Micro-canonical Ensemble and Ergodic hypothesis Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: July 25, 2016)

Hypothesis of equal a priori probability

We consider a macroscopic system with the number of particles (N), energy $(E - E + \delta E)$, and volume V in thermal equilibrium There are microscopic states in this system. The total number of the microstates is W. All of them occur at the same probability. W is called the thermodynamical weight.

For an isolated system all microstates are equally probable.

In physics and thermodynamics, the **ergodic hypothesis**^[1] says that, over long periods of time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the volume of this region, i.e., that all accessible microstates are equiprobable over a long period of time.

Liouville's Theorem states that, for Hamiltonian systems, the local density of microstates following a particle path through phase space is constant as viewed by an observer moving with the ensemble (i.e., the convective time derivative is zero). Thus, if the microstates are uniformly distributed in phase space initially, they will remain so at all times. But Liouville's theorem does *not* imply that the ergodic hypothesis holds for all Hamiltonian systems.

Canonical equation

$$\dot{q}_{i} = \frac{\partial H}{\partial p_{i}}$$
$$\dot{p}_{i} = -\frac{\partial H}{\partial q_{i}}$$

where *H* is the Hamiltonian of the system,

In the volume element $dq_1dq_2...dq_fdp_1dp_2...dp_f$ of the phase space, there are a number of microstates which is denoted by

$$d^{N}\Gamma = \frac{dqdp}{h^{3N}} = \frac{1}{h^{3N}} dq_{1}dq_{2}...dq_{f}dp_{1}dp_{2}...dp_{f}$$

with

$${}^{N}\Gamma = (q, p) = (q_1, q_2, ..., q_f, p_1, p_2, ..., p_f)$$

f = 3N (the degree of freedom)

Microscopic state

$$\rho(^{N}\Gamma) = \begin{cases} 1 & (E < H_{N} < E + \delta E) \\ 0 & (\text{otherwise}) \end{cases}$$
$$\rho(^{N}\Gamma) = \frac{\partial}{\partial E} \theta(E - H_{N}) \, \delta E = \delta(E - H_{N}) \, \delta E$$

where θ is a step function and δ is the Dirac delta function. The number of states between $E - E + \delta E$ is given by

$$W(N, E, V, \delta E) = \int d^{N} \Gamma \rho(^{N} \Gamma)$$
$$= \int d^{N} \Gamma \delta(E - H_{N}) \delta E$$
$$= D(N, E, V) \delta E$$

Note that D(N, E, V) is called the density of states (per unit energy).

$$D(N, E, V) = \int d^N \Gamma \,\delta(E - H_N)$$

We define the probability distribution function

$$f_{MC}(^{N}\Gamma) = \frac{\rho(^{N}\Gamma)}{W(N, E, V, \delta E)} = \frac{\delta(E - H_{N})\delta E}{W(N, E, V, \delta E)}$$

which is a probability which the microstate specified by the point ${}^{N}\Gamma$ contributes to. Note that

$$f_{MC}(^{N}\Gamma) = \frac{1}{W(N, E, V, \delta E)} \qquad \text{for} \qquad E < H_{N} < E + \delta E$$



The average of the physical quantity *A*;

$$\langle A \rangle_{MC} = \int d^N \Gamma f_{MC}(^N \Gamma) A(^N \Gamma).$$

The entropy S is given by

$$S(N, E, V) = k_B \ln W(N, E, V, \delta E)$$

where $k_{\rm B}$ is the Boltzmann constant. The temperature *T*, the pressures *P* and the chemical potential can be described as

$$\frac{\partial S(N, E, V)}{\partial E} = \frac{1}{T}$$
$$\frac{\partial S(N, E, V)}{\partial V} = \frac{P}{T}$$

$$\frac{\partial S(N, E, V)}{\partial N} = -\frac{\mu}{T}$$
$$E = E(N, V, T)$$

The heat capacity is

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

((Note))

