

Chapter 7

A New Approach to the Approach to Equilibrium

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Abstract Consider a gas confined to the left half of a container. Then remove the wall separating the two parts. The gas will start spreading and soon be evenly distributed over the entire available space. The gas has approached equilibrium. Why does the gas behave in this way? The canonical answer to this question, originally proffered by Boltzmann, is that the system has to be ergodic for the approach to equilibrium to take place. This answer has been criticised on different grounds and is now widely regarded as flawed. In this paper we argue that these criticisms have dismissed Boltzmann's answer too quickly and that something almost like Boltzmann's answer is true: the approach to equilibrium takes place if the system is epsilon-ergodic, i.e. ergodic on the entire accessible phase space except for a small region of measure epsilon. We introduce epsilon-ergodicity and argue that relevant systems in statistical mechanics are indeed epsilon-ergodic.

7.1 Introduction

Let us begin with a paradigmatic example. A gas is confined to the left half of a container by a dividing wall. We now remove the wall, and as a result the gas spreads uniformly across the entire container. It reaches equilibrium. Thermodynamics (TD), via its Second Law, regards this process as uniform and irreversible: once the wall is removed, the entropy increases until it reaches its maximum which it will thereafter

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never leave. Statistical mechanics (SM) tries to understand this manifest macroscopic behaviour in terms of the dynamics of the micro-constituents of the system.

One might expect SM to provide a justification of the *exact* laws of TD, in our case a justification of why systems invariably exhibit monotonic and irreversible entropy increase. This is asking for too much. In fact we have to rest content with less in two respects. First, classical Hamiltonian systems are time-reversal invariant and show Poincaré recurrence; it is therefore impossible for the entropy of such a system to increase irreversibly: sooner or later the system will move out of equilibrium again. Thermodynamics is an approximation, which, echoing Callender's [1] memorable phrase, we should not take too seriously.¹ Instead of trying to derive irreversible behaviour *stricto sensu* we should aim to show that systems in SM exhibit *thermodynamic-like behaviour* (TD-like behaviour): the entropy of the evolving system is most of the time close to its maximum value, from which it exhibits frequent small and rare large fluctuations [3, p. 255]. Second, the Second Law of TD does not allow for exceptions. However, no statistical theory can ever justify an exceptionless law. The best one could hope for is to show that something happens with probability equal to one (but even then zero-probability-events are not ruled out because zero probability is not impossibility!). But even that is a tall order since probability zero results are usually unattainable. What we have to aim for instead is showing that the desired behaviour is *very likely* [4].

These considerations suggest a new approach to the approach to equilibrium: rather than trying to derive monotonic and exceptionless entropy increase, we ought to aim to show that systems in SM are very likely to exhibit TD-like behaviour. The aim of this paper is to propose a response to this challenge. But before turning to our proposal, let us briefly comment on a recent approach which offers an explanation of TD-like behaviour in terms of the notion of typicality (see, for instance, [5]) and without explicit reference to dynamical properties of the system. In our view, such an explanation is either flawed or incomplete.²

TD-like behaviour is a dynamical phenomenon. SM is a reductionist enterprise in that its constitutive assumption is that the behaviour of large systems is determined by the behaviour of its constituents. In the case of the initial example this means that the behaviour of the gas is determined by the behaviour of the gas molecules; that is, the gas spreads because the individual molecules bounce around in such a way that they fill the space evenly and that their velocities obey the Maxwell-Boltzmann distribution. So the question is: what kind of motion do the molecules have to carry out for the gas as a whole to show TD-like behaviour? The motion of molecules is governed by the laws of mechanics, which we assume to be the laws of classical Hamiltonian mechanics. What kind of motion a Hamiltonian system carries out is determined by the Hamiltonian of the system. The question then becomes: what dynamical properties does the Hamiltonian have to possess for the system to show TD-like behaviour?

¹In passing we would like to mention that deriving the exact laws of TD from SM is also not a requirement for a successful reduction (see 2).

²For a detailed discussion of this approach see Frigg [6, 7].

