# Chapter 6

# Boltzmann's Ergodic Hypothesis.

## 6.1 The Foundations of Equilibrium Statistical Mechanics

We now begin to try to solve what might well be called the Fundamental Problem of Statistical Mechanics: Mechanical systems - isolated ones, at least - are time reversible and recurrent. However, our observations are that large isolated systems often reach a state of thermodynamic equilibrium. How do we explain our observations in such a way that there are no contradictions with the laws of mechanics? Boltzmann proposed a resolution along the following lines :

a ) Equilibrium statistical mechanics can be formulated in terms of microcanonical ensemble averages, by using the invariant measure $d\mu = \mu(dS) = \frac{dS}{|\nabla H|}$. The ensemble average of a phase-function $F(\Gamma)$, is

$$\langle F(\Gamma)\rangle_{m.c.} = \frac{\int_{H=E} d\mu F(\Gamma)}{\int_{H=E} d\mu}. \tag{6.1}$$

The density of states is

$$\Omega(E) = \int_{H=E} d\mu. \tag{6.2}$$

and the thermodynamic entropy, S, is given by $S = k_B \ln \Omega(E)$.

As an aside, one can formulate the microcanonical ensemble in terms of a phase-space density $\rho(\Gamma) = \delta(H - E)$. Then

$$\langle F(\Gamma)\rangle_{m.c.} = \frac{\int d\Gamma F(\Gamma)\delta(H-E)}{\int d\Gamma \delta(H-E)} \tag{6.3}$$

If in the laboratory one were to make very precise measurements of some quantity, $F\ (\Gamma_t)$, where $\Gamma_t$ is the location of the phase point of the system at time $t$, e.g. the force per unit area at time $t$ on a piston, the values would show wild fluctuations about a more slowly varying "mean" quantity as molecules collide with the piston. However, we might identify the thermodynamic value of some property for one system with the time-average $\overline{F}(\Gamma)$defined by

$$\overline{F}(\Gamma) = \lim_{T\to\infty} \frac{1}{T} \int_0^T F(\Gamma_t)dt \tag{6.4}$$

Boltzmann realized that one could identify the microcanonical ensemble average Eq. 6.1 with the *infinite* time average Eq. 6.4, i.e.

$$\overline{F}(\Gamma) = \langle F(\Gamma)\rangle_{m.c.} \tag{6.5}$$

if he made the hypothesis that the trajectory of a typical point on the constant-energy surface (i.e. except for a set of points of zero measure ) spends equal time in regions of equal measure. This hypothesis was called the *ergodic hypothesis* by Boltzmann and it is of central interest for the foundations of statistical mechanics.

To see how this hypothesis works, subdivide the constant energy surface into a fine grid. The average of $F(\Gamma)$ in each grid region $i$ is $F_i$(see Fig. 6.1 ) Then

$$\frac{1}{T} \int_0^T F(\Gamma_t)dt \approx \sum_i \frac{\tau_i}{T} F_i$$

where $\frac{\tau_i}{T}$ is the fraction of the time that the trajectories spend in region $i$ between $t = 0$ and $T$. Using the ergodic hypothesis, one can write

$$\frac{\tau_i}{T} = \frac{\mu_i}{\mu(E)}$$

so that

$$\overline{F}(\Gamma) = \sum_i \frac{\mu_i}{\mu(E)} F_i = \langle F(\Gamma)\rangle_{m.c.}$$

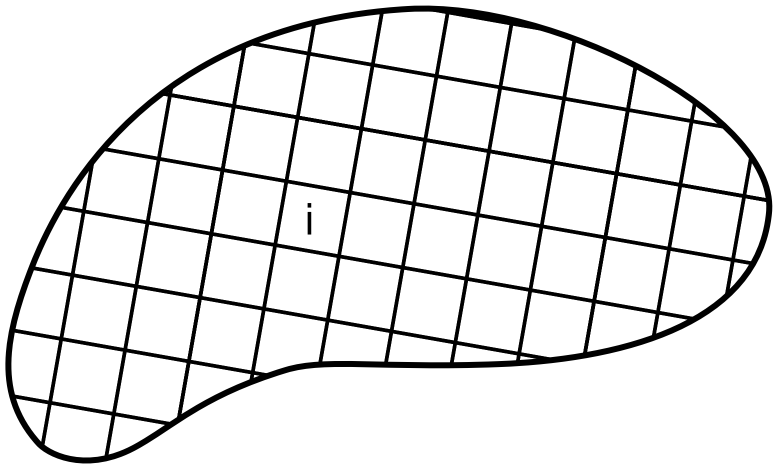


Figure 6.1: The Division of the Constant Energy Surface into Small Regions.

