

Statistical Ensembles

Ergodic hypothesis

How do we make connection between thermodynamics and mechanics?

Consider a system of N particles, each with three degrees of freedom, x, y, z . The system is described, in Hamiltonian classical mechanics, by $6N$ canonical variables

$$q_1, q_1, \dots, q_{3N}, p_1, \dots, p_{3N}$$

Hamilton's eqns
$$\begin{aligned} \dot{q}_i &= -\frac{\partial H}{\partial p_i} \\ \dot{p}_i &= \frac{\partial H}{\partial q_i} \end{aligned} \quad \left\{ \begin{array}{l} i=1, \dots, 3N \end{array} \right.$$

give the trajectory of the system $\{q_i(t), p_i(t)\}$ in "phase space" - a $6N$ dimensional space whose coordinates are the q_i and p_i .

In general, ^{total} energy will be conserved as the system moves ~~assuming there are no external time~~ ~~region~~. The condition $H[q_i, p_i] = E$ defines a $6N-1$ dimensional surface in phase space on which the system's trajectory is confined.

If one wanted to compute the ^{measured} ~~average~~ value of some quantity, averaged over an interval of time τ , it is:

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt f[q_i(t), p_i(t)]$$

In general, for large N , we expect the trajectory to be some horribly complicated curve on the constant energy surface, that we have no way of computing directly.

To compute $\langle f \rangle$ we therefore need to make an assumption. The ergodic hypothesis says: during any time interval τ , ~~this~~ sufficiently long, the location of the system in phase space $\{q_i(t), p_i(t)\}$ is equally likely to be anywhere on the surface of constant energy E .

$$\text{Therefore } \langle f \rangle = \int dq_i dp_i f[q_i, p_i] \rho(q_i, p_i)$$

$$\text{where } \rho(q_i, p_i) = C \delta(H[q_i, p_i] - E)$$

where C is a normalizing factor such that $\int dq_i dp_i \rho[q_i, p_i] = 1$

ρ is called the density matrix.

with the above form, ρ is called the microcanonical ensemble

The ergodic hypothesis cannot in general be proven. But the existence of thermodynamics, as an empirically consistent theory, suggests why it may be true.

① Liouville's Theorem (see later)

② By thermodynamics we assume that the macroscopic properties of a system are completely described by a set of a few macroscopic variables, such as total energy E , N , V , μ . If the ergodic hypothesis were not true, there would be parts of phase space with the same value of E , that never "saw" each other - i.e. a trajectory in one part would not enter the other, ad vice versa. One could imagine, therefore, that systems in these two disjoint regions of phase space might have different properties, ~~and therefore have~~ i.e. have different time averages of some particular property $F[q, p]$. One therefore might expect them to represent thermodynamically distinguishable states. But this would contradict the assumption that E alone is the important thermodynamic variable.

Alternatively, if ergodicity fails, there might be some other important macroscopic variable (for example magnetization) which one overlooked.

The disjoint regions of the constant energy surface could correspond to different values of this new macroscopic variable.

In other words, in the absence of any further information, we assume that all microscopic states $\{q_i, p_i\}$ consistent with a given set of macroscopic thermodynamic variables, E, N, V , are equally likely.

In the ensemble theory one abandons any effort to compute thermodynamic properties from the explicitly time dependent trajectory of the system in phase space. Rather one describes the thermodynamic state as represented by a particular ensemble given by the density matrix $\rho(q_i, p_i)$

The ensemble average $\langle f \rangle = \int dq_i dp_i f(q_i, p_i) \rho(q_i, p_i)$ is the value one would find not for a single isolated system moving on its trajectory, ~~but for a collection~~ but for the average of a collection of systems distributed in phase space according to the density ρ . The ergodic hypothesis asserts these two types of averages are equal.

