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The approach to equilibrium in statistical thermodynamics—do we really need coarse-graining?

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Abstract

The technique of coarse-graining is conventionally used in both introductory and more advanced textbooks on statistical mechanics and thermodynamics when discussing a thermodynamic state described by an ensemble approaching equilibrium. In quantum statistical thermodynamics there exists a natural uncertainty-limited phase space volume element, but in the case of classical statistical thermodynamics no such natural phase space volume element exists and coarse-graining by its nature can appear as a rather arbitrary and ad-hoc procedure for students first encountering it. The present work discusses the approach to equilibrium in the ensemble picture, based on observable thermodynamic properties of the system in question. We suggest that a fruitful teaching approach can be based on the perspective that the system has reached thermodynamic equilibrium (distinct from statistical equilibrium) if all its observable macroscopic thermodynamic properties are indistinguishable from those of a canonical ensemble with the same observable macroscopic properties. This differs to an approach based on whether the probability distribution function (specifically the integral of the natural logarithm of the probability distribution) match those of a canonical distribution (which they cannot do in thermally isolated systems, due to the Liouville theorem). These ideas are essentially those of ‘weak convergence’, normally encountered in more mathematically advanced treatments, but whose basic ideas can be motivated with a simple mathematical outline, and is based on a set of common and reasonable assumptions concerning the evolution of probability distribution functions in a thermally isolated system. The approach may help alleviate student concerns over the use of coarse-graining in classical statistical thermodynamics. A relatively small elevation in the mathematical level of the concepts therefore provides a considerable gain in clarity and coherence of the emergent physical picture, and aligns with previous work by Jaynes, recently highlighted by me, on the definition of entropy in the ensemble picture.

1. Introduction

The development of statistical mechanics has been strongly influenced by the seminal contributions of Josiah Willard Gibbs [1, 2]. Gibbs based his development of statistical thermodynamics on the concept of an ensemble, i.e. collections of a large (or indeed infinite) number of independent replicas of a system, characterised by a probability distribution function P in a multi-dimensional phase space. Integration of physical properties of the systems from the entire phase space, weighted by the probability distribution function, yield the macroscopic thermodynamic properties of the system.

Gibbs used the ensemble concept as the central pillar of his approach to statistical mechanics. But he took quite a mathematically based approach and did not greatly emphasise the physical aspects or links of his approach [3, 4]. One consequence of this is that he did not ever really clearly specify how he envisaged the ensemble concept was linked to the physical reality of the properties of a single system. At various points he mentions sampling of the ensemble as a method to interrogate the state of a single

system, and the idea of a time ensemble (the ensemble of phases through which a single system passes in the course of time) and also speaks about the ensemble embracing every single combination of configuration and velocities. This lack of precise and consistent definition is mirrored in the general literature on this subject also, and I discuss this further (albeit briefly) in the [appendix](#) below.

However, in the main Gibbs essentially takes the ensemble as the central quantity with which he is interested. He treats it as the key element to allow calculation of the properties of a thermodynamic system, via the ensemble average, without being overly concerned with physically motivating its origins. The concept of the ensemble average is shown in equation (1), for a property F (e.g. the system energy) where ‘ n ’ is the number of degrees of freedom of the constituent systems (proportional to the number of particles in any one system):

$$\bar{F} = \int \dots \int P(q_1, \dots, q_n, p_1, \dots, p_n) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n. \quad (1)$$

Probably the clearest statement of Gibbs’ view of the ensemble and its usage is given in the preface to his book ‘Elementary Principles in Statistical Mechanics’ [2] (referred to as EPSM hereafter):

*‘The usual point of view in the study of mechanics is that where the attention is mainly directed to the changes which take place in the course of time in a given system... For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, **not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time.**’*

The bolding of the text is my own and indicates that Gibbs views the evolution of the probability distribution as the key concern, and it is reasonable to then assume that the time evolved probability distribution is used to calculate the properties of a thermodynamic system.

