Notes for Lecture 5

Some general considerations of many particle system

Here, we will explore some general properties of a many particle system. The central topic is the irreversibility – how do we really understand the arrow of time? As we already insinuated in the last lecture, this is intimately connected to a large number. We will cover some general topics related to this, including very recent results.

5.1 Phase space

Consider a problem involving N particles. We have $3N$ variables arising from $3N$ degrees of freedom in the real space. We can write them as q_α, $\alpha = 1, ..., 3N$, a set of **generalized coordinates**. For each q_α, its **canonical conjugate momentum** p_α is given by

$$p_\alpha \equiv \frac{\partial L}{\partial \dot{q}_\alpha} \qquad L = \text{Lagrangian}. \tag{5.1}$$

The space defined by $6N$ variables, $\{q_\alpha, p_\alpha\}$, is defined as the **phase space**.

5.2 Microstate, macrostate

The states we have been referring to in lectures 1 and 2 are so-called **macrostates**, those states that can be specified by a small number of thermodynamic variables (such as T, P, N).

In contrast, **microstates** refer to those states, whose microscopic degrees of freedom are described completely.

1. In classical mechanics, a microstate corresponds to a point in the phase space.
2. In quantum mechanics, a microstate corresponds to a many body wave function.

Is there any relationship between a microstate in classical mechanics and a microstate in quantum mechanics? An important class of microstates are energy eigenstates. In the semi-classical picture of quantum mechanics, we recall that, for a bound[1] one dimensional motion, the following **Bohr-Sommerfeld quantization rule** holds for an energy eigenstate:

$$\oint dq\, p = (n+\gamma)\, h \qquad\qquad n = 0, 1, 2, \ldots \tag{5.2}$$

where γ is a constant (e.g., 1/2) that depends on the shape of the potential. We can define $S_n \equiv \oint pdq$ where S_n is the area in the two dimensional (p, q) plane. It follows that $\Delta S_n = h$. Namely, the adjacent semi-classical orbits differ in area by h. So, each orbit in the phase space *owns* an area/action quantum, which is given by h.

The above Bohr-Sommerfeld result can be re-interpreted as follows. The above result is not surprising, since we know that there must be a minimum indivisible area in the two dimensional phase space (p, q) due to the Heisenberg uncertainty principle $\Delta p \Delta q \geq \hbar/2$. So, it was to be expected that the quantum of the above action integral in the two dimensional phase space is on the order of $\hbar$. What Bohr-Sommerfeld quantization condition does is to give that area quantum, or that action quantum, precisely. Then, it is clear what to do in the general case of $6N$ dimensional phase space. As each pair of canonically conjugate variables give rise to a factor of h, we conclude the following.

Phase space volume quantum

Each quantum microstate, an energy eigenstate, corresponds, in the classical limit, to a hyper-volume of h^{3N} in the $6N$ dimensional phase space for N particles. This unit hyper-volume, h^{3N}, is defined as the **phase space volume quantum**.

In this very useful view, a quantum microstate can be considered as a fuzzy classical microstate. It should be kept in mind that a real quantum state generally

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[1] You might worry that this is a severe restriction, since not all motions are bound motions. For instance, a free particle experiences an unbound motion. However, such a motion can still be regarded as a bound motion, if the volume of the system is considered finite. This is especially helpful in statistical mechanics, where V is treated as a finite parameter, at least initially, for virtually any problem.

extends to everywhere in the phase space. Nevertheless the volume covered by the quantum state corresponds to a finite volume, due to $\Delta p \Delta q \sim \hbar$. While this argument is only semi-classical, it must be noted that the action quantum predicted by the Bohr-Sommerfeld rule is generally valid even in the quantum regime, making the above argument much more general.

5.3 Importance of semi-classical mechanics

The pure classical mechanics is not adequate in statistical physics. There are two main reasons. First, as we just saw, the volume quantum in phase space makes it possible to define the number of states. Counting the number of states is essential in statistical physics, since it is related to the entropy. Second, an equilibrium state cannot be brought about if there is no inter-molecular interaction. Such an interaction is crucially responsible for the thermodynamics of the classical ideal gas. Such an interaction is manifestly quantum mechanical, not classical mechanical! In particular, when molecules interact, they act as identical particles, as they should.