An answer to this question is an essential ingredient of an explanation of the approach to equilibrium. For one, the only way to deny that the dynamics of molecules matters is to deny reduction, but this amounts to pulling the rug from underneath SM altogether. For another, the answer to the question about dynamics is non-trivial because there are Hamiltonians under which systems do *not* show TD-like behaviour (for instance, quadratic Hamiltonians). So we need to know what properties a Hamiltonian must have for TD-like behaviour to take place. And this question must be answered in a non-trivial way. Just saying the relevant Hamiltonians possess the dynamical property of TD-likeness has no explanatory power—it would be a pseudo-explanation of the *vis dormitiva* variety. *The challenge is to identify in a non-question-begging way a dynamical property (or, indeed, properties) that those Hamiltonians whose flow is TD-like have.*

The traditional answer to this question (which can be traced back to Boltzmann) is that the system has to be ergodic. In recent discussions this answer has fallen out of favour. After introducing the formalism of Boltzmannian Statistical Mechanics (Sect. 7.2), we briefly discuss the Boltzmannian justification of TD-like behaviour along with the criticisms levelled against it (Sect. 7.3). There is indeed a serious question whether the original proposal is workable (although, rife prejudice notwithstanding, there is no *proof* that it fails). For this reason it seems sensible to look for a less uncertain solution. We point out that to justify TD-like behaviour it suffices that a system be almost ergodic, where being almost ergodic is explained in terms of epsilon-ergodicity (Sect. 7.4). The most important criticism of the ergodic programme is that relevant systems in SM are, as a matter of fact, not ergodic. We review the two most powerful arguments for this conclusion—based on the so-called KAM-Theorem and Markus-Meyer-Theorem, respectively—and argue that they have no force against epsilon-ergodicity (Sect. 7.5). Not only do these arguments have no force against epsilon-ergodicity, there are good reasons to believe that relevant systems in SM are epsilon-ergodic (Sect. 7.6). We end with a summary of our results (Sect. 7.7).

7.2 Boltzmannian Statistical Mechanics

We consider Boltzmannian SM and set Gibbsian SM aside, and we restrict attention to gases.³ Furthermore we assume systems to be classical;⁴ a discussion of quantum SM can found in Emch and Liu [10].

Consider a system of n particles moving in three-dimensional physical space. The system's *microstate* is specified by a point x in its $6n$ -dimensional phase

³The explanation of TD-like behaviour in liquids and solids demands conceptual resources we cannot discuss here. Let us just mention that an explanation of thermodynamic-like behaviour in liquids and solids might well differ from an explanation of thermodynamic-like behaviour in gases. In other words, we see no reason why for systems as different as gases and solids there has to be one single dynamical property that explains thermodynamic-like behaviour.

⁴For a discussion of Gibbsian SM see Frigg [8] and Uffink [9].

space Γ . This space is endowed with the standard Lebesgue measure μ . The time evolution of the system is governed by Hamilton's equations, and the function $s_x : \mathbb{R} \rightarrow \Gamma_E$, $s_x(t) = \phi_t(x)$ is the solution originating in x . Because the energy is conserved, the motion of the system is confined to a $6n - 1$ dimensional energy hypersurface Γ_E , where E is the value of the energy of the system. The measure μ is preserved under the dynamics of the system, and so is its restriction to Γ_E , μ_E . If normalised, μ_E is a probability measure on Γ_E . From now on we assume that μ_E be normalised. The triple $(\Gamma_E, \mu_E, \phi_t)$ is a *measure-preserving dynamical system*, where $\phi_t : \Gamma_E \rightarrow \Gamma_E (t \in \mathbb{R})$ is a family a one-to-one measurable mappings such that $\phi_{t+s} = \phi_t(\phi_s)$ for all $t, s \in \mathbb{R}$, $\phi_t(x)$ is jointly measurable in (x, t) , and $\mu_E(R) = \mu_E(\phi_t(R))$ for all measurable $R \subseteq \Gamma_E$ and all $t \in \mathbb{R}$ (which is the condition of measure-preservation).