One of the most profound results of Gibbs’ work was the association of the thermodynamic function of entropy with this probability distribution function P :

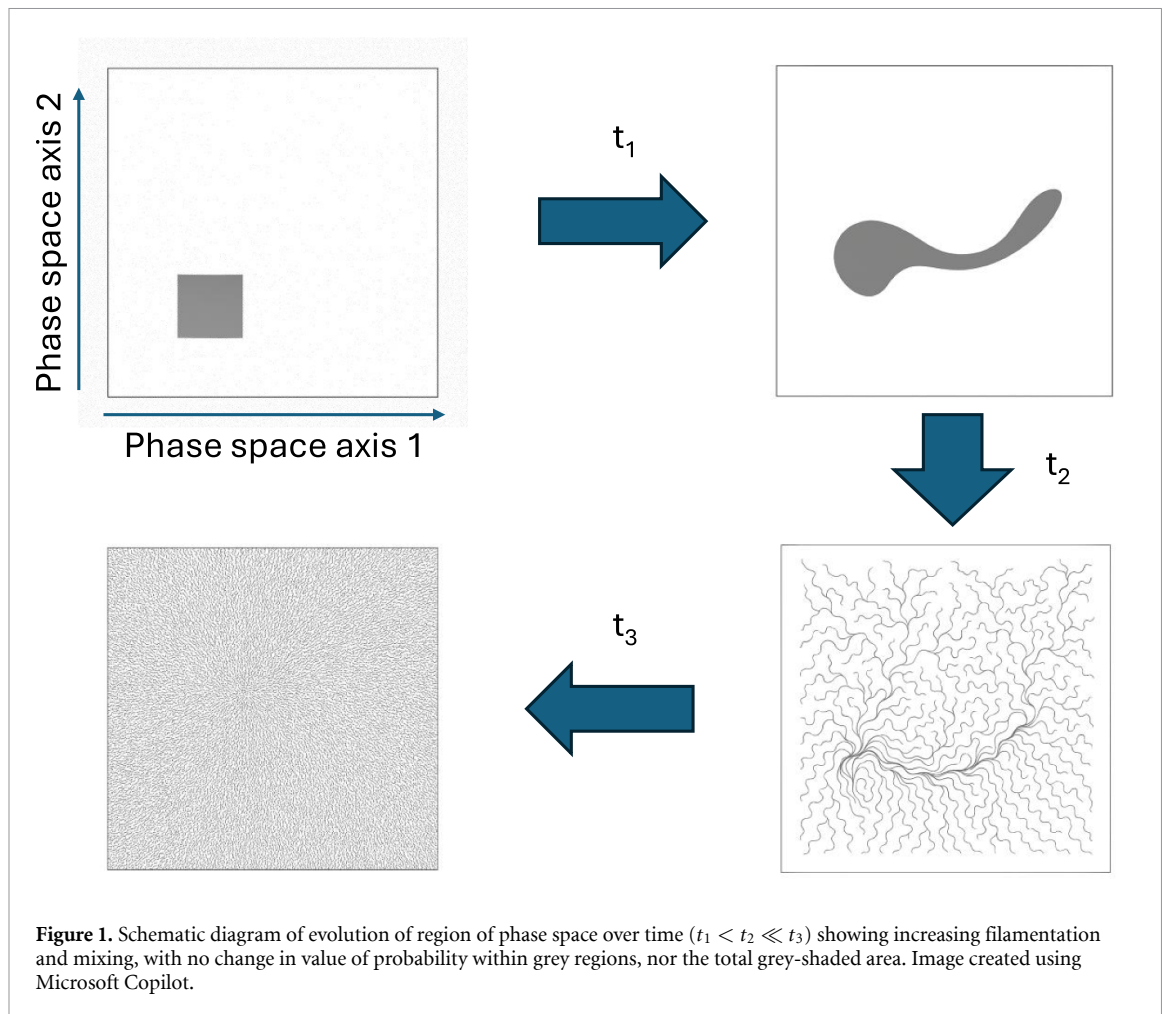
$$S_G = -k_B \int \dots \int P \cdot \ln(P) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n = -k_B \overline{\ln(P)}. \quad (2)$$

Equation (2) defines the Gibbs’ entropy (S_G). However, the Liouville theorem of classical mechanics states that the local value of the probability distribution around any moving point does not change for an isolated system. The shape of the probability distribution in phase space can become drawn out, stretch, warp and mix in a highly complex way (see the schematic illustration in figure 1) but ultimately the integral in equation (2) cannot change over time and hence neither will the Gibbs entropy in equation (2). Amongst the implications of this is that a system undergoing an irreversible adiabatic expansion does not increase in entropy, contrary to the outcomes from classical thermodynamics. One of the standard approaches to resolve this issue, which Gibbs suggested himself, was the idea of coarse-graining, whereby phase space is divided into small but finite volume elements, and a probability is associated with the element which is the average of the actual (fine-grained) probability distribution function over that element. In essence the probability distribution function is smeared out over this finite phase space volume element. While this is physically reasonable in the context of quantum mechanical systems, where a minimum-sized phase space volume element exists, in classical statistical mechanics it is an ad-hoc process without physical justification, which can be a jarring realisation for students.

