Elements of Ensemble Theory

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Ch2. Elements of Ensemble Theory

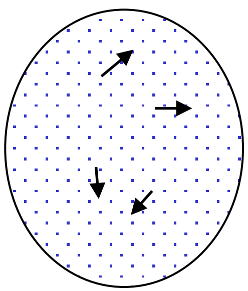
Ensemble: An ensemble is a large collection of systems in different microstates for the same macrostate (N,V,E) of the given system.

1) An ensemble element has the same macrostate as the original system (N,V,E), but is in one of all possible microstates.
2) A statistical system is in a given macrostate (N,V,E), at any time t, is equally likely to be in any one of a distinct microstate.

Ensemble theory: the ensemble-averaged behavior of a given system is identical with the time-averaged behavior.

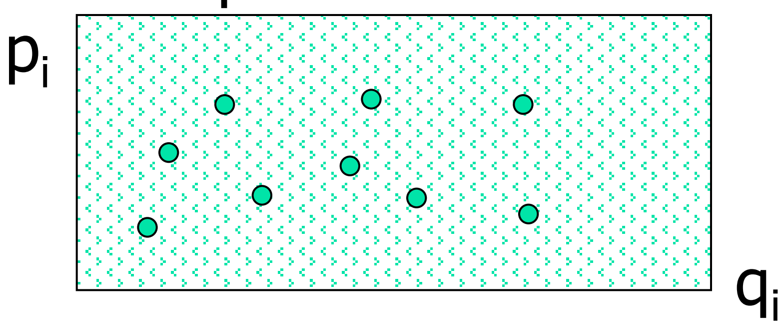
2.1 Phase space of a classical system

- Consider a classical system consisting of N-particles, each described by ($\mathbf{x_i}$,$\mathbf{v}_i$) at time t.
- A microstate at time t is



($\mathbf{x_1, x_2, \ldots, x_N; v_1, v_2, \ldots, v_N}$), or
($q_1, q_2, \ldots, q_{3N}; p_1, p_2, \ldots, p_{3N}$), or
(q_i, p_i) - position and momentum, i=1,2,.....,3N

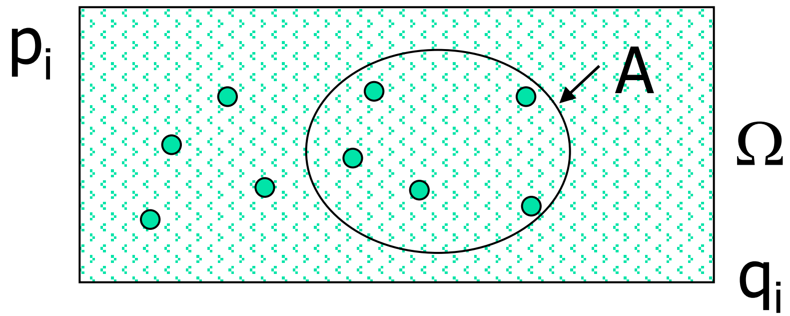
- Phase space: 6N-dimension space of (q_i, p_i).



Representative point

- Representative point: a microstate (q_i, p_i) of the given system is represented as a point in phase space.
- An ensemble is a very large collection of points in phase space Ω. The probability that the microstate is found in region A is the ratio of the number of ensemble points in A to the total number of points in the ensemble Ω.

$$P(A) = \frac{\text{Number of points in A}}{\text{Number of points in } \Omega}$$



Hamilton’s equations

- The system undergoes a continuous change in phase space as time passes by

$$\left.\begin{aligned}\dot{q}_i &= \frac{\partial H(q_i, p_i)}{\partial p_i}\\ \dot{p}_i &= -\frac{\partial H(q_i, p_i)}{\partial q_i}\end{aligned}\right\}\qquad i=1,2,\ldots,3N$$