Thus, equilibrium statistical mechanics could be justified, for isolated systems, if one could prove that the ergodic hypothesis is correct for a large class of physical systems.

One should not ignore the fact that no system of physical interest is really isolated from the rest of the universe. Thus it may be that the ergodic approach to developing the foundations for statistical mechanics is irrelevant, and the approach is governed, or at least produced by, the random perturbations on the systems caused by its environment. Our approach here is to try to determine just how much the "outside perturbations" are really needed. If in fact one could prove the truth of the ergodic hypothesis for systems of physical interest, then the mechanical properties of the system alone could be held responsible for the existence of thermodynamic equilibrium state. Then one would not need a *deus ex machina* and the results of external perturbations would not be crucial for our understanding of the success of statistical thermodynamics. If, on the other hand, one could not prove an ergodic theorem for any interesting system, or prove that there is no ergodic behavior, then the external perturbations would be absolutely necessary and we would look to them for a serious justification of our methods.

Having now stated mathematically what one needs to prove as an ergodic theorem, we now turn to seeing what one can do in this direction.

## 6.2 The Individual Ergodic Theorem

[ References: M.Toda, R. Kubo, N. Saito, *Statistical Physics* I, 2nd.ed. Springer Verlag, Berlin, (1992), chapter 5; A. Katok and B. Hasselblatt, *Introduction to the Modern Theory of Dynamical Systems,* Cambridge University Press, Cambridge, (1995)]

In 1931 Birkhoff proved a very important theorem which allows us to make some of the ideas of Boltzmann more precise. Although Birkhoff's theorem is still a long way from what is needed in Boltzmann's picture it does define in a useful way the dynamical properties that a system must possess in order to have an equilibrium state in the sense of statistical mechanics.

This theorem is concerned with the properties of individual trajectories in $\Gamma$-space. Suppose we are considering a mechanical system with an invariant measure and suppose that we consider some dynamical function $F(\Gamma)$ defined on the constant energy surface and satisfying the condition

$$\int d\mu |F(\Gamma)| < \infty$$

Birkhoff's theorem then states that

> The long-time average $\overline{F}(\Gamma) = \lim_{T\to\infty} \frac{1}{T}\int_0^T dtF(\Gamma_t)$ exists almost everywhere on the constant energy surface, that is, for almost every starting point $\Gamma$.

$\overline{F}(\Gamma)$ may depend on the trajectory, but not on the initial point of the trajectory. This can be easily seen because the time average of a function starting at phase space point $\Gamma_{t_0}$ can be written as

$$\begin{aligned}
\overline{F}(\Gamma_{t_0}) &= \frac{1}{T}\int_0^T dtF(\Gamma_{t_0+t}) = \frac{1}{T}\int_{t_0}^{T+t_0} dtF(\Gamma_t) \\
&= \frac{1}{T}\left[\int_{t_0}^{0} F(\Gamma_t)dt + \int_0^T F(\Gamma_t)dt + \int_T^{T+t_0} F(\Gamma_t)dt\right]
\end{aligned}$$

In the limit that $T\to\infty$ the first and the third term tend to zero, the second to $\overline{F}(\Gamma)$. So the long-time average is constant on a trajectory $\overline{F}(\Gamma) = \overline{F}(\Gamma_{t_0})$, and

> One can interchange the average over the invariant measure, that is, the microcanonical average of $F(\Gamma)$, with the time average, $\int d\mu F(\Gamma) = \int d\mu \overline{F}(\Gamma)$.

Finally,

> The constant energy surface can be replaced by any "invariant" set of finite measure, and the microcanonical average is replaced by an average over the invariant set, using the measure $\mu$.

By an invariant set we mean a region in phase space such that all points in the set remain in the set during the course of their time evolution, and the measure of this set of points does not change with time. This final point will be important for us when we consider some simple cases, such as the baker's transformation, where it is possible to discuss ergodic behaviour in some detail.

Birkhoff's theorem is not sufficient to show that systems of physical interest are ergodic, in the sense of Boltzmann, because the time average still depends on the trajectory and is not necessarily equal to the ensemble average. However, this gives us the opportunity to *define* a system that satisfies Boltzmann's ergodic hypothesis. We say that a system is *ergodic* if the long-time-average of a function, $\overline{F}(\Gamma)$ is a constant on the constant energy surface, which we denote by $\tilde{F}$.