In a previous paper of mine, itself centrally based on earlier work of Edwin Jaynes, it has been argued that the correct definition of the entropy to be associated with any probability distribution is the ‘experimental entropy’ S_e , i.e. the Gibbs entropy (S_G) calculated for a canonical distribution with the same average energy as that probability distribution [5, 6]. Jaynes justified this approach by saying [6]:

*‘...the experimental entropy is a measure of all conceivable ways in which the final macrostate can be realized, and **not merely of all ways in which it could be produced in one particular experiment.**’*

The bolding of the text is again my own. In my own paper I discussed this approach and gave a range of physical motivations for this definition, linking it to the definition of entropy in classical thermodynamics, amongst other points. It is argued that the concept of coarse-graining is not required in



this definition of the experimental entropy, and this is again supported by Jaynes' own comments where he says that [6]:

'Any really satisfactory demonstration of the second law must therefore be based on a different approach than coarse-graining.'

Another consequence of the Liouville theorem for the case of an isolated system is that the probability distribution P can never reach a steady state where $\partial P/\partial t = 0$ at all points in the accessible phase space. Given that Gibbs explicitly identifies this condition as the equilibrium criterion in his approach, the implication is that an isolated system undergoing an irreversible expansion can never reach equilibrium, contrary to everyday experience, and that the situation once again requires coarse-graining to rescue it.

In the present work I wish to discuss the time evolution of an isolated ensemble¹, pointing out that Gibbs' criterion for equilibrium is a statistical equilibrium, rather than a thermodynamic equilibrium, and that a useful teaching approach is to make this distinction clear at the outset. This is not limited to Gibbs, and Pathria and Beale in a recent edition of their textbook state explicitly (in the section spanning pages 26 and 27) that [7]:

'Naturally, a stationary ensemble qualifies to represent a system in equilibrium.'

This is certainly a reasonable viewpoint, but it should not be interpreted as implying that only a stationary ensemble can represent a system in thermodynamic equilibrium. I further argue that

¹ I would emphasise that the concept of a perfectly isolated system is an idealisation unattainable in practice. There will always be some residual interactions with the surrounding environment (including with the thermal radiation field), and these will always tend to blur and spread out the probability distribution (in a manner similar to coarse-graining), ultimately leading to an equilibrium distribution as I discussed in my previous paper [5]. However, the purpose of the present work is to make the point that, even in the (unattainable) idealised isolated state, coarse-graining is not required if one takes the view that the system has reached thermodynamic equilibrium if all of its observable macroscopic thermodynamic properties are indistinguishable from those of a canonical ensemble with the same observable macroscopic properties.

this teaching approach should emphasise that thermodynamic equilibrium ought to be judged by the behaviour and evolution of the thermodynamic properties predicted by ensemble averages. Assuming ergodic and mixing behaviour in the system (which are generally assumed in complex systems with large numbers of degrees of freedom), one can show that such properties calculated from ensemble averages will reach a steady state equilibrium, consistent with classical thermodynamics, without any need for coarse-graining. This behaviour is known as ‘weak convergence’ and is a more mathematically advanced topic [8–10], but nevertheless the basic ideas can certainly be motivated at the undergraduate level. The assumptions concerning the dynamical system’s behaviour which underly weak convergence are just the same as are required for the coarse-graining approach.

The use of this approach can allow teachers to provide a clear explanation of the approach to thermodynamic (as opposed to statistical) equilibrium of a system described by an evolving ensemble, without recourse to coarse-graining. In parallel with my previous paper and the work of Jaynes, it allows quite a complete and consistent explanation of how the Gibbs ensemble approach can be applied to the topics of entropy and approach to equilibrium in classical statistical mechanics, and hence may be useful to teachers and students who find the coarse-graining approach to be ad-hoc, jarring and lacking physical justification in classical statistical mechanics.

2. Time evolution of an ensemble representing an isolated system: ergodicity, mixing and weak convergence

As described above, the evolution of the ensemble representing an isolated system which undergoes an irreversible process (e.g. irreversible adiabatic expansion) is subject to the Liouville theorem and hence the local value of the probability distribution around any moving point does not change. Given that the accessible volume of phase space has increased, and since the total integral of the probability distribution over the accessible volume of phase space must remain equal to one, this implies that the probability distribution must spread out in the filamentary manner shown in figure 1, without its value in the grey regions changing. Outside the grey regions the value of the probability distribution will equal zero.