Indeed, if we simply follow the naive classical mechanics ideas alone, then we quickly discover that the entropy function is *not* extensive, the entropy of mixing is incorrectly predicted, and the entropy function is not defined uniquely. How the above considerations, the phase space volume quantum and the identical particle nature, fix these problems and give the correct classical mechanical entropy is a well-known story, explained, e.g., in Section T1.5. For this reason, the standard "Sackur-Tetrode" equation for the entropy of the classical ideal gas – Eq. T1.5.1a – has h in its expression, and it treats all molecules as identical particles!

Thus, there is really no such thing as classical statistical mechanics. **There is only semi-classical statistical mechanics.**

In a way, it is something of good news that we recognize that semi-classical mechanics, not classical mechanics, is what we must consider. What this means is that even when we seem to be dealing with pure classical mechanics, we are, in fact, not. We have in mind semi-classical mechanics where each state corresponds to a phase space volume quantum. Because of this, what we learn in classical mechanical thinking may be helpful even in the quantum regime. Of course, there are quantum effects that are completely out of reach of semi-classical picture, and they can be brought to light only by the proper quantum mechanical treatment.

With this much introduction, we will consider mostly classical mechanical problems in this lecture, with the understanding that all notions that we discuss are (1) easily generalizable to the quantum regime (as will be pointed out, as we go along), and (2) also very important in the quantum regime.

5.4 Ensemble

How is it that we are quite unaware of, or sometimes quite unconcerned with, the details of microstates for such a problem such as, e.g. chemical reactions or the cosmic soup of particles after the Big Bang, but we can apparently make meaningful statements about macrostates described by only a small number of macroscopic parameters?

The answer lies in the fact that experimentally we are apparently able to establish the laws of thermodynamics, without ever being bogged down by the worries about the microstates, and how they could be different from a macroscopic sample to another.

Therefore, it follows then that what we call a "macrostate" is necessarily a common property of all microstates sharing macroscopic thermodynamic variables. A *macrostate* is the characterization of the system only in terms of macroscopic variables such as volume, pressure, energy, entropy, etc. Thus, in general many microstates correspond to one macrostate. Such a set of microstates is called an **ensemble**. More specifically, we call it a thermodynamic ensemble, or a statistical ensemble. In subsequent lectures, we shall encounter important classes of ensembles, e.g. *microcanonical ensemble, canonical ensemble, and grand canonical ensemble.* Even if we will learn what these are only later on, it would not hurt to know these names already, since they are *so* important.

Note that the concept of ensemble is the expression of a certain type of "symmetry." It is based on the fact[2] that experiments work reproducibly when materials are prepared under the same macroscopic conditions without any intent (or capability!) of controlling all parameters of the actual microstate.

Theoretically, any closed system may be characterized by a microstate. When a system is modeled as one *microstate*, we call such a state a **pure state**. When a system is modeled as a collection of many *microstates*, we call such a state a **mixed state**. A mixed state is an ensemble, and vice versa[3].

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[2] Of course, we cannot repeat experiments for cosmological phenomena, since we have to just accept what the Universe gives us. However, the point is that we establish physical laws by reproducible well-controlled experiments, mostly here on Earth or near Earth. If these physical laws are found to explain vast amounts of data collected from different corners of the Universe, then we have good reasons to believe that our physical laws are general enough, no matter how quite miraculous this may seem sometimes!

[3] So, we will be concerned with mixed states only in this course. Generally, a pure state is of

In describing classical statistical mechanics, the phase space is a convenient place to start. It is the space where the coordinates are (q_α, p_α) where $\alpha = 1, ..., 3N$. We will often denote V_i as the phase space volume for a fixed particle index $i = 1, ..., N$. That is

$$dV_i \;\equiv\; d^3\vec{q}_i\, d^3\vec{p}_i \tag{5.3}$$

and the total infinitesimal volume ($d\Gamma$) of the phase space is given by

$$d\Gamma \;=\; \prod_i dV_i \tag{5.4}$$

Also, in this note, $\vec{\mathbf{q}} \equiv (q_1, ..., q_{3N})$ and $\vec{\mathbf{p}} \equiv (p_1, ..., p_{3N})$.

