

# Microcanonical Ensemble

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# Thermodynamics and Statistical Mechanics

- Thermodynamics: Macroscopic state from macroscopic variables
- Statistical Mechanics: Macroscopic state from microscopic variables
- Classical and Quantum Statistical Mechanics

# Thermodynamic Systems

- Isolated system  $(E, N, V) \rightarrow$  microcanonical ensemble
- Closed system  $(T, N, V) \rightarrow$  canonical ensemble
- Open system  $(T, \mu, V) \rightarrow$  grandcanonical ensemble

# Number of State & Ensembles

The number of state  $\Omega \sim \Delta x \Delta p$  in the phase space (In quantum mechanics,  $\Omega = \frac{\Delta x \Delta p}{h}$ ).

We consider a large collections or Ensemble of the system, not a single system.

# Fundamental Postulate in Statistical Mechanics

$$P = \frac{1}{\Omega_O}, \quad (1)$$

where  $\Omega_O$  is the total number of possible states. Then, the probability of  $i$  state is

$$p_i = \frac{\Omega_i}{\Omega_O}. \quad (2)$$

And, the expectation value of an observable is

$$\begin{aligned} \langle X \rangle &= \sum_i X_i p_i \\ &= \frac{\sum_i X_i \Omega_i}{\Omega_O}. \end{aligned} \quad (3)$$

# Hamiltonian Mechanics

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q}. \quad (4)$$



William Rowan Hamilton (1805 ~ 1865)

# Lagrangian Mechanics

Action minimization:

$$\delta S = \delta \int L dt. \quad (5)$$

Lagrangian:

$$L = T - V. \quad (6)$$

Lagrange Equation:

$$\frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = 0. \quad (7)$$

# Energy Conservation

We consider the Lagrangian,  $L(q, \dot{q}, t)$ . The time derivative of the Lagrangian is given by

$$\begin{aligned}\frac{dL}{dt} &= \frac{\partial L}{\partial q} \frac{dq}{dt} + \frac{\partial L}{\partial \dot{q}} \frac{d\dot{q}}{dt} + \frac{\partial L}{\partial t}, \\ &= \frac{\partial L}{\partial q} \dot{q} + \frac{\partial L}{\partial \dot{q}} \ddot{q} + \frac{\partial L}{\partial t}.\end{aligned}$$

Since the generalized momentum is  $p = \frac{\partial L}{\partial \dot{q}}$ ,

$$\begin{aligned}\frac{dL}{dt} &= \dot{p}\dot{q} + p\ddot{q} + \frac{\partial L}{\partial t}, \\ &= \frac{d}{dt}(p\dot{q}) + \frac{\partial L}{\partial t}.\end{aligned}$$

Lagrangian is not conserved with time.



# Energy Conservation

$$\frac{dL}{dt} = \frac{d}{dt}(p\dot{q}) + \frac{\partial L}{\partial t}.$$

If we define the Hamiltonian as

$$H = p\dot{q} - L, \tag{8}$$

the equation becomes:

$$\begin{aligned} \frac{dL}{dt} &= \frac{d}{dt}(H + L) + \frac{\partial L}{\partial t}. \\ \frac{dH}{dt} &= -\frac{\partial L}{\partial t}. \end{aligned}$$

Then, Hamiltonian is conserved if the Lagrangian does not depend on time explicitly.

# Hamilton's Equation

Hamiltonian is given by

$$H = p\dot{q} - L.$$

The variation of the Hamiltonian is

$$\begin{aligned}\delta H &= \dot{q}\delta p + p\delta\dot{q} - \delta L \\ &= \dot{q}\delta p + p\delta\dot{q} - \frac{\partial L}{\partial q}\delta q - \frac{\partial L}{\partial \dot{q}}\delta\dot{q}.\end{aligned}$$

Since the generalized momentum is  $p = \frac{\partial L}{\partial \dot{q}}$ ,

$$\delta H = \dot{q}\delta p - \frac{\partial L}{\partial q}\delta q.$$

Considering that  $H$  is a function of  $p$  and  $q$ ,

$$\delta H = \frac{\partial H}{\partial p}\delta p + \frac{\partial H}{\partial q}\delta q.$$

# Hamilton's Equation

We obtain the equations,

$$\dot{q} = \frac{\partial H}{\partial p}, \quad -\frac{\partial L}{\partial q} = \frac{\partial H}{\partial q}.$$

In the Lagrange equation,

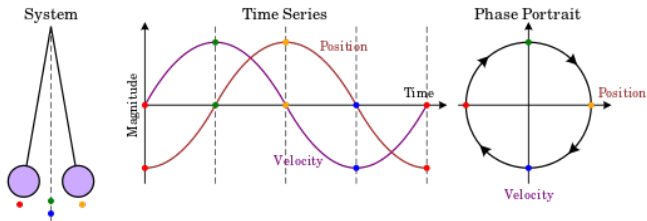
$$\frac{\partial L}{\partial q} = \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = \frac{d}{dt} p = \dot{p}.$$

Finally, we obtain the Hamilton's equations (two first order equations):

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q}.$$

# Phase Space

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q}.$$



Simple Harmonic Motion (from Wikipedia)

# Simple Harmonic Oscillators

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2.$$
$$2mH = p^2 + (m\omega q)^2.$$

Simple harmonic motion corresponds to a circular motion in phase space  $(p, q)$ .