We will assume for simplicity that the system prior to the irreversible process is distributed canonically. Each system in the ensemble will of course evolve on a constant energy surface so one could apply the arguments below equally well to a microcanonical distribution also². As time elapses this probability distribution will go through a sequence of forms P_n , where the average of P_n over any finite volume in a region will tend towards a constant value, the value for the canonical distribution, even though it remains essentially filamentary as shown. This is the generally accepted and widely taught picture of the evolution of the probability distributions [2, 9, 11, 12].

This behaviour is associated with the large number of degrees of freedom of a complex thermodynamic system and is based on a particular (and generally assumed) property of the dynamics of the system, specifically that of strong mixing (whereby phase space is essentially ‘scrambled’ so that any small subset of phase space spreads out to eventually reach all parts of available phase space, in a measure preserving manner)³ [13].

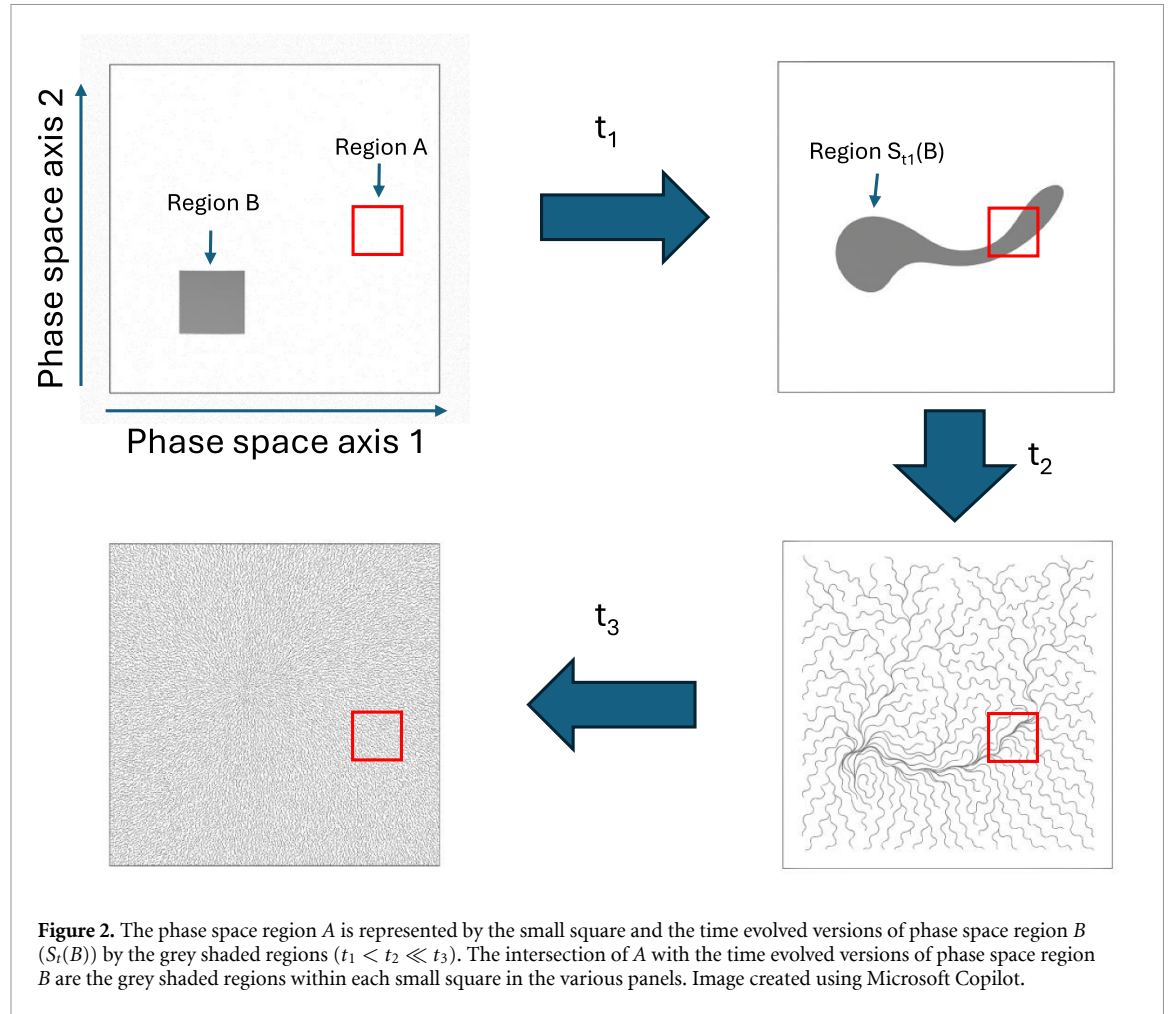
Mathematically, the strong mixing property means that on any constant energy surface (a microcanonical shell), if we have any two initial sets, A and B , whose measures are $\mu(A)$ and $\mu(B)$ (where $\mu(A)$ and $\mu(B)$ may have arbitrarily small values but must both be greater than zero), then if $S_t(B)$ is the region of phase space into which the initial region B has evolved after time t (assuming that the phase space measure is invariant under time evolution), strong mixing implies that [9]:

$$\lim_{t \rightarrow \infty} \mu(A \cap S_t(B)) = \mu(A) \frac{\mu(B)}{\mu(\Omega)} \quad (3)$$

where $\mu(\Omega)$ is the measure of the entire available phase space of the constant energy surface, Ω .

² Gibbs explicitly notes that one may regard the canonical ensemble as being composed of an infinity of microcanonical ensembles (see page 118 of EPSM).

³ If a dynamical system displays strong mixing then ergodicity (whereby the system visits every part of its phase space over very long time scales and spends an amount of time in each region of phase space proportional to the volume of that region) is assured, based on the ergodic hierarchy [13, 19]. This property is generally assumed in complex thermodynamic systems with large numbers of degrees of freedom. A simple example of strong mixing is the so-called ‘Baker’s map’, inspired by the kneading action bakers apply to dough, whereby successive cutting, stacking and stretching operations cause layers to be densely interleaved to an arbitrarily great degree. A number of nice animations are available online to demonstrate this mapping and the interleaving effect (<https://observablehq.com/@rreusser/bakers-map> and <https://demonstrations.wolfram.com/TheBakersMap/>).



Essentially, for any region of phase space A , no matter how small, the measure of the intersection of A and the region of phase space into which the initial region B has evolved after time t ($S_t(B)$) reaches a constant value, equal to the product of their initial phase space measures divided by the measure of the entire available phase space of the constant energy surface, Ω (figure 2). One can see in figure 2 that while the intersection of A and $S_t(B)$ varies as time evolves (e.g. no overlap in the top left panel, very small overlap in the top right panel), at long evolution times, as $S_t(B)$ becomes ever more mixed and filamentary, the grey shaded region within the red square becomes proportional to the product of the area of B with that of A . For example, if A had a measure of 5 and B a measure of 0.5, and the measure of the entire available phase space is 100, then equation (3) indicates that the intersection of A and $S_t(B)$ reaches a limiting measure of 0.025 as time increases, even if A and B were disjoint sets at the initial time. This holds for any region A , regardless of the value of $\mu(A)$, implying that $S_t(B)$ becomes increasingly ‘evenly distributed,’ i.e. it approaches the microcanonical distribution when integrated over any finite region (without ever reaching the microcanonical distribution). Because the phase space regions in each constant energy shell will show the same behaviour, the overall distribution will therefore approach the canonical distribution when integrated over any finite region (without ever reaching the canonical distribution).

This property may look at first glance like we are sneaking the idea of coarse-graining in by the back door through the use of the small ‘sampling’ region A , but it is important to emphasise that this is not the case. We are not suggesting that any operation should be applied to the probability distributions describing the ensemble but simply indicating the behaviour of regions of phase space under evolution through long periods of time.

At this point it is useful to introduce the property of weak convergence, which is a feature of strong mixing dynamical systems. Weak convergence refers to the behaviour over time of a sequence of probability distributions P_{sk} (where $P_{sk} = P_s(q_1, \dots, q_n, p_1, \dots, p_n, t_k)$, and the subscript ‘ k ’ indicates different times). Specifically, a sequence of probability distributions P_{sk} are said to converge weakly to P , if when P_{sk} is multiplied by any bounded continuous function of phase space $F(q_1, \dots, q_n, p_1, \dots, p_n)$, the sequence

of integrals $\overline{F}_k$:

$$\overline{F}_k = \int \dots \int P_{sk}(q_1, \dots, q_n, p_1, \dots, p_n, t_k) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n \quad (4)$$

approach a constant value $\overline{F}$ given by integration of the product of F and P over the same region of phase space, i.e. [9, 14, 15]:

$$\lim_{k \rightarrow \infty} \overline{F}_k = \overline{F} \quad (5)$$

with

$$\overline{F} = \int \dots \int P(q_1, \dots, q_n, p_1, \dots, p_n) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n. \quad (6)$$

Note that F and P are independent of time and are simply determined by the position in phase space of the element of the ensemble, whereas the probability distributions P_{sk} vary with time. If one has a uniform probability distribution on a constant energy surface in an initial region of phase, which can then evolve into a larger region of phase space (i.e. an irreversible adiabatic expansion), the strong mixing behaviour discussed above can be shown to lead to a key result, using the Frobenius–Perron operator. Specifically, the time-evolved probability distribution in the larger region of phase space converges weakly as time increases to a uniform probability distribution (with a smaller probability density value) in the larger region of phase space on the constant energy surface (i.e. converges weakly to the microcanonical distribution in the larger region). Because the phase space regions in each constant energy shell will show the same behaviour, the overall distribution will therefore converge weakly to the canonical distribution in the limit of long elapsed times.