Suppose that we consider a total of $\mathcal{N}$ points in the phase space. $\mathcal{N}$ defines the size of our ensemble, and corresponds to the number of microstates. Suppose that, corresponding to $d\Gamma$, there are $d\mathcal{N}$ points. We can form a **probability density function** $\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ as

$$\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)\, d\Gamma \;=\; \frac{d\mathcal{N}(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)}{\mathcal{N}} \tag{5.5}$$

Given this probability density function, the **ensemble average** of any dynamical variable $O(\vec{\mathbf{p}}, \vec{\mathbf{q}})$ is given by

$$\langle O \rangle \equiv \int d\Gamma\, \rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)\, O(\vec{\mathbf{p}}, \vec{\mathbf{q}}) \tag{5.6}$$

Note that $\int d\Gamma\, \rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t) = 1$, as required for a properly normalized PDF. Physically, it is essential to note that, here in this lecture note, **we are dealing with quite general states, not just equilibrium states**. The explicit time dependence in $\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ is kept for this reason.

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limited use in statistical physics. For example, the standard entropy – von Neumann entropy – is zero for any pure state, and the temperature cannot be defined for such a state. However, one can argue that the use of a pure state is at least a possible thing to do, or even the most natural thing to do, for a closed system. In this respect, it is interesting to note that there is a novel suggestion – a single eigenstate thermalization hypothesis – exists, proposed by none other than J. Deutsch. In that case, a single eigenstate describes both the system and the reservoir, and some aspects of the time evolution of such a state can be interpreted as heat exchange between the system and the reservoir.

5.5 Hamiltonian and Poisson bracket

Let us recall that the *canonical equation of motion* is given by

$$\begin{aligned} \frac{\partial H}{\partial p_\alpha} &= \dot{q}_\alpha \\ \frac{\partial H}{\partial q_\alpha} &= -\dot{p}_\alpha \\ \frac{dH}{dt} &= \frac{\partial H}{\partial t} \end{aligned} \tag{5.7}$$

where $H(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ is the so-called **Hamiltonian** function, defined as $\vec{\mathbf{p}} \cdot \dot{\vec{\mathbf{q}}} - L(\vec{\mathbf{q}}, \dot{\vec{\mathbf{q}}}, t)$, where L is the Lagrangian and $\vec{\mathbf{p}} \equiv \frac{\partial L}{\partial \dot{\vec{\mathbf{q}}}}$. It is equivalent to the Newtonian laws of motion.

This equation of motion can be derived from the Lagrangian equation of motion. However, in this course, it is quite essential to be familiar with this canonical equation of motion. Note also that in this course we will rarely consider the case when H is explicitly time dependent. However, note that certain properties (e.g., Liouville's theorem; see below) are valid even if H is explicitly time-dependent. When H is not explicitly time dependent, then H is a conserved quantity, as the last of the three equations above shows.

The Poisson bracket of two general functions $g(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ and $h(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$ is defined as

$$\{g, h\} = \sum_\alpha \left(\frac{\partial g}{\partial q_\alpha} \frac{\partial h}{\partial p_\alpha} - \frac{\partial g}{\partial p_\alpha} \frac{\partial h}{\partial q_\alpha} \right) \tag{5.8}$$

The following properties directly follow from the above definition and the canonical equations of motion (Eq. 5.7).

$$\{g, h\} = -\{h, g\} \tag{5.9}$$

$$\{g, g\} = 0 \tag{5.10}$$

$$\{g, G(g)\} = 0 \qquad G(g) \text{ is any function of } g. \tag{5.11}$$

$$\{q_\alpha, p_\beta\} = \delta_{\alpha,\beta} \tag{5.12}$$

$$\frac{dg}{dt} = \{g, H\} + \frac{\partial g}{\partial t} \qquad H \text{ is the Hamiltonian.} \tag{5.13}$$

Note that if we change $\{g, h\} \to -\frac{i}{\hbar}[g, h]$, then all of these properties are translated to those identities that are well-known for the *quantum mechanical* commutator $[g, h]$ *if* g, h were quantum mechanical operators.

5.6 Liouville's theorem

According to the canonical equation of motion written in the previous section, the time evolution in classical mechanics can be viewed as a mapping of a point $(\vec{\mathbf{p}}(t), \vec{\mathbf{q}}(t))$ to another point $(\vec{\mathbf{p}}(t+dt), \vec{\mathbf{q}}(t+dt))$, since $\vec{\mathbf{p}}(t+dt) \approx \vec{\mathbf{p}}(t) + dt\,\dot{\vec{\mathbf{p}}}$ and $\vec{\mathbf{q}}(t+dt) \approx \vec{\mathbf{q}}(t) + dt\,\dot{\vec{\mathbf{q}}}$ and since $\dot{\vec{\mathbf{p}}}$ and $\dot{\vec{\mathbf{q}}}$ are given by the canonical equation of motion.