# Liouville (Liouville-Gibbs) Theorem

## Hamiltonian Mechanics

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}, \quad H(p, q) = \Delta E.$$

We consider  $(p, q)$  as fluids with the density  $\rho$  and current  $J$  in phase space. Then, the continuity equation is

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot J,$$

where the divergence is

$$\nabla \cdot v = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0.$$

# Liouville (Liouville-Gibbs) Theorem

The current in phase space is  $J = \rho \vec{v}$ . Then, the continuity equation gives

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= -\nabla \cdot J \\ &= -\sum_i \left[ \frac{\partial \rho \dot{q}_i}{\partial q_i} + \frac{\partial \rho \dot{p}_i}{\partial p_i} \right] \\ &= -\sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right] \\ &= -\sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right].\end{aligned}$$

Note that

$$\frac{\partial \dot{q}}{\partial q} = \frac{\partial^2 H}{\partial q \partial p} = \frac{\partial^2 H}{\partial p \partial q} = -\frac{\partial \dot{p}}{\partial p}.$$

# Liouville (Liouville-Gibbs) Theorem

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot J = -\sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right].$$

Rearranging the equation:

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] \\ &= \frac{\partial \rho}{\partial t} + \sum_i \left[ \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] \\ &= \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0, \end{aligned}$$

where the Poisson bracket  $\{A, B\}$  is

$$\{A, B\} = \sum_i \left[ \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right]. \quad (9)$$



# Liouville (Liouville-Gibbs) Theorem

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

- incompressible flow
- volume in phase space is conserved
- no attractors
- microcanonical ensembles are time independent

At the stationary state ( $\frac{\partial\rho}{\partial t} = 0$ ),  $\{\rho, H\}$  becomes 0 if

- 1  $\rho = \text{const} \rightarrow$  microcanonical ensemble
- 2  $\rho = \rho[H(q, p)] \rightarrow$  canonical ensemble

# Ergodicity

- Ergodicity: energy surface in phase space is thoroughly stirred by the time evolution.
- time average = ensemble average

$$\langle f \rangle = \frac{\int f(q, p) \rho(q, p) dq dp}{\int \rho(q, p) dq dp}.$$
$$\bar{f} = \frac{1}{T} \int_0^T f(q, p) dt.$$

Can we show that our systems are ergodic? Well, usually not.

# Liouville-Gibbs Theorem & Ergodicity

Foundation of the classical statistical mechanics. Liouville-Gibbs Theorem:

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

At the stationary state ( $\frac{\partial\rho}{\partial t} = 0$ ),  $\{\rho, H\}$  becomes 0 if

- ①  $\rho = \text{const} \rightarrow$  microcanonical ensemble
- ②  $\rho = \rho[H(q, p)] \rightarrow$  canonical and grandcanonical ensemble

Ergodicity:

$$\langle f \rangle = \frac{\int f(q, p)\rho(q, p)dqdp}{\int \rho(q, p)dqdp}.$$
$$\bar{f} = \frac{1}{T} \int_0^T f(q, p)dt.$$

# Lagrange Multipliers

Before going further, we need to study a mathematical tool, “Lagrange multipliers” in order to find extreme values with constraints.

Find the extreme values of  $f(x, y)$  with the constraint equation  $g(x, y) = 0$ . Define another function  $F(x, y, \lambda) = f(x, y) + \lambda g(x, y)$ . Then,

$$\nabla F = \nabla[f + \lambda g] = 0, \quad (10)$$

at the maximum or minimum values. From this condition, we find

$$\frac{\partial F}{\partial x} = \frac{\partial F}{\partial y} = 0. \quad (11)$$

Let  $f(x, y)$  be the temperature distribution in the plane,

$$f(x, y) = x^2 + 2xy.$$

Let some bug be restricted to live in a circle of radius 2 given by the constraint equation

$$g(x, y) = x^2 + y^2 - 4 = 0.$$

What is the hottest point in this bug's world?

