

Now that we have reviewed the concepts of thermodynamics we turn our attention to describing microstates - either classically or quantum mechanically

Quantum mechanics

From the point of view of quantum mechanics, the problem we need to solve is governed by Schrodinger equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$

Where

$\hat{H} = \hat{H}(t)$ is the Hamiltonian for an isolated system at time t or for a Hamiltonian that interacts with the outside world

→ \hat{H} is independent of time if isolated, but could be dependent on time if it interacts

$|\Psi(t)\rangle$ is the state that describes the system at time t

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An equivalent formulation of the problem is given by applying a time evolution operator $U(t, t_0)$ to an initial state $|\Psi(t_0)\rangle$

The problem then is to calculate the time evolution operator which itself can be obtained by solving a Schrodinger-like equation

$$i\hbar \frac{d}{dt} U(t, t_0) = \hat{H}(t) U(t, t_0)$$

Properties: (i) The time evolution operator is unitary

$$U^\dagger(t, t_0) = U^{-1}(t, t_0)$$

(ii) satisfies the group property

$$U(t, t_0) = U(t, t_1) U(t_1, t_0)$$

(iii) If \hat{H} is time independent

$$U(t, t_0) = \exp\left[-\frac{i\hat{H}(t-t_0)}{\hbar}\right]$$

If we consider that the state evolves, but (in the case of a time independent \hat{H}) operators do not we are in the so-called Schrödinger picture (in the case of a time-varying Hamiltonian we can define time-dependent operators)

We can define another picture where the state remains fixed - and operator change with time

take $|\psi(t)\rangle$ and apply the inverse operator of the time evolution operator \rightarrow takes us back to $|\psi(t_0)\rangle$

$$|\psi_H\rangle = |\psi(t_0)\rangle = U^{-1}(t, t_0) |\psi(t)\rangle$$

The key point is that whatever picture we choose, physical quantities must remain unaltered

In the case of QM \rightarrow physical quantities $\langle A \rangle_{\psi} \equiv$ average of operator A as a function of time

In the Schrödinger picture:

$$\hat{A} = \hat{A}(t)$$

$$\langle \hat{A} \rangle_S(t) = \langle \psi(t) | \hat{A}(t) | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0) \hat{A}(t) U(t, t_0) | \psi(t_0) \rangle \quad (3)$$

$$\langle \hat{A} \rangle_H(t) = \langle \psi(t) | \hat{A}_H(t) | \psi(t_0) \rangle$$

since

$$\langle \hat{A} \rangle_S(t) = \langle \hat{A}_H \rangle(t)$$

$$\hat{A}_H(t) = U^{-1}(t, t_0) \hat{A}(t) U(t, t_0)$$

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For the special case of the Hamiltonian

$$\hat{H}_H(t) = U^{-1}(t, t_0) \hat{H}(t) U(t, t_0)$$

In the case where

\hat{H} does not depend on time

$$\hat{H}_H = \hat{H} \quad (1)$$

Proof $U(t, t_0) = \exp -i\hat{H}(t-t_0)/\hbar$

commutes with $\hat{H} \forall t$

$$\Rightarrow \hat{H}_H(t) = \hat{H} \underbrace{U^{-1}(t, t_0) U(t, t_0)}_{=I} = \hat{H}$$

■ In the special case that

$$[\hat{H}(t_1), \hat{H}(t_2)] = 0 \quad \forall t_1, t_2$$

$$U(t, t_0) = \exp \frac{-i}{\hbar} \int_{t_0}^t H(t) dt$$

and eq. (1) also holds

Let's then calculate the derivative

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$$i\hbar \frac{d\hat{A}_H}{dt} = i\hbar \frac{d[U^\dagger(t, t_0) \hat{A}(t) U(t, t_0)]}{dt} = i\hbar \left[\frac{dU^\dagger(t, t_0)}{dt} \right] \hat{A}(t) U(t, t_0) \\ + i\hbar U^\dagger(t, t_0) \frac{\partial \hat{A}(t)}{\partial t} U(t, t_0) + i\hbar U^\dagger(t, t_0) \hat{A}(t) \frac{dU(t, t_0)}{dt}$$

The complex conjugate operator obeys

$$-i\hbar \frac{dU^\dagger(t, t_0)}{dt} = \hat{A}_H^\dagger U^\dagger(t, t_0) \hat{H}$$

Proof is straight forward:
the Hamiltonian is Hermitian

$$i\hbar \frac{d\hat{A}_H}{dt} = -i\hbar \frac{\hat{A}_H^\dagger U^\dagger(t, t_0) \hat{H} \hat{A}(t) U(t, t_0)}{i\hbar} + i\hbar U^\dagger(t, t_0) \hat{A}(t) \frac{\hat{H} U(t, t_0)}{i\hbar}$$

$$+ i\hbar U^\dagger(t, t_0) \frac{\partial \hat{A}(t)}{\partial t} U(t, t_0)$$

$$\left(\frac{\partial \hat{A}(t)}{\partial t} \right)_H$$

$$= - \underbrace{U^\dagger(t, t_0) \hat{A}_H^\dagger(t)}_{\hat{A}_H^\dagger(t)} \underbrace{U(t, t_0) U^\dagger(t, t_0) \hat{A}(t) U(t, t_0)}_{\hat{A}(t)}$$

$$+ \underbrace{U^\dagger(t, t_0) \hat{A}(t) U(t, t_0)}_{\hat{A}_H(t)} \underbrace{U^\dagger(t, t_0) \hat{H} U(t, t_0)}_{\hat{H}_H(t)} + i\hbar \left(\frac{\partial \hat{A}(t)}{\partial t} \right)_H$$

$$i\hbar \frac{d\hat{A}_H}{dt} = [\hat{A}_H(t), \hat{H}_H(t)] + i\hbar \frac{\partial \hat{A}(t)}{\partial t}$$

