Statistical properties of N-particle system

Coordinates $q = (r_1, \dots, r_N) \in \mathbb{R}^n$,

$n = 3N$ is the number of degrees of freedom.

Momenta $p = (p_1, \dots, p_N) \in \mathbb{R}^n$, $p_a = m_a \dot{r}_a$

Hamilton's equations: $\dot{q} = \underbrace{\frac{\partial H}{\partial p}}_{\text{vector of derivatives}}$, $\dot{p} = -\frac{\partial H}{\partial q}$.

We are interested in the case of <u>very large</u> N.

1 mole = N for 12 grams of carbon $\approx 6 \cdot 10^{23}$ ~~particle~~ atoms.

<u>Problems</u>: (a) extremely large system (hard to solve)

(b) no initial conditions available in real-world applications.

<u>Method</u>: study statistical properties:

Consider the phase space $(p, q) \in \mathbb{R}^{2n}$ of very large dimension $\Rightarrow$

<u>probability</u> of (p, q) to be in the phase-space region $(p, q) \in V \subset \mathbb{R}^{2n}$ is

$$\boxed{\int_V \rho(p, q)\, dp\, dq}$$

$\rho(p,q)$ is a probability density function, which defines the statistical distribution in phase space.

Total probability to be somewhere: $\int_{\mathbb{R}^{2n}} \rho \, dp \, dq = 1$

(normalization cond.)

For any "observable" function $f(p,q)$ we define the mean value

$$\bar{f} = \int_{\mathbb{R}^{2n}} \underbrace{f(p,q)}_{\text{value}} \underbrace{\rho(p,q)\,dp\,dq}_{\text{probability}}$$

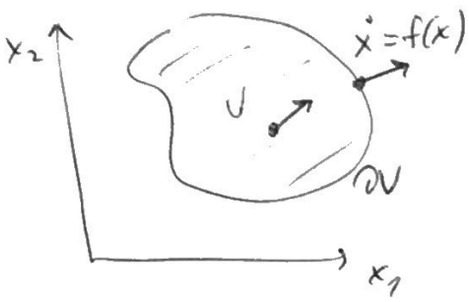
For example, f can describe the energy of a subsystem $f = H_A(p_A, q_A)$.

In practical applications, mean values are very precise: mean energy of 1 mole has $\sim 10^{-12}$ relative difference from its exact value.

Obs: central limit theorem: $E \sim N$, $\delta E \sim \sqrt{N}$

$$\Rightarrow \frac{\delta E}{E} \sim \frac{1}{\sqrt{N}} \sim 10^{-12} \quad \text{for one mole } N \sim 10^{24}.$$

Equation for the probability density



Consider (in general) a differential equation

$$\dot{x} = f(x), \quad x \in \mathbb{R}^n.$$

Consider a statistical description (ensemble of systems) with the probability density $\rho(x)$.

Probability ~~of~~ of having the system in region $x \in V$ is equal to $\int_V \rho(x)\,dx$. Since each system satisfies the equation $\dot{x} = f(x)$, we have

$$\underbrace{\frac{\partial}{\partial t} \int_V \rho(x)\,dx}_{\text{change of probability}} = \underbrace{-\int_{\partial V} f(x)\,\rho(x)\,dx}_{\text{flux through the surface } \partial V.}$$

For fixed volume V and using the divergence theorem:

$$\int_V \frac{\partial \rho}{\partial t}\,dx = -\int_V \operatorname{div}(f\rho)\,dx$$

$$\Rightarrow \int_V \left(\frac{\partial \rho}{\partial t} + \operatorname{div}(f\rho)\right) dx = 0 \qquad \text{for any } V \subset \mathbb{R}^n$$

Hence $\boxed{\dfrac{\partial \rho}{\partial t} + \operatorname{div}(f\rho) = 0}$ continuity equation for probability density.