From a macroscopic perspective the system is characterised by a set of *macrostates* $M_i, i = 1, \dots, m$. To each macrostate corresponds a macro-region Γ_{M_i} consisting of all $x \in \Gamma_E$ for which the system is in M_i . The Γ_{M_i} form a partition of Γ_E , meaning that they do not overlap and jointly cover Γ_E . The Boltzmann entropy of a macrostate M_i is $S_B(M_i) := k_B \log[\mu(\Gamma_{M_i})]$ (where k_B is the Boltzmann constant), and the Boltzmann entropy of a *system* at time t , $S_B(t)$, is the entropy of the macrostate of the system at t : $S_B(t) := S_B(M_{x(t)})$, where $x(t)$ is the microstate at t and $M_{x(t)}$ is the macrostate corresponding to $x(t)$ (cf. [11]). The equilibrium state, M_{eq} , and the macrostate at the beginning of the process, M_p , also referred to as the 'past state', are particularly important. For gases $\Gamma_{M_{eq}}$ is vastly larger (with respect to μ_E) than any other macro-region, a fact also known as the 'dominance of the equilibrium macrostate' (we briefly return to this in the conclusion); in fact Γ_E is almost entirely taken up by equilibrium microstates (see, for instance, [5], p. 45).⁵ For this reason the equilibrium state has maximum entropy. The past state is, by assumption, a low entropy state. The Boltzmann entropy is the quantity that is expected to show TD-like behaviour.

7.3 The Ergodic Programme

We now introduce the notion of ergodicity and discuss the problems that attach to it when used in the context of Boltzmannian SM. The *time-average* of the phase flow ϕ_t relative to a measurable set A of Γ_E of a solution starting at $x \in \Gamma_E$ is

$$L_A(x) = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \chi_A(\phi_\tau(x)) d\tau, \quad (7.1)$$

⁵ As Lavis [3, pp. 255–258] has pointed out, some care is needed here. Non-equilibrium states can be degenerate and *together* can take up a large part of Γ_E . However, those non-equilibrium states that occupy most of the non-equilibrium area have close to equilibrium entropy values and so one can then lump together equilibrium and close-to-equilibrium states and get an 'equilibrium or almost equilibrium' region, which indeed takes up most of Γ_E . The approach to equilibrium can then be understood as the approach to this 'equilibrium or almost equilibrium' state.

where the measure on the time axis is the Lebesgue measure and $\chi_A(x)$ is the characteristic function of A : $\chi_A(x) = 1$ for $x \in A$ and 0 otherwise. Birkhoff [12] could prove that $L_A(x)$ exists except for a set of measure zero, i.e., except for a set B in Γ_E with $\mu_E(B) = 0$. A system is ergodic (on the energy hypersurface) if and only if (iff) for all measurable A in Γ_E

$$L_A(x) = \mu_E(A) \quad (7.2)$$

for all $x \in \Gamma_E$ except for a set of measure zero.

Ergodic systems exhibit TD-like behaviour. Setting $A = \Gamma_{M_{eq}}$ and taking into account the dominance of the equilibrium macro region, it follows immediately that almost all initial conditions lie on solutions that spend most the time in equilibrium and only show relatively short fluctuations away from it (because non-equilibrium regions are small compared to $\Gamma_{M_{eq}}$). Therefore, the Boltzmann entropy is maximal most of the time and fluctuates away from its maximum only occasionally: the system behaves TD-like.⁶

In passing we would like mention that neither TD itself, nor TD-like behaviour as defined above, make any statement about how quickly a system approaches equilibrium; that is, they remain silent about relaxation times. The same holds true of ergodicity, which is also silent about how long it takes a system to reach equilibrium. This is no drawback: it is unlikely that one can say much about the speed of convergence in general because this will depend on the system under consideration. However, it is true that many gases approach equilibrium fairly quickly, and a full justification of the macroscopic behaviour of systems has to show that the relevant dynamical systems show realistic relaxation times. For want of space we do not pursue this issue further.

The two main arguments levelled against the ergodic approach are the measure zero problem and the irrelevancy charge. The measure zero problem is that $L_A(x) = \mu_E(A)$ holds only ‘almost everywhere’, i.e. except, perhaps, for initial conditions of a set of measure zero. This is seen as a problem because sets of measure zero can be rather ‘big’ (for instance, the rational numbers have measure zero within the real numbers) and because sets of measure zero need not be negligible if sets are compared with respect to properties other than their measures (see, for instance, [16], pp. 182–188).

