Calculation of Entropy from Data of Motion

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We discuss the question of determining the entropy given the phase space trajectory which describes the detailed history of a many-body system over a period of observation. Our viewpoint is that the determination of entropy, as well as all other thermodynamic properties, should require no concepts or information other than those given and defined by the trajectory. The counting of coincidence (or repetition) of states along the trajectory is presented as a way to determine entropy given the trajectory. An illustrative program based on the kinetic Ising model is described in detail.

KEY WORDS: Trajectory; coincidence.

1. INTRODUCTION

Thermodynamical properties are macroscopic properties of a large system in equilibrium. These properties are observed over a period of time long compared to the characteristic microscopic time scale, i.e., the relaxation time. The size of the system is large compared to the characteristic microscopic length scale, the correlation length. In principle, at least, if we know the complete data of the motion of all the particles in the system over the period of observation time, i.e., the detailed history, we should be able to know all there is to know about the system over that period. If over this period of time the system exhibits thermal equilibrium[2] then all the thermodynamic properties for that equilibrium state can be calculated from the detailed history. We shall refer to this view as the mechanical view.

Entropy is one of the thermodynamic properties. According to the

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[2] We define equilibrium by observed properties. A system is in equilibrium as observed over a given period of time if macroscopic properties are insensitive to the length of the period (within a range of the lengths). This is not meant to be a precise definition. Other qualifications must be added when necessary.

mechanical view it can also be determined from data of motion. It too reflects something about the history of the system. This mechanical view of entropy is the topic of discussion here.[3]

In the terminology of mechanics, the detailed history is described by a trajectory in the phase space. Phase space is the set of all possible states of the system. The trajectory is the set of states actually occurring during the time of observation. We shall limit our discussion to classical systems.

According to our mechanical view the trajectory is sufficient to determine the entropy. This view is quite different from the traditional formulation based on the Gibbs ensemble which is the mental construction of an infinite number of systems identical to the system of interest. Thermodynamic properties including entropy are regarded as properties of the ensemble in this formulation. Of course there is the whole subject of Ergodic theory which attempts to justify the ensemble formulation in terms of mechanical laws. We shall not attempt to comment on the Ergodic theory here.[4]

In this paper we are not concerned with how the trajectory is generated from the equations of motion based on the interaction between particles in the system and in the reservoir. We ask only how entropy is related to the already generated trajectory.

Many quantities such as the energy, the magnetization, and the various correlation functions are easily determined from the trajectory as time-averaged quantities. Entropy, however, is very different. It is simply defined in the ensemble formulation; but from the mechanical view, the determination is difficult. Since, as we shall argue, the mechanical view might provide a better conceptual foundation for statistical mechanics, the first task we face is to show that there exists some definite procedures to calculate the entropy from the trajectory. We present here the method of coincidence counting as such a procedure. There are most likely other procedures for the same purpose. The coincidence counting serves as a concrete example showing that such procedures exist and puts the mechanical view of entropy on firm ground.

The famous Boltzmann formula for the entropy[5]

$$S = \ln \Gamma(E) \tag{1.1}$$

is the foundation of statistical mechanics. Here E is the total energy of the system. $\Gamma(E)$ is the number of states with the energy E. It is the volume of a region Ω in the phase space. In Section 2 we discuss the basic ideas involved in counting coincidence along the trajectory for the determination

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[3] A brief summary of the discussion has been reported by the author elsewhere (unpublished works).

[4] For an introduction to more recent developments, see, for example, Ref. 1.

[5] The Boltzmann constant is chosen to be unity.

of the entropy. In Section 3 an illustrative program is presented showing how the ideas are carried out numerically. A kinetic Ising model is used for simplicity and for definiteness. The main result of this paper is simply an explicit demonstration of how, using the trajectory alone, to define Ω and measure $\Gamma(E)$.

Having presented an example of determining entropy from the trajectory, we then argue in Section 4 why the mechanical view is more preferable than the ensemble view. The major weakness of the ensemble formulation is its ambiguity in defining the ensemble when metastability is involved. Comparisons between the mechanical view and the ensemble view are made. In Section 5 we discuss the thermodynamical measurement of entropy, paying special attention to the third law of thermodynamics. Further discussion is given in Section 6.

We realize that there is a diverse range of different interpretations of the ensemble and other views. Some readers may find our mechanical view controversial and unproven. Indeed, our arguments here are not rigorous. Our numerical demonstration supplies only an evidence, not an exhaustive study. We hope that it will stimulate more rigorous work. On the other hand, some readers may regard the mechanical view as a truism. Some may even regard our discussion as merely semantic. To these readers, this paper can be taken as an introduction to a numerical technique of determining the entropy. We believe that this technique is potentially useful especially in studying random systems.