Example: Ham. eqs: $x \to (p, q)$, $f \to \left(\underbrace{-\frac{\partial H}{\partial q}}_{\dot{p}}, \underbrace{\frac{\partial H}{\partial p}}_{\dot{q}}\right)$.

We assume that the system converges to a <u>statistical equilibrium</u> if

$$\rho_{eq.}(p,q) = \lim_{t\to\infty} \rho(p,q,t).$$

from some initial condition $t=0$: $\rho = \rho_0(p,q)$.

<u>Obs</u> From the theory of dynamical systems (chaos), we expect that there is a typical <u>relaxation time</u> T such that $\rho \simeq \rho_{eq}$ for $t \gg T$.

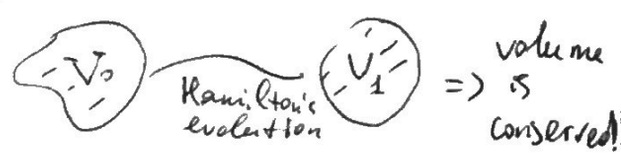
It is also expected (assumed) that both ρ_{eq} and T are independent on the initial condition.

<u>Obs</u> Usually, T is larger for a larger system (N).

<u>Liouville's theorem</u>

Consider a probability distribution $\rho(p,q,t)$ for the Hamilton's equations. Then $\frac{d\rho}{dt} = 0$, i.e. $\rho = \text{const}$ (conserved) along any trajectory of the Hamilton's equations $(\dot{p},\dot{q}) = \left(-\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p}\right)$.

<u>Obs</u> This implies "incompressibility" of the phase-space volume (exercise).



Proof of Liouville's th.

Continuity eq. for $\dot{x} = f(x)$:

$$\frac{\partial \rho}{\partial t} + \underbrace{\nabla_x \cdot}_{} (f\rho) = 0$$

div is a "scalar product" of $\nabla_x = \left(\frac{\partial}{\partial x_1}, \dots, \frac{\partial}{\partial x_n}\right)$ and $(f\rho)$.

In our case: $x \to (p, q)$, $f \to (\dot{p}, \dot{q}) = \left(-\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p}\right)$

Hence,
$$\frac{\partial \rho}{\partial t} + \underbrace{\nabla_p \cdot (\dot{p}\rho)}_{} + \underbrace{\nabla_q \cdot (\dot{q}\rho)}_{} = 0$$

open derivatives of the product

$$\frac{\partial \rho}{\partial t} + \left[(\nabla_p \rho)\cdot\dot{p} + (\nabla_q \rho)\cdot\dot{q}\right] + \left[\nabla_p \cdot \dot{p} + \nabla_q \cdot \dot{q}\right]\rho = 0$$

$$\nabla_p \cdot \dot{p} + \nabla_q \cdot \dot{q} = \underbrace{\sum_i \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i}\right)}_{\text{(use Hamilt. eqs)}} = \sum_i \left(-\frac{\partial^2 H}{\partial p_i \partial q_i} + \frac{\partial^2 H}{\partial q_i \partial p_i}\right) = 0$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + (\nabla_p \rho)\cdot\dot{p} + (\nabla_q \rho)\cdot\dot{q} = 0 \Rightarrow \frac{d\rho}{dt} = 0.$$

for $\rho = \rho(p(t), q(t), t)$.

$\blacksquare$

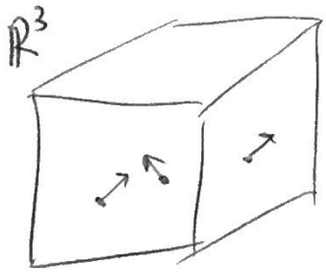
<u>Corollary</u>: probability density of a system in the statistical equilibrium is the invariant of motion (conservation law): $\frac{d}{dt}\rho_{eq}(p,q) = 0$.

<u>Obs</u> For non-stationary $\rho(p,q,t)$, we have $\frac{d\rho}{dt} = 0$, but the invariant of motion should depend only on (p,q).