Now, consider an arbitrary volume Γ in phase space whose points evolve in time as so. Liouville's theorem says that Γ may deform but its volume cannot change. One can also interpret this result as follows. Consider the volume as consisting of a certain number of points, each of which occupies a small identical phase space volume element $\Delta\Gamma$ (like the phase space volume quantum!). So, we can consider the flow of phase space volume as the flow of $\Gamma/\Delta\Gamma$ "particles" where each small volume element is christened as a particle. As the volume is invariant, **this "fluid" acts as an incompressible fluid**.

While there are many proofs of this theorem[4], the following proof is the best in my opinion.

Consider the movement of the phase space volume as the motion of a fluid. By the continuity, we know that the density of the fluid must satisfy

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \left(\rho \vec{\mathcal{V}}\right) = 0 \tag{5.14}$$

Here, $\vec{\mathcal{R}} \equiv (q_1, ..., q_{3N}, p_1, ..., p_{3N})$ and $\vec{\mathcal{V}} \equiv \frac{d\vec{\mathcal{R}}}{dt}$. The above continuity equation is the consequence of observing that $\rho\vec{\mathcal{V}}$ is the current density of the fluid in the phase space. It is easily derived by considering the flow of particles in and out of a small fixed volume, without any sink or source for the particles.

We can expand the above equation as $\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} + \rho \frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = 0$. Now, note that the third term on the left side is zero, since $\frac{\partial}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = \sum_\alpha \left(\frac{\partial \dot{q_\alpha}}{\partial q_\alpha} + \frac{\partial \dot{p_\alpha}}{\partial p_\alpha} \right)$ and $\frac{\partial \dot{q_\alpha}}{\partial q_\alpha} = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha} = -\frac{\partial \dot{p_\alpha}}{\partial p_\alpha}$ from the canonical equation (Eq. 5.7). Thus what we get is $\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial \vec{\mathcal{R}}} \cdot \vec{\mathcal{V}} = 0$, which just means that $\frac{d\rho}{dt} = 0$, since $\rho = \rho(\vec{\mathcal{R}}, t)$. This means that the density of the fluid remains constant, proving the Liouville's theorem. Here are four different ways that

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[4] They can be found in standard texts such as Landau, Goldstein, Marion-and-Thornton, etc.

the Liouville's theorem can be stated.

$$\begin{aligned} \frac{d\rho}{dt} &= 0 && (5.15) \\ \frac{\partial\rho}{\partial t} + \sum_\alpha \dot{q}_\alpha \frac{\partial\rho}{\partial q_\alpha} + \sum_\alpha \dot{p}_\alpha \frac{\partial\rho}{\partial p_\alpha} &= 0 && (5.16) \\ \frac{\partial\rho}{\partial t} + \{\rho, H\} &= 0 && (5.17) \\ d\Gamma(t) \equiv \prod_\alpha dq_\alpha(t) dp_\alpha(t) &= d\Gamma(0) \equiv \prod_\alpha dq_\alpha(t=0) dp_\alpha(t=0) && (5.18) \end{aligned}$$

The first two equations mean that the total time derivative of $\rho = \rho(\vec{\mathbf{q}}, \vec{\mathbf{p}}, t)$ is zero. The third equation has the same content as the second, and is the consequence of the first equation upon applying Eq. 5.13. Due to the conceptual advantage of the Poisson bracket, the third equation should be viewed as a better form of the second equation, while content-wise they are completely identical. The fourth equation also means the same thing as the other three. As we follow the fluid in a small volume element $d\Gamma$ containing our "particles" of interest, this volume element can deform in shape but its volume must be conserved, since the density of particles does not change.

Keep in mind that in this fluid analogy, the "particle" is actually a small volume of microstates of the real system. It should never be confused with a real particle, such as a gas molecule.

5.7 Poincaré recurrence

For a Hamiltonian system, one can prove that any bound motion is "almost periodic." Below, we will state what this means in classical mechanics and quantum mechanics, and prove this statement, which goes by the name of Poincaré recurrence theorem.

Historically, this theorem was used against the Boltzmann argument for the irreversibility. However, in fact, this theorem must be viewed as supporting Boltzmann's argument or the general inevitability of the emergence of the irreversibility, if anything.

