# Chapter 7

# Gibbs' Picture-Mixing Systems

## 7.1 The Definition of a Mixing System

[Reference: V.I. Arnol'd and A. Avez, *Ergodic Problems of Classical Mechanics,* Benjamin Publ. Co. New York, (1968).]

While Boltzmann fixed his attention on the motion of the phase point for a single system and was led to the concept of ergodicity, Gibbs took another approach to the same problem. Since one never knows precisely what the initial phase point of a system is, Gibbs decided to consider the average behavior of a set of points on the constant energy surface with more or less the same macroscopic initial state. Without worrying too much about how such a set might be defined precisely, let's consider an initial set of points $A$. As the set travels through $\Gamma$-space it changes shape, but its measure stays the same; $\mu(A) = \mu(A_t)$ . The set gets stretched and folded and may eventually appear on a coarse enough scale to fill the energy surface uniformly. However the set $A_t$ has the same topological structure as the set $A$ and the initial set is not 'forgotten', in the sense that a time reversal operation on the set $A_t$ will produce the set $A$. There is a nice lecture demonstration apparatus that illustrates this time reversal operation: a drop of immiscible ink is added to a container of glycerine. If you stir the glycerine slowly, the drop will stretch and form a thin line. Eventually it seems to fill the whole space, but if the stirring is reversed, the initial configuration of the drop of ink surprisingly reappears.

Gibbs thought that the apparently uniform distribution of the set $A_t$ on the energy surface was the key to understanding how mechanically reversible systems could approach an equilibrium state. To make this idea more precise, Gibbs called a system *mixing* if the following identity holds for each set $B$ of non-zero measure

$$\lim_{t\to\infty} \frac{\mu(B \cap A_t)}{\mu(B)} = \frac{\mu(A)}{\mu(E)} \tag{7.1}$$

As we will see presently the requirement that a system be mixing is a stronger condition than ergodicity. However, more can be said about the approach to equilibrium for a mixing system than for an ergodic one.

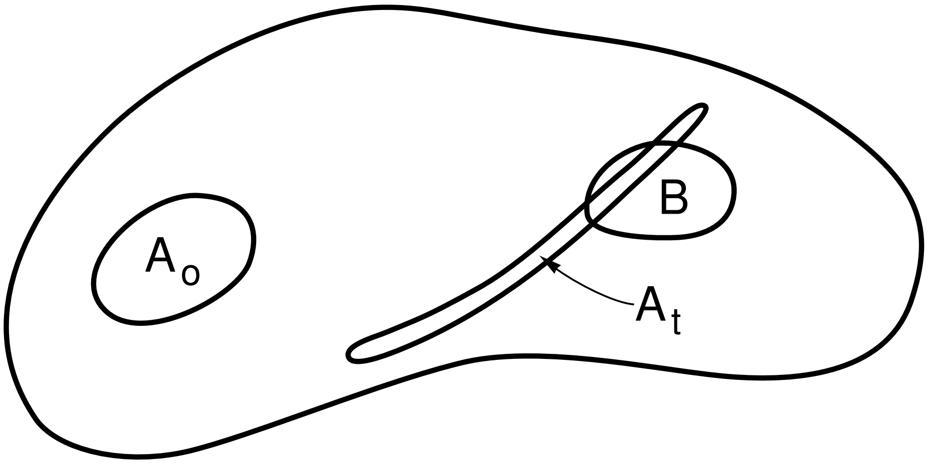


Figure 7.1: The Time Development of Phase Space Regions and the Mixing Property.

To discuss the difference between ergodic and mixing systems we need the notion of *metric indecomposability.*

A *metrically decomposable* system is one for which there exists a subdivision of the constant-energy surface (or in general, Γ-space) into two regions of non-zero measure, each of which is invariant under the mechanical flow in Γ-space . That is, a phase point starting out in one region will always stay in that region. A system is ergodic if and only if it is metrically *in*decomposable:

1 ) decomposable $\rightarrow$ non-ergodic : On a surface that can be subdivided into two invariant regions 1 and 2, let $F(\Gamma)$ be the characteristic function of region 1 ,

$$F(\Gamma) = \chi_1(\Gamma)$$

Due to the invariance, the time-average of $F$ is

$$\overline{F}(\Gamma) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \chi_1(\Gamma_t) dt = \chi_1(\Gamma)$$

$$= \begin{cases} 0 \text{ if } \Gamma \in 2 \\ 1 \text{ if } \Gamma \in 1 \end{cases}$$

Since this is not constant over $\Gamma$-space the system is not ergodic.

The converse argument is as follows :

2 ) non-ergodic $\rightarrow$ decomposable : For a non-ergodic system $\overline{F}(\Gamma)$ is not constant, but depends on the trajectory. For *some* $\gamma$ the sets of points $\{\Gamma | \overline{F}(\Gamma) \geq \gamma\}$ and $\{\Gamma | \overline{F}(\Gamma) < \gamma\}$ both contain complete trajectories, because $\bar{F}(\Gamma)$ is constant on a trajectory. Therefore, the sets are invariant and form a decomposition into two sets, each of positive measure. If this were not true for some $\gamma$ then our assumption that $\bar{F}$ is not constant would be violated.