It is important to be clear again that the actual probability distribution does not converge pointwise to the canonical distribution, that it retains its filamentary structure; weak convergence solely refers to the convergence as time evolves of integrals involving the product of a function and the probability distribution. Again, we are not suggesting that any operation should be applied to the probability distributions describing the ensemble but simply indicating the behaviour of a sequence of integrals under evolution through long periods of time.

But happily, the integrals $\overline{F}_k$ in question are exactly the type used to calculate ensemble averages of thermodynamic properties (denoted by F) of the system associated with the evolving probability distributions P_{sk} (increasing k implying later times). While the functions F representing the thermodynamic properties may be complicated functions of the phase space variables, they are necessarily continuous since they describe physical properties of systems as a function of phase space coordinates and all thermodynamic properties can be described by such functions. The total system energy is one example, and the pressure can be written as the rate of variation of the total energy with respect to the volume for an isolated system. The temperature can also be uniquely related to the total system energy since a requirement for thermal stability in a uniform material is that the specific heat capacity at constant volume should always be positive [16, 17]. Hence the thermodynamic properties of the system, as predicted by the sequence of ensemble averages, do indeed reach a limit, and the value of the limit will be that for an ensemble average calculated using the canonical distribution.

The approach above is quite mathematical, but the general idea can be motivated relatively simply in a step-wise fashion. In figure 2 we showed schematically how the increasingly filamentary probability distribution $S_t(B)$ evolves within a ‘sampling’ region of phase space A (a ‘set’ in the language used in relation to equation (3)). We can write the evolving sequence of probability distributions P_{sk} within the region A as follows:

$$P_{sk} = P_{mc} + \Delta P_{sk} \quad (7)$$

where P_{mc} is the microcanonical distribution and ΔP_{sk} the difference between the actual and microcanonical distribution. This will be an increasingly rapidly-varying function of the phase space variables as time evolves. The weak convergence of P_{sk} to P_{mc} discussed after equation (6) above implies that as time evolves the integral of ΔP_{sk} over A approaches zero, and also that as time evolves one can use ever smaller and smaller sets A and the integral again approaches zero. So, for any region of phase space A , no matter how small:

$$\lim_{k \rightarrow \infty} \int \dots \int_A \Delta P_{sk}(q_1, \dots, q_n, p_1, \dots, p_n, t_k) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n = 0. \quad (8)$$

We can then write the ensemble average over A of any bounded continuous function of phase space $F(q_1, \dots, q_n, p_1, \dots, p_n)$ using the sequence of distribution functions P_{sk} can be written as:

$$\overline{F}_k^A = \int_A \dots \int_A P_{sk}(q_1, \dots, q_n, p_1, \dots, p_n, t_k) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n. \quad (9)$$

This may be written as the sum of two terms:

$$\begin{aligned} \overline{F}_k^A &= \int_A \dots \int_A P_{mc}(q_1, \dots, q_n, p_1, \dots, p_n) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n \\ &\quad + \int_A \dots \int_A \Delta P_{sk}(q_1, \dots, q_n, p_1, \dots, p_n, t_k) \cdot F(q_1, \dots, q_n, p_1, \dots, p_n) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n. \end{aligned} \quad (10)$$

The first term in equation (10) is simply the ensemble average over the phase space region A of the thermodynamic property F using the microcanonical distribution (which will be called $\overline{F}_{mc}^A$). When looking at the second term, we must recall that F is a bounded continuous function and consequently, if we let the time evolve for sufficiently long, we can choose a sufficiently small set A within which we integrate so that the integral of ΔP_{sk} is as small as we wish, and also that the variation of F within A is sufficiently small that we can replace the function F within A by its mean value within A with arbitrarily small error over A . Consequently, we can take this average value of F outside the integral sign to yield:

$$\overline{F}_k^A = \overline{F}_{mc}^A + F_{mean}^A \int_A \dots \int_A \Delta P_{sk}(q_1, \dots, q_n, p_1, \dots, p_n, t_k) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n. \quad (11)$$

In the limit as $k \rightarrow \infty$, the second term in equation (11) will vanish because of equation (8), and we are left with the result that:

$$\lim_{k \rightarrow \infty} \overline{F}_k^A = \overline{F}_{mc}^A. \quad (12)$$

Physically this means that we can choose the size of the phase space region A to be so small that the variation of the bounded continuous function F is negligible, while ΔP_{sk} shows strong variations and averages as close to zero as we wish within region A . The strong mixing property of the dynamics ensures this.