If a system is completely isolated, the system will stay forever in a definite state if it is initially in that state. But, it is useless to speak of a completely isolated system. We have some uncertainty in the energy of the system because of uncontrollable interaction between the system and the external world. Nevertheless, we can consider a system which is nearly isolated, and assume the validity of Liouville's theorem during some interval of time. We shall further admit that the time average of a mechanical quantity of a system under a macroscopic equilibrium state is equal to the ensemble average (ergodic hypothesis). This ensemble must be time-independent or stationary. It is a consequence of Liouville's theorem that, if the ensemble is stationary, its density is a function of the energy of the system. Such an ensemble was first clearly mentioned by W. Gibbs, and thus it is called Gibbs' ensemble. It satisfies the requirement that the statistical ensemble should be compatible with mechanics. The requirement is fundamental to statistical mechanics. Thus, energy plays an important special role in statistical mechanics, and it is usually assumed that there is no invariant other than energy conservation. In mechanics, there are total momentum and total angular momentum as conserved quantities. However, for a system confined in a box, we have no momentum conservation, and if some asymmetry of the shape of the box is introduced, the total angular momentum will be no longer conserved.

The Principles of Statistical Mechanics

From the classical Liouville's theorem, we conclude that the weight is proportional to the volume of the portion of phase space for a stationary statistical ensemble. The correspondence with quantum mechanics leads to the assertion that every quantum state of the same energy E has the same weight w(E). This is the fundamental principle, which is called the *principle of equal probability* or the assumption of equal *a priori* probability. In short, every quantum state is considered on equal footing. In other words, the a priori probability for a system to be in a particular energy level is the same for all levels. That the time-average is the same as the ensemble-average and the principle of equal a priori probability, are two basic principles of statistical mechanics. After adopting these principles, we have only to construct the general probabilistic theory. The ergodic problem aims at deriving the above principles from mechanics.

Phase space: canonical co-ordinate and canonical momentum:

$$(q, p) = (q_1, q_2, ..., q_f, p_1, p_2, p_3 ..., p_f);$$

$$H(q, p) = H(q_1, q_2, ..., q_f, p_1, p_2, p_3 ..., p_f)$$
(1)

Hamilton's equation

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \qquad \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}$$
(2)

$$(i = 1, 2, 3, \dots, f = 3N)$$

Each state of the system is represented by a point in the phase space. As the time changes, the representative point moves in phase space, showing the trajectory of the system, the following properties result directly from Eq.(2).

- (i) The trajectory never cross each other. More than one trajectory never pass through the same point. If they cross at an certain instant, their values at an adjacent instant are uniquely determined by Eq.(2)
- (ii) Two representative points infinitely close to each other at a certain time t_1 will always be so at any other time t_2 in the course of motion.
- (iii) We define the (2*f*-1)-dimensional surface (so called, equi-energy surface), defined by

$$H(q_1, q_2, ..., q_f, p_1, p_2, p_3 ..., p_f) = \text{const} = E$$
(3)

Because of the energy conservation, the representative point starting from a certain point on this surface remains for all time on the same surface in the phase space.

((Ergodic hypothesis))

We assume that the trajectory will cover the entire surface of the equi-energy surface. The equi-energy surface does not extend to infinity, but forms a closed surface in the phase sspace. The aggregate of all the phases which the dynamical system assumes during its temporal development is called the temporal ensemble. This temporal ensemble of the system is made up all the phases on the equi-energy surface.