This consideration actually sheds light on how an irreversibility can come into play, as we start from perfectly reversible problem. In the following, we assume a Hamiltonian that is time-invariant and time-reversal-invariant. That is, the Hamiltonian is not explicitly time dependent, and $H(\vec{q}, \vec{p}) = H(\vec{q}, -\vec{p})$.

5.7.1 Poincaré recurrence in classical mechanics

Consider a bound motion. Here, by bound motion, we mean a motion bound both in $\vec{p}$ and in $\vec{x}$. Besides, we do not place any restriction on the degrees of freedom – and so the motion can involve any many particles as it is realistic to do so. Poincaré recurrence theorem states that after sufficient time, the system comes back to the original point, or infinitesimally close to it, in phase space.

Proof ✎ Let us suppose that this is not true. Then, there must be a point, z_0, in phase space that never returns however long a time passes. Here, a point in phase space $z \equiv \{\vec{q}_1, \vec{q}_2, ..., \vec{q}_N, \vec{p}_1, ..., \vec{p}_N\}$, where N is the number of particles involved. Assume that $z(t=0) \equiv z_0$. Since we assumed that z_0 is never reached thereafter, it follows that after an arbitrary finite time τ, z_τ must be at a finite distance away from z_0. Furthermore, it must be possible to enclose a finite volume v_0 around z_0 such that the trajectory will never cross its interior for any $t \geq \tau$. Note that, by definition, v_0 cannot enclose the point z_τ.

Now, let us consider the volume v_0 as an initial phase space volume at $t = 0$. At time τ, this volume will have mapped to another volume v_τ. Now, consider the total volume V_0 that is covered by the time evolution of the initial volume v_0 at $t=0$. I.e., V_0 is the total volume that is swept by all the phase space trajectories as $t \to \infty$ starting from all the points of the volume v_0 as separate initial conditions. Similarly, we consider the total volume V_τ that is covered by the time evolution of the phase space volume v_τ at $t=\tau$. Note that V_τ and V_0 are both finite, due to our assumption of the boundedness of the system. Furthermore, since v_τ is the time evolution of v_0, we have $V_0 \supset V_\tau$, when these volumes are considered as subsets of the phase space. An important point to keep in mind is that V_τ cannot include the set v_0, by our first assumption in this proof, while V_0 does include the set v_0, by definition.

Next, we in turn treat the volume V_0 as a set of initial conditions, and consider its time evolution. Moreover, at any time, the set of evolved points cannot contain points that are not already contained in V_0. This is clear, since if any such spurious point existed, then that point is clearly a time-evolution of a point from V_0. By the time-invariance of the Hamiltonian, one can see that such a point can be considered as a result of time-evolution of a point from v_0. That is, it must belong in V_0 by definition. In addition, by Liouville theorem, at any time of the evolution, the volume must be equal to the initial volume. To satisfy these two conditions, we see that as a function of time, V_0 is ''almost invariant'' -- at any given time, the set of points evolved from the set V_0 can be different from from V_0 by a set of points of measure zero, at the most. The same argument holds for V_τ as well.

Now, consider evolving V_τ backwards to time 0. Such a backward evolution must cover the set v_0, by definition. By the time-reversal invariance, we also know that V_τ must be almost invariant upon this backward evolution as well. The only way that V_τ remains almost invariant and include v_0 is that $V_\tau = V_0$ up to a set of measure zero. But this leads to a contradiction. V_τ cannot contain v_0! QED. ✎

5.7.2 Poincaré recurrence in quantum mechanics

In the quantum mechanical version, the recurrence theorem can be stated as follows. While we are not doing the quantum statistical mechanics just yet, the following consideration turns out to be important when one considers the physics of the Poincaré recurrence in a *classical* system as well. So, we spend some time to prove the following theorem.

As above, consider a time-invariant Hamiltonian system. The wave function of the system for a bound motion can be made as close to the initial wave function as any precision required at a later time. In other words, for any $\epsilon > 0$, it is possible to find T_ϵ such that

$$|\Psi(t+T_\epsilon) - \Psi(t)| < \epsilon \tag{5.19}$$

where Ψ is the normalized wave function of the system. This is the quantum mechanical definition of an "almost periodic" state.

