every a.c. measure converges to the microcanonical measure, which is of course stationary in time. Note however that the fine-grained entropy remains constant and does not converge to the fine-grained entropy of the microcanonical ensemble.

On the basis of our previous association of thermodynamic equilibrium with time-independent probability distributions, we would be forced to conclude that a mixing system will not reach equilibrium, despite the fact that in the long run not a single ensemble average can be discriminated from the microcanonical average. That is, we have no –macroscopic– means to discriminate our system from one which would be regarded as being in equilibrium. With our new definition on the other hand, mixing systems will indeed reach equilibrium. Note that it is not necessary for this conclusion to assume the mixing property. It suffices if we demand mixing only with respect to the class Ω .⁵

6. Retrieving the zeroth and second law in statistical mechanics. Having accepted a definition of equilibrium of the kind discussed in the previous section, we have to investigate further in what respects thermodynamical behaviour can be reproduced. We have seen that we can avoid the inconsistency, but can we also achieve our more general goal of retrieving the laws of thermodynamics? For the zeroth law the prospects are good. In case of mixing (even only w.r.t. Ω) we can immediately prove that the system will reach equilibrium, no matter what state it started in, from the definitions in the previous section. If the ϵ_f are finite, equilibrium will be reached in finite time; if they are zero, it may take an infinite amount of time. For more general systems much work still has to be done, but the fact that we have weakened the standard definition of equilibrium at least guarantees that we’re in a better position than proponents of the other approaches are.

Turning now to the second law, the obvious way to go is to define entropy only for systems in equilibrium. Of course we want to recover the nice results for the Gibbsian ensembles we discussed earlier. We don’t use, however, the fine-grained entropy (1) as the identification of entropy. Instead, we rely on the procedure of introducing entropy as a total differential, as discussed in section 3. We have seen that this procedure led to the fine-grained entropy in case of the Gibbsian ensembles. The idea is now, that we, for all equilibrium ensembles, repeat the derivation of the entropy, and so obtain the entropy for equilibrium states and consequently for quasistatic processes as well.

To be concrete, let’s consider the case that the stationary distribution μ in (8) is a canonical ensemble. Moreover, we suppose that during quasistatic processes the distribution remains in the same equilibrium class as a canonical distribution. We know, from the definition of equilibrium, that

⁴In fact, for a.c. measures (9) and (10) are equivalent conditions. For a proof, see Mackey (1993), p. 63.

⁵That is, we require relation (10) to hold only for all $f \in \Omega$. Interestingly, Earman and Rédei (1996) come to the same requirement in their discussion of why equilibrium statistical mechanics works in predicting observed values of macroscopic quantities.

all macroscopically relevant ensemble averages approximate the canonical averages. Since in the calculation of the total differential belonging to δQ only ensemble averages occur, the resulting entropy will also approximate the canonical fine-grained entropy. That is, the entropy of at least this special class of equilibrium distributions is found to be the same as the thermodynamical entropy. It is an open question whether this procedure can be pursued in general.

Again, if the system is mixing we can straightforwardly get all we want. The above-mentioned procedure then assigns to a general equilibrium distribution the fine-grained entropy S_{fg} of the limiting, microcanonical distribution. For quasistatic processes, we then have the following picture. Under the influence of small external perturbations, the system will stay in equilibrium all the time; its entropy therefore at any time equals the entropy of a microcanonically distributed system undergoing a quasistatic process (cf. section 3). Consequently, its entropy equals S_{TD} . In conclusion, we see that for quasistatic processes the actual distribution function ρ_t of mixing systems has the proper thermodynamical behaviour, since both its entropy and all relevant ensemble averages coincide with those of a microcanonical curve. We have gained a description that is consistent with the dynamics, without losing the thermodynamical results.

In general, the time evolution of the entropy for quasistatic processes resulting from the above-mentioned procedure needn't coincide with the time evolution of S_{fg} as given in (6), and we have shaken off the yoke of Liouville's theorem. In the above example of mixing systems, we attribute at any stage during the quasistatic process the fine-grained entropy of the limiting, microcanonical distribution to the actual distribution. Had we taken (1) as a definition, that is, had we stuck to the fine-grained entropy of the actual distribution, this would have led to undesirable time behaviour.

The final step to make in retrieving the laws of thermodynamics is the second law for irreversible processes. Here, we are in much the same position as Uhlenbeck and Ford were; that is, no rigorous results are available as yet. But note that we are now better off in the following sense. Once we are capable of showing the second law for processes that begin and end in one of the Gibbsian ensembles, this result immediately transfers to more general processes. This is due to the fact that we attribute the fine-grained entropy of these stationary Gibbsian ensembles also to non-stationary, but equilibrium ensembles. Also in comparison to advocates of the coarse-grained entropy we are in a better position, since we don't need to prove monotonic increase of entropy during non-equilibrium processes.

7. Conclusion. We have seen that, after relaxing the condition that thermal equilibrium be identified with a stationary probability distribution, the approach to equilibrium is compatible with the underlying Hamiltonian dynamics, and the inconsistency that existed in the standard account of equilibrium theory has been removed. In fact, for systems of the mixing type it can be proved that they will approach equilibrium, starting from an arbitrary initial state. Also, the entropy of all equilibrium states coincides with the thermodynamical entropy.

It might be objected that the reliance on mixing dynamics is a serious shortcoming of the theory here presented. After all, thermodynamic behaviour is also exhibited by systems that are demonstrably not mixing, or even not ergodic. Therefore, as is convincingly argued by Earman and Rédei (1996), ergodic theory can't be the basis of the explanation why classical statistical mechanics works as a description of thermal phenomena. But note that ergodic theory doesn't play such a key role in the explanation of irreversible phenomena here. The reason for the prominent place of mixing systems in this paper is only that this case provides such a nice example, for which exact theorems are available. However, there seem to be no fundamental obstacles for non-mixing systems to approach equilibrium, or to display an increase of entropy.

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