((Liouville's theorem))

We look at one of the representative points at t = dt

$$(q', p') = (q'_1, q'_2, ..., q'_f, p'_1, p'_2, p'_3, ..., p'_f)$$

According to the Hamilton's equation, this point is related to the point at t = 0

$$(q, p) = (q_1, q_2, ..., q_f, p_1, p_2, p_3, ..., p_f)$$

by

$$q_{1} = q_{1}' - \left(\frac{\partial H}{\partial p_{1}'}\right) dt, \qquad q_{2} = q_{2}' - \left(\frac{\partial H}{\partial p_{2}'}\right) dt, \dots,$$
$$p_{1} = p_{1}' + \left(\frac{\partial H}{\partial q_{1}'}\right) dt, \qquad p_{2} = p_{2}' + \left(\frac{\partial H}{\partial q_{2}'}\right) dt, \dots,$$

The infinitesimally volume element of the phase space (q', p') is related to that of the phase space (q, p) though the Jacobian

$$dq'dp' = dq'_{1}dq'_{2}...dq'_{f}dp'_{1}dp'_{2}...dp'_{f}$$

= $\frac{\partial(q'_{1}, q'_{2}, ..., q'_{f}, p'_{1}, p'_{2}, p'_{3}..., p'_{f})}{\partial(q_{1}, q_{2}, ..., q_{f}, p_{1}, p_{2}, p_{3}..., p_{f})}dq_{1}dq_{2}...dq_{f}dp_{1}dp_{2}...dp_{f}$

Here we note that

$$\left[\frac{\partial(q_{1}', q_{2}', ..., q_{f}', p_{1}', p_{2}', p_{3}'..., p_{f}')}{\partial(q_{1}, q_{2}, ..., q_{f}, p_{1}, p_{2}, p_{3}..., p_{f})}\right]^{-1} = \begin{vmatrix} 1 - \frac{\partial}{\partial q_{1}'} \left(\frac{\partial H}{\partial p_{1}'}\right) dt & -\frac{\partial}{\partial q_{1}'} \left(\frac{\partial H}{\partial p_{2}'}\right) dt & ...\\ - \frac{\partial}{\partial q_{2}'} \left(\frac{\partial H}{\partial p_{1}'}\right) dt & 1 - \frac{\partial}{\partial q_{2}'} \left(\frac{\partial H}{\partial p_{2}'}\right) dt & ...\\ ... & ... & ...\\ = 1 - \sum_{s} \left[\frac{\partial}{\partial q_{s}'} \left(\frac{\partial H}{\partial p_{s}'}\right) - \frac{\partial}{\partial p_{s}'} \left(\frac{\partial H}{\partial q_{s}'}\right)\right] dt \end{vmatrix}$$

to the order of dt. Making the use of the identity

$$\frac{\partial}{\partial q_{s}'} \left(\frac{\partial H}{\partial p_{s}'} \right) = \frac{\partial}{\partial p_{s}'} \left(\frac{\partial H}{\partial q_{s}'} \right)$$

we get the result

$$\frac{\partial(q'_1, q'_2, ..., q'_f, p'_1, p'_2, p'_3 ..., p'_f)}{\partial(q_1, q_2, ..., q_f, p_1, p_2, p_3 ..., p_f)} = 1$$

and

$$dq'_{1}dq'_{2}...dq'_{f}dp'_{1}dp'_{2}...dp'_{f} = dq_{1}dq_{2}...dq_{f}dp_{1}dp_{2}...dp_{f}$$
(4)

Then the volume of the phase space is conserved.



The volume in the phase space is given by

$$\Delta n_{\perp} d^{N} A = \int \delta(H - E) d^{N} \Gamma = W(N, E, V, \delta E)$$

where

$$\frac{\Delta H}{\Delta n_{\perp}} = \frac{\delta E}{\Delta n_{\perp}} = \left| \nabla H \right|$$

and

$$\left|\nabla H\right| = \sqrt{\sum_{i=1}^{3N} \left[\left(\frac{\partial H}{\partial q_i}\right)^2 + \left(\frac{\partial H}{\partial p_i}\right)^2\right]} = \sqrt{\sum_{i=1}^{3N} \left[\left(\frac{dp_i}{dt}\right)^2 + \left(\frac{dq_i}{dt}\right)^2\right]} = v(^N \Gamma)$$

