Contents

Chapter 3

Ergodicity and the Approach to Equilibrium

3.1 References

- R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, 1975)
  An advanced text with an emphasis on fluids and kinetics.
- R. Balian, *From Macrophysics to Microphysics* (2 vols., Springer-Verlag, 2006)
  A very detailed discussion of the fundamental postulates of statistical mechanics and their implications.)

3.2 Modeling the Approach to Equilibrium

3.2.1 Equilibrium

A thermodynamic system typically consists of an enormously large number of constituent particles, a typical 'large number' being Avogadro's number, $N_{\text{A}} = 6.02 \times 10^{23}$. Nevertheless, in *equilibrium*, such a system is characterized by a relatively small number of thermodynamic state variables. Thus, while a complete description of a (classical) system would require us to account for $\mathcal{O}\big(10^{23}\big)$ evolving degrees of freedom, with respect to the physical quantities in which we are interested, the details of the initial conditions are effectively forgotten over some microscopic time scale τ, called the collision time, and over some microscopic distance scale, ℓ, called the mean free path[1]. The equilibrium state is time-independent.

3.2.2 The Master Equation

Relaxation to equilibrium is often modeled with something called the *master equation*. Let $P_i(t)$ be the probability that the system is in a quantum or classical state i at time t. Then write

$$\frac{dP_i}{dt} = \sum_j \big(W_{ij}\,P_j - W_{ji}\,P_i\big) \ . \tag{3.1}$$

Here, W_{ij} is the rate at which j makes a transition to i. Note that we can write this equation as

$$\frac{dP_i}{dt} = -\sum_j \Gamma_{ij}\,P_j \ , \tag{3.2}$$

where

$$\Gamma_{ij} = \begin{cases} -W_{ij} & \text{if } i \neq j \\ \sum_k' W_{kj} & \text{if } i = j \ , \end{cases} \tag{3.3}$$

where the prime on the sum indicates that $k = j$ is to be excluded. The constraints on the W_{ij} are that $W_{ij} \geq 0$ for all i, j, and we may take $W_{ii} \equiv 0$ (no sum on i). Fermi's Golden Rule of quantum mechanics says that

$$W_{ij} = \frac{2\pi}{\hbar}\,\big|\langle\, i \,|\, \hat{V} \,|\, j \,\rangle\big|^2\,\rho(E_j) \ , \tag{3.4}$$

where $\hat{H}_0 \,\big|\, i \,\big\rangle = E_i \,\big|\, i \,\big\rangle$, $\hat{V}$ is an additional potential which leads to transitions, and $\rho(E_i)$ is the density of final states at energy E_i. The fact that $W_{ij} \geq 0$ means that if each $P_i(t=0) \geq 0$, then $P_i(t) \geq 0$ for all $t \geq 0$. To see this, suppose that at some time $t > 0$ one of the probabilities P_i is crossing zero and about to become negative. But then eqn. 3.1 says that $\dot{P}_i(t) = \sum_j W_{ij} P_j(t) \geq 0$. So $P_i(t)$ can never become negative.

3.2.3 Equilibrium distribution and detailed balance

If the transition rates W_{ij} are themselves time-independent, then we may formally write

$$P_i(t) = \big(e^{-\Gamma t}\big)_{ij}\,P_j(0) \ . \tag{3.5}$$

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[1] Exceptions involve quantities which are conserved by collisions, such as overall particle number, momentum, and energy. These quantities relax to equilibrium in a special way called *hydrodynamics*.

Here we have used the Einstein 'summation convention' in which repeated indices are summed over (in this case, the j index). Note that

$$\sum_i \Gamma_{ij} = 0 \ , \tag{3.6}$$

which says that the total probability $\sum_i P_i$ is conserved:

$$\frac{d}{dt}\sum_i P_i = -\sum_{i,j} \Gamma_{ij}\, P_j = -\sum_j \bigg(P_j \sum_i \Gamma_{ij}\bigg) = 0 \ . \tag{3.7}$$

We conclude that $\vec{\phi} = (1, 1, \ldots, 1)$ is a left eigenvector of Γ with eigenvalue $\lambda = 0$. The corresponding right eigenvector, which we write as $P_i^{\rm eq}$, satisfies $\Gamma_{ij} P_j^{\rm eq} = 0$, and is a stationary (*i.e.* time independent) solution to the master equation. Generally, there is only one right/left eigenvector pair corresponding to $\lambda = 0$, in which case any initial probability distribution $P_i(0)$ converges to $P_i^{\rm eq}$ as $t \to \infty$, as shown in Appendix I (§3.7).

In equilibrium, the net rate of transitions into a state $|\, i \,\rangle$ is equal to the rate of transitions out of $|\, i \,\rangle$. If, for each state $|\, j \,\rangle$ the transition rate from $|\, i \,\rangle$ to $|\, j \,\rangle$ is equal to the transition rate from $|\, j \,\rangle$ to $|\, i \,\rangle$, we say that the rates satisfy the condition of *detailed balance*. In other words,

$$W_{ij}\, P_j^{\rm eq} = W_{ji}\, P_i^{\rm eq}. \tag{3.8}$$

Assuming $W_{ij} \neq 0$ and $P_j^{\rm eq} \neq 0$, we can divide to obtain

$$\frac{W_{ji}}{W_{ij}} = \frac{P_j^{\rm eq}}{P_i^{\rm eq}} \ . \tag{3.9}$$

Note that detailed balance is a stronger condition than that required for a stationary solution to the master equation.

If $\Gamma = \Gamma^{\rm t}$ is symmetric, then the right eigenvectors and left eigenvectors are transposes of each other, hence $P^{\rm eq} = 1/N$, where N is the dimension of Γ. The system then satisfies the conditions of detailed balance. See Appendix II (§3.8) for an example of this formalism applied to a model of radioactive decay.

3.2.4 Boltzmann's H-theorem

Suppose for the moment that Γ is a symmetric matrix, *i.e.* $\Gamma_{ij} = \Gamma_{ji}$. Then construct the function

$$\mathsf{H}(t) = \sum_i P_i(t)\, \ln P_i(t) \ . \tag{3.10}$$

Then

$$\begin{aligned} \frac{d\mathsf{H}}{dt} &= \sum_i \frac{dP_i}{dt}\,\big(1 + \ln P_i\big) = \sum_i \frac{dP_i}{dt}\, \ln P_i \\ &= -\sum_{i,j} \Gamma_{ij}\, P_j \ln P_i \\ &= \sum_{i,j} \Gamma_{ij}\, P_j \big(\ln P_j - \ln P_i\big) \ , \end{aligned} \tag{3.11}$$

where we have used $\sum_i \Gamma_{ij} = 0$. Now switch $i \leftrightarrow j$ in the above sum and add the terms to get

$$\frac{d\mathsf{H}}{dt} = \frac{1}{2}\sum_{i,j} \Gamma_{ij} \big(P_i - P_j\big)\, \big(\ln P_i - \ln P_j\big) \ . \tag{3.12}$$

Note that the $i = j$ term does not contribute to the sum. For $i \neq j$ we have $\varGamma_{ij} = -W_{ij} \leq 0$, and using the result

$$(x - y)\,(\ln x - \ln y) \geq 0 \ , \tag{3.13}$$

we conclude

$$\frac{d\mathsf{H}}{dt} \leq 0 \ . \tag{3.14}$$

In equilibrium, $P_i^{\rm eq}$ is a constant, independent of i. We write

$$P_i^{\rm eq} = \frac{1}{\Omega} \quad , \quad \Omega = \sum_i 1 \quad \Longrightarrow \quad \mathsf{H} = -\ln \Omega \ . \tag{3.15}$$

If $\varGamma_{ij} \neq \varGamma_{ji}$, we can still prove a version of the H-theorem. Define a new symmetric matrix

$$\overline{W}_{ij} \equiv W_{ij}\, P_j^{\rm eq} = W_{ji}\, P_i^{\rm eq} = \overline{W}_{ji} \ , \tag{3.16}$$

and the generalized H-function,

$$\mathsf{H}(t) \equiv \sum_i P_i(t)\, \ln\!\left(\frac{P_i(t)}{P_i^{\rm eq}}\right) \ . \tag{3.17}$$

Then

$$\frac{d\mathsf{H}}{dt} = -\frac{1}{2} \sum_{i,j} \overline{W}_{ij} \left(\frac{P_i}{P_i^{\rm eq}} - \frac{P_j}{P_j^{\rm eq}}\right) \left[\ln\!\left(\frac{P_i}{P_i^{\rm eq}}\right) - \ln\!\left(\frac{P_j}{P_j^{\rm eq}}\right)\right] \leq 0 \ . \tag{3.18}$$

3.3 Phase Flows in Classical Mechanics

3.3.1 Hamiltonian evolution

The master equation provides us with a semi-phenomenological description of a dynamical system's relaxation to equilibrium. It explicitly breaks time reversal symmetry. Yet the microscopic laws of Nature are (approximately) time-reversal symmetric. How can a system which obeys Hamilton's equations of motion come to equilibrium?

Let's start our investigation by reviewing the basics of Hamiltonian dynamics. Recall the Lagrangian $L = L(q, \dot{q}, t) = T - V$. The Euler-Lagrange equations of motion for the action $S\big[q(t)\big] = \int\! dt\, L$ are

$$\dot{p}_\sigma = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_\sigma}\right) = \frac{\partial L}{\partial q_\sigma} \ , \tag{3.19}$$

where p_σ is the canonical momentum conjugate to the generalized coordinate q_σ:

$$p_\sigma = \frac{\partial L}{\partial \dot{q}_\sigma} \ . \tag{3.20}$$

The Hamiltonian, $H(q, p)$ is obtained by a Legendre transformation,

$$H(q, p) = \sum_{\sigma=1}^{r} p_\sigma\, \dot{q}_\sigma - L \ . \tag{3.21}$$

Note that

$$\begin{aligned} dH &= \sum_{\sigma=1}^{r}\bigg(p_\sigma\, d\dot{q}_\sigma + \dot{q}_\sigma\, dp_\sigma - \frac{\partial L}{\partial q_\sigma}\, dq_\sigma - \frac{\partial L}{\partial \dot{q}_\sigma}\, d\dot{q}_\sigma\bigg) - \frac{\partial L}{\partial t}\, dt \\ &= \sum_{\sigma=1}^{r}\bigg(\dot{q}_\sigma\, dp_\sigma - \frac{\partial L}{\partial q_\sigma}\, dq_\sigma\bigg) - \frac{\partial L}{\partial t}\, dt \ . \end{aligned} \tag{3.22}$$

Thus, we obtain Hamilton's equations of motion,

$$\frac{\partial H}{\partial p_\sigma} = \dot{q}_\sigma \quad , \quad \frac{\partial H}{\partial q_\sigma} = -\frac{\partial L}{\partial q_\sigma} = -\dot{p}_\sigma \tag{3.23}$$

and

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \ . \tag{3.24}$$

Define the rank $2r$ vector $\boldsymbol{\varphi}$ by its components,

$$\varphi_i = \begin{cases} q_i & \text{if } 1 \le i \le r \\ \\ p_{i-r} & \text{if } r \le i \le 2r \ . \end{cases} \tag{3.25}$$

Then we may write Hamilton's equations compactly as

$$\dot{\varphi}_i = J_{ij}\, \frac{\partial H}{\partial \varphi_j} \ , \tag{3.26}$$

where

$$J = \begin{pmatrix} 0_{r\times r} & 1_{r\times r} \\ -1_{r\times r} & 0_{r\times r} \end{pmatrix} \tag{3.27}$$

is a rank $2r$ matrix. Note that $J^{\rm t} = -J$, *i.e.* J is antisymmetric, and that $J^2 = -1_{2r\times 2r}$.