Define  $F(x, y, \lambda) = x^2 + 2xy + \lambda(x^2 + y^2 - 4)$ . Then, we have

$$\frac{\partial F}{\partial x} = 2x + 2y + 2\lambda x = 0, \quad (12)$$

$$\frac{\partial F}{\partial y} = 2x + 2\lambda y = 0. \quad (13)$$

Therefore,  $x = -\lambda y$  (Eq. 13) and  $\lambda^2 - \lambda + 1 = 0$  (Eq. 12). Finally,  $\lambda_{\pm} = \frac{-1 \pm \sqrt{5}}{2}$  and  $x = -\lambda y$ .

# Microcanonical Ensemble

Fixed energy and the number of particles. We define  $\Omega$  is the accessible volume in phase space with  $E \leq H \leq E + \Delta E$ .

$$\Omega = \int_{E \leq H \leq E + \Delta E} dP dQ,$$

where  $P = (p_1, p_2, \dots, p_{3N})$  and  $Q = (q_1, q_2, \dots, q_{3N})$ . The probability and the expectation value is then

$$P = \frac{1}{\Omega},$$
$$\langle O \rangle = \frac{1}{\Omega} \int_{E \leq H \leq E + \Delta E} O(P, Q) dP dQ.$$

Conceptually the microcanonical ensemble approach is extremely simple, in practice it is not so easy.

## Ideal Gas in a box

The Hamiltonian of  $N$ -ideal gas molecules in a box with volume  $V$  (i.e, helium atoms at high temperatures and low densities):

$$H = \sum_i^{3N} \frac{p_i^2}{2m} + V(x_i). \quad (14)$$

where the potential  $V(x_i)$  is given by 0 if  $x \in V$  and otherwise  $V = \infty$ . The number (or volume) of states is

$$\begin{aligned} \Omega &= \int_{E \leq H \leq E + \Delta E} dP dQ \\ &= \int dQ \int_{E \leq H \leq E + \Delta E} dP \\ &= \Omega_Q \Omega_P = V^N \Omega(P), \end{aligned}$$

since there is  $V = 0$  in a box.

# Momentum Space

The constant energy surface is a sphere in  $3N$ -dimensional space,

$$\sum_{i=1}^{3N} p_i^2 = 2mE = R^2,$$

where radius  $R = \sqrt{2mE}$ . If we define  $\Sigma(E)$  as the volume of region  $H \leq E$ ,

$$\begin{aligned}\Omega_P &= \int_{E \leq H \leq E + \Delta E} dP \\ &= \Sigma(E + \Delta E) - \Sigma(E).\end{aligned}$$

Then, the volume  $\Sigma$  can be computed as

$$\begin{aligned}\Sigma(E) &= \int_{H \leq E} dP \\ &= \int_{\sum_{i=1}^{3N} p_i^2 \leq 2mE} dP.\end{aligned}$$



# Volume of $n$ -dimensional Sphere

The volume of  $n$ -dimensional sphere with radius  $R$  is

$$\begin{aligned}V_N(R) &= \int_{\sum_i^N x_i^2 \leq R^2} dx_1 dx_2 \cdots dx_N \\ &= R^N \int_{\sum_i^N y_i^2 \leq 1} dy_1 dy_2 \cdots dy_N \\ &= R^N C_N,\end{aligned}$$

where  $C_N = \int_{\sum_i^N y_i^2 \leq 1} dy_1 dy_2 \cdots dy_N$ .

$$\begin{aligned}\sqrt{\pi}^N &= \left[ \int_{-\infty}^{\infty} e^{-x^2} dx \right]^N = \int_{-\infty}^{\infty} dx_1 dx_2 \cdots dx_N e^{-(x_1^2+x_2^2+\cdots+x_N^2)} \\ &= \int_{-\infty}^{\infty} dV_N(R) e^{-(x_1^2+x_2^2+\cdots+x_N^2)}\end{aligned}$$

where  $dV_N(R) = dx_1 dx_2 \cdots dx_N = NR^{N-1} C_N dR$ . In  $n$ -dimensional polar coordinates,

$$\begin{aligned}\sqrt{\pi}^N &= \int_0^{\infty} NR^{N-1} C_N e^{-R^2} dR \\ &= C_N \frac{N}{2} \int_0^{\infty} X^{\frac{N}{2}-1} e^{-X} dX = C_N \frac{N}{2} \Gamma\left(\frac{N}{2}\right) \\ &= C_N \Gamma(N/2 + 1) = C_N (N/2)!,\end{aligned}$$

where  $X = R^2$  and  $dX = 2RdR$ . Therefore,

$$C_N = \frac{\pi^{N/2}}{(N/2)!}, \quad V_N(R) = R^N \frac{\pi^{N/2}}{(N/2)!}.$$

# Momentum Space

The volume of region  $H \leq E$

$$\begin{aligned}\Omega_P &= \Sigma(E + \Delta E) - \Sigma(E) \\ &= \Delta E \frac{\Sigma(E + \Delta E) - \Sigma(E)}{\Delta E} \\ &\approx \Delta E \frac{d\Sigma(E)}{dE},\end{aligned}$$

where

$$\begin{aligned}\frac{d\Sigma(E)}{dE} &= \frac{d}{dE} \frac{\pi^{3N/2} (2mE)^{3N/2}}{(3N/2)!} \\ &= \frac{3N}{2} \frac{\pi^{3N/2} (2mE)^{3N/2-1}}{(3N/2)!} \\ &= \frac{(2\pi m)^{3N/2} E^{3N/2-1}}{(3N/2-1)!}.\end{aligned}$$