Other conservation laws (invariants) known are:

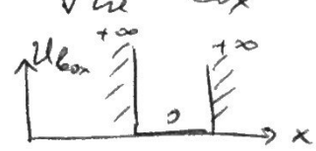
$$\left.\begin{array}{ll} \text{energy} & E = H(p,q) \in \mathbb{R} \\ \text{momentum} & P = \sum_{a=1}^{N} \vec{p}_a \in \mathbb{R}^3 \\ \text{angular momentum} & M = \sum_{a=1}^{N} r_a \times p_a \in \mathbb{R}^3 \end{array}\right\} \text{7 invariants}$$

<u>A trick</u>: we will consider the system <u>in a box</u>.



All particles are confined within a box with rigid walls.
Later we will "remove" the box and will see what will change.

<u>Obs</u> In the Lagrangian formulation, the box is introduced via the potential

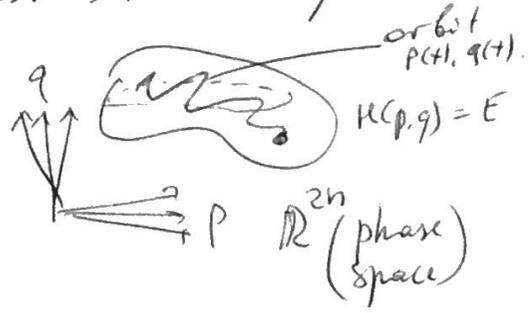


$$U_b = \sum_{a=1}^{N} U_{box}(r_a), \quad U_{box}(r) = \begin{cases} 0, & r \text{ is in the box} \\ +\infty, & r \text{ is outside the box.} \end{cases}$$

Since $E = \underbrace{K}_{\text{kinetic}} + U + U_b = \text{const} \Rightarrow$ all particles remain inside the box.

Ergodicity hypothesis:

The energy surface $H(p,q) = E = \text{const}$ of the system contains a dense orbit



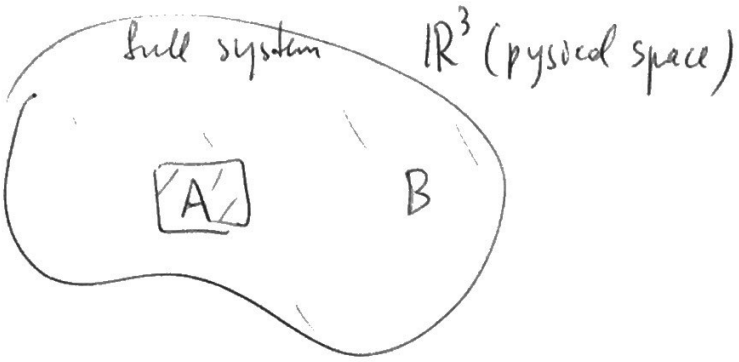
Since $\rho_{eq}(p,q) = \text{const}$ along every orbit, hence $\rho_{eq}(p,q) = \text{const}$ in the energy surface (dense orbit) and $\rho_{eq}(p,q) = 0$ outside energy surface (energy is conserved):

$$\boxed{\rho(p,q) = \underbrace{\text{const}}_{\text{normalization factor: } \int \rho \, dp\, dq = 1} \cdot \underbrace{\delta\big(H(p,q) - E\big)}_{\text{Dirac's delta-function}}}$$

This distribution is called the <u>microcanonical ensemble</u>.

<u>Obs</u> Ergodicity hypothesis is <u>generally WRONG</u>! (KAM-theory!). Perhaps it is true as $N \to \infty$, in the limit of large number of particles.

Statistical distribution of a macroscopic SUB system



Let us divide the system into two parts A and B, with phase variables (p_A, q_A) and (p_B, q_B).