3.3.2 Dynamical systems and the evolution of phase space volumes

Consider a general dynamical system,

$$\frac{d\boldsymbol{\varphi}}{dt} = \boldsymbol{V}(\boldsymbol{\varphi}) \ , \tag{3.28}$$

where $\boldsymbol{\varphi}(t)$ is a point in an n-dimensional phase space. Consider now a compact[2] region $\mathcal{R}_0$ in phase space, and consider its evolution under the dynamics. That is, $\mathcal{R}_0$ consists of a set of points $\big\{\boldsymbol{\varphi} \,|\, \boldsymbol{\varphi} \in \mathcal{R}_0\big\}$, and if we regard each $\boldsymbol{\varphi} \in \mathcal{R}_0$ as an initial condition, we can define the time-dependent set $\mathcal{R}(t)$ as the set of points $\boldsymbol{\varphi}(t)$ that *were* in $\mathcal{R}_0$ at time $t = 0$:

$$\mathcal{R}(t) = \big\{\boldsymbol{\varphi}(t) \,\big|\, \boldsymbol{\varphi}(0) \in \mathcal{R}_0\big\} \ . \tag{3.29}$$

Now consider the volume $\Omega(t)$ of the set $\mathcal{R}(t)$. We have

$$\Omega(t) = \int\limits_{\mathcal{R}(t)} \! d\mu \tag{3.30}$$

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[2] 'Compact' in the parlance of mathematical analysis means 'closed and bounded'.

where

$$d\mu = d\varphi_1\, d\varphi_2 \,\cdots\, d\varphi_n \ , \tag{3.31}$$

for an n-dimensional phase space. We then have

$$\Omega(t+dt) = \int\limits_{\mathcal{R}(t+dt)} \!\! d\mu' = \int\limits_{\mathcal{R}(t)} \!\! d\mu \left| \frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} \right| , \tag{3.32}$$

where

$$\left| \frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} \right| \equiv \frac{\partial(\varphi'_1, \ldots, \varphi'_n)}{\partial(\varphi_1, \ldots, \varphi_n)} \tag{3.33}$$

is a determinant, which is the Jacobean of the transformation from the set of coordinates $\big\{\varphi_i = \varphi_i(t)\big\}$ to the coordinates $\big\{\varphi'_i = \varphi_i(t+dt)\big\}$. But according to the dynamics, we have

$$\varphi_i(t+dt) = \varphi_i(t) + V_i\big(\boldsymbol{\varphi}(t)\big)\, dt + \mathcal{O}(dt^2) \tag{3.34}$$

and therefore

$$\frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} = \delta_{ij} + \frac{\partial V_i}{\partial\varphi_j}\, dt + \mathcal{O}(dt^2) \ . \tag{3.35}$$

We now make use of the equality

$$\ln\det M = \mathsf{Tr}\, \ln M \ , \tag{3.36}$$

for any matrix M, which gives us[3], for small ε,

$$\det\big(1+\varepsilon A\big) = \exp \mathsf{Tr}\, \ln\big(1+\varepsilon A\big) = 1 + \varepsilon\ \mathsf{Tr}\, A + \tfrac{1}{2}\,\varepsilon^2 \Big(\big(\mathsf{Tr}\, A\big)^2 - \mathsf{Tr}\,(A^2)\Big) + \ldots \tag{3.37}$$

Thus,

$$\Omega(t+dt) = \Omega(t) + \int\limits_{\mathcal{R}(t)} \!\! d\mu\ \boldsymbol{\nabla}\!\cdot\! \boldsymbol{V}\ dt + \mathcal{O}(dt^2) \ , \tag{3.38}$$

which says

$$\frac{d\Omega}{dt} = \int\limits_{\mathcal{R}(t)} \!\! d\mu\ \boldsymbol{\nabla}\!\cdot\! \boldsymbol{V} = \int\limits_{\partial\mathcal{R}(t)} \!\! dS\ \hat{\boldsymbol{n}} \cdot \boldsymbol{V} \tag{3.39}$$

Here, the divergence is the *phase space divergence*,

$$\boldsymbol{\nabla}\!\cdot\! \boldsymbol{V} = \sum_{i=1}^{n} \frac{\partial V_i}{\partial\varphi_i} \ , \tag{3.40}$$

and we have used the divergence theorem to convert the volume integral of the divergence to a surface integral of $\hat{\boldsymbol{n}} \cdot \boldsymbol{V}$, where $\hat{\boldsymbol{n}}$ is the surface normal and dS is the differential element of surface area, and $\partial\mathcal{R}$ denotes the boundary of the region $\mathcal{R}$. We see that if $\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} = 0$ everywhere in phase space, then $\Omega(t)$ is a constant, and phase space volumes are *preserved* by the evolution of the system.

For an alternative derivation, consider a function $\varrho(\boldsymbol{\varphi}, t)$ which is defined to be the *density* of some collection of points in phase space at phase space position $\boldsymbol{\varphi}$ and time t. This must satisfy the continuity equation,

$$\frac{\partial\varrho}{\partial t} + \boldsymbol{\nabla}\!\cdot\!(\varrho\boldsymbol{V}) = 0 \ . \tag{3.41}$$

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[3] The equality $\ln\det M = \mathsf{Tr}\, \ln M$ is most easily proven by bringing the matrix to diagonal form via a similarity transformation, and proving the equality for diagonal matrices.

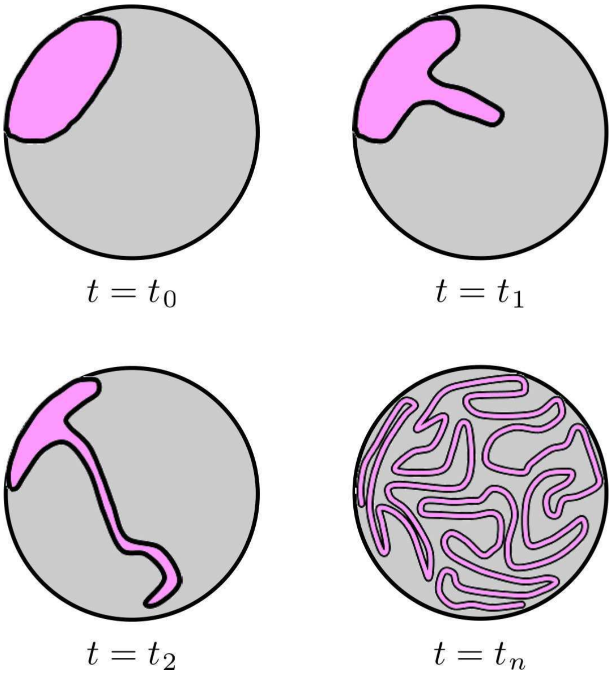

Figure 3.1: Time evolution of two immiscible fluids. The local density remains constant.

This is called the *continuity equation*. It says that 'nobody gets lost'. If we integrate it over a region of phase space $\mathcal{R}$, we have

$$\frac{d}{dt}\int\limits_{\mathcal{R}} d\mu\, \varrho = -\int\limits_{\mathcal{R}} d\mu\, \boldsymbol{\nabla}\cdot(\varrho \boldsymbol{V}) = -\int\limits_{\partial\mathcal{R}} dS\, \hat{\boldsymbol{n}}\cdot(\varrho\boldsymbol{V}) \ . \tag{3.42}$$

It is perhaps helpful to think of ϱ as a charge density, in which case $\boldsymbol{J} = \varrho\boldsymbol{V}$ is the current density. The above equation then says

$$\frac{dQ_{\mathcal{R}}}{dt} = -\int\limits_{\partial\mathcal{R}} dS\, \hat{\boldsymbol{n}}\cdot\boldsymbol{J} \ , \tag{3.43}$$

where $Q_{\mathcal{R}}$ is the total charge contained inside the region $\mathcal{R}$. In other words, the rate of increase or decrease of the charge within the region $\mathcal{R}$ is equal to the total integrated current flowing in or out of $\mathcal{R}$ at its boundary.

The Leibniz rule lets us write the continuity equation as

$$\frac{\partial\varrho}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla}\varrho + \varrho\,\boldsymbol{\nabla}\cdot\boldsymbol{V} = 0 \ . \tag{3.44}$$

But now suppose that the phase flow is divergenceless, *i.e.* $\boldsymbol{\nabla}\cdot\boldsymbol{V} = 0$. Then we have

$$\frac{D\varrho}{Dt} \equiv \left(\frac{\partial}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla}\right)\varrho = 0 \ . \tag{3.45}$$

The combination inside the brackets above is known as the *convective derivative*. It tells us the total rate of change of ϱ for an observer *moving with the phase flow*. That is

$$\begin{aligned} \frac{d}{dt}\,\varrho\big(\boldsymbol{\varphi}(t),t\big) &= \frac{\partial\varrho}{\partial\varphi_i}\,\frac{d\varphi_i}{dt} + \frac{\partial\varrho}{\partial t} \\ &= \sum_{i=1}^{n} V_i\,\frac{\partial\rho}{\partial\varphi_i} + \frac{\partial\varrho}{\partial t} = \frac{D\varrho}{Dt} \ . \end{aligned} \tag{3.46}$$

If $D\varrho/Dt = 0$, the local density remains the same during the evolution of the system. If we consider the 'characteristic function'

$$\varrho(\boldsymbol{\varphi}, t = 0) = \begin{cases} 1 & \text{if } \boldsymbol{\varphi} \in \mathcal{R}_0 \\ 0 & \text{otherwise} \end{cases} \tag{3.47}$$

then the vanishing of the convective derivative means that the image of the set $\mathcal{R}_0$ under time evolution will always have the same volume.

Hamiltonian evolution in classical mechanics is volume preserving. The equations of motion are

$$\dot{q}_i = + \frac{\partial H}{\partial p_i} \qquad , \qquad \dot{p}_i = - \frac{\partial H}{\partial q_i} \tag{3.48}$$

A point in phase space is specified by r positions q_i and r momenta p_i, hence the dimension of phase space is $n = 2r$:

$$\boldsymbol{\varphi} = \begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{p} \end{pmatrix} \qquad , \qquad \boldsymbol{V} = \begin{pmatrix} \dot{\boldsymbol{q}} \\ \dot{\boldsymbol{p}} \end{pmatrix} = \begin{pmatrix} \partial H/\partial \boldsymbol{p} \\ -\partial H/\partial \boldsymbol{q} \end{pmatrix} . \tag{3.49}$$

Hamilton's equations of motion guarantee that the phase space flow is divergenceless:

$$\begin{aligned} \nabla \!\cdot\! \boldsymbol{V} &= \sum_{i=1}^{r} \left\{ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right\} \\ &= \sum_{i=1}^{r} \left\{ \frac{\partial}{\partial q_i} \left(\frac{\partial H}{\partial p_i} \right) + \frac{\partial}{\partial p_i} \left(- \frac{\partial H}{\partial q_i} \right) \right\} = 0 \, . \end{aligned} \tag{3.50}$$

Thus, we have that the convective derivative vanishes, *viz.*

$$\frac{D\varrho}{Dt} \equiv \frac{\partial \varrho}{\partial t} + \boldsymbol{V} \!\cdot\! \nabla \varrho = 0 \, , \tag{3.51}$$

for any distribution $\varrho(\boldsymbol{\varphi}, t)$ on phase space. Thus, the value of the density $\varrho(\boldsymbol{\varphi}(t), t)$ is constant, which tells us that the phase flow is *incompressible*. In particular, phase space volumes are preserved.