2. BASIC IDEAS

2.1. Coincidence and the Size of a Region

The basic idea of using coincidence counting to calculate entropy is extremely simple. Suppose that the trajectory is a set of n points randomly distributed in a region of Γ positions. Even if n is much smaller than Γ, there is a nonzero chance for coincidence, i.e., some positions will get more than one point. Since the probability for a point to fall in any given position is $1/\Gamma$, the number of coincidences is easily estimated:

$$N_c = n(n-1)/2 \times 1/\Gamma \qquad (2.1)$$

Let us define R to be the coincidence rate which is the probability of finding a coincidence per trial. There are $n(n-1)/2$ trials; therefore,

$$R = 1/\Gamma \qquad (2.2)$$

$$\Gamma = N_t/N_c$$

$$N_t = n(n-1)/2$$

$$S = \ln(1/R) \qquad (2.3)$$

Knowing n and N_c one can calculate Γ. The advantage of this way of calculating Γ is that it is very straightforward. No consideration of the "shape" or other geometrical properties of the region is necessary. However, there are many problems in applying this idea to the trajectory of interest. The most serious problem is already evident from (2.1). In order to get a good estimate of Γ we need to have N_c greater than 1, i.e.,

$$n \gtrsim \sqrt{\Gamma} \tag{2.4}$$

The number of states must be very large because we need to deal with extremely large Γ. We now discuss this problem in more detail.

2.2. Statistical Independence

As is well known, over a reasonable period of time $\mathfrak{T}$ the trajectory by no means passes through all Γ states. For a many-particle system, the number of states which the trajectory actually passes through is roughly

$$n \sim N(\mathfrak{T}/\tau) \tag{2.5}$$

where N is the number of degrees of freedom of the system and τ is the time between two changes for each variable. However, Γ is of the order of the exponential of N

$$\Gamma = e^S \tag{2.6}$$

$$S \propto N$$

Therefore, if N is large the criterion (2.4) cannot be met for any reasonable time $\mathfrak{T}$.

This difficulty is not as serious as it appears. The exponential dependence of Γ on N only reflects the statistical independence of subsystems, i.e., the fact that a large system is made up of approximately independent subsystems. The total entropy is the sum of the entropies of the subsystems. The number of subsystems is proportional to N and that is why the total entropy is proportional to N.

The coincidence rate for the combined system of two independent subsystems A and B is just the product $R_A R_B$ which is the probability of finding a coincidence for A and one for B simultaneously. Thus, we have

$$S_{A+B} = \ln(1/R_A R_B)$$
$$= S_A + S_B \tag{2.7}$$

This shows that the measurement of entropy by coincidence is consistent with the additive property of entropy for independent systems. For large systems, we can therefore write total entropy as

$$S = \sum_A S_A + \sum_{A,B} S_{AB} \tag{2.8}$$

where S_A is the entropy for the subsystem A. We expect some correlation between neighboring subsystems. The S_{AB} terms are the corrections due to such correlations. The correction term S_{AB} can be calculated by calculating the entropy for the combined system $A + B$ and

$$S_{AB} = S_{A+B} - S_A - S_B \qquad (2.9)$$

One has to choose the subsystems in such a way that they are large enough to be approximately independent. Of course we would like to have these subsystems be small so that the entropies can be determined by coincidence counting.

At this point we emphasize that the physics of a many-body system rests on the correlation among a relatively small number of dynamical variables, i.e., correlations within a subsystem, and the combinations of approximately independent subsystems. Once the properties of the subsystems are known, the extrapolation to a larger system (the thermodynamic limit) is relatively simple when statistical independence holds. This is the basic reason why it is possible to calculate thermodynamic properties by numerical simulations which have so far been limited to model systems of less than a few thousand particles or spins. Very often model systems of much smaller sizes can already adequately give accurate descriptions of thermodynamic properties. Correlations in many systems of interest extend not much more than ten particles or spins. Statistical independence is already evident before the sizes get to about 100. Generally if the size is sufficient to account for the correlations, further increase in size would simply reflect only the statistical independence property. Of course, the minimum size required would depend on the particular problem of interest. When there are long-range correlations such as those occurring near a critical point, direct simulation would require sizes that are too large for today's computers. However, special techniques such as renormalization group can be combined to extract certain information.

2.3. Relaxation Time

In general the states in a trajectory are not quite randomly distributed. Each state is correlated to other states which occur within a relaxation time. The statistical independence property discussed above implies that fluctuations separated by large distances in a large system are uncorrelated. A system in equilibrium also has the property that fluctuations separated by large times are uncorrelated. Thermodynamic properties are obtained by observations over a period much longer than the relaxation time. The length of the relaxation time again depends on the particular system of interest. Many model systems studied in the numerical simulation literature

typically have a relaxation time of several flips per spin or a few moves per particle. Again, there are interesting systems with long relaxation times such as those near critical points.