Proof ✎ The normalized wave function of the system can be written as

$$|\Psi(t)\rangle = \sum_{j=0}^{\infty} C_j \exp(-iE_j t/\hbar)\,|\psi_j\rangle \tag{5.20}$$

where $|\psi_i\rangle$ is the i-th eigenstate of H. That we have a discrete sum here is due to the assumption of a bound state. These eigenstates form an ortho-normal set of states.

First, note that

$$\begin{aligned}
|\Psi(t+T_\epsilon) - \Psi(t)\rangle &= -2i\sum_{j=0}^{\infty} C_j e^{-iE_j(t+T_\epsilon/2)/\hbar} \sin\left[E_j T_\epsilon/(2\hbar)\right]|\psi_j\rangle \\
|\Psi(t+T_\epsilon) - \Psi(t)|^2 &= 4\sum_{j=0}^{\infty} |C_j|^2 \sin^2\left[E_j T_\epsilon/(2\hbar)\right]
\end{aligned}$$

As this infinite sum converges (the difference of two finite vectors is finite), it follows that we can truncate the sum to include the sum only up to a large integer $j = N_\epsilon$ so that the truncation error for the sum is less than $\epsilon^2/2$. Then, the proof would be complete if we showed that

$$4\sum_{j=0}^{N_\epsilon - 1} |C_j|^2 \sin^2\left[E_j T_\epsilon/(2\hbar)\right] < \epsilon^2/2 \tag{5.21}$$

with a suitable choice of T_ϵ.
Consider adding two periodic functions, characterized by periods T_1 and T_2 respectively. The question is whether the sum of the two periodic functions is also periodic. Clearly, if the two periods are commensurate, $T_1 N_1 = T_2 N_2$ (for some positive integers N_1 and N_2), then the sum is periodic with $N_1 T_1 = N_2 T_2$ as the new period. However, even if T_1 and T_2 are incommensurate, we can approximate the ratio T_1/T_2 as a rational number to any precision required. This fact can be repeatedly used when more than 2, but finite, periods are involved. Thus, one can find a very large period $T_\epsilon \approx N_j T_j = N_j 2\pi\hbar/E_j$ for any $j = 0, \ldots, N_\epsilon - 1$ to any required precision.
So, we have $E_j T_\epsilon/\hbar = 2\pi N_j + \delta_j$ where N_j is an integer and δ_j is some prescribed small real number, for any $j = 0, \ldots, N_\epsilon - 1$. The smaller δ_j we require, the larger T_ϵ we must choose, and subsequently the larger N_j we will get. Since we can meet this requirement for any precision for δ_j, we can require

$$|\delta_j| < \frac{\epsilon}{\sqrt{2}} \tag{5.22}$$

for any $j = 0, \ldots, N_\epsilon - 1$.
Then, $4|C_j|^2 \sin^2\left[E_j T_\epsilon/(2\hbar)\right] = 4|C_j|^2 \sin^2\left[\pi N_j + \delta_j/2\right] = 4|C_j|^2 \sin^2(\delta_j/2) \le |C_j|^2 \delta_j^2 < |C_j|^2 \epsilon^2/2$. By summing over j, while noting that $\sum_{j=0}^{N_\epsilon} |C_j|^2 \le \sum_{j=0}^{\infty} |C_j|^2 = 1$, we can see that Eq. 5.21 is satisfied by our choice of T_ϵ. QED. ✎

5.7.3 Poincaré cycle

At first, the Poincaré recurrence theorem, as proved above, may sound like it precludes the emergence of the irreversibility. Indeed, this theorem was used to disqualify the work by Boltzmann, whose theory as we shall discuss below strictly respects the irreversibility.

The funny thing is that the Poincaré recurrence theorem can be proven rigorously as shown above, while Boltzmann's theory cannot be proven rigorously. Nevertheless, Boltzmann's theory is still living and the Poincaré recurrence argument that was used to attack Boltzmann is long disqualified. Mindless math does not necessarily shed light on physics.

So, one should imbue some life to the above math with some physical consideration. If we do so, we come to deal with the matter of the magnitude of the recurrence time scale. The period of the motion that is (nearly) periodic in the Poincaré recurrence theorem is called the *Poincaré cycle*.

What is the typical value of the Poincaré cycle? It is very large! It is one of those unfathomably large numbers. The point is that it is so large, exponentially larger than the age of the Universe, that it actually supports the emergence of the irreversibility, if anything.