We can sum the contributions from all the sets A which completely cover (without overlapping; a partition in set theoretical language) the total phase space in the constant energy shell to yield:

$$\lim_{t \rightarrow \infty} \overline{F} = \overline{F}_{mc} \quad (13)$$

where $\overline{F}_{mc}$ is the ensemble average over the total phase space in the constant energy shell using the microcanonical ensemble. Because the phase space regions in each constant energy shell show the same behaviour, the ensemble average over the entire phase space will therefore approach the value obtained using the canonical distribution, as explained above. There has been no coarse-graining of the probability distribution, with the derivation relying solely on the behaviour of a sequence of integrals under evolution through long periods of time, as determined by the dynamical behaviour of the systems.

Using this reasoning, we have shown that the thermodynamic properties of the system as derived from ensemble averages of the evolving probability distribution approach a steady state value, and specifically the value associated with an ensemble average using the canonical probability distribution. Taking the reasonable and physically motivated standpoint that a system is deemed to have reached thermodynamic equilibrium if all its observable macroscopic thermodynamic properties are unchanging over time and indistinguishable from those of a canonical ensemble with the same observable macroscopic properties, we can say that the system has reached thermodynamic equilibrium. Furthermore, any system which displays all the same observable macroscopic properties when it has reached equilibrium must be regarded as being in the same thermodynamic state (even if its underlying ensemble probability distribution is different). This approach has not required us to change the nature of the probability distribution via a process such as coarse-graining, but rather to focus our attention, and the criterion for equilibrium, on observable macroscopic properties of a system.

This final part of the argument dovetails precisely, consistently and coherently with Jaynes' view (expressed above) that the correct definition of the entropy to be associated with any probability distribution is the 'experimental entropy' S_e , i.e. the Gibbs entropy (S_G) calculated for a canonical distribution with the same average energy as that probability distribution [6]. This allows us to ensure that we include '*...all conceivable ways in which the final macrostate can be realized, and not merely...all ways in which it could be produced in one particular experiment.*'

Based on the entirety of the argument above (and referring also to my previous paper and the work of Edwin Jaynes [5, 6]), we can now provide a coherent and consistent description of the process for the definition of entropy based on the probability distribution function of an ensemble, as well as a way to describe the approach to thermodynamic equilibrium, without any requirement for coarse-graining.

One final question which may well concern students is: why do the thermodynamic properties calculated by the sequence of ensemble averages, as shown in equations (4)–(6) above approach a steady thermodynamic limit, while the Gibbs entropy in equation (2) above does not? The key point here is that the Gibbs entropy formula involves multiplying the probability distribution by its own logarithm and then integrating. Hence as time elapses the sequence of integrals for the evolution of the Gibbs entropy will be:

$$S_{G,k} = -k_B \int \dots \int P_k \ln(P_k) \cdot dp_1, \dots, dp_n, dq_1, \dots, dq_n = -k_B \overline{\ln(P_k)}. \quad (14)$$

However, a key requirement for weak convergence property is that the probability distribution be multiplied by a bounded **continuous function of phase space** $F(q_1, \dots, q_n, p_1, \dots, p_n)$. While the functions representing thermodynamic properties are continuous, the functions $\ln(P_k)$ clearly are not, since P_k switches abruptly from finite values to zero as one moves across the filaments. As time elapses (increasing k) the phase space structure and complexity of $\ln(P_k)$ evolves in a way which matches that of P_k , unlike the functions representing thermodynamic properties which are time independent. Hence, we can never reach a time where locally it seems like $\ln(P_k)$ varies slowly compared to P_k . Hence the weak convergence limit is not reached and the Gibbs entropy remains unchanged.