In order to use coincidence counting to calculate entropy via Eqs. (2.1)–(2.3) the set of n states must be randomly distributed. Therefore, in calculating the coincidence rate we must collect coincidences between states which occur far apart in time, i.e., farther than a relaxation time.

2.4. Nonuniform Probability Distribution

The assumption that we can sample from the trajectory a set of states which are randomly distributed, i.e., distributed with uniform probability, over Γ positions is crucial in order to define Γ by the trajectory. We now generalize the above results to cover cases where the probability distribution is not entirely uniform.

We separate the states into groups labeled by λ. Let $\mathfrak{T}_\lambda$ be the total time which the trajectory spends in states of the group λ and

$$P_\lambda = \mathfrak{T}_\lambda/\mathfrak{T} \tag{2.10}$$

be defined as the probability of finding a group-λ state. $\mathfrak{T}$ is the total time duration of the trajectory. Now suppose that uniform probability can be assumed for states in each group. Let the number of trials done in each group be $N_{t\lambda}$ and the coincidence count be $N_{c\lambda}$. The generalization of (2.3) is then the average over λ:

$$S = \sum_\lambda P_\lambda \ln(1/R_\lambda) \tag{2.11}$$

where R_λ is the probability of finding a state along the trajectory to coincide with a given state in the group λ. This coincidence rate is

$$R_\lambda = P_\lambda/\Gamma_\lambda \tag{2.12}$$

since the probability that a trial state be picked in the group λ is P_λ. If there are Γ_λ positions in the λ phase space, the coincidence probability is clearly given by (2.12). Thus, we have

$$S = \sum_\lambda P_\lambda \ln(\Gamma_\lambda/P_\lambda)$$

$$\Gamma_\lambda = N_{t\lambda}/N_{c\lambda} \tag{2.13}$$

The separation into groups depends on the particular problem of interest. For example, the total energy is not fixed if the system is in contact with an energy reservoir. Assuming uniform probability for each energy interval, we may choose λ to label the energy intervals.

3. ILLUSTRATIVE PROGRAM

The coincidence counting program is a program to calculate entropy given the trajectory for the system of interest. For the purpose of illustrating basic ideas we study the kinetic Ising model whose trajectory is easy to analyze on a computer. We actually need two programs. First a simulation program which generates the trajectory and second the counting program which calculates the entropy given the trajectory as the input. The program of interest here is the second program. The first is just a standard simulation program, but the second program cannot be designed independent of the first. We shall discuss the model and its simulation first.

3.1. The Kinetic Ising Model

The state of the kinetic Ising system is specified by N spins, s_1, $s_2, \ldots, s_N$. Each s_i can assume two values, ± 1. The spins flip according to certain dynamical laws which we specify as follows. Given a state we define the flip probability per unit time W_i for each spin

$$W_i = \frac{\exp(-s_i h_i / T)}{\cosh(h_i / T)} \tag{3.1}$$

Here T is the temperature of the system and

$$h_i = \sum_j J_{ij} s_j \tag{3.2}$$

is the effective field seen by the ith spin and J_{ij} is the coupling constant for the interaction between spins i and j. The model is now completely defined. The trajectory generated by (3.1) will contain all information concerning the system in contact with a reservoir of temperature T. Given the state at time t the probability that no spin has flipped by the time t' later is $\exp(-\Omega t')$ where

$$\Omega = \sum_i W_i \tag{3.3}$$

is the probability per unit time that one of the spins flips. Therefore the probability that nothing happens during the period t' and then one spin flips t' in the subsequent interval dt' is

$$e^{-\Omega t'} \Omega \, dt' \tag{3.4}$$

The probability that the spin which flips is s_i is

$$W_i / \Omega \tag{3.5}$$

Therefore, the generation of the trajectory has three steps.

(1) Given the state at t, compute W_i and Ω according to (3.1), (3.2), and (3.3).

(2) Generate two numbers x and y by a generator of random numbers uniformly distributed between zero and 1 and set

$$t' = (-\ln x)/\Omega \tag{3.6}$$

and add t' to t.

(3) Divide the interval $(0,1)$ into N portions of lengths given by (3.5). If the number y generated above falls in the jth portion, then change s_j to $-s_j$. Go to step 1.

These three steps faithfully generate the trajectory according to the model. We now proceed to discuss various aspects of the counting program.

3.2. The Counting Program—Memory and Comparison

This program is to compare the n states of the trajectory generated above and to see if some of the states coincide. Each state is a configuration of N spins. We essentially need to make about $n^2/2$ pairwise comparisons. The task is to memorize n configurations and then compare them. We have not searched for the latest art of accomplishing such a task although very likely ingenious methods already exist in computer science literature. Here we shall discuss only a simple program with very limited efficiency and generality. It is catered to the kinetic Ising model discussed above.