 $v(^{N}\Gamma)$ is the velocity on the surface element. Since

$$\Delta n_{\perp} = \frac{\Delta E}{\left|\nabla H\right|} = \frac{\delta E}{v(^{N}\Gamma)}$$
(5)

the surface element is obtained as

$$d^{N}A = \frac{1}{\Delta n_{\perp}} \delta(H - E) d^{N}\Gamma = \frac{v({}^{N}\Gamma)}{\delta E} \delta(H - E) d^{N}\Gamma$$

or

$$\frac{d^{N}A}{v(^{N}\Gamma)} = \frac{\delta(H-E)d^{N}\Gamma}{\delta E},$$

leading to

$$\frac{1}{\Omega(N, E, V)} \frac{d^{N}A}{v(^{N}\Gamma)} = \frac{1}{\Omega(N, E, V)\delta E} \delta(H - E)d^{N}\Gamma$$
$$= \frac{\rho(^{N}\Gamma)}{W(N, E, V, \delta E)}$$
$$= f_{MC}(^{N}\Gamma)$$
(6)

Note that we use the following formula in the above discussion.

$$f_{MC}(^{N}\Gamma) = \frac{\rho(^{N}\Gamma)}{W(N, E, V, \delta E)} = \frac{\delta(E - H_{N})\delta E}{W(N, E, V, \delta E)}$$
$$W(N, E, V, \delta E) = \int d^{N}\Gamma \,\delta(E - H_{N})\delta E = \Omega(N, E, V)\delta E$$
$$\rho(^{N}\Gamma) = \delta(E - H_{N})\delta E$$

In the right side of Eq.(6), $\frac{d^N A}{v({}^N \Gamma)}$ is a time for the system staying at the surface element ${}^N \Gamma$. In the microscopic ensemble theory, the probability distribution function $f_{MC}({}^N \Gamma)$ is proportional to this time (Ergodic theorem).

Liouville theorem

$$W(N, E, V, \delta E) = \int d^{N} \Gamma \rho(^{N} \Gamma) ,$$

$$1 = \int d^{N} \Gamma \frac{\rho(^{N} \Gamma)}{W(N, E, V, \delta E)} = \int d^{N} \Gamma f_{MC}(^{N} \Gamma)$$

We assume that the continuity of equation is valid,

$$d^{N}\Gamma(t)f_{MC}[^{N}\Gamma(t)] = d^{N}\Gamma(t+dt)f_{MC}[^{N}\Gamma(t+dt)]$$

where

$$d^{N}\Gamma(t) = d^{N}\Gamma(t+dt)$$



Then we get

$$f_{MC}[{}^{N}\Gamma(t)] = f_{MC}[{}^{N}\Gamma(t+dt)]$$

We use the Taylor expansion for $f_{MC}[{}^{N}\Gamma(t+dt)] - f_{MC}[{}^{N}\Gamma(t)]$

$$f_{MC}[^{N}\Gamma(t+dt)] - f_{MC}[^{N}\Gamma(t)] = \sum_{i=1}^{3N} \left(\frac{\partial f_{MC}}{\partial q_{i}}\frac{\partial q_{i}}{\partial t}\right) dt + \sum_{i=1}^{3N} \left(\frac{\partial f_{MC}}{\partial p_{i}}\frac{\partial p_{i}}{\partial t}\right) dt + \frac{\partial f_{MC}}{\partial t} dt$$
$$= \sum_{i=1}^{3N} \left(\frac{\partial f_{MC}}{\partial q_{i}}\frac{\partial H}{\partial p_{i}}\right) dt - \sum_{i=1}^{3N} \left(\frac{\partial f_{MC}}{\partial p_{i}}\frac{\partial H}{\partial q_{i}}\right) dt + \frac{\partial f_{MC}}{\partial t} dt$$
$$= 0$$

or

$$\frac{\partial f_{MC}}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial f_{MC}}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f_{MC}}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0$$

We use the Poisson bracket which is defined by

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

Thus we have the Liouville equation for $f_{\rm MC}$,

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

REFERENCES

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