Now it will be shown that mixing implies ergodicity. Consider a mixing system and an invariant set $A = A_t$. Then for all $B$ Eq. 7.1 gives

$$\lim_{t \to \infty} \frac{\mu(A_t \cap B)}{\mu(B)} = \frac{\mu(A)}{\mu(E)}$$

or, equivalently,

$$\lim_{t \to \infty} \mu(A_t \cap B) = \frac{\mu(A)\mu(B)}{\mu(E)}.$$

If we set $B = A = A_t$ (since $A$ is an invariant set) then $A_t \cap B = A$ and

$$\mu(A) = \frac{\mu(A)\mu(A)}{\mu(E)}$$

This equation has two solutions :

1) $\mu(A) = 0$ then one trivial invariant set is a set of zero measure, and the other solution is

2) $\mu(A) = \mu(E)$; the invariant set is effectively the whole energy-surface.

Therefore, if a system is mixing the only invariant set with positive measure is the constant energy surface, with the possible exception of special set of measure zero. Such sets might be a countable set of periodic orbits. Consequently, a mixing system is ergodic, but the converse is not true as can be seen from a simple counter example. Consider the rotations on the circle discussed in the previous chapter. When an initial point is moved an irrational distance around the circle the transformation is ergodic, and the point is the course of its trajectory, spends an equal amount of time in all regions of the circle with the same measure. However to determine if this system is mixing, we need to look at the time evolution of a set of points. Suppose we take a small connected interval on the circle as our initial set $A$. Then the set $A_t$ will remain a small connected set of points rotating rigidly around the circle. As a result of this it is easy to see that the limit as $t \to \infty$ of the measure of the set $A_t \cap B$ does not exist for any arbitrary set $B$ of positive measure on the circle. Hence the irrational rotations on the circle are ergodic but not mixing.

## 7.2 Distribution Functions for Mixing Systems

Consider an isolated system that initially is in a non-equilibrium state. For example it may have a temperature- or pressure-gradient. We wish to calculate the ensemble-average at time $t$ of a dynamical quantity $F(\Gamma)$,

$$\langle F(\Gamma) \rangle_t = \frac{\int d\mu \rho(\Gamma, t) F(\Gamma)}{\int d\mu \rho(\Gamma, t)} \tag{7.2}$$

where $\rho\,(\Gamma, t)$ is the time dependent phase space distribution function for the system. It satisfies Liouville's equation,

$$\frac{d}{dt}\rho(\Gamma, t) = 0.$$

Suppose the system is mixing. Again, think of the constant-energy surface as a patchwork, where for each patch, $i$, there's a characteristic function, $\chi_i$. Then $F(\Gamma)$ can approximately be described by typical values of $F$ on each patch, $F_i$:

$$F(\Gamma) \approx \sum_j F_j \chi_j$$

We can express $\rho(\Gamma, 0)$ in this way also as :

$$\rho(\Gamma, 0) = \sum_j \rho_j \chi_j$$

Now, from Liouville's equation, Eq. 4.3, it follows that $\rho(\Gamma, t) = \rho(\Gamma_{-t}, 0)$ where $\Gamma_{-t}$ is the phase point that evolves to $\Gamma$ after a time interval $t$. So

$$\rho(\Gamma, t) = \sum_j \rho_j \chi_j(\Gamma_{-t})$$

When this expression is substituted into Eq. 7.2, we find:

$$\langle F(\Gamma) \rangle_t = \frac{\sum_j \sum_k F_j \rho_k \int d\mu \chi_j(\Gamma) \chi_k(\Gamma_{-t})}{\sum_k \rho_k \int d\mu \chi_k(\Gamma_{-t})} \tag{7.3}$$

The integrand in the numerator is 1 if $\Gamma$ is in the $j$-th patch and $\Gamma_{-t}$ is in the $k$-th patch, otherwise it is zero. The second condition means that $\Gamma \in k_t$, the $k$-th patch after a time $t$. The integral becomes

$$\int d\mu \chi_j(\Gamma) \chi_k(\Gamma_{-t}) = \mu(j \cap k_t)$$

Because the system is mixing

$$\mu(j \cap k_t) \to \frac{\mu(j)\mu(k)}{\mu(E)}$$

as $t \to \infty$. The denominator doesn't actually depend on the time and can also be approximated,

$$\lim_{t \to \infty} \langle F(\Gamma) \rangle_t = \frac{\sum_j \sum_k F_j \rho_k (\frac{\mu(j)\mu(k)}{\mu(E)})}{\sum_k \rho_k \mu(k)} = \frac{1}{\mu(E)} \sum_j F_j \mu(j) = \langle F(\Gamma) \rangle_{\text{m.c.}}$$

This shows that the time dependent ensemble average of any well behaved dynamical quantity for a mixing system approaches an equilibrium value as $t \to \infty$. This is equivalent to the statement that for a mixing system, the time dependent phase space distribution function approaches its equilibrium value as $t \to \infty$. Here we have a nice illustration of the value for physics of what mathematicians call a *weak limit*. That is, suppose that the initial distribution function is concentrated on some set $A$ and zero elsewhere. Then in the course of time the distribution function is non-zero on some very long extended set determined by the time evolution of $A$ and zero elsewhere. This long "stringy" set has the same measure as $A$ itself, of course. What we have just shown, though, is that averages computed with the distribution function on this "stringy" set are, after a long enough time, equal to averages computed with a smooth equilibrium distribution function. In this *weak* sense we can say that the distribution function approaches its equilibrium value. This phenomenon is at the core of what are called SRB measures (Sinai-Ruelle-Bowen) which we will discuss in later chapters.