Instead of memorizing all states in the trajectory, we keep in the memory the labels of spins $i_1, i_2, \ldots, i_n$ which are flipped sequentially. To compare two states we calculate the difference between the two states. The difference is defined as the difference in the number of spins between the two configurations. It can be calculated from the flips which happen between the two states. For example, to compare the state before i_2 and the state after i_{10} we count the number of spins in the set $i_2, \ldots, i_{10}$ which were flipped an odd number of times (those flipped an even number of times are the same as not flipped at all). This number is the difference between these two states. If the difference is zero, we have a coincidence. In this manner the program calculates the differences between the two states of pairs of states sampled along the trajectory. As stressed in the previous section, each pair of states sampled must be well separated in time. One has to first estimate the relaxation time and then make the separations longer than it is.

3.3. Energy and Cross Section

Because of the contact to an energy reservoir the trajectory goes through states of different energies and we need to calculate $\Gamma(E)$ for all E

with an appreciable probability $P(E)$. The entropy is then calculated via (2.13),

$$S = \sum_E P(E)\ln\left[\Gamma(E)/P(E)\right] \tag{3.7}$$

The probability $P(E)$ is readily available from the simulation program.

$$P(E) = \mathfrak{T}(E)/\mathfrak{T} \tag{3.8}$$

where $\mathfrak{T}(E)$ is the total time spent in states with energy E and $\mathfrak{T}$ is the total time of the trajectory. Thus, in addition to the labels of the flipped spins the energies of all the states in the trajectory are memorized also. The coincidences for each energy level are recorded and $\Gamma(E)$ computed separately.

The cross section V_s of a state s is defined as the total number of states having the same energy as s but differs from s by no more than m spins. The number m is chosen to be a small number like 0, 1, or 2 so that the cross sections are easily computed in simulation programs. The purpose of introducing the cross sections is to enhance the coincidence counts. Given a state s, if another state s' differs from s by no more than m spins, then we record a coincidence count. In other words, if s' is within the cross section of s, we count it. (If $m = 0$, then s and s' must be the same state to be counted as a coincidence.) In computing the coincidence rate, we have to appropriately divide the coincidence counts by a sample number weighted by the V_s. The cross sections of all states in the trajectory are calculated and memorized along with the energies and the labels of flipped spins. Nothing else needs to be memorized from the simulation program.

3.4. Examples of Calculation, Estimate of Limitation

At this primitive stage of development, an explicit calculation is most illustrative. We have applied the above described program to one-dimensional kinetic Ising models with nearest neighbor interactions. We describe first the case of a uniform model of 12 spins.

Table I shows the results from a trajectory of 2000 flips. The "number of trials" listed are weighted by the cross sections V_s as described in Section

Table I.   Coincidence Counting for a Uniform Chain of 12 Spins[a]

Excitation energy	Number of trials	Coincidence counts	$\Gamma(E)$	$P(E)$
0	2,680	1,334	1.99 (2)	0.515 (0.42)
4	2,845,392	22,440	126.8 (132)	0.425 (0.51)
8	369,635	377	980.5 (990)	0.059 (0.07)
12	69	0	(1848)	0.001 (0.002)

[a] Nearest-neighbor interaction $J = 1$, periodic boundary condition. V_s calculated with $m = 2$. 2000 flips at $T = 1$. Measured entropy $S = 3.7$.

3.3. The two states of each trial are further apart than 60 flips. The number of trials divided by the coincidence count gives $\Gamma(E)$. These $\Gamma(E)$'s are the output of the coincidence counting program. For this model, $\Gamma(E)$ can be calculated analytically quite easily. The two ground states are those with all spins parallel. The excited states are those with even numbers of "kinks" (or domain walls) present. Note that the periodic boundary condition is imposed. The analytic results are given in Table I in parentheses. We see that the agreement is very good except for $E = 12$ where there is no coincidence recorded.

Using $\Gamma(E)$, we can calculate the entropy via (3.7) and obtain $S = 3.7$. This is quite a bit lower than the value 4.1 calculated analytically. This discrepancy is due to the lack of good data for $P(E)$, which needs a longer time for the simulation program; 2000 flips are too short. It happens that $E = 4$ gives the major contribution to S and $P(E)$ for this energy is off by 10%. Note that as far as the coincidence program is concerned, 2000 flips already give very good $\ln \Gamma(E)$. For $E = 12$, where the coincidence counting fails, the contribution to entropy is about 0.03. Thus, disregarding errors of the simulation program, we can say that the error due to the coincidence counting program at 2000 flips is about 2% for this particular calculation. The same conclusion is observed for other temperatures tested.

Since we will eventually be interested in applying the counting program to random systems, we test the program on a nonuniform Ising chain. For nonuniform models, the energy levels are often more spread out. They are more difficult to evaluate analytically.