What lies in the background of this criticism is the quest for a justification of a strict version of the Second Law. However, as we have pointed out in the introduction, this is an impossible goal. At best SM can show that TD-like behaviour is very likely, and there is no way to rule out that there are initial conditions for which this is not the case. As long as the probability for this to happen is low, this is no threat to the programme. In fact, our explanation (in the next section) for why systems behave TD-like is even more permissive than the traditional ergodic programme:

⁶ We can then interpret μ_E as a time-average. For a discussion of this interpretation see Frigg [13], Lavis [14] and Werndl [15].

it allows for sets of ‘bad’ initial conditions that have finite (yet very small) measure.⁷

The second objection, the irrelevancy challenge, is that ergodicity is irrelevant to SM because real systems are not ergodic. In effect, by appealing to ergodicity we are like the proverbial fool who searches for his lost wallet underneath the lantern. This is a serious objection, and the aim of this paper is to develop a response to it. Our response departs from the observation that less than full-fledged ergodicity is sufficient to explain why systems behave TD-like most of the time. We introduce epsilon-ergodicity and then argue that epsilon-ergodicity gives us what we need. We then revisit the main two arguments for the conclusion that SM systems are not ergodic and show that they have no force against epsilon-ergodicity (or ergodicity).

7.4 Epsilon-Ergodicity and Thermodynamic-Like Behaviour

Roughly speaking, a system is epsilon-ergodic if it is ergodic on the entire energy hypersurface except, perhaps, on a set of measure ε , where ε is very small or zero.⁸ In order to eventually introduce epsilon-ergodicity, we first define the (different!) notion of ε -ergodicity. The latter captures the idea that a system is ergodic on a set of measure $1 - \varepsilon$: $(\Gamma_E, \mu_E, \phi_t)$ is ε -ergodic, $\varepsilon \in \mathbb{R}$, $0 \leq \varepsilon < 1$, iff there is a set $Z \subset \Gamma_E$, $\mu(Z) = \varepsilon$, with $\phi_t(\hat{\Gamma}_E) \subseteq \hat{\Gamma}_E$ for all $t \in \mathbb{R}$, where $\hat{\Gamma}_E := \Gamma_E \setminus Z$, such that the system $(\hat{\Gamma}_E, \mu_{\hat{\Gamma}_E}, \phi_t^{\hat{\Gamma}_E})$ is ergodic, where $\mu_{\hat{\Gamma}_E}(\cdot) := \mu_E(\cdot) / \mu_E(\hat{\Gamma}_E)$ for any measurable set in $\hat{\Gamma}_E$ and $\phi_t^{\hat{\Gamma}_E}$ is ϕ_t restricted to $\hat{\Gamma}_E$. Trivially, a 0-ergodic system is simply an ergodic system. We now say that a dynamical system $(\Gamma_E, \mu_E, \phi_t)$ is epsilon-ergodic iff there exists a very small ε (i.e. $\varepsilon \ll 1$) for which the system is ε -ergodic.

An epsilon-ergodic system $(\Gamma_E, \mu_E, \phi_t)$ is ergodic on $\Gamma_E \setminus Z$, and, therefore, it shows thermodynamic-like behaviour for the initial conditions in $\Gamma_E \setminus Z$. If ε is very small compared to $\mu_E(\Gamma_{M_p})$, then the system will behave TD-like for most initial conditions (i.e. for all initial conditions except, perhaps, ones that form a set of measure ε).⁹ If we now interpret μ_E as a probability density (which we are free to do because it has the formal properties of a probability measure),¹⁰ then it follows that

⁷ This solution (or rather: dissolution) of the measure zero problem presupposes that the initial conditions are measured with respect to the Lebesgue measure. Justifying this choice is a well-known and thorny problem which we cannot address here. In what follows we assume that such a justification can be given and that the Lebesgue measure is the right measure to use in these cases.

⁸ Epsilon-ergodicity has been introduced into the foundations of SM by Vranas [17]. However, Vranas uses it to justify Gibbsian equilibrium theory, while we use it within Boltzmannian SM. For a discussion of Vranas’ views, see Frigg [8, pp. 149–151].

⁹ A weaker antecedent still warrants the consequent: $\mu_E(\Gamma_{M_p} \setminus Z) / \mu_E(\Gamma_{M_p})$ has to be close to one. This is trivially true if $\mu_E(Z)$ is small compared to $\mu_E(\Gamma_{M_p})$, but it can also be true if $\mu_E(Z)$ is larger (but substantial parts of Z come to lie in other macro-regions).