3.3.3 Liouville's equation and the microcanonical distribution

Let $\varrho(\boldsymbol{\varphi}) = \varrho(\boldsymbol{q}, \boldsymbol{p})$ be a distribution on phase space. Assuming the evolution is Hamiltonian, we can write

$$\frac{\partial \varrho}{\partial t} = -\dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla} \varrho = - \sum_{k=1}^{r} \left(\dot{q}_k \frac{\partial}{\partial q_k} + \dot{p}_k \frac{\partial}{\partial p_k} \right) \varrho = -i \hat{L} \varrho \, , \tag{3.52}$$

where $\hat{L}$ is a differential operator known as the *Liouvillian*:

$$\hat{L} = -i \sum_{k=1}^{r} \left\{ \frac{\partial H}{\partial p_k} \frac{\partial}{\partial q_k} - \frac{\partial H}{\partial q_k} \frac{\partial}{\partial p_k} \right\} . \tag{3.53}$$

Eqn. 3.52, known as *Liouville's equation*, bears an obvious resemblance to the Schrödinger equation from quantum mechanics.

Suppose that $\Lambda_a(\boldsymbol{\varphi})$ is conserved by the dynamics of the system. Typical conserved quantities include the components of the total linear momentum (if there is translational invariance), the components of the total angular momentum (if there is rotational invariance), and the Hamiltonian itself (if the Lagrangian is not explicitly time-dependent). Now consider a distribution $\varrho(\boldsymbol{\varphi},t) = \varrho(\Lambda_1,\Lambda_2,\ldots,\Lambda_k)$ which is a function only of these various conserved quantities. Then from the chain rule, we have

$$\dot{\boldsymbol{\varphi}}\cdot\boldsymbol{\nabla}\varrho = \sum_a \frac{\partial\varrho}{\partial\Lambda_a}\,\dot{\boldsymbol{\varphi}}\cdot\boldsymbol{\nabla}\Lambda_a = 0\ , \tag{3.54}$$

since for each a we have

$$\frac{d\Lambda_a}{dt} = \sum_{\sigma=1}^{r}\bigg(\frac{\partial\Lambda_a}{\partial q_\sigma}\,\dot{q}_\sigma + \frac{\partial\Lambda_a}{\partial p_\sigma}\,\dot{p}_\sigma\bigg) = \dot{\boldsymbol{\varphi}}\cdot\boldsymbol{\nabla}\Lambda_a = 0\ . \tag{3.55}$$

We conclude that any distribution $\varrho(\boldsymbol{\varphi},t) = \varrho(\Lambda_1,\Lambda_2,\ldots,\Lambda_k)$ which is a function solely of conserved dynamical quantities is a stationary solution to Liouville's equation.

Clearly the microcanonical distribution,

$$\varrho_E(\boldsymbol{\varphi}) = \frac{\delta\big(E-H(\boldsymbol{\varphi})\big)}{D(E)} = \frac{\delta\big(E-H(\boldsymbol{\varphi})\big)}{\int\! d\mu\,\delta\big(E-H(\boldsymbol{\varphi})\big)}\ , \tag{3.56}$$

is a fixed point solution of Liouville's equation.

3.4 Irreversibility and Poincaré Recurrence

The dynamics of the master equation describe an approach to equilibrium. These dynamics are irreversible: $d\mathsf{H}/dt \le 0$, where H is Boltzmann's H-function. However, the microscopic laws of physics are (almost) time-reversal invariant[4], so how can we understand the emergence of irreversibility? Furthermore, any dynamics which are deterministic and volume-preserving in a finite phase space exhibits the phenomenon of *Poincaré recurrence*, which guarantees that phase space trajectories are arbitrarily close to periodic if one waits long enough.

3.4.1 Poincaré recurrence theorem

The proof of the recurrence theorem is simple. Let g_τ be the 'τ-advance mapping' which evolves points in phase space according to Hamilton's equations. Assume that g_τ is invertible and volume-preserving, as is the case for Hamiltonian flow. Further assume that phase space volume is finite. Since energy is preserved in the case of time-independent Hamiltonians, we simply ask that the volume of phase space *at fixed total energy* E be finite, *i.e.*

$$\int\! d\mu\,\delta\big(E-H(\boldsymbol{q},\boldsymbol{p})\big) < \infty\ , \tag{3.57}$$

where $d\mu = d\boldsymbol{q}\,d\boldsymbol{p}$ is the phase space uniform integration measure.

Theorem: In any finite neighborhood $\mathcal{R}_0$ of phase space there exists a point $\boldsymbol{\varphi}_0$ which will return to $\mathcal{R}_0$ after m applications of g_τ, where m is finite.

Proof: Assume the theorem fails; we will show this assumption results in a contradiction. Consider the set Υ formed from the union of all sets $g_\tau^k\,\mathcal{R}$ for all m:

$$\Upsilon = \bigcup_{k=0}^{\infty} g_\tau^k\,\mathcal{R}_0 \tag{3.58}$$

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[4] Actually, the microscopic laws of physics are *not* time-reversal invariant, but rather are invariant under the product PCT, where P is parity, C is charge conjugation, and T is time reversal.

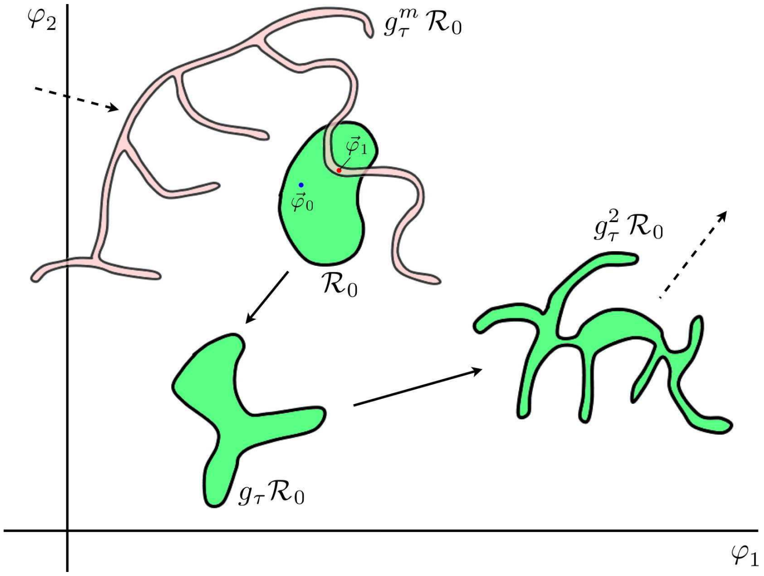

Figure 3.2: Successive images of a set $\mathcal{R}_0$ under the τ-advance mapping g_τ, projected onto a two-dimensional phase plane. The Poincaré recurrence theorem guarantees that if phase space has finite volume, and g_τ is invertible and volume preserving, then for any set $\mathcal{R}_0$ there exists an integer m such that $\mathcal{R}_0 \cap g_\tau^m\,\mathcal{R}_0 \neq \emptyset$.

We assume that the set $\{g_\tau^k\,\mathcal{R}_0 \,|\, k \in \mathbb{N}\}$ is disjoint[5]. The volume of a union of disjoint sets is the sum of the individual volumes. Thus,

$$\begin{aligned}\text{vol}(\Upsilon) &= \sum_{k=0}^{\infty} \text{vol}\big(g_\tau^k\,\mathcal{R}_0\big) \\ &= \text{vol}(\mathcal{R}_0) \cdot \sum_{k=0}^{\infty} 1 = \infty\ ,\end{aligned} \tag{3.59}$$

since $\text{vol}\big(g_\tau^k\,\mathcal{R}_0\big) = \text{vol}\big(\mathcal{R}_0\big)$ from volume preservation. But clearly Υ is a subset of the entire phase space, hence we have a contradiction, because by assumption phase space is of finite volume.

Thus, the assumption that the set $\{g_\tau^k\,\mathcal{R}_0 \,|\, k \in \mathbb{Z}_+\}$ is disjoint fails. This means that there exists some pair of integers k and l, with $k \neq l$, such that $g_\tau^k\,\mathcal{R}_0 \cap g_\tau^l\,\mathcal{R}_0 \neq \emptyset$. Without loss of generality we may assume $k < l$. Apply the inverse g_τ^{-1} to this relation k times to get $g_\tau^{l-k}\,\mathcal{R}_0 \cap \mathcal{R}_0 \neq \emptyset$. Now choose any point $\boldsymbol{\varphi}_1 \in g_\tau^m\,\mathcal{R}_0 \cap \mathcal{R}_0$, where $m = l - k$, and define $\boldsymbol{\varphi}_0 = g_\tau^{-m}\boldsymbol{\varphi}_1$. Then by construction both $\boldsymbol{\varphi}_0$ and $g_\tau^m\,\boldsymbol{\varphi}_0$ lie within $\mathcal{R}_0$ and the theorem is proven.

Poincaré recurrence has remarkable implications. Consider a bottle of perfume which is opened in an otherwise evacuated room, as depicted in fig. 3.3. The perfume molecules evolve according to Hamiltonian evolution. The positions are bounded because physical space is finite. The momenta are bounded because the total energy is conserved, hence no single particle can have a momentum such that $T(\boldsymbol{p}) > E_{\text{TOT}}$, where $T(\boldsymbol{p})$ is the single particle kinetic energy function[6]. Thus, phase space, however large, is still bounded. Hamiltonian evolution, as we have seen, is invertible and volume preserving, therefore the system is recurrent. All the molecules must eventually return to the bottle. What's more, they all must return with momenta arbitrarily close to their initial momenta![7]

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[5] The natural numbers $\mathbb{N}$ is the set of non-negative integers $\{0, 1, 2, \ldots\}$.

[6] In the nonrelativistic limit, $T = p^2/2m$. For relativistic particles, we have $T = (p^2c^2 + m^2c^4)^{1/2} - mc^2$.

[7] Actually, what the recurrence theorem guarantees is that there is a configuration arbitrarily close to the initial one which recurs, to within the same degree of closeness.

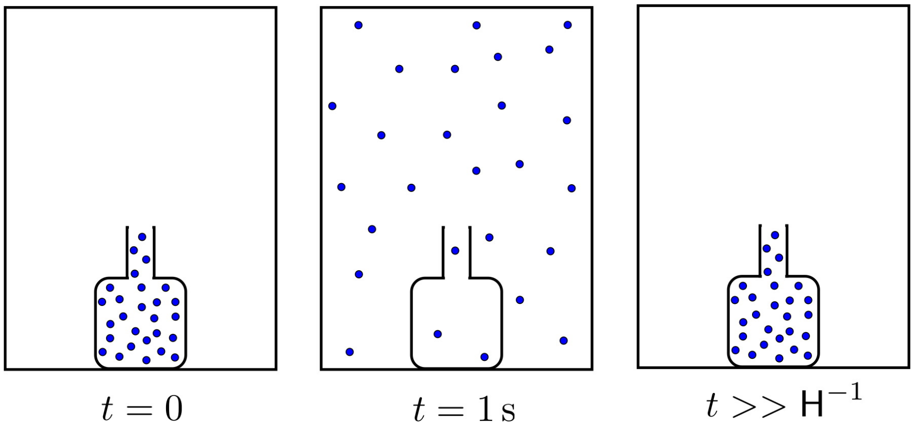

Figure 3.3: Poincaré recurrence guarantees that if we remove the cap from a bottle of perfume in an otherwise evacuated room, all the perfume molecules will eventually return to the bottle! (Here H is the Hubble constant.)

