Appendix C
Ergodicity

Ergodic theory asks questions which lie at the very foundations of statistical mechanics [53, 54, 163]. The phase space of conservative Newtonian systems is of a very special type because there are no diffusion processes present. For systems with ergodic flow, we can obtain a unique stationary probability density (a constant on the energy surface) which characterizes systems with a fixed energy at equilibrium. However, a system with ergodic flow cannot necessarily reach this equilibrium state if it does not start out there. For decay to equilibrium, we must have at least the additional property of mixing. Mixing systems are ergodic (the converse is not always true, however) and can exhibit random behavior even though Newton's laws are fully deterministic.

Let us now define ergodic flow. Consider a Hamiltonian system with $3N$ degrees of freedom with Hamiltonian $H(\boldsymbol{p}^N, \boldsymbol{r}^N) = E$. If we relabel the momentum coordinates so $p_1 = p_{x,1}, p_2 = p_{y,1}, p_3 = p_{z,1}, p_4 = p_{x,2}, \dots, p_{3N} = p_{z,N}$ (with similar relabeling for the position coordinates), then Hamilton's equations can be written

$$\frac{\mathrm{d}q_1}{(\partial H/\partial p_1)} = \cdots = \frac{\mathrm{d}q_{3N}}{(\partial H/\partial p_{3N})} = \cdots = -\frac{\mathrm{d}p_1}{(\partial H/\partial x_1)} = \cdots = -\frac{\mathrm{d}x_{3N}}{(\partial H/\partial q_{3N})} = \mathrm{d}t\,. \tag{C.1}$$

Equation (C.1) provides $6N-1$ equations relating phase space coordinates which, when solved, give us $6N-1$ constants, or integrals, of the motion,

$$f_i(p_1, \dots, p_{3N}, x_1, \dots, x_{3N}) = C_i\,, \tag{C.2}$$

where $i = 1, 2, \dots, 6N-1$ and C_i is a constant. However, these integrals of the motion can be divided into two kinds: isolating and nonisolating. Isolating integrals define a whole surface in the phase space and are important in ergodic theory, while nonisolating integrals do not define a surface and are unimportant [53]. One of the main problems of ergodic theory is to determine how many isolating integrals a given system has. An example of an isolating integral is the total energy, $H(\boldsymbol{p}^N, \boldsymbol{r}^N) = E$. For N hard-sphere particles in a box, it is the only isolating integral.

Let us consider a system for which the only isolating integral of the motion is the total energy and assume that the system has total energy, E. Then trajectories in Γ

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face in phase space which exists because of the isolating integral of the motion, $H(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N}) = E$. The flow of state points on the energy surface is defined to be *ergodic* if almost all points, $\boldsymbol{X}(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N})$, on the surface move in such a way that they pass through every small finite neighborhood, R_E, on the energy surface. In other words, each point samples small neighborhoods over the entire surface during the course of its motion (a given point, $\boldsymbol{X}(p_1, \ldots, p_{3N}, x_1, \ldots, x_{3N})$ cannot pass through every point on the surface, because a line which cannot intersect itself cannot fill a surface of two or more dimensions). Note that not all points need sample the surface, only "almost all." We can exclude a set of measure zero from this requirement.

A criterion for determining if a system is ergodic was established by Birkhoff and is called the *ergodic theorem*. Let us consider an integrable phase function $f(\boldsymbol{X}^N)$ of the state point $\boldsymbol{X}^N$. We may define a phase average of the function $f(\boldsymbol{X}^N)$ on the energy surface by the equation

$$\langle f \rangle_S = \frac{1}{\Sigma(E)} \int_{S_E} f(\boldsymbol{X}^N)\, \mathrm{d}S_E = \frac{1}{\Sigma(E)} \int_{\Gamma} \delta(H^N(\boldsymbol{X}^N) - E) f(\boldsymbol{X}^N)\, \mathrm{d}\boldsymbol{X}^N \,, \quad \text{(C.3)}$$

where $\mathrm{d}S_E$ is an area element of the energy surface which is invariant (does not change size) during the evolution of the system and $\Sigma(E)$ is the area of the energy surface and is defined as

$$\Sigma(E) = \int_{S_E} \mathrm{d}S_E = \int_{\Gamma} \delta(H^N(\boldsymbol{X}^N) - E)\, \mathrm{d}\boldsymbol{X}^N \,. \quad \text{(C.4)}$$

We may define a time average of the function $f(\boldsymbol{X}^N)$ by the equation

$$\langle f \rangle_T = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} f(\boldsymbol{X}^N(t))\, \mathrm{d}t \quad \text{(C.5)}$$

for all trajectories for which the time average exists. Birkhoff showed that the time average in Eq. (C.5) exists for all integrable phase functions of physical interest (i. e., for smooth functions).