- Trajectory evolution and velocity vector v
- Hamiltonian

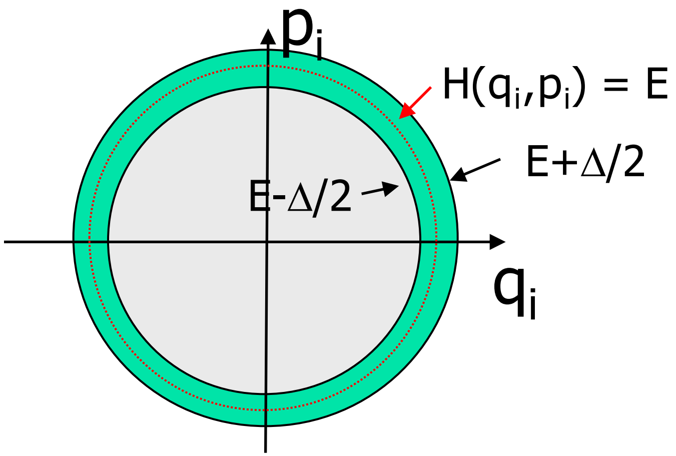
$$H(q_i, p_i) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} U(\vec{r}_i) + \sum_{i<j}^{N} \phi\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

Hypersurfce

- Hypersurface is the trajectory region of phase space if the total energy of the system is E, or (E-Δ/2, E+Δ/2).

$$H(q_i,p_i) = E$$

Hypershell (E-Δ/2, E+Δ/2).



- e.g. One dimensional harmonic oscillator

$$H(q_i,p_i) = (½)kq^2 + (1/2m)p^2 = E$$

Ensemble average

- For a given physical quantity f(q, p), which may be different for systems in different microstates,

$$\langle f \rangle = \frac{\int f(q,p)\rho(q,p;t)d^{3N}q\,d^{3N}p}{\int \rho(q,p;t)d^{3N}q\,d^{3N}p}$$

where

$d^{3N}q\ d^{3N}p$ – volume element in phase space

$\rho(q,p;t)$ – density function of microstates

Microstate probability density

- The number of representative points in the volume element ($d^{3N}q\ d^{3N}p$) around point (q,p) is given by

$$\rho(q,p;t)\, d^{3N}q d^{3N}p$$

- Microstate probability density:

$$(1/C)\rho(q,p;t) \qquad C = \int \rho(q,p;t) d^{3N}q\, d^{3N}p$$

- Stationary ensemble system: $\rho(q,p)$ does not explicitly depend on time t. <f> will be independent of time. $\frac{\partial \rho}{\partial t} = 0$

2.2 Liouville's theorem and its consequences

- The equation of continuity

At any point in phase space, the density function $\rho(q_i, p_i; t)$ satisfies

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

$$where \quad \vec{v} = (\dot{q}_i, \dot{p}_i)$$

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

So, $$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right\} = 0$$

Liouville's theorem

From above

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial\rho}{\partial q_i} \dot{q}_i + \frac{\partial\rho}{\partial p_i} \dot{p}_i \right\} = 0$$

Use Hamilton's equations

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial\rho}{\partial q_i} \left(\frac{\partial H}{\partial p_i} \right) - \frac{\partial\rho}{\partial p_i} \left(\frac{\partial H}{\partial q_i} \right) \right\}$$

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + [\rho, H] = 0$$

where $$[\rho, H] = \sum_{i=1}^{3N} \left\{ \frac{\partial\rho}{\partial q_i} \left(\frac{\partial H}{\partial p_i} \right) - \frac{\partial\rho}{\partial p_i} \left(\frac{\partial H}{\partial q_i} \right) \right\}$$

Consequences

For thermal equilibrium

$$\frac{\partial \rho}{\partial t} = 0 \quad \rightarrow [\rho, H] = \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} = 0$$

- One solution of stationary ensemble

$$\rho(q, p) = const$$ (Uniform distribution over all possible microstates)

$$\langle f \rangle = \frac{1}{\omega} \int_{\omega} f(q, p) d\omega$$

where $d\omega = d^{3N} q \, d^{3N} p$ Volume element on phase space

Consequences-cont.

$$\frac{\partial \rho}{\partial t} = 0 \quad \rightarrow [\rho, H] = \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} = 0$$

- Another solution of stationary ensemble

$$\boxed{\rho(q, p) = \rho[H(q, p)]}$$

satisfying $[\rho, H] = \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} = 0$