Table II summarizes the results for the more complicated case of a nonuniform model. We arbitrarily choose the interactions of a 16-spin system as

$$J_{i,i+1} = 1, 4, 4, 7, 7, 4, 4, 2, 2, 3, 3, 6, 6, 2, 2 \tag{3.9}$$

for $i = 1, 2, \ldots , 15$, respectively. The average and the rms of the J's are, respectively,

$$\begin{aligned} \bar{J} &= 3.56 \\ \Delta J &= 2.03 \end{aligned} \tag{3.10}$$

The usual canonical calculation gives

$$S_{\text{canon}} = \sum_{i=1}^{15} S_1(J_{i,i+1}) + \ln 2$$

$$S_1(J) \equiv \frac{2J/T}{e^{2J/T} + 1} + \ln(1 + e^{-2J/T}) \tag{3.11}$$

The entropy is again calculated via (3.7). The data of Table II give $S = 6.3$. For the energies with zero coincidence count, a lower limit of $\Gamma(E)$ was

Table II. Coincidence Counting for a Nonuniform Chain of 16 Spins[a]

Excitation energy	Number of trials	Coincidence counts	$\Gamma(E)$	$P(E)$
0	108	48	2.25	0.0771
2	36	18	2	0.0463
4	1,116	116	9.6	0.1094
6	1,592	115	13.8	0.0970
8	1,486	54	27.5	0.1008
10	4,215	75	56.2	0.1140
12	4,120	41	100	0.1003
14	3,023	32	95	0.0793
16	4,459	34	131	0.0659
18	3,038	18	169	0.0408
20	1,960	14	140	0.0361
22	2,343	5	469	0.0392
24	1,550	4	388	0.0268
26	569	4	142	0.0188
28	281	1	281	0.0139
30	351	0	351[b]	0.0132
32	87	0	87[b]	0.0068
34	32	0	32[b]	0.0066
36	122	0	122[b]	0.0037
38	13	0	13[b]	0.0035
40	0	0		0.0003

[a] V_s calculated with $m = 2$. $S = 6.3$. 1000 flips at $T = 3.5$.
[b] Low estimate.

estimated by simply taking $\Gamma(E)$ to be the number of trials. These energies give 5% of the entropy. Note that the statistical error is already significant at the energy 20, where the coincidence count is very low. The value of $P(E)$ at this energy gives a rough estimate of the overall statistical error, about 5%. At lower temperatures the error is lower because of fewer levels and higher coincidence counts. The error is higher at higher temperatures. Equation (3.11) gives $S_{canon} = 6.1$. Agreement within 5% between the measured entropy and S_{canon} is also found at other temperatures tested, except for very low temperature ($T = 1.5$), at which the measured value of entropy is significantly lower than S_{canon} and depending on how the system was cooled down. This discrepancy is a result of metastability (see Section 4).

The above example shows that for $n = 1000$ an entropy of 6 can be measured within 5%. Clearly, 1000 is a rather small value for n. The usual simulation programs run much longer. Let us estimate roughly the limitation of the counting program, in general, for a given n. Suppose that the n

states of the trajectory are divided into k groups of states. States in the same group have approximately the same energy. Each group thus has $\sim n/k$ states and gives coincidence counts at that energy

$$N_c(E) \sim \frac{1}{2} \left(\frac{n}{k} \right)^2 \frac{V}{\Gamma(E)} \tag{3.12}$$

where V is a typical value of V_s. The larger N_c, the more accurate the results. Suppose that we demand $N_c \gtrsim 25$, then the maximum measurable entropy is

$$S \sim \ln \left(\frac{V}{k^2} \right) + \ln \left(\frac{n^2}{50} \right) \tag{3.13}$$

One should make the energy intervals large to increase the size of the groups in order to decrease k and increase V. However, the intervals must be smaller than T so that a randomly distributed set of states can be chosen in each group. The value of V can be increased by making m larger, namely, by allowing a larger difference in comparing states in counting coincidence. For systems with simple structures of energy levels (uniform systems) the cross sections V are large ($V \sim 10$ in the first example), but for nonuniform systems (in the second example above $V \sim 1$), they are relatively small. Suppose that V can be made large enough so that the first logarithm of (3.13) is unimportant. Then the crucial number is n, the number of states in the trajectory. For $n \sim 10^6$, (3.13) gives $S \sim 23$. Clearly, even if we make n much larger, the maximum measurable S would not be much greater simply because of the logarithmic dependence on n. If the entropy per spin is 0.5, the counting program can cover about 40 spins. It can cover more at lower temperatures and fewer at higher temperatures. Therefore, to measure the entropy of a large system, the subdivision of the system into approximately statistical independent subsystems smaller than 40 spins is crucial. The application of the counting program is therefore limited to systems for which such a subdivision is possible. This limitation is not serious for many models of interest. To extend the range of application, one needs to improve the choice of dynamic variables so that correlations are more efficiently represented (e.g., using normal coordinates in vibrational problems). This improvement seems to be the most important, although there are clearly many other aspects of the program which can be improved.

