Léonard classroom

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 \( \rho(\mathbf{q}, \mathbf{p}; t) \). We therefore want to see what general condition \( \rho \) must satisfy in order that \( \frac{\partial \rho}{\partial t} = 0 \), i.e., steady-state.

Consider an initial density \( \rho \) 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 \( \rho \) like particles in a fluid.

The probability density \( \rho \) must obey a local conservation equation:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot ( \rho \mathbf{V} ) = 0
\]

Where \( \mathbf{V} \) is the "velocity" vector of the probability "current" \( \rho \mathbf{V} \), that tells how the points in \( \rho \) flow in phase space. \( \mathbf{V} \) is the \( 6N \) dimensional vector \( (\dot{\mathbf{q}}_1, \ldots, \dot{\mathbf{q}}_N, \dot{\mathbf{p}}_1, \ldots, \dot{\mathbf{p}}_N) \), and

\[
\nabla \cdot ( \rho \mathbf{V} ) = \sum_{i=1}^{3N} \left[ \frac{\partial}{\partial \mathbf{q}_i} (\rho \dot{\mathbf{q}}_i) + \frac{\partial}{\partial \mathbf{p}_i} (\rho \dot{\mathbf{p}}_i) \right] = \sum_{i=1}^{3N} \left[ \frac{\partial \rho}{\partial \mathbf{q}_i} \dot{\mathbf{q}}_i + \rho \frac{\partial \dot{\mathbf{q}}_i}{\partial \mathbf{q}_i} + \frac{\partial \rho}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i + \rho \frac{\partial \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i} \right]
\]
\[ \nabla \cdot (\rho \mathbf{v}) = \sum_i \left[ \frac{\partial \rho}{\partial x_i} \mathbf{v}_i + \frac{\partial \rho}{\partial p_i} \mathbf{v}_i \right] + \sum_i \left[ \frac{\partial \mathbf{v}_i}{\partial x_i} \rho + \frac{\partial \mathbf{v}_i}{\partial p_i} \right] \]

\[ \mathbf{v}_i = \frac{\partial H}{\partial p_i}, \quad \rho_i = -\frac{\partial H}{\partial \mathbf{v}_i} \]

\[ \Rightarrow \frac{\partial \mathbf{v}_i}{\partial \mathbf{v}_i} = \frac{\partial H}{\partial \mathbf{v}_i}, \quad \frac{\partial \mathbf{v}_i}{\partial p_i} = -\frac{\partial H}{\partial \mathbf{v}_i} \]

\[ \Rightarrow \frac{\partial \mathbf{v}_i}{\partial \mathbf{v}_i} + \frac{\partial \rho_i}{\partial \mathbf{v}_i} = 0 \]

\[ \nabla \cdot (\rho \mathbf{v}) = \sum_i \left[ \frac{\partial \rho}{\partial x_i} \mathbf{v}_i + \frac{\partial \rho}{\partial p_i} \mathbf{v}_i \right] = [\rho, H] \quad \text{defines the "Poisson bracket"} \]

\[ \Rightarrow \frac{\partial H}{\partial \mathbf{v}_i} + [\rho, H] = 0 \]

\[ \frac{\partial \rho}{\partial t} + \frac{3N}{\rho} \sum_i \left( \frac{\partial \rho}{\partial x_i} \frac{d\mathbf{v}_i}{dt} + \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} \right) = \frac{d\rho}{dt} = 0 \]

\[ \frac{d\rho}{dt} \text{ is also called the convective derivative, it is how } \frac{\partial \rho}{\partial t} \text{ changes in time if one moves along with "particles" (ie the systems or their trajectories).} \]

\[ \frac{d\rho}{dt} = 0 \Rightarrow \text{density in phase space is constant in time as it flows - like an incompressible fluid.} \]
Equilibrium requires a stronger condition, namely \( \frac{\partial}{\partial t} \langle \phi \rangle = 0 \), so that ensemble averages will not vary in time.

\[
\frac{\partial}{\partial t} \langle \phi \rangle = \frac{\partial}{\partial \phi_i} \left[ \sum_i \frac{2 \phi_i \partial \phi_i}{\partial \phi_i} \right] = 0
\]

we see that \( [\rho, H] = 0 \) if \( \rho (\phi_i, p_i) \) depends
on \( \phi_i, p_i \) only via the function \( H(\phi_i, p_i) \), i.e.,
\( f = f (H(\phi_i, p_i)) \). Then \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho = \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \), \( \frac{\partial}{\partial \phi_i} \frac{\partial}{\partial \phi_i} \rho \).

\[
[\rho, H] = \sum_i \left[ 2 \phi_i \frac{\partial \phi_i}{\partial \phi_i} \right] = 0
\]

so \( f (\phi_i, p_i) \) must be constant on constant energy surfaces, if \( f \) is to describe equilibrium.