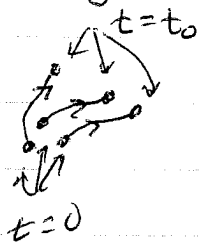
$\rho(q_i, p_i)$ can be viewed as the probability density that the system will be found in phase space at $\{q_i, p_i\}$

Equilibrium is described by a density matrix that does not vary in time.

Liouville's theorem

The concept of density matrix will soon be expanded beyond the particular example of the microcanonical ensemble. It can also be generalized to non-equilibrium situations. $\rho(q_i, p_i, t)$. We therefore want to see what general condition ρ must satisfy in order that $\frac{\partial \rho}{\partial t} = 0$, i.e. steady-state

Consider an initial density ρ of points in phase space. As the systems represented by these initial points evolve in time, their trajectories give the density $\rho(t)$ at later times. Think of the points in ρ like particles in a fluid.



The probability density ρ must obey a local conservation equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

where $\vec{v}$ is the "velocity" vector of the probability "current" $\rho \vec{v}$, that tells how the points in ρ flow in phase space.

$\vec{v}$ is the $6N$ dimensional vector $(\dot{q}_1, \dots, \dot{q}_{6N}, \dot{p}_1, \dots, \dot{p}_{6N})$

and

$$\begin{aligned} \vec{\nabla} \cdot (\rho \vec{v}) &= \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right] \\ &= \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right] \end{aligned}$$

$$\vec{\nabla} \cdot (f \vec{v}) = \sum_i \left[\frac{\partial f}{\partial g_i} \dot{g}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right] + f \left[\frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right]$$

use $\dot{g}_i = \frac{\partial H}{\partial p_i}$ $\dot{p}_i = -\frac{\partial H}{\partial g_i}$

$$\Rightarrow \frac{\partial \dot{g}_i}{\partial g_i} = \frac{\partial H}{\partial p_i \partial g_i} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial H}{\partial g_i \partial p_i}$$

$$\text{so } \frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$$

and

$$\vec{\nabla} \cdot (f \vec{v}) = \sum_i \left\{ \frac{\partial f}{\partial g_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial g_i} \right\}$$

$$= [f, H] \quad \leftarrow \text{defines the "Poisson bracket"}$$

so

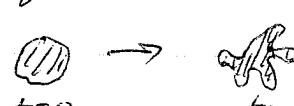
$$\frac{\partial f}{\partial t} + [f, H] = 0$$

$$\approx \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial f}{\partial g_i} \frac{dg_i}{dt} + \frac{\partial f}{\partial p_i} \frac{dp_i}{dt} \right\} = \frac{df}{dt} = 0$$

↑
total time derivative

$\frac{df}{dt}$ is also called the convective derivative. It is how f changes in time if one moves along with "particles" (i.e. the systems on their trajectories)

$\frac{df}{dt} = 0 \Rightarrow$ density in phase space is ~~independent of~~ ^{constant} in time as it flows - like an incompressible fluid.

 $t=0 \rightarrow t$ density of points..

Equilibrium requires a stronger condition, namely $\frac{\partial \rho}{\partial t} = 0$,
so that ensemble averages will not vary in time.

$$\frac{\partial \rho}{\partial t} = 0 \Rightarrow [\rho, H] = 0$$

$$[\rho, H] = \sum_i \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$$

we see that $[\rho, H] = 0$ if $\rho(q_i, p_i)$ depends
on q_i, p_i only via the function $H[q_i, p_i]$, i.e.

$\rho = \rho(H(q_i, p_i))$. Then $\frac{\partial \rho}{\partial q_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i}$, $\frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i}$

$$[\rho, H] = \sum_i \left[\frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0$$

so $\rho(q_i, p_i)$ must be constant on constant
energy surfaces, if ρ is to describe equilibrium.

We already saw one example

microcanonical ensemble $\rho(q_i, p_i) \sim \delta(H(q_i, p_i) - E)$

another choice later will be

canonical ensemble $\rho(q_i, p_i) \sim e^{-H[q_i, p_i]/k_B T}$