¹⁰ For a discussion of how to interpret these probabilities see Frigg and Hoefer [18].

the system is overwhelmingly likely to behave TD-like. Therefore, we find that if a system is epsilon-ergodic, then it is overwhelmingly likely to behave TD-like. This is the sought after result.

7.5 Threats from the Sidelines

This result is relevant only if real systems are actually epsilon-ergodic. In this section we discuss two general mathematical theorems that are often marshaled against ergodicity and argue that these arguments are based on a misinterpretation of the theorems. In the next section we look at some important systems in SM and provide evidence (both mathematical and numerical) that they are indeed epsilon-ergodic.

The Kolmogorov-Arnold-Moser theorem (KAM-Theorem). Physically speaking, a first integral of a dynamical system is constant of motion. Formally, a function G is a *first integral* of a dynamical system with Hamiltonian H just in case the Poisson bracket $\{H, G\}$ equals zero. A dynamical system with n degrees of freedom is called integrable (in the sense of Liouville) just in case there are n independent first integrals G_i which are in involution (the G_i are in involution iff $\{G_i, G_j\} = 0$ for all $i, j, 1 \leq i, j \leq n$). If a dynamical system is not integrable, it is called *nonintegrable*. For an integrable system the energy hypersurface is foliated into tori, and on each torus there is either periodic motion or quasi-periodic motion with a specific frequency [19, 20].

The KAM-theorem gives an answer to the question of what happens when an integrable system is perturbed by a small perturbation which is nonintegrable. According to the KAM-theorem, under certain conditions,¹¹ there are two kinds of motion on the hypersurface of constant energy. Namely, first, there is the motion on tori with sufficiently irrational frequencies; the solutions on these tori behave like the ones in the integrable case, meaning that there is quasi-periodic motion (these tori are said to “survive the perturbation”). Second, between the surviving tori the motion is irregular and unpredictable. As the perturbation decreases, the measure of the tori which survive the perturbation goes to one. Thus the hypersurface of constant energy splits into two regions invariant under the dynamics: the region where the tori survive and the region where this is not the case; moreover, the measure of the former goes to one as the perturbation goes to zero. The motion on the region where the tori survive cannot be ergodic or epsilon-ergodic because the solutions are confined to tori. Consequently, dynamical systems to which the KAM-Theorem applies fail to be ergodic, and for a small enough perturbations they also fail to be epsilon-ergodic (cf. [20]).

¹¹ It is required that (i) one of the frequencies never vanishes, and (ii) that the ratios of the non-vanishing frequency to the remaining $n - 1$ frequencies are functionally independent on the entire energy hypersurface (this means that the ratios depend on the action) [20, pp. 182–183].

This consequence of the KAM-theorem is often taken to show that many, or even all, systems in SM fail to be ergodic. Consider, for instance, the following quotations:

[T]he evidence against the applicability [of ergodicity in SM] is strong. The KAM-Theorem leads one to expect that for systems where the interactions among the molecules are non-singular, the phase space will contain islands of stability where the flow is non-ergodic. [21, p. 70]

Actually, demonstrating that the conditions sufficient for the regions of KAM-stability to exist can only be done for simple cases. But there is strong reason to suspect that the case of a gas of molecules interacting by typical intermolecular potential forces will meet the conditions for the KAM result to hold. [...] So there is plausible theoretical reason to believe that more realistic models of typical systems discussed in statistical mechanics will fail to be ergodic. [16, p. 72]

First appearances notwithstanding, these claims are unfounded. The KAM-Theorem does not show that gases in SM fail to be ergodic (and hence does not show that they fail to be epsilon-ergodic). The crucial point, which is often ignored, is that the KAM-theorem only applies to *extremely small* perturbations of integrable systems. For systems in SM it has been found that the largest admissible perturbation parameter rapidly converges toward zero as the number of degrees of freedom n goes to infinity [22, 23]. Consequently, as Pettini points out, “for large n -systems – which are dealt with in statistical mechanics – the admissible perturbation amplitudes for the KAM-theorem to apply drop down to exceedingly tiny values of no physical meaning” [22, p. 60]. For larger perturbations the surviving tori disappear and the motion can be epsilon-ergodic or even ergodic. Thus the KAM-theorem is simply irrelevant because it does not apply to gases in SM.