We can also define a projection operator on a state $|\psi\rangle$

$$D = |\psi\rangle\langle\psi|$$

We note that

$$\text{Tr } |\psi\rangle\langle\psi| = \sum_n \langle n|\psi\rangle\langle\psi|n\rangle$$

the trace is invariant under basis transformation so the choice of $\{|n\rangle\}$ is arbitrary.

where $\{|n\rangle\}$ forms a complete basis of orthonormal states

$$\Rightarrow \sum_n |n\rangle\langle n| = I$$

$$= \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = \langle\psi|\left[\sum_n |n\rangle\langle n|\right]|\psi\rangle = \langle\psi|\psi\rangle$$

$$\langle A \rangle_\psi = \langle\psi|A|\psi\rangle = \langle\psi|\underbrace{|\psi\rangle}_{|\psi\rangle}\langle\psi|A = \langle\psi|\left[\sum_n |n\rangle\langle n|\right]|\psi\rangle = \sum_n \underbrace{\langle n|\psi\rangle}_{\langle n|\psi\rangle}\langle\psi|n\rangle$$

$$= \sum_n \langle n|[A|\psi\rangle\langle\psi|]n\rangle = \sum_n \langle n|AD|n\rangle = \text{Tr } AD$$

Let's now do the same thing but write the projection operator on a particular basis $\{|i\rangle\}$

$$|\psi\rangle = \sum_i c_i |i\rangle$$

$$\Rightarrow D = |\psi\rangle\langle\psi| = \sum_{ij} c_i^* c_j |i\rangle\langle j| \Rightarrow D_{ij} = c_i c_j^*$$

But what if we don't know what state the system is in?

Suppose all we know is the probability p_n of finding the system in a state $|\psi_n\rangle$

$$|\psi_n\rangle = \sum_i c_i^{(n)} |i\rangle$$

It is important to note here that we are not talking about our system being in a particular state that is a combination of $|\psi_n\rangle$

$$|\Psi\rangle = \sum_n d_n |\psi_n\rangle \quad d_n = \sqrt{p_n}$$

This would also imply that we "know" the exact state ~~the~~ system is in. We could apply a basis transformation to go back to $\{|i\rangle\}$, for example

The key point here is that we introduce a probability distribution for the microstates, thus defining a macrostate

$$\begin{aligned} |\Psi\rangle &\equiv \text{pure state} \\ \Rightarrow \{|\psi_n\rangle, p_n\} &\equiv \text{Statistical mixture} \end{aligned}$$

We then define the density operator

$$\mathcal{D} = \sum_n |\psi_n\rangle p_n \langle \psi_n|$$

In the special case that \mathcal{D} is given by a pure state is always possible to find a single $|\Psi\rangle$ for which

$$\mathcal{D} = |\Psi\rangle\langle\Psi|$$

Projection operator on state $|\Psi\rangle$

For a pure state

$$\langle A \rangle = \text{Tr } A \mathcal{D} = \langle \Psi | A | \Psi \rangle$$

For a mixed state

$$|\Psi\rangle = \sum_i c_i |i\rangle$$

$$\langle A \rangle_{\Psi} = \sum_j c_j^* \langle j | \hat{A} \sum_i c_i |i\rangle = \sum_{ij} c_j^* c_i \langle j | \hat{A} |i\rangle$$

Because the basis is arbitrary I'll choose a basis that is an eigenbasis of \hat{A}

$$\hat{A}|i\rangle = a_i|i\rangle \quad \langle i|j\rangle = \delta_{ij}$$

$$\langle A \rangle_{\Psi} = \sum_i |c_i|^2 a_i$$

↑
probability of measuring the particle in state $|i\rangle$

We then define the average of an operator in a mixed state

$$\langle A \rangle = \sum_n p_n \langle \tau_n | \hat{A} | \tau_n \rangle$$

↑
the microstates are independent

$$= \sum_i \sum_n p_n \langle \tau_n |i\rangle \langle i | \hat{A} | \tau_n \rangle = \sum_{in} \langle i | \hat{A} | \tau_n \rangle p_n \langle \tau_n |i\rangle$$

$$= \sum_i \langle i | \hat{A} \underbrace{\sum_n p_n |\tau_n\rangle \langle \tau_n|}_{\mathcal{D}} |i\rangle = \text{Tr } \hat{A} \mathcal{D}$$