We already saw one example

**microcanonical ensemble** \( \rho (\phi_i, p_i) \sim \delta (H(\phi_i, p_i) - E) \)

another choice like will be

**canonical ensemble** \( \rho (\phi_i, p_i) \sim e^{-\frac{H(\phi_i, p_i)}{k_B T}} \)


Microcanonical Ensemble and Entropy

We saw that the microcanonical ensemble, at energy \( E \), assigned equal weight to all systems on the surface in phase space of constant energy \( H [ q_i, p_i ] = E \).

To count the number of such states on the energy surface, we define the "density of states"

\[
\rho (E) = \frac{\int dq_i dp_i \delta (H [ q_i, p_i ] - E)}{\mathcal{V}^{3N}}
\]

where \( \mathcal{V} \) is a constant with units of \( q_i p_i \). \( \mathcal{V}^{3N} \) represents the volume of phase space occupied by one "state". Classically, \( \mathcal{V} \) is totally arbitrary so our thermodynamic results should not depend on it. Quantum mechanically, we will see that it turns out to be Planck's constant.

At this stage, the factor \( \frac{1}{\mathcal{V}^{3N}} \) is introduced so that \( \rho (E) \) has the units of \( 1/\text{energy} \).

We can now define the number of states in a shell of thickness \( \Delta \) about the energy surface \( E \).

\[
\mathcal{D} (E, V, N) = \int_{E - \frac{\Delta}{2}}^{E + \frac{\Delta}{2}} dE \rho (E')
\]

\( \mathcal{D} \) is a pure number. Again, \( \Delta \) is arbitrary, but
\[ E \leq \frac{V}{N} \]

assumed to be \( \mathcal{N}_0 \). It can be thought of as representing the finite accuracy with which one knows \( E \). Our thermodynamic results should not depend on \( \mathcal{N}_0 \).

[Both \( \mathcal{N}_0 \) and \( \Delta \) are introduced so that the dimensionless pure number that we can think of as being the \( \mathcal{N}_0 \) number of microscopically states occupied in the microcanonical ensemble at \( E \).]

**Example:** Compute \( S_2 \) for the ideal gas of non-interacting particles confined to a volume \( V \)

\[ H = \sum_i \frac{p_i^2}{2m} \]

\[ q(E) = \frac{1}{\hbar^{3N}} \int d^3p_i \int d^3p_j \delta \left( \sum_i \frac{p_i^2}{2m} - E \right) \]

\[ = \frac{V^N}{\hbar^{3N}} \int d^3p_i \delta \left( \sum_i \frac{p_i^2}{2m} - E \right) \]

The surface of constant energy is just the surface of a sphere in \( 3N \) dimensional momentum space given by the coordinates \( p_1x, p_2y, p_3z \ldots \). The radius of the sphere is \( \sqrt{2mE} \)

Let \( P = \sqrt{\frac{2}{m} \sum p_i^2} \) be the length of the momentum vector in the \( 3N \) dimensional momentum space
\[ \prod_{i=1}^{N} d^3p_i = dp P^{3N-1} d\Omega_{3N} \quad \text{diff. solid angle} \]

\[ g(E) = \frac{V^N}{\frac{4}{3} \pi^{3N}} \int_{0}^{\infty} d\Omega_{3N} \int_0^{p_{\text{max}}} dp P^{3N-1} S \left( \frac{P^2}{2m} - E \right) \]

\[ = \frac{V^N}{\frac{4}{3} \pi^{3N}} S_{3N} \int_0^{p_{\text{max}}} dp P^{3N-1} \frac{S \left( \frac{P^2}{2m} - E \right)}{\left( \frac{P}{m} \right)^{3N-2}} \]

\[ = \frac{V^N}{\frac{4}{3} \pi^{3N}} S_{3N} m \left( \frac{2mE}{m} \right)^{\frac{3N-2}{2}} \]

From Appendix C of Pathria (Eqn C.76) or elsewhere, one has the area of unit sphere in d-dim space:

\[ S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} \]

where \( \Gamma(n) = (n-1)! \)

\( \Gamma \) is the Gamma function

\[ S_d = \frac{2\pi^{3N/2}}{\Gamma(\frac{3N}{2}-1)} \]

\[ g(E) = \frac{V^N}{\frac{4}{3} \pi^{3N}} \frac{2\pi^{3N/2}}{\Gamma(\frac{3N}{2})} m \left( \frac{2mE}{m} \right)^{\frac{3N}{2}} \]
\[ g(E) = \frac{V^N}{(2\pi mE)^{3N/2}} \frac{1}{E} \]

\[ \Omega(E) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' \, g(E') \approx g(E) \Delta \]

\[ \Omega(E) = \frac{V^N}{(2\pi mE)^{3N/2}} \frac{1}{E} \frac{\Delta}{E} \]

For large \( N \), \( \Omega(E) \) is a very rapidly increasing function of \( E \), \( \Omega \propto E^{3N/2-1} \).