How would one go about estimating the Poincaré cycle? This is an interesting question, which involves some math and physics. You will be able to make a competent estimate in a homework problem. Also, you will see that there is an interesting connection between the very large period of the Poincaré cycle and the very short time scale of the irreversibility.

5.8 Boltzmann's H theorem

Historically, Boltzmann's H theorem was the first one to microscopically address the question of the irreversibility. Here, we will briefly state it, without going through the so-called "derivation." The derivation of the H theorem relies on an *ad hoc* assumption of a certain asymmetry in the scattering process, and so it has the feel of being unsatisfactory, since the irreversibility is the direct result of such an *ad hoc* assumption. Indeed, Boltzmann was severely attacked for this reason. Some viewed Boltzmann's H theorem non-rigorous. In contrast, the Poincaré recurrence appeared much more rigorous. In the hindsight, Boltzmann's theory was a correct one in a bigger sense, since it pointed out the nature of the irreversible dynamics in a large system. At the same time, the Poincaré recurrence should not be interpreted as not supporting irreversible dynamics, but rather quite the opposite.

5.8.1 Single particle density function

Consider a collection of N identical particles. We ask, what is the density of N particles? The answer is the following function, f_1, the **single particle density function**.

$$f_1(\vec{p},\vec{q},t) \equiv \left\langle \sum_{i=1}^{N} \delta(\vec{p}-\vec{p}_i)\delta(\vec{q}-\vec{q}_i) \right\rangle \tag{5.23}$$

where the angular bracket is the ensemble average as defined by Eq. 5.6.

It is essential to note that, here, we are being quite general, in the sense that the ensemble of microstates that we are considering do not necessarily correspond to an equilibrium state.

As the phase-space probability distribution function ρ (Eq. 5.5) must be symmetric with respect to swapping identical particles (exchange symmetry), we get

$$\begin{aligned} f_1(\vec{p},\vec{q},t) &= \int d\Gamma \rho(\vec{p}_1,\vec{q}_1,...,\vec{p}_N,\vec{q}_N,t) \sum_{i=1}^{N} \delta(\vec{p}-\vec{p}_i)\delta(\vec{q}-\vec{q}_i) \\ &= N \int d\Gamma \rho(\vec{p}_1,\vec{q}_1,...,\vec{p}_N,\vec{q}_N,t)\, \delta(\vec{p}-\vec{p}_1)\delta(\vec{q}-\vec{q}_1). \end{aligned}$$

By effecting the integral, and using Eq. 5.4, we get

$$\begin{aligned} f_1(\vec{p},\vec{q},t) &= N \int dV_2...dV_N\, \rho(\vec{p},\vec{q},\vec{p}_2,\vec{q}_2,...,\vec{p}_N,\vec{q}_N,t) && (5.24) \\ &= N\rho_1(\vec{p},\vec{q},t) \qquad \rho_1\text{, an unconditional PDF.} && (5.25) \end{aligned}$$

As defined in previous lectures, the unconditional probability distribution function is defined as the one with all other variables integrated out, as here. So, f_1 is the single particle density in the phase space that integrates to the total number of particles, and f_1/N is the corresponding PDF.

5.8.2 Boltzmann's H theorem

Boltzmann showed that, assuming that the f_1 function satisfies the "Boltzmann equation," the Boltzmann H function

$$H(\vec{p},\vec{q},t) = \int d^3\vec{p}d^3\vec{q}\, f_1(\vec{p},\vec{q},t) \log f_1(\vec{p},\vec{q},t) \qquad (5.26)$$

satisfies

$$\frac{dH}{dt} \le 0. \qquad (5.27)$$

While this theorem was important in the history of statistical mechanics, it was also mired in controversy due to the empirical nature of the Boltzmann equation, which appears to include the irreversibility by hand even though the microscopic laws are time-reversal invariant. We will not go into details about this old issue, but will remark that (1) Boltzmann equation does include an *ad-hoc* assumption which amounts to acknowledging the entropy increase, and (2) it is still in wide use today due to its usefulness.