4. COMPARISON TO THE ENSEMBLE VIEW

We have presented above a definite procedure which determines the entropy given the trajectory. This is a procedure of direct measurement. We now proceed to examine to what extent this measured entropy would

coincide with the entropy defined via the traditional Gibbs ensemble and in what ways mechanical views differ conceptually from the ensemble formulation. Let us review briefly some of the features of the ensemble formulation.

4.1. The Ensemble Formulation

The traditional formulation of statistical mechanics has been in terms of the Gibbs ensemble.[6] In this formulation the calculation of thermodynamic properties of a given system requires the mental construction of an ensemble. The ensemble is an infinite number of systems identical to the system of interest. The states of these systems thus form a "cloud" in the phase space. Assuming that the cloud spreads uniformly in an allowed region Ω in phase space, the equilibrium properties are then calculated as averages taken over the ensemble. The entropy is simply given by the number of states in the allowed region by (1.1). From this ensemble formulation, equilibrium properties including entropy are conceptually regarded as properties of the ensemble of systems, not the properties of a single system. There is no longer any need to consider the actual trajectory of the system of interest. In fact, many theorists today would regard the ensemble as the conceptual, as well as the mathematical, foundation of the physics of many-particle systems.

An essential step in the ensemble formulation is the choice of the ensemble. In general, the ensemble is fixed by the assumption of the uniform distribution over the allowed region in phase space (from which the canonical and grand canonical ensembles can be derived). Although the ensemble formulation does not give a precise rule of defining the allowed region, there has been little difficulty in choosing the right one. For most cases, the allowed region can be defined by the consideration of the particle number and other conservation laws and the walls containing the system. For decades the success of the ensemble has been overwhelming. However, as more and more study is done on metastable systems, one begins to realize the ambiguity of the ensemble formulation. Now we turn to the subject of metastability.

4.2. Metastable Systems

Metastable means stable for a short time and unstable for a long time of observation. Strictly speaking, all the real systems which we regard as in

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[6] For a detailed and eloquent presentation of the ensemble viewpoint, see Ref. 2.

equilibrium are metastable. Any solid under shear or tension is metastable. The very container which helps us define an "isolated" system is metastable. Some metastable states last very long and some quite short. As long as the period of observation is short enough, metastable systems have very well-defined thermodynamic properties.

From the mechanical view, the qualitative picture of metastability is very simple. The trajectory over a limited period of time is restricted to a certain region of phase space but it would eventually go beyond this region if a much longer period of time is allowed. The very slow rate of transition out of the region may be due to high energy barriers surrounding the region or due to some other reasons.

It seems clear that time is a crucial consideration. Therefore a formulation of statistical mechanics which excludes time from its conceptual foundation is expected to have serious difficulties. The ensemble formulation does not take time into consideration. However, over the years the practitioners who apply it to physical problems always have, in fact, considered the time element. Most often the consideration required is minimal. The working rule is simple. Dynamical variables which do not change much over the observation period are considered fixed. The sum over allowed region is the sum over variables which do change during the period. A classic example is the hydrogen gas. The transition between the triplet nuclear spin state of H_2 and the singlet state is so slow (in the absence of a catalyst) that over the usual period of observation in a laboratory virtually no such transition occurs.[7] Thus the populations of the triplet states and the singlet states must be considered as fixed conserved quantities when the ensemble formulation is applied.

This simple rule may look trivial and indeed has been taken for granted. Nevertheless, it does show that at least some consideration of how the actual trajectory spends its time is necessary. When the mechanism responsible for metastability is more complicated, it is no longer easy to define the allowed region. Research on systems with quenched random impurities and glassy systems has shown that metastability can result from rather complicated energy barriers in phase space. The only concrete concept one can hold on to seems to be the trajectory.

The conclusion is then that the only secure way to obtain the correct definition of the allowed region is through the examination of the trajectory. Therefore it seems clear that although the ensemble can very often serve as a convenient formal concept it cannot be regarded as a fundamental physical concept.

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[7] Early workers got wrong results by applying the canonical ensemble without realizing the smallness of the transition rate. For a discussion, see, for example, Ref. 3.

4.3. Statistical Assumptions

In principle we could define the entropy directly in terms of the coincidence counting without ever mentioning any region in the phase space. However, at this stage of development it is intuitively more transparent to look upon the coincidence counting program as a means of measuring the size of the phase space region which the trajectory explores. In this way a comparison to the ensemble view is made very easy.