We will now argue that \( \Omega(E) \) is related to the entropy of the system.

Consider two subsystems separated by a wall

\[
\begin{array}{c|c|c|c}
E_1 & E_2 & E_1 + E_2 & \text{energy conserved} \\
V_1 & V_2 & & \\
N_1 & N_2 & & \\
\end{array}
\]

Let \( g_1(E_1) \) is density of states of system 1 with energy \( E_1 \),

\( g_2(E_2) \) is density of states of system 2 with energy \( E_2 \).

Now suppose the wall is thermally conducting so that energy can be transferred between the two systems, \( \Rightarrow E \) can vary but \( E_1 + E_2 \) is fixed. What will be the value of \( E_1 \) when the system comes to equilibrium?
The density of states of the combined system will be

\[ g_T(E_T) = \int dE_1 g_1(E_1) g_2(E_T - E_1) \]

Now if \( \Omega_T(E_T) = g_T(E_T) \Delta \)
\[ \Omega_1(E_1) = g_1(E_1) \Delta \]
\[ \Omega_2(E_2) = g_2(E_2) \Delta \]

Then the above can be written as

\[ \Omega_T(E_T) = \int \frac{dE_1}{\Delta} \Omega_1(E_1) \Omega_2(E_T - E_1) \]

The integrand is the number of states with total energy \( E_T \) that also have system 1 with energy \( E_1 \).

REMARK: Consider the behavior of the integrand
\[ \Omega_1(E_1) \] is a rapidly increasing function of \( E_1 \)
\[ \Omega_2(E_2) \] is a rapidly increasing function of \( E_2 \)
\[ \Rightarrow \Omega_2(E_T - E_1) \] is a rapidly decreasing function of \( E_1 \)

\[ \Rightarrow \text{the product } \Omega_1(E_1) \Omega_2(E_T - E_1) \text{ has a sharp maximum at some particular value of } E_1 \]
In the microcanonical ensemble, all states with total energy $E_T$ are equally likely. But the value of $E_1$ that one is most likely to find as the energy of system 1 is the particular value that maximizes $\Omega_1(E_1)\Omega_2(E_T-E_1)$. That is, there are more states with this particular value of $E_1$ than with any other value of $E_1$, and since all microscopic states are equally likely, this value of $E_1$ is the most likely. Moreover, since $\Omega_1(E_1)$ is rapidly increasing in $E_1$ and $\Omega_2(E_T-E_1)$ is rapidly decreasing in $E_1$, the maximum is extremely sharp. So one is almost certain to find the maximum value of $E_1$. (The probability to find any other value of $E_1$ will vanish as the size of the system gets infinitely large.)

What condition determines this maximizing value of $E_1$?

\[
\frac{\partial}{\partial E_1}\left[\Omega_1(E_1)\Omega_2(E_T-E_1)\right] = 0
\]

\[
\Rightarrow \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_T-E_1) + \Omega_1(E_1) \frac{\partial \Omega_2(E_T-E_1)}{\partial E_1} = 0
\]

\[
\Rightarrow \frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_T-E_1) - \Omega_1(E_1) \frac{\partial \Omega_2(E_T-E_1)}{\partial E_2} = 0
\]

\[
\Rightarrow \frac{1}{\Omega_1} \frac{\partial \Omega_1(E_1)}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2(E_T-E_1)}{\partial E_2}
\]
\[
\frac{\partial}{\partial E_1} \left( \ln \Omega_1 \right) = \frac{\partial}{\partial E_2} \left( \ln \Omega_2 \right)
\]

But from thermodynamics we know that the equilibrium value of \( E_1 \) will be determined by the condition

\[
\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T_2}
\]

Therefore, following Boltzmann, we identify

\[
S(E) \propto \ln \Omega(E)
\]

as the entropy.

Since the relation between thermodynamics and mechanics should be fundamentally, Boltzmann postulated that the proportionality constant in the above should be a universal number, and not depend on the particular system. This constant is Boltzmann's constant \( k_B \).

\[
S(E) = k_B \ln \Omega(E)
\]

\( k_B \) states with energy \( E \)

\( S(E) \) is a monotonic increasing function of \( E \)
as it should be.