In this case, we could define the region $\mathcal{R}_0$ as

$$\mathcal{R}_0 = \big\{ (q_1, \ldots, q_r, p_1, \ldots, p_r) \; \big| \; |q_i - q_i^0| \leq \Delta q \text{ and } |p_j - p_j^0| \leq \Delta p \;\forall\; i, j \big\} \;, \tag{3.60}$$

which specifies a hypercube in phase space centered about the point $(\boldsymbol{q}^0, \boldsymbol{p}^0)$.

Each of the three central assumptions – finite phase space, invertibility, and volume preservation – is crucial. If any one of these assumptions does not hold, the proof fails. Obviously if phase space is infinite the flow needn't be recurrent since it can keep moving off in a particular direction. Consider next a volume-preserving map which is not invertible. An example might be a mapping $f : \mathbb{R} \to \mathbb{R}$ which takes any real number to its fractional part. Thus, $f(\pi) = 0.14159265\ldots$. Let us restrict our attention to intervals of width less than unity. Clearly f is then volume preserving. The action of f on the interval $[2, 3)$ is to map it to the interval $[0, 1)$. But $[0, 1)$ remains fixed under the action of f, so no point within the interval $[2, 3)$ will ever return under repeated iterations of f. Thus, f does not exhibit Poincaré recurrence.

Consider next the case of the damped harmonic oscillator. In this case, phase space volumes contract. For a one-dimensional oscillator obeying $\ddot{x} + 2\beta\dot{x} + \varOmega_0^2\, x = 0$ one has $\nabla \!\cdot\! \boldsymbol{V} = -2\beta < 0$, since $\beta > 0$ for physical damping. Thus the convective derivative is $D_t \varrho = -(\nabla \!\cdot\! \boldsymbol{V})\varrho = 2\beta\varrho$ which says that the density increases exponentially in the comoving frame, as $\varrho(t) = e^{2\beta t}\,\varrho(0)$. Thus, phase space volumes collapse: $\Omega(t) = e^{-2\beta 2}\,\Omega(0)$, and are not preserved by the dynamics. The proof of recurrence therefore fails. In this case, it is possible for the set Υ to be of finite volume, even if it is the union of an infinite number of sets $g_\tau^k\, \mathcal{R}_0$, because the volumes of these component sets themselves decrease exponentially, as $\mathrm{vol}(g_\tau^n\, \mathcal{R}_0) = e^{-2n\beta\tau}\, \mathrm{vol}(\mathcal{R}_0)$. A damped pendulum, released from rest at some small angle θ_0, will not return arbitrarily close to these initial conditions.

3.4.2 Kac ring model

The implications of the Poincaré recurrence theorem are surprising – even shocking. If one takes a bottle of perfume in a sealed, evacuated room and opens it, the perfume molecules will diffuse throughout the room. The recurrence theorem guarantees that after some finite time T all the molecules will go back inside the bottle (and arbitrarily close to their initial velocities as well). The hitch is that this could take a very long time, *e.g.* much much longer than the age of the Universe.

On less absurd time scales, we know that most systems come to thermodynamic equilibrium. But how can a system both exhibit equilibration *and* Poincaré recurrence? The two concepts seem utterly incompatible!

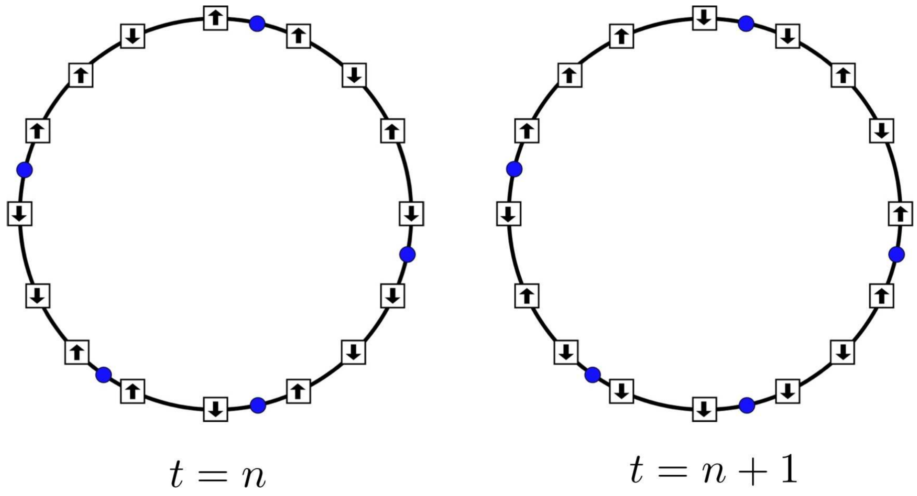

Figure 3.4: Left: A configuration of the Kac ring with $N = 16$ sites and $F = 4$ flippers. The flippers, which live on the links, are represented by blue dots. Right: The ring system after one time step. Evolution proceeds by clockwise rotation. Spins passing through flippers are flipped.

A beautifully simple model due to Kac shows how a recurrent system can exhibit the phenomenon of equilibration. Consider a ring with N sites. On each site, place a 'spin' which can be in one of two states: up or down. Along the N links of the system, F of them contain 'flippers'. The configuration of the flippers is set at the outset and never changes. The dynamics of the system are as follows: during each time step, every spin moves clockwise a distance of one lattice spacing. Spins which pass through flippers reverse their orientation: up becomes down, and down becomes up.

The 'phase space' for this system consists of 2^N discrete configurations. Since each configuration maps onto a unique image under the evolution of the system, phase space 'volume' is preserved. The evolution is invertible; the inverse is obtained simply by rotating the spins counterclockwise. Figure 3.4 depicts an example configuration for the system, and its first iteration under the dynamics.

Suppose the flippers were not fixed, but moved about randomly. In this case, we could focus on a single spin and determine its configuration probabilistically. Let p_n be the probability that a given spin is in the up configuration at time n. The probability that it is up at time $(n+1)$ is then

$$p_{n+1} = (1-x)\, p_n + x\,(1-p_n) \ , \tag{3.61}$$

where $x = F/N$ is the fraction of flippers in the system. In words: a spin will be up at time $(n+1)$ if it was up at time n and did not pass through a flipper, or if it was down at time n and did pass through a flipper. If the flipper locations are randomized at each time step, then the probability of flipping is simply $x = F/N$. Equation 3.61 can be solved immediately:

$$p_n = \tfrac{1}{2} + (1-2x)^n\, (p_0 - \tfrac{1}{2}) \ , \tag{3.62}$$

which decays exponentially to the equilibrium value of $p_{\text{eq}} = \frac{1}{2}$ with time scale

$$\tau(x) = -\frac{1}{\ln|1-2x|} \ . \tag{3.63}$$

We identify $\tau(x)$ as the microscopic relaxation time over which local equilibrium is established. If we define the magnetization $m \equiv (N_\uparrow - N_\downarrow)/N$, then $m = 2p - 1$, so $m_n = (1-2x)^n\, m_0$. The equilibrium magnetization is $m_{\text{eq}} = 0$. Note that for $\frac{1}{2} < x < 1$ that the magnetization reverses sign each time step, as well as decreasing exponentially in magnitude.

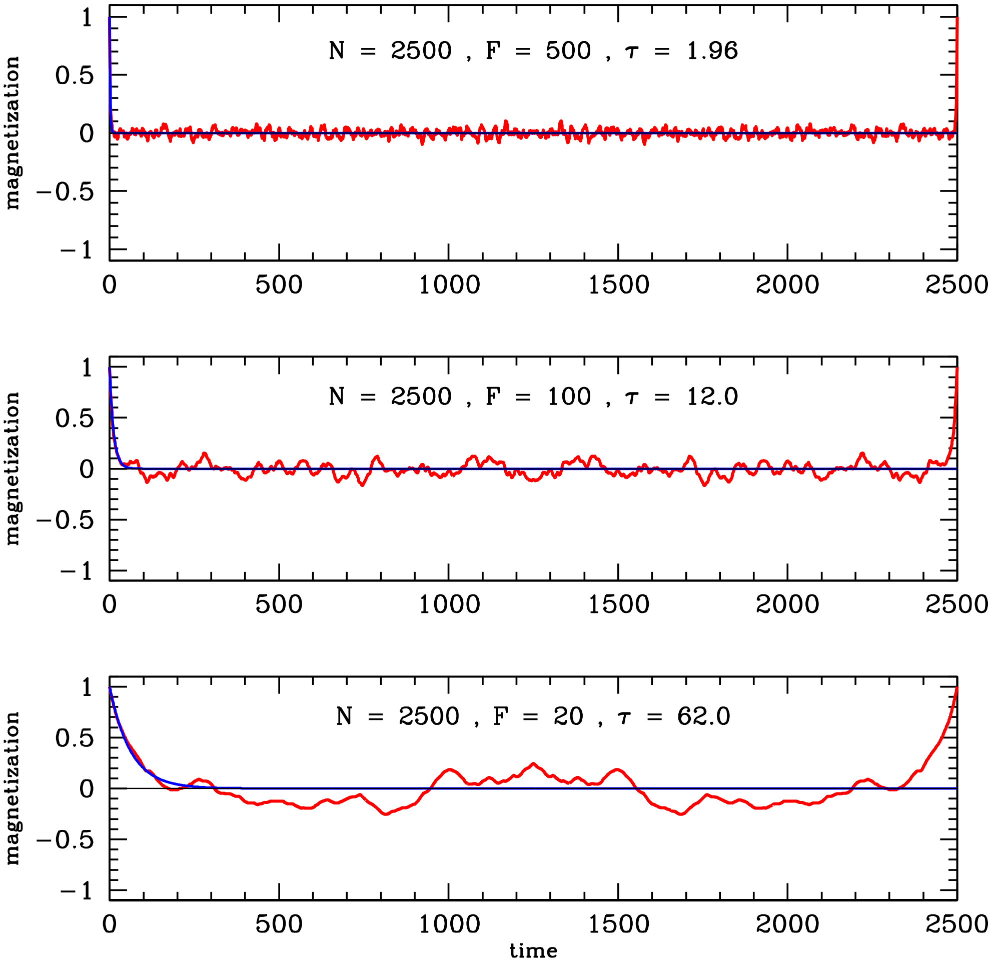

Figure 3.5: Three simulations of the Kac ring model with $N = 2500$ sites and three different concentrations of flippers. The red line shows the magnetization as a function of time, starting from an initial configuration in which 100% of the spins are up. The blue line shows the prediction of the *Stosszahlansatz*, which yields an exponentially decaying magnetization with time constant τ.

The assumption that leads to equation 3.61 is called the *Stosszahlansatz*[8], a long German word meaning, approximately, 'assumption on the counting of hits'. The resulting dynamics are irreversible: the magnetization inexorably decays to zero. However, the Kac ring model is purely deterministic, and the *Stosszahlansatz* can at best be an approximation to the true dynamics. Clearly the *Stosszahlansatz* fails to account for correlations such as the following: if spin i is flipped at time n, then spin $i+1$ will have been flipped at time $n-1$. Also if spin i is flipped at time n, then it also will be flipped at time $n+N$. Indeed, since the dynamics of the Kac ring model are invertible and volume preserving, it must exhibit Poincaré recurrence. We see this most vividly in figs. 3.5 and 3.6.