An ergodic system is such that the time average of a dynamical quantity is equal to its microcanonical average, for one easily sees that $\int d\mu F(\Gamma) = \int d\mu \overline{F}(\Gamma) = \tilde{F} \int d\mu$ . So

$$\tilde{F} = \frac{\int d\mu F(\Gamma)}{\int d\mu} = \langle F(\Gamma) \rangle_{m.c.}$$

Moreover, Boltzmann's hypothesis that the time spent in a region of the constant energy surface is proportional to its microcanonical measure is indeed true for an ergodic system. To prove this, refer to the grid-picture of the last section (see Fig. 6.1), and take for $F(\Gamma)$ the characteristic function of a grid region $i$, $\chi_i(\Gamma)$, where

$$\chi_i(\Gamma) = \begin{cases} 1 & \text{if } \Gamma \in \text{ region } i \\ 0 & \text{if } \Gamma \notin \text{ region } i. \end{cases} \tag{6.6}$$

Then $\bar{\chi}(\Gamma) = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt \chi_i(\Gamma_t) = \lim_{T\to\infty} \frac{\tau_i}{T}$, which is the fraction of time that the system spends in region $i$, and also $\bar{\chi}(\Gamma) = \langle \chi(\Gamma) \rangle_{m.c.} = \frac{\int d\mu \chi_i(\Gamma)}{\int d\mu} = \frac{\mu_i}{\mu(E)}$.

AS an example of an ergodic system consider a circle with circumference 1. The time is a discrete variable. In a time-step the points $x \in [0,1]$ on the circle are rotated :

$$\phi : x \to \phi(x) = x + \alpha \quad mod\, 1 \quad \phi^2 : x \to x + 2\alpha \quad mod\, 1$$

and so on. If $\alpha$ is a rational number, $n/m$, where $n$ and $m$ are integers, then after a finite number of steps, $m$ , $\phi^m$ maps all points to their initial positions. A trajectory starting at some initial point will be periodic and will not spend equal time in regions of equal (Lebesgue) measure, and hence the trajectory is not in any way dense on the circle. In this case the system is not ergodic. But if $\alpha$ is irrational no trajectory is periodic and the system is ergodic! To see this consider the time-average of an integrable function on a trajectory starting at $x$ :

$$\overline{F}(x) = \lim_{N\to\infty} \frac{1}{N} \sum_{g=0}^{N-1} F(\phi^g(x)) = \lim_{N\to\infty} \frac{1}{N} \sum_{g=0}^{N-1} F(x + g\alpha)$$

Consider the Fourier-series for $F(x)$ : $F(x) = \sum_{n=0}^{\infty} a_n e^{2\pi i n x}$:

$$F(x + g\alpha) = \sum_{n=0}^{\infty} a_n e^{2\pi i n x + 2\pi i n \alpha g}$$

Substitution in the expression for the time-average gives

$$\begin{aligned} \overline{F}(x) &= \lim_{N\to\infty} \frac{1}{N} \sum_{g=0}^{N-1} \sum_{n=0}^{\infty} a_n e^{2\pi i n x + 2\pi i n \alpha g} \\ &= a_0 + \lim_{N\to\infty} \frac{1}{N} \sum_{n=1}^{\infty} a_n e^{2\pi i n x} \frac{1 - e^{2\pi i \alpha N n}}{1 - e^{2\pi i \alpha n}} \end{aligned} \tag{6.7}$$

The terms with $n \geq 1$ don't survive the limit $N \to \infty$. Thus $\overline{F}(x) = a_0$ for $\alpha$ irrational . In this case the time-average is a constant - independent of the starting point $x$-and the system is ergodic; where the ensemble average is the average over the circle with the usual Lebesgue measure,

$$\overline{F}(x) = \int_0^1 dx F(x) = \langle F(x) \rangle_{\mathrm{m.c.}}.$$

Sequences of numbers may also have ergodic properties (see exercise 3.1 )

We now can fill in some details of Boltzmann's picture: If we can prove that a system is *ergodic* then we know that it's time average properties are equal to the appropriate microcanonical ensemble average properties, and equilibrium statistical mechanics can be used to determine the time average properties of the system. Boltzmann then argued, as we know from all of our statistical mechanics courses, that if: (a) the system spends equal times in regions of equal measures, and (b) the region of the energy surface that corresponds to a macroscopic equilibrium state ( i.e. with Maxwell-Boltzmann velocity distributions, and equilibrium many particle distribution functions) has overwhelmingly the largest measure, then all of the usual results of equilibrium thermodynamics follow from a mechanical argument. The Poincaré recurrence issue is not a problem since it is of no consequence if a phase point returns to its initial region every once in a while, and the reversibility of the dynamics is no problem either, since in this picture both the forward and time reversed motion will eventually have the same - equilibrium - values for time averages. (We didn't prove this yet, but it is an easy consequence of ergodicity and we will prove it when we look more carefully at how one proves that interesting systems are ergodic.)

What remains to be done then is to show that systems of physical interest are in fact ergodic. Before we turn to this problem, it is appropriate to consider a somewhat deeper idea - mixing- and also to discuss an equivalent way of characterizing ergodic systems as being metrically indecomposable.