Moreover, it is at best unclear whether systems in SM can be represented as integrable systems plus a small perturbation.¹² Hamiltonians of that kind are extremely special. And not only is there no reason to believe that SM systems are of this special kind; the systems commonly studied in SM are not (as becomes clear in the next section). Hence, once again, the KAM-Theorem is just irrelevant to the question of whether or not systems in SM are epsilon-ergodic (or ergodic), and dismissals of the ergodic approach based on the KAM-Theorem are misguided.

The Markus-Meyer Theorem (MM-Theorem). The MM-theorem is about the class of infinitely differentiable Hamiltonians on a compact manifold. It says that in this class nonergodic systems are generic in a topological sense (of first Baire category) [24]. Furthermore, when studying the proof of the MM-Theorem, one sees that the proof implies that the set of Hamiltonians which are not epsilon-ergodic are also generic. Here an *ergodic Hamiltonian* (*epsilon-ergodic Hamiltonian*) (as opposed to a dynamical system) is defined to be a Hamiltonian which is ergodic (epsilon-ergodic) on the energy hypersurface for a dense set of energy values. So is the MM-Theorem a threat to the claim that all gases in SM are epsilon-ergodic?

¹²Thanks to Pierre Lochack for making us aware of this.

We do not think so for two reasons. First, the proof of the MM-theorem shows that those Hamiltonians which are generic are not epsilon-ergodic because there is exactly one minimum value of the energy (where the motion is a general elliptic equilibrium point). And for energy values which are arbitrarily close to this minimum the motion on the energy hypersurface is not epsilon-ergodic. However, these very low energy values are of no relevance to gases in SM. Either for very low energy values quantum effects come in, rendering these energy values irrelevant for SM. Or these low energy values do not correspond to gases but to glasses or solids [17, 25–28].

Second, the MM-Theorem only holds for compact phase spaces. However, for systems considered in SM the phase space is usually not compact (see, e.g., [19]).¹³ The proof of the MM-Theorem cannot be easily transferred to noncompact phase spaces; but this is exactly what would be needed. For these reasons, also the MM-Theorem is no threat to the claim that all gases in SM are epsilon-ergodic (or ergodic).

7.6 Relevant Cases

A different line of attack draws attention to particular systems that fail to be ergodic and yet behave TD-like, from which it is concluded that ergodicity cannot explain TD-like behaviour. We will argue that these examples are besides the point and that there are good reasons to believe that gases in SM are epsilon-ergodic.

Common counterexamples to the ergodic programme are the following. First, solids show thermodynamic-like behaviour; however, in a solid the molecules oscillate around fixed positions in a lattice, implying that a state can only access a small part of the energy hypersurface [9, p. 1017]. Second, a system of n uncoupled anharmonic oscillators of identical mass shows TD-like behaviour, but it is not ergodic [29]. Third, the Kac Ring Model is known not to be ergodic, but it still shows TD-like behaviour (*ibid.*). Fourth, a system of non-interacting point particles is not ergodic, yet it is still often studied in SM [30, p. 381].

None of these examples threatens our claim that gases in SM are epsilon-ergodic. Clearly, solids are not gases and hence can be set aside. Similarly, uncoupled harmonic oscillators and the Kac-ring model are irrelevant because they seem to have nothing to do with gases. The properties of ideal gases are very different from the properties of real gases because there are no collisions in ideal gases and collisions are essential to the behaviour of gases. So while ideal gases may be an expedient in certain context, no conclusion about the dynamics of real gases should be drawn from them. Hence, the well-rehearsed examples do not establish that there is a gas-like system which behaves TD-like while failing to be

¹³The hypersurface of constant energy is usually compact, but the phase space is not, and the theorem cannot be rephrased as one about the energy hypersurface.

ergodic.¹⁴ We now argue that this is not an artifact of the way the examples have been chosen; gases do seem to be epsilon-ergodic. We should point out that there are only few rigorous results about the dynamical properties of gases. Nevertheless, these, together with the results of some numerical studies, support the hypothesis that gases in SM are epsilon-ergodic.