The model is trivial to simulate. The results of such a simulation are shown in figure 3.5 for a ring of $N = 1000$ sites, with $F = 100$ and $F = 24$ flippers. Note how the magnetization decays and fluctuates about the equilibrium value $m_{\rm eq} = 0$, but that after N iterations m recovers its initial value: $m_N = m_0$. The recurrence time for this system is simply N if F is even, and $2N$ if F is odd, since every spin will then have flipped an even number of

---

[8] Unfortunately, many important physicists were German and we have to put up with a legacy of long German words like *Gedankenexperiment*, *Zitterbewegung*, *Brehmsstrahlung*, *Stosszahlansatz*, *Kartoffelsalat*, *etc.*

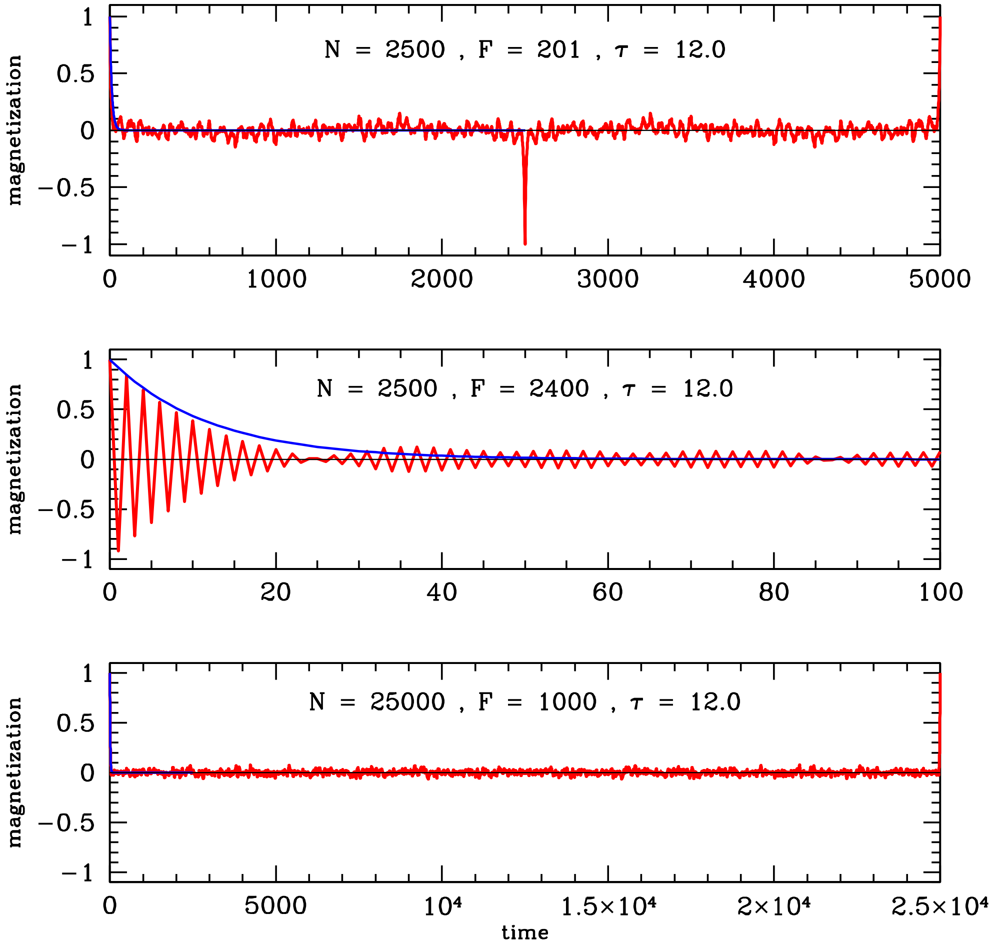

Figure 3.6: Simulations of the Kac ring model. Top: $N = 2500$ sites with $F = 201$ flippers. After 2500 iterations, each spin has flipped an odd number of times, so the recurrence time is $2N$. Middle: $N = 2500$ with $F = 2400$, resulting in a near-complete reversal of the population with every iteration. Bottom: $N = 25000$ with $N = 1000$, showing long time equilibration and dramatic resurgence of the spin population.

times.

In figure 3.6 we plot two other simulations. The top panel shows what happens when $x > \frac{1}{2}$, so that the magnetization wants to reverse its sign with every iteration. The bottom panel shows a simulation for a larger ring, with $N = 25000$ sites. Note that the fluctuations in m about equilibrium are smaller than in the cases with $N = 1000$ sites. Why?

3.5 Remarks on Ergodic Theory

3.5.1 Definition of ergodicity

A mechanical system evolves according to Hamilton's equations of motion. We have seen how such a system is *recurrent* in the sense of Poincaré.

There is a level beyond recurrence called *ergodicity*. In an ergodic system, time averages over intervals $[0,T]$ with $T \to \infty$ may be replaced by phase space averages. The time average of a function $f(\boldsymbol{\varphi})$ is defined as

$$\big\langle f(\boldsymbol{\varphi}) \big\rangle_T = \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \! dt\, f\big(\boldsymbol{\varphi}(t)\big) \ . \tag{3.64}$$

For a Hamiltonian system, the *phase space average* of the same function is defined by

$$\big\langle f(\boldsymbol{\varphi}) \big\rangle_S = \int \! d\mu\, f(\boldsymbol{\varphi})\, \delta\big(E - H(\boldsymbol{\varphi})\big) \Big/ \int \! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ , \tag{3.65}$$

where $H(\boldsymbol{\varphi}) = H(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian, and where $\delta(x)$ is the Dirac δ-function. Thus,

$$\text{ergodicity} \quad \Longleftrightarrow \quad \big\langle f(\boldsymbol{\varphi}) \big\rangle_T = \big\langle f(\boldsymbol{\varphi}) \big\rangle_S \ , \tag{3.66}$$

for all smooth functions $f(\boldsymbol{\varphi})$ for which $\big\langle f(\boldsymbol{\varphi}) \big\rangle_S$ exists and is finite. Note that we do not average over *all* of phase space. Rather, we average only over a hypersurface along which $H(\boldsymbol{\varphi}) = E$ is fixed, *i.e.* over one of the *level sets* of the Hamiltonian function. This is because the dynamics *preserves the energy*. Ergodicity means that almost all points $\boldsymbol{\varphi}$ will, upon Hamiltonian evolution, move in such a way as to eventually pass through every finite neighborhood on the energy surface, and will spend equal time in equal regions of phase space.

Let $\chi_{\mathcal{R}}(\boldsymbol{\varphi})$ be the characteristic function of a region $\mathcal{R}$:

$$\chi_{\mathcal{R}}(\boldsymbol{\varphi}) = \begin{cases} 1 & \text{if } \boldsymbol{\varphi} \in \mathcal{R} \\ 0 & \text{otherwise,} \end{cases} \tag{3.67}$$

where $H(\boldsymbol{\varphi}) = E$ for all $\boldsymbol{\varphi} \in \mathcal{R}$. Then

$$\big\langle \chi_{\mathcal{R}}(\boldsymbol{\varphi}) \big\rangle_T = \lim_{T\to\infty} \left(\frac{\text{time spent in } \mathcal{R}}{T} \right) \ . \tag{3.68}$$

If the system is ergodic, then

$$\big\langle \chi_{\mathcal{R}}(\boldsymbol{\varphi}) \big\rangle_T = P(\mathcal{R}) = \frac{D_{\mathcal{R}}(E)}{D(E)} \ , \tag{3.69}$$

where $P(\mathcal{R})$ is the *a priori* probability to find $\boldsymbol{\varphi} \in \mathcal{R}$, based solely on the relative volumes of $\mathcal{R}$ and of the entire phase space. The latter is given by

$$D(E) = \int \! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ , \tag{3.70}$$

called the *density of states*, is the surface area of phase space at energy E, and

$$D_{\mathcal{R}}(E) = \int\limits_{\mathcal{R}} \! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ . \tag{3.71}$$

is the density of states for the phase space subset $\mathcal{R}$. Note that

$$D(E) \equiv \int \! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) = \int\limits_{\mathcal{S}_E} \! \frac{dS}{|\boldsymbol{\nabla} H|} \tag{3.72}$$

$$= \frac{d}{dE} \int \! d\mu\, \Theta\big(E - H(\boldsymbol{\varphi})\big) = \frac{d\Omega(E)}{dE} \ . \tag{3.73}$$

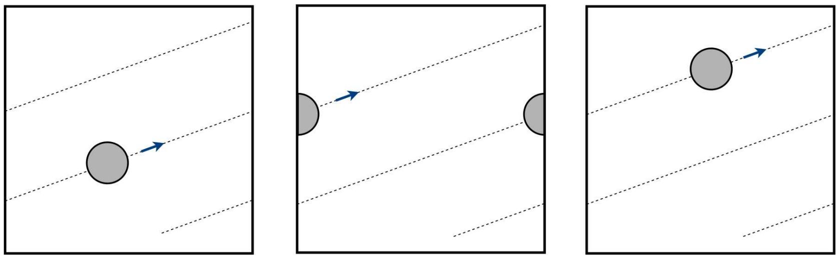

Figure 3.7: Constant phase space velocity at an irrational angle over a toroidal phase space is ergodic, but not mixing. A circle remains a circle, and a blob remains a blob.

Here, dS is the differential surface element, $\mathcal{S}_E$ is the constant H hypersurface $H(\boldsymbol{\varphi}) = E$, and $\Omega(E)$ is the volume of phase space over which $H(\boldsymbol{\varphi}) < E$. Note also that we may write

$$d\mu = dE\, d\Sigma_E \; , \tag{3.74}$$

where

$$d\Sigma_E = \frac{dS}{|\boldsymbol{\nabla} H|}\bigg|_{H(\boldsymbol{\varphi})=E} \tag{3.75}$$

is the the *invariant surface element*.

3.5.2 The microcanonical ensemble

The distribution,

$$\varrho_E(\boldsymbol{\varphi}) = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{D(E)} = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{\int d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big)} \; , \tag{3.76}$$

defines the *microcanonical ensemble* (μCE) of Gibbs.

We could also write

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_S = \frac{1}{D(E)} \int\limits_{\mathcal{S}_E} d\Sigma_E\, f(\boldsymbol{\varphi}) \; , \tag{3.77}$$

integrating over the hypersurface $\mathcal{S}_E$ rather than the entire phase space.

3.5.3 Ergodicity and mixing

Just because a system is ergodic, it doesn't necessarily mean that $\varrho(\varphi, t) \to \varrho^{\text{eq}}(\varphi)$, for consider the following motion on the toroidal space $\big(\boldsymbol{\varphi} = (q,p) \,\big|\, 0 \le q < 1 \; , \; 0 \le p < 1\big\}$, where we identify opposite edges, *i.e.* we impose periodic boundary conditions. We also take q and p to be dimensionless, for simplicity of notation. Let the dynamics be given by

$$\dot{q} = 1 \qquad , \qquad \dot{p} = \alpha \; . \tag{3.78}$$

The solution is

$$q(t) = q_0 + t \qquad , \qquad p(t) = p_0 + \alpha t \; , \tag{3.79}$$

hence the phase curves are given by

$$p = p_0 + \alpha(q - q_0) \; . \tag{3.80}$$

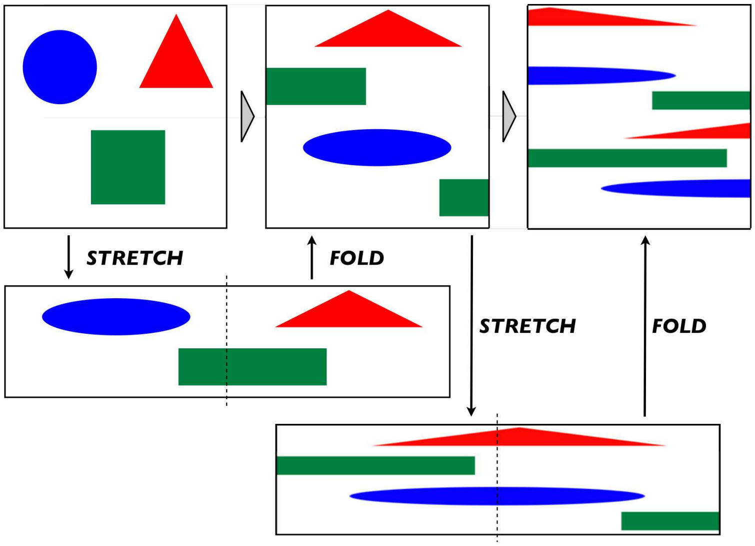

Figure 3.8: The baker's transformation is a successive stretching, cutting, and restacking.