As emphasized in Section 2, a crucial assumption which allows us to translate coincidence counts into the size of the explored region is that correlation between states far apart in time shall vanish. This assumption allows us to get a sample of points along the trajectory which are randomly distributed. Effectively this means uniform distribution of probability in a region of phase space explored by a trajectory. This assumption is the same as the uniform probability assumption used in the ensemble formulation. The only new ingredient which the mechanical view adds is that the trajectory alone defines the region over which the probability is assumed to be uniformly distributed.

In Section 2, we emphasized the necessity of statistical independence among subsystems. This assumption is also necessary for the ensemble formulation to work.

These statistical assumptions, i.e., the lack of correlation between fluctuations far apart in space and/or in time are taken for granted here as properties of the trajectory (note that correlations can be measured; a correlation function is calculated by sampling the states upon the trajectory; no mentally constructed ensemble is needed). They are not just properties of the stochastic models such as the kinetic Ising model discussed previously. They are also properties observed in many-body systems in equilibrium with completely deterministic dynamics (as shown by numerical calculations).

4.4. Relaxation Times in Metastable Systems

As emphasized above, relaxation time plays a crucial role in determining the entropy in our mechanical view. For many metastable systems, there is a clear separation of long and short time scales. For example, a spin-1 to spin-0 transition time in H_2 gas is much larger than the mean time between collisions. The latter is the relevant relaxation time. As long as the observation period is long compared to the shorter time scale and still short compared to the longer time scale, the measured entropy is independent of the length of the observation period.

The more complicated cases are those with distributions of transition rates extending over a wide range. These cases appear often in glassy

materials. The phase space is divided by energy barriers of different heights. The time to climb over low barriers is short and that required over high barriers is long. Therefore the measured entropy is expected to depend on the length of the observation period. This dependence can be roughly estimated as follows. The time needed to climb over a barrier of height Λ is roughly

$$t \sim \tau_0 e^{\Lambda/T} \tag{4.1}$$

where τ_0 is a short time scale which is the relaxation time in the absence of the barrier. For t much larger than τ_0 the barriers higher than

$$\Lambda_c \sim T \ln(t/\tau_0) \tag{4.2}$$

are effectively formidable while there is ample time to climb barriers lower than Λ_c. Therefore, we expect the measured entropy to vary only logarithmically with the length of the observation period. This time dependence is insensitive especially for small T.

5. COMPARISON TO THE THERMODYNAMIC FORMULA

5.1. The Thermodynamic Formula

We now turn to the discussion of entropy as defined by thermodynamics. The entropy difference between equilibrium states 1 and 2 is given by

$$S_2 - S_1 = \int_1^2 \frac{dT}{T} \frac{\partial Q}{dT} \tag{5.1}$$

where $\partial Q/dT$ is the specific heat measured along a sequence of reversible processes connecting states 1 and 2. Latent heat terms must be added if there are first-order phase transitions in the sequence. This equation defines the entropy up to an additive constant. The additive constant can be defined by fixing the value of entropy at very high temperature in the gas phase according to the theory of dilute gas or by setting the entropy to zero at $T = 0$ (the third law of thermodynamics). Equation (5.1) is not only of experimental importance, it can also be used as the basis for determining entropy by numerical simulation. Since the specific heat is directly obtained from the time average of (energy fluctuation) squared of the model system of interest, entropy is thereby connected to the trajectories. However, this connection is very different from the coincidence counting discussed above. The entropy of a given equilibrium state cannot be measured directly from (5.1) by observing that state alone. One has to measure the specific heats of a sequence of other equilibrium states. Therefore, one needs to know the trajectories of equilibrium states other than the one of interest. This is not satisfactory from the mechanical view.

The sequence of processes connecting states 1 and 2 in (5.1) must be reversible. This means that if the temperature is varied through a complete cycle the system must return to its original equilibrium state. This condition is rather restrictive and not satisfied by many processes involving metastability, which introduces irreversibility. From the mechanical view, irreversibility means that a trajectory would end up in a different region in phase space after the temperature has been varied and returned to the original temperature. Very often macroscopic properties remain the same to a good approximation even when the trajectory ends up in a different region. For example, a glassy material can assume many molecular structures with the same macroscopic properties. These different structures correspond to different regions in phase space. Each region is surrounded by energy barriers. Within a reasonable observation time the trajectory is restricted in one of these regions.

In spite of the difficulty of irreversibility one can of course still define the entropy by (5.1) with a definite choice of additive constant. In fact, this is the definition used for experimental determination and in many cases by numerical simulations.

5.2. The Third Law of Thermodynamics

This law says that the entropy should vanish in the limit of zero temperature. If we fix the additive constant in (5.1) using the theoretical high-temperature entropy, then with the experimentally measured specific heat, (5.1) would in many cases give a nonzero entropy for T approaching 0, i.e., a violation of the third law (an extensive review can be found in a book by Wilks[4]). This nonzero entropy is often referred to as the "frozen entropy" which reflects the irreversibility due to metastable states as mentioned above.