5.9 Entropy and the H function

The entropy of a probability distribution is defined as

$$\begin{aligned} s &= -\sum_i p_i \log p_i && \text{discrete} && (5.28)\\ &= -\int dx\, p(x) \log p(x) && \text{continuous} && (5.29) \end{aligned}$$

Note that the discrete case is clearly defined, but the continuous case *is* problematic. Why so? If one discretizes the x axis, in unit of ε, then one sees that $s = -\int dx\, p(x) \log p(x) \approx -\sum_i \varepsilon p(x_i) \log p(x_i)$. Rewriting $p(x_i)\varepsilon \to p_i$, we get $s \approx -\sum_i p_i \log \frac{p_i}{\varepsilon}$. Thus, s is *dependent on* ε. Another way of seeing this problem is that if we make a scale transformation[5] $y = Ax$, then $dx \to dy/A$, and $p(x) \to p(y)A$: $s \to s - \log A$. This problem is symptomatic of the classical mechanical way of thinking, and can be saved only by realizing the phase space quantum as we discussed in Section 5.2. We will assume this in the following. Namely, when we see an integral in phase space, what we really mean is the discrete sum where the infinitesimal volume is taken to be h^{3N}, which is taken to be the unit volume for the purpose of the sum!

If N particles are independent (and identical), then

$$\rho(\vec{p}_1, \vec{q}_1, ..., \vec{p}_N, \vec{q}_N) = \rho_1(\vec{p}_1, \vec{q}_1)\rho_1(\vec{p}_2, \vec{q}_2)...\rho_1(\vec{p}_N, \vec{q}_N)$$

and so

$$\begin{aligned} s &= -\int d\Gamma\, \rho_1(\vec{p}_1, \vec{q}_1)...\rho_1(\vec{p}_N, \vec{q}_N) \sum_{j=1}^{N} \log \rho_1(\vec{p}_j, \vec{q}_j)\\ &= -N \int d^3\vec{p} d^3\vec{q}\, \rho_1(\vec{p}, \vec{q}) \log \rho_1(\vec{p}, \vec{q})\\ &= -\int d^3\vec{p} d^3\vec{q}\, f_1(\vec{p}, \vec{q})\, \log \frac{f_1}{N}\\ &= -H + N \log N \end{aligned}$$

Therefore, the H function is, up to a constant, a negative entropy. The thermodynamic entropy can be defined as k_B (Boltzmann constant) times s.

For this reason, it is standard to define the thermodynamic entropy as

$$S = -k_B \int d\Gamma\, \rho(\mathbf{\vec{p}}, \mathbf{\vec{q}}, t) \log \rho(\mathbf{\vec{p}}, \mathbf{\vec{q}}, t) \tag{5.30}$$

which is applicable for non-equilibrium states as well as equilibrium states.

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[5] A similar argument can be made for any one-to-one mapping $y = F(x)$. In that case, $A \equiv |F'(x)|$, and $s \to s - \langle \log |F'(x)| \rangle$.

It is important to note three things. (1) While the notation did not make it clear so far, the single particle distribution $f_1(\vec{p}, \vec{q}, t)$, or the density function $\rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t)$, considered by Boltzmann is a *coarse-grained* quantity, not a microscopic quantity. It is an averaged quantity over a length scale and a time scale, that are much longer than a collision length scale and a collision time scale, respectively. In the gas problem that Boltzmann addressed, these scales are Å and pico-second respectively. (2) If one considers a microscopic function, instead, then one can show the following startling result. Due to Liouville's theorem, the H function, or the entropy function, $S = -\int d\Gamma\, \rho \log \rho$, *remains constant.* This startling results has a counter part in quantum mechanics, as well, as we shall see later on. (3) Lastly, you are reminded that the H theorem is an empirical theorem, in the sense that it requires an *ad hoc* assumption, which essentially amounts to using the conclusion before it is proven.

5.10 Recent results

If the discussion in the previous two sections makes you feel uneasy about how much what we know about the entropy and the irreversibility implied by the second law of thermodynamics, then you are quite right to feel so. This topic is a topic of much investigation even today.

The research on this topic is going on, and is not completely resolved. However, recent progress in this field gives a certain hope. More specifically, recent results on so-called "fluctuation theorems" or similar theorems[6] suggest the following type of behavior

$$\frac{P_F(\Delta S)}{P_R(-\Delta S)} = e^{\frac{\Delta S}{k_B}}$$

where $P_F(\Delta S)$ is the probability for a forward process involving ΔS, and $P_R(-\Delta S)$ is the probability for its time-reversed process. So, in this view, the entropy decreasing process is possible, but is exponentially unlikely, compared to the entropy increasing process.

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[6] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997); G. Crooks, Phys. Rev. E, **60**, 2721 (1999); D. J. Evans, and D. J. Searles, Adv. in Phys. **51** (7), 1529 (2002).