Now consider the average of some function $f(q,p)$. We can write $f(q,p)$ in terms of its Fourier transform,

$$f(q,p) = \sum_{m,n} \hat{f}_{mn}\, e^{2\pi i(mq+np)} \ . \tag{3.81}$$

We have, then,

$$f\big(q(t),p(t)\big) = \sum_{m,n} \hat{f}_{mn}\, e^{2\pi i(mq_0+np_0)}\, e^{2\pi i(m+\alpha n)t} \ . \tag{3.82}$$

We can now perform the time average of f:

$$\begin{aligned} \big\langle f(q,p)\big\rangle_T &= \hat{f}_{00} + \lim_{T\to\infty} \frac{1}{T} \sum_{m,n}{}' \hat{f}_{mn}\, e^{2\pi i(mq_0+np_0)}\, \frac{e^{2\pi i(m+\alpha n)T} - 1}{2\pi i(m+\alpha n)} \\ &= \hat{f}_{00} \quad \text{if } \alpha \text{ irrational.} \end{aligned} \tag{3.83}$$

Clearly,

$$\big\langle f(q,p)\big\rangle_S = \int\limits_0^1 \!dq \int\limits_0^1 \!dp\, f(q,p) = \hat{f}_{00} = \big\langle f(q,p)\big\rangle_T \ , \tag{3.84}$$

so the system is ergodic.

The situation is depicted in fig. 3.7. If we start with the characteristic function of a disc,

$$\varrho(q,p,t=0) = \Theta\big(a^2 - (q-q_0)^2 - (p-p_0)^2\big) \ , \tag{3.85}$$

then it remains the characteristic function of a disc:

$$\varrho(q,p,t) = \Theta\big(a^2 - (q-q_0-t)^2 - (p-p_0-\alpha t)^2\big) \ , \tag{3.86}$$

A stronger condition one could impose is the following. Let A and B be subsets of $\mathcal{S}_E$. Define the *measure*

$$\nu(A) = \int \! d\Sigma_E\, \chi_A(\varphi) \bigg/ \!\! \int \! d\Sigma_E = \frac{D_A(E)}{D(E)} \ , \tag{3.87}$$

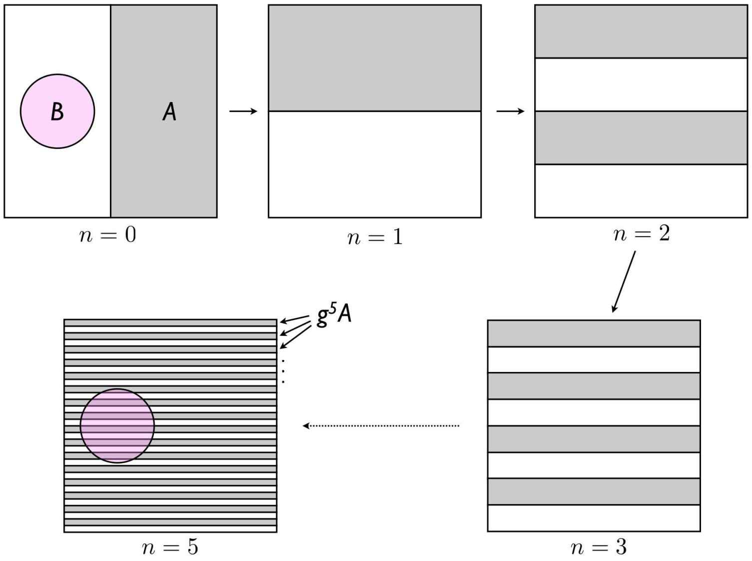

Figure 3.9: The multiply iterated baker's transformation. The set A covers half the phase space and its area is preserved under the map. Initially, the fraction of B covered by A is zero. After many iterations, the fraction of B covered by g^nA approaches $\frac{1}{2}$.

where $\chi_A(\boldsymbol{\varphi})$ is the characteristic function of A. The measure of a set A is the fraction of the energy surface $\mathcal{S}_E$ covered by A. This means $\nu(\mathcal{S}_E) = 1$, since $\mathcal{S}_E$ is the entire phase space at energy E. Now let g be a volume-preserving map on phase space. Given two measurable sets A and B, we say that a system is *mixing* if

$$\text{mixing} \qquad \Longleftrightarrow \qquad \lim_{n\to\infty} \nu\Big(g^n A \cap B\Big) = \nu(A)\,\nu(B)\ . \tag{3.88}$$

In other words, the fraction of B covered by the n^{th} iterate of A, *i.e.* $g^n A$, is, as $n \to \infty$, simply the fraction of $\mathcal{S}_E$ covered by A. The iterated map g^n distorts the region A so severely that it eventually spreads out 'evenly' over the entire energy hypersurface. Of course by 'evenly' we mean 'with respect to any finite length scale', because at the very smallest scales, the phase space density is still locally constant as one evolves with the dynamics.

Mixing means that

$$\begin{aligned}\big\langle f(\boldsymbol{\varphi})\big\rangle &= \int\! d\mu\; \varrho(\boldsymbol{\varphi},t)\, f(\boldsymbol{\varphi}) \\ &\xrightarrow[t\to\infty]{} \int\! d\mu\, f(\boldsymbol{\varphi})\,\delta\big(E - H(\boldsymbol{\varphi})\big) \Big/ \!\int\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \\ &\equiv \mathsf{Tr}\Big[f(\boldsymbol{\varphi})\,\delta\big(E - H(\boldsymbol{\varphi})\big)\Big] \Big/ \,\mathsf{Tr}\Big[\delta\big(E - H(\boldsymbol{\varphi})\big)\Big]\ .\end{aligned} \tag{3.89}$$

Physically, we can imagine regions of phase space being successively stretched and folded. During the stretching process, the volume is preserved, so the successive stretch and fold operations map phase space back onto itself.

An example of a mixing system is the *baker's transformation*, depicted in fig. 3.8. The baker map is defined by

$$g(q,p) = \begin{cases} \big(2q\,,\,\frac{1}{2}p\big) & \text{if} \quad 0 \le q < \frac{1}{2} \\ \\ \big(2q-1\,,\,\frac{1}{2}p + \frac{1}{2}\big) & \text{if} \quad \frac{1}{2} \le q < 1\ . \end{cases} \tag{3.90}$$

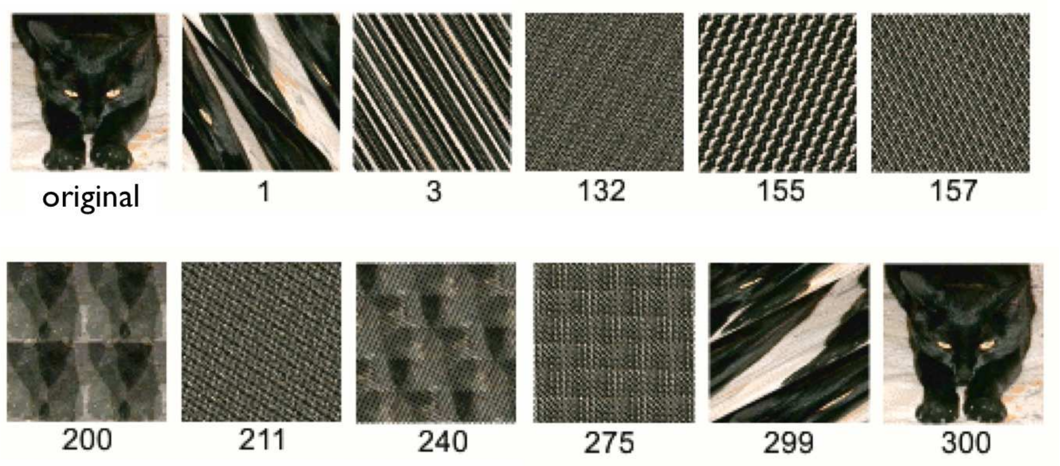

Figure 3.10: The Arnold cat map applied to an image of 150×150 pixels. After 300 iterations, the image repeats itself. (*Source: Wikipedia*)

Note that g is invertible and volume-preserving. The baker's transformation consists of an initial stretch in which q is expanded by a factor of two and p is contracted by a factor of two, which preserves the total volume. The system is then mapped back onto the original area by cutting and restacking, which we can call a 'fold'. The inverse transformation is accomplished by stretching first in the vertical (p) direction and squashing in the horizontal (q) direction, followed by a slicing and restacking. Explicitly,

$$g^{-1}(q,p) = \begin{cases} \big(\frac{1}{2}q\,,\,2p\big) & \text{if} \quad 0 \le p < \frac{1}{2} \\ \\ \big(\frac{1}{2}q + \frac{1}{2}\,,\,2p-1\big) & \text{if} \quad \frac{1}{2} \le p < 1\ . \end{cases} \tag{3.91}$$

Another example of a mixing system is Arnold's 'cat map'[9]

$$g(q,p) = \big(\,[q+p]\,,\,[q+2p]\,\big)\ , \tag{3.92}$$

where $[x]$ denotes the fractional part of x. One can write this in matrix form as

$$\begin{pmatrix} q' \\ p' \end{pmatrix} = \overbrace{\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}}^{M} \begin{pmatrix} q \\ p \end{pmatrix} \ \text{mod}\ \mathbb{Z}^2\ . \tag{3.93}$$

The matrix M is very special because it has integer entries and its determinant is $\det M = 1$. This means that the inverse also has integer entries. The inverse transformation is then

$$\begin{pmatrix} q \\ p \end{pmatrix} = \overbrace{\begin{pmatrix} 2 & -1 \\ -1 & 1 \end{pmatrix}}^{M^{-1}} \begin{pmatrix} q' \\ p' \end{pmatrix} \ \text{mod}\ \mathbb{Z}^2\ . \tag{3.94}$$

Now for something cool. Suppose that our image consists of a set of discrete points located at $(n_1/k\,,\,n_2/k)$, where the denominator $k \in \mathbb{Z}$ is fixed, and where n_1 and n_2 range over the set $\{1,\ldots,k\}$. Clearly g and its inverse

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[9] The cat map gets its name from its initial application, by Arnold, to the image of a cat's face.