$p = (p_A, p_B)$

$q = (q_A, q_B)$

Hamiltonian of the full system:

$$\mathcal{H}(p,q) = \underbrace{H_A(p_A, q_A)}_{\text{(Hamiltonian of system A)}} + \underbrace{H_B(p_B, q_B)}_{\text{(Hamiltonian of system B)}} + \underbrace{\mathcal{U}_{int}(p,q)}_{\text{(interaction between A and B)}}$$

Interaction among particles is usually local. Then, only particles near the boundary of A contribute to $\mathcal{U}_{int}$. For a macroscopic (large) system: $H_A \sim N_A$ (volume particles) $\gg \mathcal{U}_{int} \sim N_A^{2/3}$ (surface particles)

$\Rightarrow$ We can approximately neglect $\mathcal{U}_{int}$. $\Rightarrow$

$\Rightarrow$ Systems A and B are approximately decoupled.

Hence, in the statistical equilibrium, distributions of systems A and B are independent:

$$\boxed{\rho(p,q) = \rho_A(p_A, q_A) \cdot \rho_B(p_B, q_B)}.$$

Equivalently,

$$\log \rho = \log \rho_A + \log \rho_B$$

Also, ρ_A is (approximately, neglecting U_{int}) an invariant of system A with the Hamiltonian $H_A(p_A, q_A)$.

Hence, the equilibrium probability density yields an additive invariant of motion: $\underline{\log \rho}$.

<u>Poincaré</u>: in a generic (typical) Hamiltonian system, there are no analytic invariants of motion besides the energy!

Hence $\log \rho$ should be related to the energy E. Both $\log \rho$ and E are additive functions of subsystems (approximately, neglecting U_{int}).

The only possible choice for $\log \rho$ is:

$$\log \rho_A = \alpha_A + \beta H_A(p_A, q_A)$$

where α_A depends on a subsystem; β is the same constant for all subsystems.

hence, $\rho_A = \exp\left[\alpha_A + \beta H_A(p_A, q_A)\right]$,

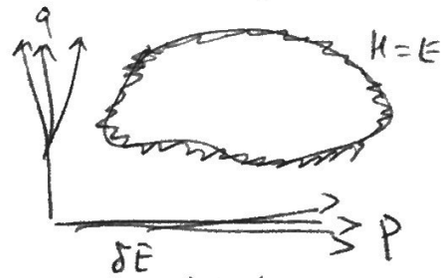
and α_A is defined by the normalization condition: $\int \rho_A \, dp_A \, dq_A = 1$.

<u>Obs</u> Note that <u>energy of a subsystem is not constant</u>, it is different for <u>each chosen full system</u>; and also it changes due to U_{int}.

<u>Summary</u>:

<u>Microcanonical ensemble</u> (for a full system)	<u>Canonical ensemble</u> (for a subsystem)
$\rho = \text{const} \cdot \delta(H(p,q) - E)$	$\rho = \exp\left[\alpha + \beta H(p,q)\right]$
(const $\leftarrow \int \rho \, dp \, dq = 1$)	($\alpha \leftarrow \int \rho \, dp \, dq = 1$)

<u>Obs</u> In fact both ensembles are very similar: in canonical ensemble, all systems are found near the energy surface $H(p,q) = E = \overline{H}$ (mean)



$\frac{\delta E}{E} \ll 1 \quad (\sim 10^{-12})$

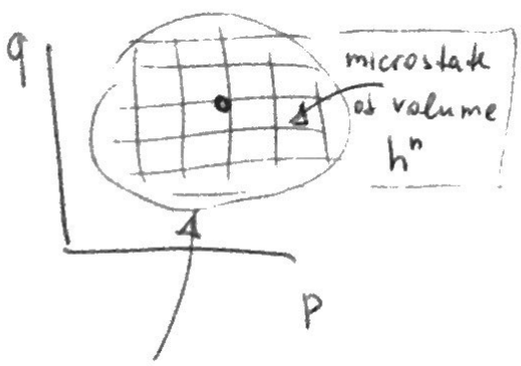
Entropy

Definition. $S = k_B \overline{\log \Omega}$, $\Omega = \dfrac{1}{\rho h^n}$

Here: $k_B = 1.38 \cdot 10^{-23} \left[\frac{J}{K}\right]$ is the Boltzmann constant (it will match units of energy and temperature later)

