Classical phase space

Phase space and probability density

We consider a system of N particles in a d-dimensional space. Canonical coordinates and momenta

$$\begin{aligned} q &= (q_1, \ldots, q_{dN}) \\ p &= (p_1, \ldots, p_{dN}) \end{aligned}$$

determine exactly the microscopic state of the system.
The *phase space* is the $2dN$-dimensional space $\{(p, q)\}$, whose every point $P = (p, q)$ corresponds to a possible state of the system.
A *trajectory* is such a curve in the phase space along which the point $P(t)$ as a function of time moves.
Trajectories are determined by the classical equations of motion

$$\begin{aligned} \frac{dq_i}{dt} &= \frac{\partial H}{\partial p_i} \\ \frac{dp_i}{dt} &= -\frac{\partial H}{\partial q_i}, \end{aligned}$$

where

$$\begin{aligned} H &= H(q_1, \ldots, q_{dN}, p_1, \ldots, p_{dN}, t) \\ &= H(q, p, t) = H(P, t) \end{aligned}$$

is the Hamiltonian function of the system.
The trajectory is *stationary*, if H does not depend on time: trajectories starting from the same initial point P are identical.
Let $F = F(q, p, t)$ be a property of the system. Now

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\},$$

where $\{F, G\}$ stands for Poisson brackets

$$\{F, G\} \equiv \sum_i \left(\frac{\partial F}{\partial q_i} \frac{\partial G}{\partial p_i} - \frac{\partial G}{\partial q_i} \frac{\partial F}{\partial p_i} \right).$$

We define the *volume measure of the phase space*

$$d\Gamma = \prod_{i=1}^{dN} \frac{dq_i dp_i}{h} = h^{-dN} dq_1 \cdots dq_{dN} dp_1 \cdots dp_{dN}.$$

Here $h = 6.62608 \cdot 10^{-34}$Js is the Planck constant.
Note $[dq\, dp] =$ Js, so $d\Gamma$ is dimensionless.
Note $\Delta_0 \Gamma = 1$ corresponds to the smallest possible volume element of the phase space where a point representing the system can be localized in accordance with the uncertainty principle. The volume $\Delta\Gamma = \int d\Gamma$ is then roughly equal to the number of quantum states in the part of the space under consideration.
The *ensemble* or *statistical set* consists, at a given moment, of all those phase space points which correspond to identical macroscopic systems.
Corresponding to a *macro state* of the system there are thus a set of *micro states* which belong to the ensemble with the probability $\rho(P)\, d\Gamma$. $\rho(P)$ is the *probability density* which satisfies the condition

$$\int d\Gamma\, \rho(P) = 1.$$

The statistical average, or the ensemble expectation value, of a measurable quantity $f = f(P)$ is

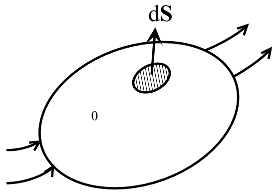
$$\langle f \rangle = \int d\Gamma\, f(P) \rho(P).$$

We associate every phase space point with the velocity field

$$\boldsymbol{V} = (\dot{q}, \dot{p}) = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q} \right).$$

The probability current is then $\boldsymbol{V}\rho$. The probability weight of an element Γ_0 evolves then like

$$\frac{\partial}{\partial t} \int_{\Gamma_0} \rho\, d\Gamma = -\int_{\partial \Gamma_0} \boldsymbol{V}\rho \cdot d\boldsymbol{S}.$$



Because

$$\int_{\partial \Gamma_0} \boldsymbol{V}\rho \cdot d\boldsymbol{S} = \int_{\Gamma_0} \nabla \cdot (\boldsymbol{V}\rho)\, d\Gamma,$$

we get in the limit $\Gamma_0 \to 0$ the *continuity equation*

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\boldsymbol{V}\rho) = 0.$$

According to the equations of motion

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned}$$

we have

$$\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0,$$

so we end up with the *incompressibility condition*

$$\nabla \cdot \boldsymbol{V} = \sum_i \left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] = 0.$$

From the continuity equation we get then

$$\begin{aligned} 0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot (\boldsymbol{V}\rho) \\ &= \frac{\partial \rho}{\partial t} + \rho \nabla \cdot \boldsymbol{V} + \boldsymbol{V} \cdot \nabla \rho \\ &= \frac{\partial \rho}{\partial t} + \boldsymbol{V} \cdot \nabla \rho. \end{aligned}$$

When we employ the *convective time derivative*

$$\begin{aligned} \frac{d}{dt} &= \frac{\partial}{\partial t} + \boldsymbol{V} \cdot \nabla \\ &= \frac{\partial}{\partial t} + \sum_i \left(\dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} \right), \end{aligned}$$

the continuity equation can be written in the form known as the *Liouville theorem*

$$\frac{d}{dt}\,\rho(P(t),t) = 0.$$

The points in the phase space move like an incompressible fluid which carries with it the constant probability describing the ensemble.