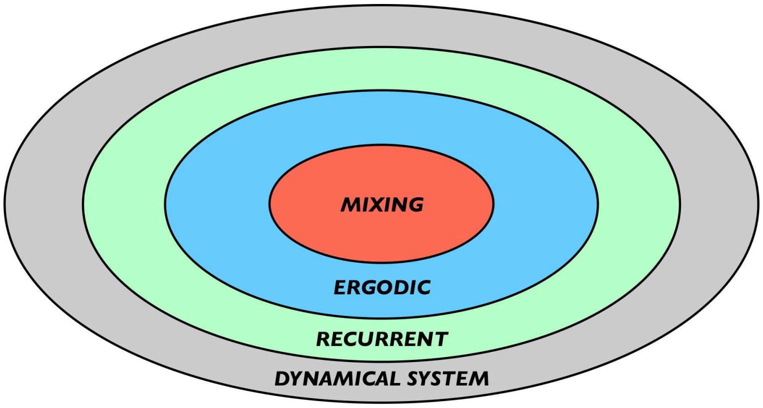

Figure 3.11: The hierarchy of dynamical systems.

preserve this set, since the entries of M and M^{-1} are integers. If there are two possibilities for each pixel (say off and on, or black and white), then there are $2^{(k^2)}$ possible images, and the cat map will map us invertibly from one image to another. Therefore it must exhibit Poincaré recurrence! This phenomenon is demonstrated vividly in fig. 3.10, which shows a $k = 150$ pixel (square) image of a cat subjected to the iterated cat map. The image is stretched and folded with each successive application of the cat map, but after 300 iterations the image is restored! How can this be if the cat map is mixing? The point is that only the discrete set of points $(n_1/k\,,\,n_2/k)$ is periodic. Points with different denominators will exhibit a different periodicity, and points with irrational coordinates will in general never return to their exact initial conditions, although recurrence says they will come arbitrarily close, given enough iterations. The baker's transformation is also different in this respect, since the denominator of the p coordinate is doubled upon each successive iteration.

The student should now contemplate the hierarchy of dynamical systems depicted in fig. 3.11, understanding the characteristic features of each successive refinement[10].

3.6 Thermalization of Quantum Systems

3.6.1 Quantum dephasing

Thermalization of quantum systems is fundamentally different from that of classical systems. Whereas time evolution in classical mechanics is in general a nonlinear dynamical system, the Schrödinger equation for time evolution in quantum mechanics is linear:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \,, \tag{3.95}$$

where $\hat{H}$ is a many-body Hamiltonian. In classical mechanics, the thermal state is constructed by time evolution – this is the content of the ergodic theorem. In quantum mechanics, as we shall see, the thermal distribution must be encoded in the eigenstates themselves.

Let us assume an initial condition at $t = 0$,

$$|\Psi(0)\rangle = \sum_\alpha C_\alpha \,|\Psi_\alpha\rangle \,, \tag{3.96}$$

---

[10] There is something beyond mixing, called a *K-system*. A K-system has positive Kolmogorov-Sinai entropy. For such a system, closed orbits separate exponentially in time, and consequently the Liouvillian L has a Lebesgue spectrum with denumerably infinite multiplicity.

where $\big\{|\,\Psi_\alpha\,\rangle\big\}$ is an orthonormal eigenbasis for $\hat{H}$ satisfying $\hat{H}\,|\Psi_\alpha\rangle = E_\alpha\,|\Psi_\alpha\rangle$Ṫhe expansion coefficients satisfy $C_\alpha = \langle\Psi_\alpha|\Psi(0)\rangle$ and $\sum_\alpha |C_\alpha|^2 = 1$. Normalization requires

$$\langle\,\Psi(0)\,|\,\Psi(0)\,\rangle = \sum_\alpha |C_\alpha|^2 = 1\ . \tag{3.97}$$

The time evolution of $|\Psi\rangle$ is then given by

$$|\Psi(t)\rangle = \sum_\alpha C_\alpha\, e^{-iE_\alpha t/\hbar}\,|\Psi_\alpha\rangle\ . \tag{3.98}$$

The energy is distributed according to the time-independent function

$$P(E) = \langle\,\Psi(t)\,|\,\delta(E-\hat{H})\,|\,\Psi(t)\,\rangle = \sum_\alpha |C_\alpha|^2\,\delta(E-E_\alpha)\ . \tag{3.99}$$

Thus, the average energy is time-independent and is given by

$$\langle E\rangle = \langle\,\Psi(t)\,|\,\hat{H}\,|\,\Psi(t)\,\rangle = \int\limits_{-\infty}^{\infty}\! dE\; P(E)\,E = \sum_\alpha |C_\alpha|^2\,E_\alpha\ . \tag{3.100}$$

The root mean square fluctuations of the energy are given by

$$(\Delta E)_{\rm rms} = \Big\langle\big(E-\langle E\rangle\big)^2\Big\rangle^{1/2} = \sqrt{\sum_\alpha |C_\alpha|^2\,E_\alpha^2 - \Big(\sum_\alpha |C_\alpha|^2\,E_\alpha\Big)^2}\ . \tag{3.101}$$

Typically we assume that the distribution $P(E)$ is narrowly peaked about $\langle E\rangle$, such that $(\Delta E)_{\rm rms} \ll E - E_0$, where E_0 is the ground state energy. Note that $P(E) = 0$ for $E < E_0$, *i.e.* the eigenspectrum of $\hat{H}$ is bounded from below.

Now consider a general quantum observable described by an operator $\mathcal{A}$. We have

$$\langle\mathcal{A}(t)\rangle = \langle\,\Psi(t)\,|\,\mathcal{A}\,|\,\Psi(t)\,\rangle = \sum_{\alpha,\beta} C_\alpha^*\,C_\beta\,e^{i(E_\alpha-E_\beta)t/\hbar}\,\mathcal{A}_{\alpha\beta}\ , \tag{3.102}$$

where $\mathcal{A}_{\alpha\beta} = \langle\Psi_\alpha|\mathcal{A}|\Psi_\beta\rangle$. In the limit of large times, we have

$$\langle\mathcal{A}\rangle_T \equiv \lim_{T\to\infty}\frac{1}{T}\int\limits_0^T\! dt\;\langle\mathcal{A}(t)\rangle = \sum_\alpha |C_\alpha|^2\,\mathcal{A}_{\alpha\alpha}\ . \tag{3.103}$$

Note that this implies that all coherence between different eigenstates is lost in the long time limit, due to *dephasing*.

3.6.2 Eigenstate thermalization hypothesis

The essential ideas behind the *eigenstate thermalization hypothesis* (ETH) were described independently by J. Deutsch (1991) and by M. Srednicki (1994). The argument goes as follows. If the total energy is the only conserved quantity, and if $\mathcal{A}$ is a local, translationally-invariant, few-body operator, then the time average $\langle\mathcal{A}\rangle$ is given by its microcanonical value,

$$\langle\mathcal{A}\rangle_T = \sum_\alpha |C_\alpha|^2\,\mathcal{A}_{\alpha\alpha} = \frac{\sum_\alpha \mathcal{A}_{\alpha\alpha}\,\Theta(E_\alpha\in I)}{\sum_\alpha \Theta(E_\alpha\in I)} \equiv \langle\mathcal{A}\rangle_E\,, \tag{3.104}$$

where $I = \big[E, E + \Delta E\big]$ is an energy interval of width ΔE. So once again, time averages are micro canonical averages.

But how is it that this is the case? The hypothesis of Deutsch and of Srednicki is that thermalization in isolated and bounded quantum systems occurs *at the level of individual eigenstates*. That is, for all eigenstates $|\Psi_\alpha\rangle$ with $E_\alpha \in I$, one has

$$\mathcal{A}_{\alpha\alpha} = \langle \mathcal{A} \rangle_{E_\alpha} \ . \tag{3.105}$$

This means that *thermal information is encoded in each eigenstate*. This is called the *eigenstate thermalization hypothesis* (ETH).

An equivalent version of the ETH is the following scenario. Suppose we have an infinite or extremely large quantum system U (the 'universe') fixed in an eigenstate $|\Psi_\alpha\rangle$. Then form the projection operator $P_\alpha = |\Psi_\alpha\rangle\langle\Psi_\alpha|$. Projection operators satisfy $P^2 = P$ and their eigenspectrum consists of one eigenvalue 1 and the rest of the eigenvalues are zero[11]. Now consider a partition of $U = W \cup S$, where $W \gg S$. We imagine S to be the 'system' and W the 'world'. We can always decompose the state $|\Psi_\alpha\rangle$ in a complete product basis for W and S, *viz.*

$$|\Psi_\alpha\rangle = \sum_{p=1}^{N_W} \sum_{j=1}^{N_S} \mathcal{Q}^\alpha_{pj} \, |\psi^W_p\rangle \otimes |\psi^S_j\rangle \ . \tag{3.106}$$

Here $N_{W/S}$ is the size of the basis for W/S. The *reduced density matrix* for S is defined as

$$\rho_S = \mathop{\mathsf{Tr}}_W P_\alpha = \sum_{j,j'=1}^{N_S} \Bigg(\sum_{p=1}^{N_W} \mathcal{Q}^\alpha_{pj} \, \mathcal{Q}^{\alpha *}_{pj'} \Bigg) \, |\psi^S_j\rangle\langle\psi^S_{j'}| \ . \tag{3.107}$$

The claim is that ρ_S is a *thermal density matrix* on S, *i.e.*

$$\rho_S = \frac{1}{Z_S} \, e^{-\beta \hat{H}_S} \ , \tag{3.108}$$

where $\hat{H}_S$ is the Hamiltonian restricted to S, and $Z_S = \mathsf{Tr}\, e^{-\beta \hat{H}_S}$, so that $\mathsf{Tr}\,\rho_S = 1$ and ρ_S is properly normalized. Here $\beta = 1/k_{\rm B}T$ with T the temperature. The temperature is fixed by the requirement that $\mathsf{Tr}\,(\rho_S \, \hat{H}_S) = E_\alpha \cdot (V_S/V_U)$, where the last factor is a ratio of volumes.

3.6.3 When is the ETH true?

There is no rigorous proof of the ETH. Deutsch showed that the ETH holds for the case of an integrable Hamiltonian weakly perturbed by a single Gaussian random matrix. Horoi *et al.* (1995) showed that nuclear shell model wavefunctions reproduce thermodynamic predictions. Recent numerical work by M. Rigol and collaborators has verified the applicability of the ETH in small interacting boson systems. ETH fails for so-called integrable models, where there are a large number of conserved quantities, which commute with the Hamiltonian. Integrable models are, however, quite special, and as Deutsch showed, integrability is spoiled by weak perturbations, in which case ETH then applies.

Note again that in contrast to the classical case, time evolution of a quantum state does not create the thermal state. Rather, it *reveals* the thermal distribution which is encoded in all eigenstates after sufficient time for dephasing to occur, so that correlations between all the wavefunction expansion coefficients $\{C_\alpha\}$ for $\alpha \neq \alpha'$ are all lost.

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[11] More generally, we could project onto a K-dimensional subspace, in which case there would be K eigenvalues of $+1$ and $N - K$ eigenvalues of 0, where N is the dimension of the entire vector space.