Ω is the number of occupied "microstates" in the phase space $(p, q) \in \mathbb{R}^{2n}$

h is the volume of a "microstate" per 1 degree of freedom.



typical volume occupied $\sim 1/\rho$

n is the number of degrees of freedom (in our case $n = 3N$).

Obs $\log \Omega \sim$ dimension of phase space $\sim n$

Obs h is the Plank constant (justified by quantum mechanics)

$$S = k_B \overline{\log \frac{1}{\rho h^n}} = -k_B \overline{\log \rho} + \text{const} = \boxed{-k_B \int \rho \log \rho \, dp\, dq} + \text{const}$$

Entropy measures a (log of) number of possible microscopic configurations.

Larger $S \Rightarrow$ more possible states $\Rightarrow$ larger disorder.

For simplicity, we put $k_B \to 1$, const $\to 0$, (e.g. by choosing appropriate unit system).

Obs for systems with discrete states (e.g. quantum)

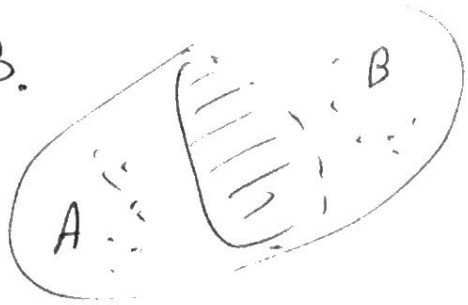
$$S = -\sum_i p_i \log p_i$$

where p_i is a probability of state i.

$S=0$ corresponds to the deterministic system with $p_i = 1$ for some state i and 0 otherwise.

Entropy in statistical equilibrium

Consider two subsystems A and B.



Relate S_A, S_B to the entropy of the whole system S_{A+B}.

$\rho_{A+B} \approx \rho_A \rho_B$ - approximate stat. independence

Phase space element: $dp\,dq = dp_A\,dq_A\,dp_B\,dq_B$

$$S_{A+B} = -\int \rho_{A+B} \log \rho_{A+B}\, dp\,dq = -\int \rho_A \rho_B \log(\rho_A \rho_B)\, dp\,dq$$

$$= -\int \rho_A \log \rho_A\, dp_A\,dq_A \underbrace{\int \rho_B\, dp_B\,dq_B}_{\substack{1 \\ \text{(total probab.} \\ \text{in state B)}}} - \underbrace{\int \rho_A\, dp_A\,dq_A}_{\substack{1 \\ \text{(total probability} \\ \text{in state A)}}} \int \rho_B \log \rho_B\, dp_B\,dq_B$$

$$= S_A + S_B.$$

$$\boxed{S_{A+B} = S_A + S_B}$$

Entropy is an additive macroscopic quantity.

Entropy of whole system is equal to the sum of entropies of subsystems.

Obs This is also true for systems not in equilibrium.

$S \stackrel{\text{def}}{=} \sum_i S_i$ sum of entropies of subsystems, where each subsystem i is in local stat. equilibrium.

2d law of thermodynamics

- The total entropy of an isolated system can never decrease over time.
- Systems evolve towards thermodynamic equilibrium, where the entropy attains its maximum value.
- Entropy is constant in time if and only if all processes are reversible.

Obs It can be proved in some cases: see the Boltzmann H-theorem (later in the course) $\longrightarrow$ Simon

Obs Idea: system goes to stat. eq $\Longrightarrow$ ~~ergodicity occupies phase space with probability~~

$\Rightarrow$ occupies all phase space at given E (ergodicity) $\Rightarrow$ max disorder