Flow in phase space

The *energy surface* Γ_E is the manifold determined by the equation

$$H(q,p) = E.$$

Since the energy is a constant of motion every phase point $P^i(t)$ moves on a certain energy surface Γ_{Ei}.
The expectation value of the energy of the system

$$E = \langle H \rangle = \int d\Gamma\, H\rho$$

is also a constant of motion.
The volume of the energy surface is

$$\Sigma_E = \int d\Gamma_E = \int d\Gamma\, \delta(H(P)-E).$$

The volume of the phase space is

$$\int d\Gamma = \int_{-\infty}^{\infty} dE\, \Sigma_E.$$

Let us consider the element $\Delta\Gamma_E$ of an energy surface.

Non ergodic flow: In the course of time the element $\Delta\Gamma_E$ traverses only a part of the energy surface Γ_E.

Ergodic flow: Almost all points of the surface Γ_E are sometimes arbitrarily close to any point in $\Delta\Gamma_E$.

$\Leftrightarrow$

The flow is ergodic if $\forall f(P)$, $f(P)$ "smooth enough",

$$\bar f = \langle f \rangle_E$$

holds. Here $\bar f$ is the time average

$$\bar f = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, f(P(t))$$

and $\langle f \rangle_E$ the energy surface expectation value

$$\langle f \rangle_E = \frac{1}{\Sigma_E} \int d\Gamma_E\, f(P).$$

We define the *microcanonical ensemble* so that its density distribution is

$$\rho_E(P) = \frac{1}{\Sigma_E}\,\delta(H(P)-E).$$

Every point of the energy surface belongs with the same probability to the microcanonical ensemble.
The microcacnonical ensembel is stationary, i.e. $\frac{\partial \rho_E}{\partial t} = 0$ and the expectation values over it temporal constants.

The *mixing flow* is such an ergodic flow where the points of an energy surface element $d\Gamma_E$ disperse in the course of time all over the energy surface.
If $\hat\rho_E(P,t)$ is an arbitrary non stationary density distribution at the moment $t = t_0$, then

$$\lim_{t\to\infty} \hat\rho_E(P,t) = \frac{1}{\Sigma_E}\,\delta(H(P)-E) = \rho_E(P)$$

and

$$\begin{aligned}\lim_{t\to\infty}\langle f\rangle &= \lim_{t\to\infty}\int d\Gamma\, \hat\rho_E(P,t) f(P)\\ &= \int d\Gamma\, f(P)\rho_E(P)\end{aligned}$$

i.e. the density describing an arbitrary (non equilibrium) state evolves towards a microcanonical ensemble.

Microcanonical ensemble and entropy

If the total energy of a macroscopic system is known exactly its equilibrium state can be described by a microcanonical ensemble. The corresponding probability density is

$$\rho_E(P) = \frac{1}{\Sigma_E}\,\delta(H(P)-E).$$

For a convenience we allow the energy to have some "tolerance" and define

$$\rho_{E,\Delta E}(P) = \frac{1}{Z_{E,\Delta E}}\,\theta(E+\Delta E - H(P))\theta(H(P)-E).$$

Here the normalization constant

$$Z_{E,\Delta E} = \int d\Gamma\, \theta(E+\Delta E-H(P))\theta(H(P)-E)$$

is the *microcanonical state sum* or *partition function.* $Z_{E,\Delta E}$ is the number of states contained in the energy slice $E < H < E+\Delta E$ (see the volume measure of the phase space). In the microcanonical ensemble the probability is distributed evenly in every allowed part of the phase space.

Entropy

We define the *Gibbs entropy* as

$$S = -k_B \int d\Gamma\, \rho(P)\ln\rho(P).$$

Let $\Delta\Gamma_i$ the volume of the phase space element i and ρ_i the average probability density in i. The state of the system is, with the probability

$$p_i = \rho_i\,\Delta\Gamma_i,$$

in the element i and

$$\sum p_i = 1.$$

We chooce the sizes of all elements to be smallest possible, i.e. $\Delta\Gamma_i = 1$. Then

$$\begin{aligned} S &= -k_B \sum_i \Delta\Gamma_i \rho_i \ln\rho_i = -k_B \sum_i \rho_i\Delta\Gamma_i \ln \rho_i\Delta\Gamma_i\\ &= -k_B \sum_i p_i \ln p_i,\end{aligned}$$

since $\ln \Delta\Gamma_i = 0$.
If ρ is smooth in the range $\Delta\Gamma = W$ we have

$$\rho = \frac{1}{W},$$

so that

$$S = -k_B \frac{1}{W} \ln \frac{1}{W} \int d\Gamma.$$

We end up with the *Boltzmann entropy*

$$S = k_B \ln W.$$

Here W is the *thermodynamic probability*: the number of all those states that correspond to the macroscopical properties of the system.
One can show that the entropy is *additive*, i.e. if the system is composed of two partial systems 1 and 2 its entropy is

$$S_{1+2} = S_1 + S_2.$$

If we require that the entropy has a maximum under the condition

$$\int d\Gamma\, \rho(P) = 1,$$

ρ takes the form

$$\rho(P) = \rho_0 \ \forall P \in \Gamma_E.$$

The maximum principle of the entropy leads thus to the microcanonical distribution.

Entropy and disorder
The maximum of entropy
$\Leftrightarrow$
Microcanonical ensemble
$\Leftrightarrow$
Every microscopic state which satisfies

$$E < H < E + \Delta E,$$

is present with the same probability, i.e. there is the complete lack of information
$\Leftrightarrow$
Disorder is at maximum.