3.7 Appendix I : Formal Solution of the Master Equation

Recall the master equation $\dot{P}_i = -\Gamma_{ij}\, P_j$. The matrix Γ_{ij} is real but not necessarily symmetric. For such a matrix, the left eigenvectors ϕ^α_i and the right eigenvectors ψ^β_j are not the same: general different:

$$\begin{aligned} \phi^\alpha_i\, \Gamma_{ij} &= \lambda_\alpha\, \phi^\alpha_j \\ \Gamma_{ij}\, \psi^\beta_j &= \lambda_\beta\, \psi^\beta_i\ . \end{aligned} \tag{3.109}$$

Note that the eigenvalue equation for the right eigenvectors is $\Gamma\psi = \lambda\psi$ while that for the left eigenvectors is $\Gamma^{\rm t}\phi = \lambda\phi$. The characteristic polynomial is the same in both cases:

$$F(\lambda) \equiv \det\,(\lambda - \Gamma) = \det\,(\lambda - \Gamma^{\rm t})\ , \tag{3.110}$$

which means that the left and right eigenvalues are the same. Note also that $\big[F(\lambda)\big]^* = F(\lambda^*)$, hence the eigenvalues are either real or appear in complex conjugate pairs. Multiplying the eigenvector equation for ϕ^α on the right by ψ^β_j and summing over j, and multiplying the eigenvector equation for ψ^β on the left by ϕ^α_i and summing over i, and subtracting the two results yields

$$\big(\lambda_\alpha - \lambda_\beta\big)\,\big\langle\, \phi^\alpha \,\big|\, \psi^\beta \,\big\rangle = 0\ , \tag{3.111}$$

where the inner product is

$$\big\langle\, \phi \,\big|\, \psi \,\big\rangle = \sum_i \phi_i\, \psi_i\ . \tag{3.112}$$

We can now demand

$$\big\langle\, \phi^\alpha \,\big|\, \psi^\beta \,\big\rangle = \delta_{\alpha\beta}\ , \tag{3.113}$$

in which case we can write

$$\Gamma = \sum_\alpha \lambda_\alpha \,\big|\, \psi^\alpha \,\big\rangle\big\langle\, \phi^\alpha \,\big| \qquad \Longleftrightarrow \qquad \Gamma_{ij} = \sum_\alpha \lambda_\alpha\, \psi^\alpha_i\, \phi^\alpha_j\ . \tag{3.114}$$

We have seen that $\vec{\phi} = (1, 1, \ldots, 1)$ is a left eigenvector with eigenvalue $\lambda = 0$, since $\sum_i \Gamma_{ij} = 0$. We do not know *a priori* the corresponding right eigenvector, which depends on other details of Γ_{ij}. Now let's expand $P_i(t)$ in the right eigenvectors of Γ, writing

$$P_i(t) = \sum_\alpha C_\alpha(t)\, \psi^\alpha_i\ . \tag{3.115}$$

Then

$$\begin{aligned} \frac{dP_i}{dt} &= \sum_\alpha \frac{dC_\alpha}{dt}\, \psi^\alpha_i \\ &= -\Gamma_{ij}\, P_j = -\sum_\alpha C_\alpha\, \Gamma_{ij}\, \psi^\alpha_j \\ &= -\sum_\alpha \lambda_\alpha\, C_\alpha\, \psi^\alpha_i\ . \end{aligned} \tag{3.116}$$

This allows us to write

$$\frac{dC_\alpha}{dt} = -\lambda_\alpha\, C_\alpha \qquad \Longrightarrow \qquad C_\alpha(t) = C_\alpha(0)\, e^{-\lambda_\alpha t}\ . \tag{3.117}$$

Hence, we can write

$$P_i(t) = \sum_\alpha C_\alpha(0)\, e^{-\lambda_\alpha t}\, \psi^\alpha_i\ . \tag{3.118}$$

It is now easy to see that $\mathrm{Re}\,(\lambda_\alpha) \geq 0$ for all λ, or else the probabilities will become negative. For suppose $\mathrm{Re}\,(\lambda_\alpha) < 0$ for some α. Then as $t \to \infty$, the sum in eqn. 3.118 will be dominated by the term for which λ_α has the largest negative real part; all other contributions will be subleading. But we must have $\sum_i \psi_i^\alpha = 0$ since $\big|\,\psi^\alpha\,\big\rangle$ must be orthogonal to the left eigenvector $\vec{\phi}^{\alpha=0} = (1,1,\ldots,1)$. Therefore, at least one component of ψ_i^α (*i.e.* for some value of i) must have a negative real part, which means a negative probability![12] As we have already proven that an initial nonnegative distribution $\{P_i(t=0)\}$ will remain nonnegative under the evolution of the master equation, we conclude that $P_i(t) \to P_i^{\mathrm{eq}}$ as $t \to \infty$, relaxing to the $\lambda = 0$ right eigenvector, with $\mathrm{Re}\,(\lambda_\alpha) \geq 0$ for all α.

3.8 Appendix II : Radioactive Decay

Consider a group of atoms, some of which are in an excited state which can undergo nuclear decay. Let $P_n(t)$ be the probability that n atoms are excited at some time t. We then model the decay dynamics by

$$W_{mn} = \begin{cases} 0 & \text{if } m \geq n \\ n\gamma & \text{if } m = n-1 \\ 0 & \text{if } m < n-1\ . \end{cases} \tag{3.119}$$

Here, γ is the decay rate of an individual atom, which can be determined from quantum mechanics. The master equation then tells us

$$\frac{dP_n}{dt} = (n+1)\,\gamma\, P_{n+1} - n\,\gamma\, P_n\ . \tag{3.120}$$

The interpretation here is as follows: let $\big|\,n\,\big\rangle$ denote a state in which n atoms are excited. Then $P_n(t) = \big|\langle\,\psi(t)\,|\,n\,\rangle\big|^2$. Then $P_n(t)$ will increase due to spontaneous transitions from $|\,n{+}1\,\rangle$ to $|\,n\,\rangle$, and will decrease due to spontaneous transitions from $|\,n\,\rangle$ to $|\,n{-}1\,\rangle$.

The average number of particles in the system is

$$N(t) = \sum_{n=0}^{\infty} n\,P_n(t)\ . \tag{3.121}$$

Note that

$$\begin{aligned} \frac{dN}{dt} &= \sum_{n=0}^{\infty} n\Big[(n+1)\,\gamma\,P_{n+1} - n\,\gamma\,P_n\Big] \\ &= \gamma \sum_{n=0}^{\infty} \Big[n(n-1)\,P_n - n^2 P_n\Big] \\ &= -\gamma \sum_{n=0}^{\infty} n\,P_n = -\gamma\,N\ . \end{aligned} \tag{3.122}$$

Thus,

$$N(t) = N(0)\,e^{-\gamma t}\ . \tag{3.123}$$

The relaxation time is $\tau = \gamma^{-1}$, and the equilibrium distribution is

$$P_n^{\mathrm{eq}} = \delta_{n,0}\ . \tag{3.124}$$

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[12] Since the probability $P_i(t)$ is real, if the eigenvalue with the smallest (*i.e.* largest negative) real part is complex, there will be a corresponding complex conjugate eigenvalue, and summing over all eigenvectors will result in a real value for $P_i(t)$.

Note that this satisfies detailed balance.

We can go a bit farther here. Let us define

$$P(z,t) \equiv \sum_{n=0}^{\infty} z^n \, P_n(t) \; . \tag{3.125}$$

This is sometimes called a *generating function*. Then

$$\begin{aligned} \frac{\partial P}{\partial t} &= \gamma \sum_{n=0}^{\infty} z^n \Big[(n+1) \, P_{n+1} - n \, P_n \Big] \\ &= \gamma \, \frac{\partial P}{\partial z} - \gamma z \, \frac{\partial P}{\partial z} \; . \end{aligned} \tag{3.126}$$

Thus,

$$\frac{1}{\gamma} \, \frac{\partial P}{\partial t} - (1-z) \, \frac{\partial P}{\partial z} = 0 \; . \tag{3.127}$$

We now see that any function $f(\xi)$ satisfies the above equation, where $\xi = \gamma t - \ln(1-z)$. Thus, we can write

$$P(z,t) = f\big(\gamma t - \ln(1-z)\big) \; . \tag{3.128}$$

Setting $t=0$ we have $P(z,0) = f\big(-\ln(1-z)\big)$, and inverting this result we obtain $f(u) = P(1-e^{-u},0)$, *i.e.*

$$P(z,t) = P\big(1 + (z-1) \, e^{-\gamma t} \, , \, 0\big) \; . \tag{3.129}$$

The total probability is $P(z\!=\!1,t) = \sum_{n=0}^{\infty} P_n$, which clearly is conserved: $P(1,t) = P(1,0)$. The average particle number is

$$N(t) = \sum_{n=0}^{\infty} n \, P_n(t) = \frac{\partial P}{\partial z}\bigg|_{z=1} = \, e^{-\gamma t} \, P(1,0) = N(0) \, e^{-\gamma t} \; . \tag{3.130}$$

3.9 Appendix III : Canonical Transformations in Hamiltonian Mechanics

The Euler-Lagrange equations of motion of classical mechanics are invariant under a redefinition of generalized coordinates,

$$Q_\sigma = Q_\sigma(q_1, \ldots, q_r, t) \; , \tag{3.131}$$

called a *point transformation*. That is, if we express the new Lagrangian in terms of the new coordinates and their time derivatives, *viz.*

$$\tilde{L}\big(Q, \dot{Q}, t\big) = L\big(q(Q,t) \, , \, \dot{q}(Q,\dot{Q},t) \, , \, t\big) \; , \tag{3.132}$$

then the equations of motion remain of the form

$$\frac{\partial \tilde{L}}{\partial Q_\sigma} = \frac{d}{dt}\bigg(\frac{\partial \tilde{L}}{\partial \dot{Q}_\sigma}\bigg) \; . \tag{3.133}$$

Hamilton's equations[13],

$$\dot{q}_\sigma = \frac{\partial H}{\partial p_\sigma} \qquad , \qquad \dot{p}_\sigma = -\frac{\partial H}{\partial q_\sigma} \tag{3.134}$$

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[13] We revert to using H for the Hamiltonian in this section, rather than $\hat{H}$ as before.

are invariant under a much broader class of transformations which mix all the $q's$ and $p's$, called *canonical transformations*. The general form for a canonical transformation is

$$q_\sigma = q_\sigma\big(Q_1\,,\,\ldots\,,\,Q_r\,,\,P_1\,,\,\ldots\,,\,P_r\,,\,t\big) \tag{3.135}$$

$$p_\sigma = p_\sigma\big(Q_1\,,\,\ldots\,,\,Q_r\,,\,P_1\,,\,\ldots\,,\,P_r\,,\,t\big)\ , \tag{3.136}$$

with $\sigma \in \{1, \ldots, r\}$. We may also write

$$\xi_i = \xi_i\big(\Xi_1\,,\,\ldots\,,\,\Xi_{2r}\,,\,t\big)\ , \tag{3.137}$$

with $i \in \{1, \ldots, 2r\}$. Here we have

$$\xi_i = \begin{cases} q_i & \text{if } 1 \le i \le r \\ p_{i-r} & \text{if } n \le i \le 2r \end{cases} \quad , \quad \Xi_i = \begin{cases} Q_i & \text{if } 1 \le i \le r \\ P_{i-r} & \text{if } r \le i \le 2r\ . \end{cases} \tag{3.138}$$

The transformed Hamiltonian is $\tilde{H}(Q, P, t)$.

What sorts of transformations are allowed? Well, if Hamilton's equations are to remain invariant, then

$$\dot{Q}_\sigma = \frac{\partial \tilde{H}}{\partial P_\sigma} \quad , \quad \dot{P}_\sigma = -\frac{\partial \tilde{H}}{\partial Q_\sigma}\ , \tag{3.139}$$

which gives

$$\frac{\partial \dot{Q}_\sigma}{\partial Q_\sigma} + \frac{\partial \dot{P}_\sigma}{\partial P_\sigma} = 0 = \frac{\partial \dot{\Xi}_i}{\partial \Xi_i}\ . \tag{3.140}$$

I.e. the flow remains incompressible in the new (Q, P) variables. We will also require that phase space volumes are preserved by the transformation, *i.e.*

$$\det\!\left(\frac{\partial \Xi_i}{\partial \xi_j}\right) = \left|\left|\frac{\partial(Q, P)}{\partial(q, p)}\right|\right| = 1\ . \tag{3.141}$$

This last condition guarantees the invariance of the phase space measure

$$d\mu = h^{-r} \prod_{\sigma=1}^{r} dq_\sigma\, dp_\sigma\ , \tag{3.142}$$

where h in the normalization prefactor is Planck's constant.