A natural choice in Canonical ensemble is

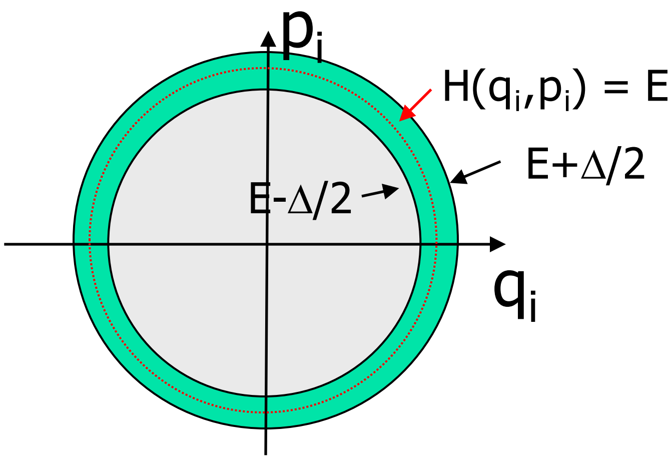
$$\rho(q, p) \propto \exp[-H(q, p)/(kT)]$$

2.3 The microcanonical ensemble

- Microcanonical ensemble is a collection of systems for which the density function r is, at all time, given by

$$\rho(q,p) = const \quad \text{If } E-\Delta/2 \leq H(q,p) \leq E+\Delta/2$$
$$= 0 \quad \text{otherwise}$$

- In phase space, the representative points of the microcanonical ensemble have a choice to lie anywhere within a "hypershell" defined by the condition



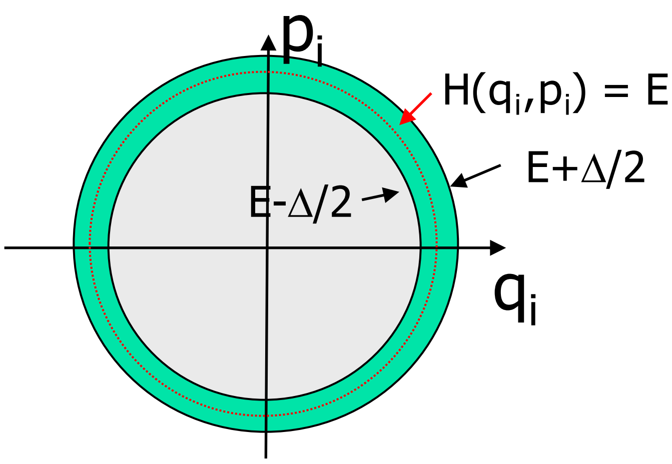
$$E-\Delta/2 \leq H(q,p) \leq E+\Delta/2$$

Microcanonical ensemble and thermodynamics

- Γ – the number of microstates accessible;
  ω – allowed region in phase space;
  ω_0 – fundamental volume equivalent to one microstate

$$\Gamma(N, V, E, \Delta) = \omega / \omega_0$$

$$S = k \ln \Gamma = k \ln\left(\frac{\omega}{\omega_0}\right)$$

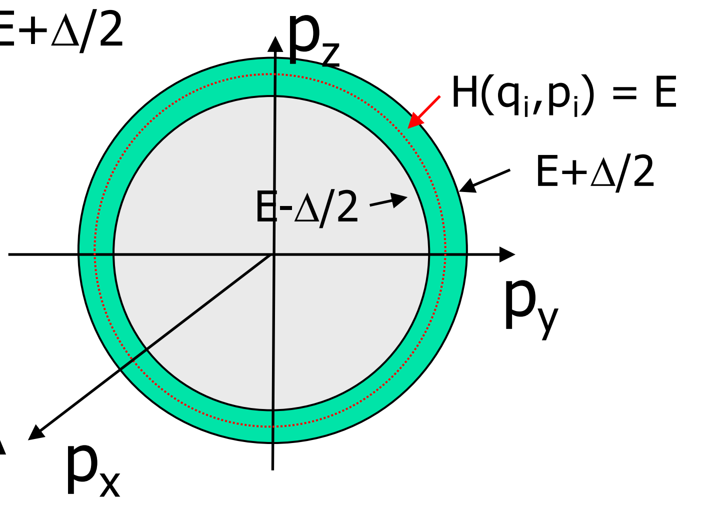


- Microcanonical ensemble describes isolated sysstems of known energy. The system does not exchange energy with any external system so that (N,V,E) are fixed.