## 7.3 Chaos

[Reference: See the papers published in *Dynamical Systems II,* Ya. G. Sinai, ed. Springer-Verlag, Berlin, (1989).]

We have now reached a point in our discussions where we can begin to understand some of the central ideas of this approach to non-equilibrium statistical mechanics based on dynamical systems theory. We have argued that in order for the dynamical functions of an isolated system to approach well defined equilibrium values and for the system itself to be described by a distribution function that approaches an equilibrium distribution, the system should be mixing. This condition on the dynamical properties has some astounding consequences which have been described, collectively, as *chaotic* behavior. To be more precise, consider some set of points on the constant energy surface with arbitrarily small, but still positive measure. If the system is mixing then no matter how small the measure of the set of points, the set will be spread out uniformly on the energy surface as the system develops in time. This means that any two points in this set will typically head to very different regions of phase space no matter how close the two points may have been initially. The trajectories of the points must then be very sensitive functions of the initial coordinates and momenta of the particles of the system. This sensitive dependence of trajectories on initial conditions is the characteristic feature of chaotic systems.

A simple example of this separation of nearby trajectories is illustrated in Fig. 7.2. Here we illustrate the classical Lorentz gas. A collection of fixed scatterers is placed at random in space - here we use hard disks on a plane - and a point particle moves with constant velocity along straight line paths until it collides with a scatterer whereupon it makes a specular, energy conserving collision. This is a well known model for studying the diffusion of electrons in amorphous materials. We show two trajectories that start at the same point in space, but with slightly different directions of the velocity vector. Note that the two trajectories separate at each collision with a scatterer in exactly the same way that a beam of light is dispersed by a convex mirror. After a number of collisions the two trajectories are sufficiently far apart that one trajectory includes a collision with a scatterer that is just missed by the other one. After that, the two trajectories are completely different, each exploring a different region of space. Something like this takes place in the much higher dimensional phase space for systems where all of the particles are moving, and this picture is at the heart of the ergodic theory of billiard systems developed by Sinai and others.

Moreover, one can argue that most of the constants of the motion for a mixing system must be very singular functions of the initial coordinates and momenta, as well. One knows from elementary mechanical considerations that a system of $N$ particles in three dimensions has $6N$ constants of the motion. One of these constants is the total energy of the system, another constant fixes the initial point on the trajectory. Except for perhaps a few

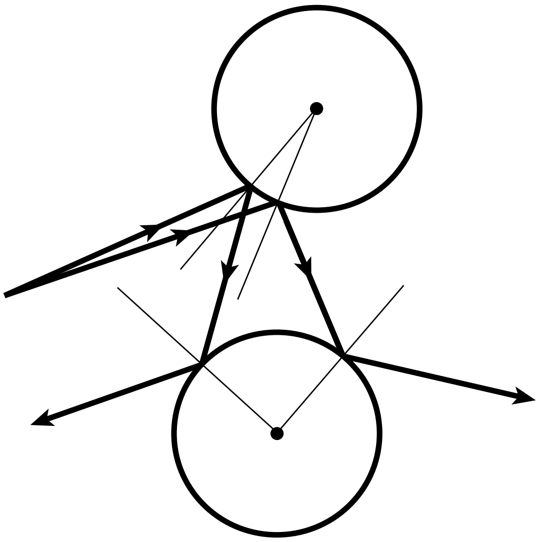

Figure 7.2: Separation of Trajectories in a Lorentz Gas.

other constants of the motion, such as the total momentum, we cannot fix the other constants of the motion when we prepare a system in the laboratory. Now if the system is ergodic its trajectory must pass arbitrarily close to almost every point on the constant energy surface. All of these other points may have very different values for these "uncontrolled" constants of the motion, so the values of these other constants of the motion must be such singular functions of the phase points that in any close neighborhood of almost every point the "uncontrolled" constants take on all possible values! In the theory of functions of complex variables one defines an "essential singularity" of a function as a point where the function takes on all values (for example, the point $z = 0$ for the function $f(z) = \exp(-1/z)$). We might say that the "uncontrolled" constants of the motion have essential singularities at almost every point on the constant energy surface.

Consequently, we are able to justify the methods of non-equilibrium statistical mechanics for systems that show sensitive dependence on initial conditions, and very complex behavior of the phase space trajectories, such that we can prove them to be mixing systems.

As the first example of the application of the idea that phase space trajectories may depend very sensitively upon the parameters used to specify the state of the system, we turn to one of the most interesting controversies in non-equilibrium statistical mechanics: van Kampen's objections to linear response theory.