The dynamics of a gas is specified by the potential which models the force between the particles. Two potentials are of particular importance: *the Lennard-Jones potential* and *the hard-sphere potential*. For two particles the Lennard-Jones potential has the form:

$$U(r) = 4\alpha \left(\left(\frac{\rho}{r} \right)^{12} - \left(\frac{\rho}{r} \right)^6 \right), \quad (7.3)$$

where r is the distance between the particles, α corresponds to the depth of the potential well and ρ is the distance at which the inter-particle potential is 0. From this one obtains the potential of the entire system by summing over all two-particle interactions or by considering only the interactions between the nearest neighbours. The Lennard-Jones potential is among the most widely-used potentials because it agrees well with the data about inter-particle forces [31, pp. 236–237, 32, pp. 502–505].

The hard-sphere potential models the motion of impenetrable spheres of radius R that bounce off elastically. For two particles the hard-sphere potential is:

$$U(r) = \infty \quad \text{for } r < R \quad \text{and } 0 \text{ otherwise,} \quad (7.4)$$

where r is the distance between the particles. Again, one obtains the potential of the entire system by summing over all two-particles interactions. The hard-sphere potential simulates the steep repulsive part of realistic potentials [31, p. 234]. It is widely used in mathematical as well as numerical studies because it is the simplest potential.

Let us start by discussing the hard-sphere potential. Boltzmann [33] already studied this potential and conjectured that hard-sphere systems are ergodic when the number of balls is large. From a mathematical viewpoint it is easier to study the movement of particles on a *torus* rather than the movement of particles in box or in other containers with walls. For particles moving on a torus there are no walls; it is like if a ball reappears at the opposite side of the box instead of bouncing off the wall. Studying the motion of hard-spheres on a torus is important: if anything, the walls cause the motion to be more random than the motion on a torus (relative to the trivial invariants of motion; see Chernov [34]). Thus if the motion of hard-spheres on a torus is ergodic, this provides good evidence that the motion of hard

¹⁴ However, the case of solids highlights an important issue. Namely that the approach to equilibrium in solids is an unsolved problem and that this problem deserves more attention than it has received so far.

spheres in a box (or other containers) is ergodic. Sinai [35] hypothesised that a system of N hard-spheres moving on T^2 and on T^3 is ergodic for all $N \geq 2$ where T^m is the m -torus [36]; this hypothesis became known later as the ‘Boltzmann-Sinai ergodic hypothesis’. The first step towards proving this hypothesis was made by Sinai [37], who showed that the motion of two hard spheres on T^2 is ergodic.¹⁵ Since then several important proofs have been accomplished; taken together, they add up to an almost complete proof of the Boltzmann-Sinai ergodic hypothesis (and mathematicians in this field expect that a full proof will be forthcoming soon). Three results are particularly important. First, Simányi [42] showed that a system of N hard-spheres moving on T^m is ergodic for all $m \geq N$, $N \geq 2$. Second, Simányi [43] proved that a system of N hard spheres moving on T^m is ergodic for all $N \geq 2$ and all $m \geq 2$ and for almost all values (M_1, \dots, M_N, r) , where M_i is the mass of the i -th ball and r is the radius of the balls.¹⁶ Third, Simányi [44] showed that a system of N hard spheres moving on T^m is ergodic for all N and all m provided that the Sinai-Chernov Ansatz is true (mathematicians who work in this field widely expect that the Sinai-Chernov Ansatz holds).¹⁷

Obtaining strict mathematical results about the more realistic case of hard-spheres moving in a box (rather than on a torus) is more difficult. Only few results have been obtained here. Most importantly, Simányi [45] proved that the system of two balls moving in an m -dimensional box is ergodic for all m . Numerical studies suggest that the same result holds true for an arbitrary number of balls. Zheng et al. [46] found evidence that systems of identical hard-spheres in a two-dimensional and a three-dimensional box are ergodic. Dellago and Posch [47] studied systems of a large number of identical hard-spheres in a three-dimensional box, and obtained numerical evidence that the motion is ergodic.

We now turn to the Lennard-Jones potential, which is much harder to treat mathematically. Donnay [48] showed that a system of two particles moving on T^2 where there is a generalised Lennard-Jones type potential is not ergodic for certain values of the energy of the system.¹⁸ However, this result does not say anything

¹⁵ All hard-sphere systems which are discussed in this section are not only ergodic but are also strongly chaotic – they are Bernoulli systems (for a discussion of the meaning of Bernoulli systems, see [38–41]).

¹⁶ We are most interested in the case where the system has equal masses. Unfortunately, it is unknown whether the system is ergodic for equal masses because the proof does not provide an effective method of checking whether a given (M_1, \dots, M_N, r) is among the values where the system is ergodic [44, p. 383].