Example – one particle in 3-D motion

- Hamilton: $H(q,p) = (p_x^2+p_y^2+p_z^2)/(2m)$
- Microcanonical ensemble

$$\rho(q,p) = const \quad \text{If } E-\Delta/2 \le H(q,p) \le E+\Delta/2$$
$$= 0 \quad \text{otherwise}$$



- Fundamental volume, $\omega_0 \sim h^3$
- Accessible volume

$$\omega = \int dxdydz \int dp_x dp_y dp_z = V 4\pi\left(\sqrt{2mE}\right)^2 \Delta$$

$$\Gamma = \omega / \omega_0 = V 4\pi\left(\sqrt{2mE}\right)^2 \Delta / h^3$$

2.4 Examples

1. Classical ideal gas of N particles
   a) particles are confined in physical volume V;
   b) total energy of the system lies between $E-\Delta/2$ and $E+\Delta/2$.

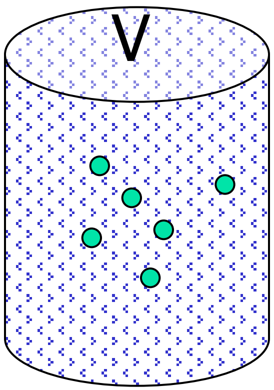
2. Single particle
   a) particles are confined in physical volume V;
   b) total energy of the system lies between $E-\Delta/2$ and $E+\Delta/2$.

3. One-dimensional harmonic oscillator

2.4 Examples

1. Classical ideal gas of N particles
   - Particles are confined in physical volume V
   - The total energy of system lies between (E-Δ/2, E+Δ/2)

Hamiltonian $$H(q_i, p_i) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$



Volume ω of phase space accessible to representative points of microstates

$$\omega = \int_{q \in V} \cdot \int_{E-\Delta/2 \le \sum_{i=1}^{3N}\left(\frac{p_i^2}{2m}\right) \le E+\Delta/2} d^{3N}q\, d^{3N}p = V^N \int_{E-\Delta/2 \le \sum_{i=1}^{3N}\left(\frac{p_i^2}{2m}\right) \le E+\Delta/2} d^{3N}p$$

Examples-ideal gas

$$\omega = V^N \int_{2m(E-\Delta/2)\le\sum_{i=1}^{3N}\left(y_i^{\,2}\right)\le 2m(E+\Delta/2)} d^{3N}y = V^N \frac{\pi^{3N/2}\,3N}{\left(3N/2\right)!}\left(2mE\right)^{\frac{3N-1}{2}}\left(\sqrt{\frac{2m}{E}}\frac{\Delta}{2}\right)$$

$$\approx \frac{\Delta}{E} V^N \frac{\left(2\pi mE\right)^{3N/2}}{\left(3N/2-1\right)!}$$

where

$$V_N\left(R\right) = \int_{0\le\sum_{i=1}^{3N}\left(y_i^{\,2}\right)\le R^2} d^{3N}y = \frac{\pi^{N/2}}{\left(N/2\right)!}R^N, \quad R=\sqrt{2mE}$$

$$dV_N\left(R\right) = \frac{\pi^{N/2}N}{\left(N/2\right)!}R^{N-1}dR, \quad dR = \sqrt{\frac{2m}{E}}\frac{\Delta}{2}$$

Examples-ideal gas

The fundamental volume: $\omega_0 = h^{3N}$

* A representative point (q,p) in phase space has a volume of uncertainty $\sim \eta$, for N particle, we have 3N (qi,pi) so, $\omega_0 = h^{3N}$

- The multiplicity Γ (microstate number)

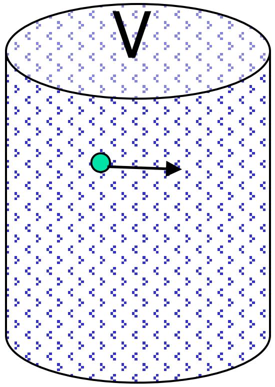
$$\Gamma = \frac{\omega}{\omega_0} = \frac{\Delta}{E}\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2-1)!}$$

and $\ln\Gamma \approx N\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}N$

$$S(N,V,E) = k\ln\Gamma \approx Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk$$