The qualitative interpretation of this frozen entropy is that it accounts for the regions which could be visited by the trajectory but actually not visited owing to the lack of time.

The entropy as defined by the coincidence counting program automatically satisfies the third law. This is because it measures the region of phase space which the trajectory actually explores. It measures the amount of motion. As T approaches zero, all transition rates go to zero. This cessation of motion is, of course, the essence of the third law. Exception occurs if the system has highly degenerate ground states and no energy barriers separate them. In this case, transitions among these states can still occur at an appreciable rate for T approaching zero.

At very high temperatures the entropy defined by coincidence counting agrees with (5.1). Therefore, there is a range of temperatures over which

there is disagreement whenever (5.1) violates the third law. The discrepancy can be defined as the frozen entropy at nonzero temperatures:

$$S_{\text{frozen}} = S_{\text{spec heat}} - S_{\text{coinc}} \tag{5.2}$$

This quantity is a measure of "glassiness." It is also clear that if (5.2) is nonzero there will be some range of temperature over which

$$T \, dS_{\text{coinc}} > dQ \tag{5.3}$$

when the heat dQ is added, since by definition

$$T \, dS_{\text{spec heat}} = dQ \tag{5.4}$$

Equation (5.3) is a clear indication of irreversibility and so is a nonzero S_{frozen}.

6. FURTHER DISCUSSION

6.1. Entropy in Terms of Probabilities for All States

Another well-known formula for the entropy is

$$S = - \sum_s p_s \ln p_s \tag{6.1}$$

where p_s is the probability of finding the state s. At first sight, this formula may seem to be a way to calculate entropy from the trajectory since p_s can be defined as the fraction of time spent in the state s. [After all, (1.1) and (2.13) can be regarded as special cases of (6.1).] However, (6.1) is useful only if the number of states is small enough so that the time spent in each state is sufficiently long to define p_s. This formula is useful in the theory of information and communication where the number of the symbols (corresponding to states) is small and messages (corresponding to the trajectories) are long. Each symbol appears many times in a message and p_s can be evaluated. In statistical mechanics, the number of states is large and the trajectories short. The trajectory does not have time to visit all the states. For as few as 12 spins, there are already about 4000 states. However, for systems which are very small, (6.1) is useful.[5]

6.2. Nonequilibrium States

The coincidence counting program, which is just an algorithm, can be applied to the trajectory of a nonequilibrium system, e.g., a system with a heat current and a temperature gradient. Such applications should provide new probes in studying nonequilibrium systems. However, there are features of nonequilibrium which are very different from those found in

equilibrium. The interpretation of the measured entropy would therefore be more complicated. An important feature is the strong low-frequency noise, the so-called $1/f$ noise, which is believed to be a consequence of a steady current. Such noise implies long-time correlations of fluctuations. The entropy obtained from the coincidence counting would therefore depend on the length of the period of observation. The precise form of this dependence and its implications are yet to be worked out.

6.3. Remarks on the Relevant Size

As we have emphasized in Section 2, the properties of a many-body system are well manifested by the behaviors of relatively small subsystems over a relatively short period of time. The extrapolation to larger systems and longer time can be done easily by combining the subsystems, which are approximately statistically independent. From this viewpoint, the traditional approach of studying the phase space of the entire many-body system might not be the most illuminating. It would be hard to sort out the correlation effects from those effects which are merely results of statistical independence. It would be more efficient and illuminating to study the phase spaces of the subsystems.

Of course, statistical properties should be understood within the framework of mechanics. Recently, there has been much interest and progress in the study of nonlinear dynamics. Systems with several degrees of freedom have been studied. One has begun to see chaotic behavior generated by deterministic equations of motion and recursion formulas. Statistical properties of such systems are being measured.[5] The main purpose of these studies has been dynamics and not statistical mechanics. From the viewpoint of many-body physics, the systems studied have been too small. We expect that the study of systems of the size of the order of 15 spins (a phase space of an order of a few thousand states) is needed to gain insight on the interplay of correlations and statistical independence from a mechanical viewpoint. The crucial question is how nonlinear dynamics depend on the number of degrees of freedom in the range from 2 or 3 to 10 or 20.

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REFERENCES

1. J. Ford, Transition from analytic dynamics to statistical mechanics, *Adv. Chem. Phys.* **24**:155 (1973).
2 R. C. Tolman, *Principles of Statistical Mechanics* (Cambridge University Press, Cambridge, England, 1962).
3. G. H. Wannier, *Statistical Physics* (Wiley, New York, 1966), p. 218.
4. J. Wilks, *The Third Law of Thermodynamics* (Oxford University Press, New York, 1961).
5. A. N. Kaufman, H. D. I. Abarbanel, and C. Grebogi, in Proceedings of the International Conference on Plasma Physics, Nagaya, Japan, April 1981.