Teachers may wish to encourage students to probe this last issue further. One useful perspective concerns the nature of the use of the probability distribution and the ensemble average. One could discuss whether there is in fact a significant philosophical difference between using probability distributions to predict an ensemble average value of a thermodynamic property, which is a defined function of phase space coordinates, compared to the calculation of the Gibbs entropy. The former calculation uses the probability distribution along with an independent continuous function in phase space, to yield an average for the independent function. The latter calculation however is inherently self-referential, for want of a better term. One is essentially using the probability distribution to measure a property of itself, rather than to measure an independent quantity. While this can, and does, yield unique and meaningful values for certain probability distributions such as the canonical distribution (due to the particular properties of these specific distributions, such as the extremal properties of a canonical distribution compared to any other probability distribution with the same average energy), more generally the fact that both functions in the integral will mirror each other's structures in phase space at all scales means that the physical relevance of the results obtained can be questioned.

3. Conclusions

By re-focussing our attention on observable thermodynamic properties of the system in question, as deduced from integration over the ensemble which represents it, we can describe the approach to equilibrium of a system in a precise, consistent and coherent manner, which also dovetails with Jaynes' definition of the 'experimental entropy.' This is achieved using only well-known properties of dynamical systems which show the property of strong mixing (which itself is generally assumed in complex systems with large numbers of degrees of freedom) and without recourse to ad-hoc and artificial measures such as coarse-graining for classical mechanical systems. While this approach requires some knowledge of slightly more advanced mathematical topics such as weak convergence, these concepts can be motivated physically and visually quite easily at the undergraduate level, so that even if the mathematical proofs are beyond the desired level of the course, the general concepts should be readily understandable. Thus, a small increase in the mathematical level of the approach yields great dividends in terms of the clarity of the physical description which emerges.

A key point is a teaching approach based on the perspective that the system has reached thermodynamic equilibrium if all its observable macroscopic thermodynamic properties are indistinguishable from those of a canonical ensemble with the same observable macroscopic properties, and that any two systems whose observable macroscopic thermodynamic properties are identical should be considered thermodynamically identical and therefore must have identical values of state variable such as entropy. This differs sharply from the approach often encountered which simply defines the integral yielding the average of the natural logarithm of the probability distribution as the entropy, and which therefore

can never show the required approach to equilibrium based on such a definition due to the Liouville theorem.

This approach may help to alleviate concerns students may have over the use of coarse-graining in classical statistical thermodynamics as well as helping to introduce them, in a well-known physical context, to a range of more advanced mathematical tools for the study of dynamical systems, chaotic behaviour etc.

Acknowledgments

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Data availability statement

No new data were created or analysed in this study.

Appendix

A lack of uniform definition and understanding of the physical meaning and interpretation of the ensemble concept is not unique to Gibbs [4, 18]. Humpty Dumpty's words in 'Through the Looking Glass': '*When I use a word, it means just what I choose it to mean—neither more nor less...*' seem a good description of this situation. For example, Landau and Lifshitz specify that the ensemble at one instant of time should be identified with the points representing the state of one system at a series of equally spaced times during its evolution over a very long time, which is an approach that is strongly linked to ergodic behaviour [16]. Other authors take a view that the ensemble is the set of states through which a system would move during the period of time of an individual measurement, as discussed critically in [19], or relate it to issues concerned with the experimental precision associated with measurement, and/or uncertainty in initial specification, of a thermodynamic state [20]. There is a such a range of interpretations that it is impossible to do justice to them here, but further details can be found in references [4, 21, 22]. From a teaching standpoint however this situation offers both positives and negatives. Certainly, from a positive perspective, it allows a variety of approaches to motivate the ensemble concept physically, but it can also be quite unsatisfactory and confusing, particularly for more advanced students, since it is clear that while these different viewpoints all occupy the same general physical and philosophical 'territory' it is equally clear that they are far from being either philosophically, mathematically or physically identical standpoints.

It also seems that sometimes the logical consequences of some of these perspectives are perhaps not fully followed through. For example, in the Landau and Lifshitz perspective, i.e. that the ensemble at one instant of time should be identified with the points representing the state of one system at a series of equally spaced times during its evolution over a very long time, one might reasonably take a view (based on the ergodic dynamical behaviour the approach relies upon) in a process such as a sudden irreversible adiabatic expansion of e.g. an ideal gas represented by an initially canonical ensemble in the smaller configuration space, that the effect of the sudden expansion would be to discontinuously change the ensemble probability distribution to a new canonical ensemble probability distribution in the larger configuration space. This is because the implication of the ergodic dynamics is that any trajectory of an individual system will thereafter visit all the locations in the now larger configuration space during its evolution over a very long time. However, clearly this is not how discussions of the evolution of an ensemble over time normally proceed, and generally in more modern treatments the evolution of the initially smaller phase space region into the enlarged phase space region after expansion are treated using Liouville's theorem and ideas of strong mixing. This is the approach that Gibbs and most modern writers use and is hence the one used in this paper.

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