Example-single free particle

2. Classical ideal gas of 1 particles
   - Particle confined in physical volume V
   - The total energy lies between (E-Δ/2, E+Δ/2)



Hamiltonian $$H(q,p) = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^{\ 2} + p_y^{\ 2} + p_z^{\ 2}\right)$$

Volume of phase space with p< P=sqrt(2mE) for a given energy E

$$\omega = \int \cdot \underset{\substack{q\in V \\ p_1^{\ 2}+p_2^{\ 2}+p_3^{\ 2}\le P^2}}{} \int (dq_1 dq_2 dq_3)(dp_1 dp_2 dp_3) = V\,\frac{4\pi}{3}P^2$$

Examples-single particle

- The number of microstates with momentum lying btw p and p+dp,

$$g(p)dp = \frac{d}{dp}\left(\frac{\omega}{\omega_0}\right)dp = \frac{V}{h^3}4\pi p^2 dp$$

- The number of microstates of a free particle with energy lying btw ε and ε+dε,

$$a(\varepsilon)d\varepsilon = \frac{d}{d\varepsilon}\left(\frac{\omega}{\omega_0}\right)d\varepsilon = \frac{V}{h^3}2\pi(2m)^{3/2}\varepsilon^{1/2}d\varepsilon$$

where $\varepsilon = \frac{p^2}{2m}, \quad \omega_0 \sim h^3$

Example-One-dimensional simple harmonic oscillator

3. Harmonic oscillator

Hamiltonian $$H(q,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2$$

Where k – spring constant
m – mass of oscillating particle

Solution for space coordinate and momentum coordinate

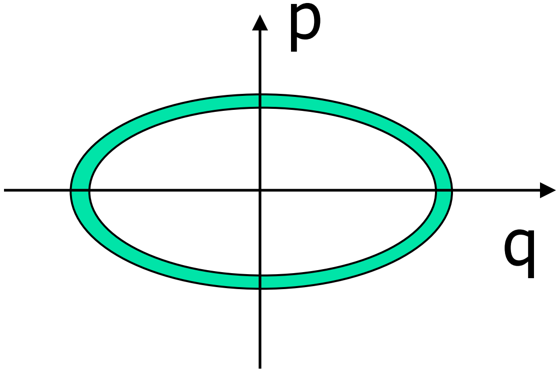
$$q = A\cos(\omega t + \phi)$$

$$p = m\dot{q} = -m\omega A\sin(\omega t + \phi)$$

$$with \quad \omega = \sqrt{k/m}, \quad E = \frac{1}{2}m\omega^2 A^2$$

Example-One-dimensional simple harmonic oscillator

- The phase space trajectory of representative point (q,p) is determined by



$$H(q,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2 = E$$

$$or \quad \frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{(2mE)} = 1$$

With restriction of E to E-Δ/2 ≤ H(q,p) ≤ E+Δ/2

- The "volume" of accessible in phase space

$$\omega_v = \int_{E-\Delta/2 \le H(q,p) \le E+\Delta/2} \int (dq)(dp) = \frac{2\pi}{\omega}\left[\left(E+\Delta/2\right) - \left(E-\Delta/2\right)\right]$$

$$A_v = \pi q_0 p_0 = \pi\sqrt{\frac{2E}{m\omega^2}}\sqrt{2mE}$$

$$\omega_v = \frac{2\pi\Delta}{\omega}$$

$$= \frac{2\pi E}{\omega}$$

Example-One-dimensional simple harmonic oscillator

- If the area of one microstate is $\omega_0 \sim h$

The number of microstates (eigenstates) for a harmonic oscillator with energy btw E-Δ/2 and E+Δ/2 is given by

$$\Sigma(E) = \frac{\omega_v}{\omega_0} = \frac{\Delta}{\eta\omega}$$

So, entropy

$$S = k \ln \Sigma(E) = k \ln\left(\frac{\Delta}{\eta\omega}\right)$$

Problem 3.5

- For a collection of N 3-D quantum harmonic oscillators of frequency w and total energy E, compute the entropy S and temperature T.