(15)

# Information and Entropy

- A measure for the lack of information (ignorance):  $s_i = -\log P_i = \log \frac{1}{P_i}$ .
- An average ignorance:  $S = k_B \sum_i P_i s_i = -k_B \sum_i P_i \log P_i = -k_B \langle \log P_i \rangle$ .
- We call  $S$  as “entropy” (Shannon’s Entropy).
- $k_B$ : Boltzmann’s constant.

# Maximum Entropy

The prior probability distribution maximizes entropy (the average ignorance) while respecting macroscopic constraints. A natural constraint of normalization is  $\sum_i P_i = 1$ . Applying the Lagrange multiplier method,

$$\nabla[S + \lambda(\sum_i P_i - 1)] = 0,$$

where  $\nabla$  stands for the derivative with respect to  $P$ . To be specific,

$$\begin{aligned}\frac{\partial}{\partial P} \left[ S + \lambda(\sum_i P_i - 1) \right] &= \frac{\partial}{\partial P} \left[ -\sum_i P_i \log P_i + \lambda(\sum_i P_i - 1) \right] \\ &= \sum_i \left[ -\log P_i - P_i \frac{d \log P_i}{d P_i} + \lambda \right] \\ &= \sum_i [-\log P_i - 1 + \lambda] = 0.\end{aligned}$$

# Maximum Entropy

It leads

$$-\log P_i - 1 + \lambda = 0.$$

Finally, we get

$$P_i = e^{\lambda-1} = \text{const.} \equiv \frac{1}{\Omega}.$$

# Boltzmann's Entropy

In an equilibrium state, the probability of  $i$  state is given by

$$p_i = \frac{1}{\Omega}.$$

Then the entropy can be expressed as

$$\begin{aligned} S &= -\langle \log P_i \rangle = -\langle \log \frac{1}{\Omega} \rangle \\ &= \log \Omega. \end{aligned}$$

We will see the meaning of entropy later.

# Boltzmann and Shannon



Ludwig Boltzmann and Claude Shannon



# Number of States & Entropy

The total number (volume) of states is

$$\Omega = V^N \Delta E \frac{(2\pi m)^{3N/2} E^{3N/2-1}}{(3N/2 - 1)!}. \quad (16)$$

The entropy is then  $k_B \log \Omega$ , and

$$\begin{aligned} \log \Omega &= \log V^N + \log \Delta E + \frac{3N}{2} \log(2\pi m) \\ &+ \left( \frac{3N}{2} - 1 \right) \log E - \log(3N/2 - 1)! \\ &\approx N \log V + \frac{3N}{2} \log(2\pi m E) - (3N/2) \log(3N/2) + (3N/2). \end{aligned}$$

# Entropy for Ideal Gas

The entropy is

$$S \approx Nk_B \log V + \frac{3Nk_B}{2} \log(2\pi mE) - (3Nk_B/2) \log(3N/2) + (3Nk_B/2).$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{3Nk_B}{2E},$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk_B}{V}.$$

Therefore, we can derive equipartition theorem and the equation of state for the ideal gas,

$$E = \frac{3}{2}Nk_B T, \quad PV = Nk_B T.$$

# Gibbs Paradox

Compare  $2N$  particles in two boxes with volume  $V$  and  $2N$  particles in a box with volume  $2V$ :

$$S_1 = 2k_B \log V^N,$$

$$S_2 = k_B \log(2V)^{2N}.$$

# Gibbs Paradox & Gibbs factor

All particles are perfectly identical or indistinguishable:

$$S_1 = 2k_B \log V^N / N!,$$

$$S_2 = k_B \log (2V)^{2N} / (2N)!.$$

# Planck Constant

- $h$  has the unit of momentum  $\times$  distance.
- The uncertainty principle:  $\delta x \delta p \geq h$ .

Applying two factors, we find the Sackur-Tetrode formula:

$$\begin{aligned} S(N, V, E) &= k_B \log \Omega / (N! h^{3n}) \\ &= N k_B \log \left[ \frac{V}{N} \left( \frac{4\pi m E}{3N h^2} \right)^{3/2} \right] + N k_B \frac{5}{2}. \end{aligned} \quad (17)$$