In terms of averages, the *ergodic theorem* may be stated as follows: *A system is ergodic if for all phase functions, $f(\boldsymbol{X}^N)$: (i) the time average, $\langle f \rangle_T$, exists for almost all $\boldsymbol{X}^N$ (all but a set of measure zero), and (ii) when it exists it is equal to the phase average, $\langle f \rangle_T = \langle f \rangle_S$.*

To determine the form of the invariant area element, $\mathrm{d}S_E$, we write an expression for the volume of phase space, $\Omega(E)$, with energy less than E – that is, the region of phase space for which $0 < H^N(X^N) < E$. We then assume that the phase space can be divided into layers, each with different energy, and that the layers can be arranged in the order of increasing energy. (This is possible for all systems

$$\Omega(E) = \int_{0<H^N(X^N)<E} \mathrm{d}\boldsymbol{X}^N = \int_{0<H^N(X^N)<E} \mathrm{d}A_H \, \mathrm{d}n_H \,, \tag{C.6}$$

where $\mathrm{d}A_H$ is an area element on a surface of constant energy and $\mathrm{d}n_H$ is normal to that surface. Since $\nabla_x H^N$ is a vector perpendicular to the surface $H^N(X^N) =$ constant, we can write $\mathrm{d}H^N = |\nabla_x H^N| \, \mathrm{d}n_H$ and the volume becomes

$$\Omega(E) = \int_0^E \mathrm{d}H^N \int_{S_H} \frac{\mathrm{d}A_H}{|\nabla_x H^N|} \,. \tag{C.7}$$

If we take the derivative of $\Omega(E)$, we find

$$\frac{\mathrm{d}\Omega(E)}{\mathrm{d}E} = \Sigma(E) = \int_{S_E} \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H=E}} \,. \tag{C.8}$$

The area, $\Sigma(E)$, is called the *structure function*. If we wish to take the average value of a function $f(\boldsymbol{X}^N)$ over the surface, we can write

$$\langle f \rangle_S = \frac{1}{\Sigma(E)} \int_{S_E} f(\boldsymbol{X}^N) \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H^N=E}} \,. \tag{C.9}$$

Thus, the differential

$$\mathrm{d}S_E = \frac{\mathrm{d}A_E}{|\nabla_X H^N|_{H^N=E}} \tag{C.10}$$

is the invariant surface area element.

If a system is ergodic, the fraction of time that its state, $X^N(\boldsymbol{p}^N, \boldsymbol{q}^N)$, spends in a given region R_E of the energy surface will be equal to the fraction of the surface S_E occupied by R_E. Let us consider a function $\phi(R_E)$ such that $\phi(R_E) = 1$ when X^N is in R_E and $\phi(R_E) = 0$ otherwise. Then it is easy to see that, for an ergodic system,

$$\lim_{T\to\infty} \frac{\tau_{R_E}}{T} = \frac{\Sigma(R_E)}{\Sigma(E)} \,, \tag{C.11}$$

where τ_{R_E} is the time the trajectory spends in R_E and $\Sigma(R_E)$ is the area occupied by R_E.

A system can exhibit ergodic flow on the energy surface only if there are no other isolating integrals of the motion which prevent trajectories from moving freely on the energy surface. If no other isolating integrals exist, the system is said to be metrically transitive (trajectories move freely on the energy surface). If a system is ergodic, it will spend equal times in equal areas of the energy surface. If we perform measurements to decide where on the surface the system point is, we

region from another, the best choice we can make is to assume that the probability $P(R_E)$ of finding the system in R_E is equal to the fraction of the energy surface occupied by R_E. Thus,

$$P(R_E) = \frac{1}{\Sigma(E)} \int_{R_E} \mathrm{d}S_E = \frac{\Sigma(R_E)}{\Sigma(E)} \,. \tag{C.12}$$

From Eq. (C.12) it is a simple matter to write down a normalized probability density for the energy surface, namely,

$$\rho(\boldsymbol{X}^N, S_E) = \frac{1}{\Sigma(E)} \,. \tag{C.13}$$

Equation (C.13) is called the *fundamental distribution law* by Khintchine and called the *microcanonical ensemble* by Gibbs. Since it is a function only of the energy, it is a stationary state of the Liouville equation (see Appendix A). It says that all states on the energy surface are equally probable. Equation (C.13) forms the foundation upon which all of equilibrium and most of nonequilibrium statistical mechanics are built.