¹⁷ Consider ∂M , the boundary of all possible states M of the hard-sphere system. Define SR^+ as the set of all states x in ∂M which correspond to singular reflections with the post-collision velocity v_0 , for any arbitrary v_0 . According to the Chernov-Sinai Ansatz, the forward solution originating from x is geometrically hyperbolic for almost every $x \in SR^+$ [44, p. 392].

¹⁸ The set of generalised Lennard-Jones potentials consists of potentials of the same general shape as the Lennard-Jones potential and potentials which share some characteristics with the Lennard-Jones potential. More specifically, generalised Lennard-Jones potentials as considered by Donnay are smooth potentials where (a) for large r the potential is attracting, (b) as r goes to zero the

about the cases of interest in *SM*, namely systems with a large number of particles. And there is a general tendency that the larger the number of particles, the more often systems are ergodic. Important for us is that even if systems with Lennard-Jones potentials and with a large number of particles should turn out to be non-ergodic, they are likely to be epsilon-ergodic [49]. Donnay [48, p. 1024] expresses this as follows:

Even if one could find such examples [generalised Lennard-Jones systems with a large number of particles that are non-ergodic], the measure of the set of solutions constrained to lie near the elliptic periodic orbits is likely to be very small. Thus from a practical point of view, these systems may appear to be ergodic.

Indeed, it is widely believed that Lennard-Jones type systems are epsilon-ergodic because similar systems are epsilon-ergodic and numerical studies provide evidence that they are epsilon-ergodic. More specifically, numerical studies of systems with Lennard-Jones potentials have found that there exists an energy threshold (a specific value of the energy) such that the system is epsilon-ergodic for values above the energy threshold and fails to be epsilon-ergodic for values below the threshold. Whether for energy values below the threshold the system is really not epsilon-ergodic, or is epsilon-ergodic but appears to be not so because it needs a very long time to approach equilibrium is still discussed [49–51]. Important for our purpose is that the energy values below the energy threshold are very low. This implies that the classical statistical mechanical description breaks down because quantum effects cannot be ignored any longer [17, 27, 32]. Consequently, the behaviour of these systems with very low energy values is irrelevant. In conclusion, there is evidence that gases with a Lennard-Jones potential are epsilon-ergodic for the relevant energy values.

After having discussed the hard-sphere potential and the Lennard-Jones potential, we want to briefly mention two important results about other potentials of relevance in *SM*. First, Donnay and Liverani [52] proved that the motion of two particles moving on T^2 is ergodic for three types of potentials, namely for a general class of repelling potentials, a general class of attracting potentials, and a class of potentials with attracting and repelling parts (the latter are called mixed potentials). Of particular importance here are the mixed potentials because they are everywhere smooth. Everywhere smooth potentials are regarded as more realistic than potentials with singularities, and Donnay and Liverani's [52] mixed potentials were the first smooth potentials which were proven to lead to ergodic motion. Second, among the systems with many degrees of freedom which have been most extensively investigated is the one-dimensional self-gravitating system consisting of N plane-parallel sheets with uniform density; this system models processes in plasma physics. Numerical investigations suggest that for $N \geq 11$ the system is

potential approaches infinity, and (c) the potential has finite range, i.e., there exists an $R > 0$ such that $U(r) = 0$ for all $r \geq R$ ((c) is assumed because it considerably simplifies the mathematical treatment).

ergodic [53–55]. To conclude, the mathematical and numerical results provide evidence for the claim that all gases in SM are epsilon-ergodic.

7.7 Conclusion

This paper aimed to explain why gases exhibit thermodynamic-like behaviour. We have argued that there is thermodynamic-like behaviour when the system is epsilon-ergodic, i.e., ergodic on the entire accessible phase space except for a small region of measure epsilon. Then we have shown that the common objections against the ergodic approach are misguided and that there are good reasons to believe that the relevant systems in statistical mechanics are indeed epsilon-ergodic. Therefore, epsilon-ergodicity seems to be the sought-after explanation of why gases show thermodynamic-like behaviour. However, our approach presupposes that the equilibrium macro region is dominant, which can be shown only for gases. The situation might well be different in liquids and solids. Whether, and if so how, the current approach generalises to liquids and solids is an open question.

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