Properties of \mathcal{D}

(i) $\mathcal{D} = \mathcal{D}^\dagger$ Hermitian (the p_n 's are real)

(ii) $\text{Tr } \mathcal{D} = \sum_n p_n = 1$

$$\sum_i \langle i | \mathcal{D} |i\rangle = \sum_i \sum_n \langle \tau_n |i\rangle p_n \langle i | \tau_n \rangle = \sum_i \sum_n \sum_j c_j^{*(n)} \underbrace{\langle i | j \rangle}_{\delta_{ij}} p_n c_j^{(n)} \underbrace{\langle j | i \rangle}_{\delta_{ji}}$$

$$|\tau_n\rangle = \sum_j c_j^{(n)} |j\rangle$$

$$1 = \langle \tau_n | \tau_n \rangle = \sum_j |c_j^{(n)}|^2 \quad \text{for } n = 1, \dots, N$$

$$= \sum_i \sum_n p_n |c_i^{(n)}|^2 = \sum_n p_n \sum_i |c_i^{(n)}|^2 = 1$$

(iv) $D^2 = D$ for a pure state

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If D is a pure state

$$D = |\psi\rangle\langle\psi| \quad p=1 \quad \Rightarrow \quad D^2 = |\psi\rangle\langle\psi| \underbrace{|\psi\rangle\langle\psi|}_{\substack{\downarrow \\ \text{(normalized)}}} = |\psi\rangle\langle\psi| = D$$

If D is a statistical mixture

$$D = \sum_n |\psi_n\rangle\langle\psi_n| p_n$$

$$D^2 = \sum_{n,n'} |\psi_n\rangle\langle\psi_n| p_n |\psi_{n'}\rangle\langle\psi_{n'}| p_{n'} a_{nn'} = \sum_{n,n'} |\psi_n\rangle p_n a_{nn'} p_{n'} \langle\psi_{n'}|$$

In the special case that all states are orthogonal

not the same state

$$a_{nn'} = \delta_{nn'}$$

$$= \sum_n p_n^2 |\psi_n\rangle\langle\psi_n|$$

This would mean

$$p_n^2 = p_n \quad \forall n$$

$$\Rightarrow p_n = \begin{cases} 1 \\ 0 \end{cases}$$

and there can be only one value of $p_n = 1$, all the remaining ones must be zero

pure state

Now, considering our definition of the density operator we can define its evolution

$$D(t_0) = \sum_n p_n |\psi_n(t_0)\rangle\langle\psi_n(t_0)|$$

The density operator is in a statistical mixture of states at time t_0

$$\begin{aligned} \mathcal{D}(t) &= \sum_n |\gamma_n(t)\rangle p_n \langle \gamma_n(t)| = \sum_n U(t, t_0) |\gamma_n(t_0)\rangle p_n \langle \gamma_n(t_0)| U^{-1}(t, t_0) \\ &= U(t, t_0) \underbrace{\sum_n |\gamma_n(t_0)\rangle p_n \langle \gamma_n(t_0)|}_{\mathcal{D}(t_0)} U^{-1}(t, t_0) \end{aligned}$$

$$\mathcal{D}(t) = \underbrace{U(t, t_0) \mathcal{D}(t_0) U^{-1}(t, t_0)}_{\text{different from typical operators.}}$$

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$$i\hbar \frac{d\mathcal{D}(t)}{dt} = i\hbar \frac{dU(t, t_0)}{dt} \mathcal{D}(t_0) U^{-1}(t, t_0) + i\hbar U(t, t_0) \mathcal{D}(t_0) \frac{dU^{-1}(t, t_0)}{dt}$$

$\mathcal{D}(t_0)$ does not depend on

$$= i\hbar \underbrace{\hat{H} U(t, t_0) \mathcal{D}(t_0) U^{-1}(t, t_0)}_{\mathcal{D}(t)} - \underbrace{U(t, t_0) \mathcal{D}(t_0) U^{-1}(t, t_0) \hat{H}(t)}_{\mathcal{D}(t)}$$

$$= [\hat{H}(t), \mathcal{D}(t)]$$

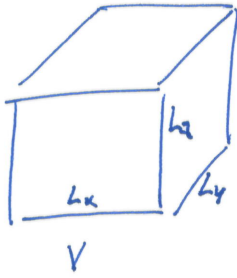
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⌈ We note that in the Heisenberg picture the state does not depend on time \Rightarrow the density operator does not depend on time ⌋

Generalizing for a mixed state evolving in time
 $\langle A \rangle(t) = \text{Tr} A(t) \mathcal{D}(t) = \text{Tr} A_H(t) \mathcal{D}_H$

$$\mathcal{D}_H = \mathcal{D}(t_0)$$

Let's now solve the problem of particles in a box



The particles are free inside the box

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = \epsilon \psi(\vec{r})$$

Taking the limit of a large box with periodic boundary conditions

$$\psi(0, y, z) = \psi(L_x, y, z)$$

$$\psi(x, 0, z) = \psi(x, L_y, z)$$

$$\psi(x, y, 0) = \psi(x, y, L_z)$$

Equation is separable with solution

$$\psi(\vec{r}) = \frac{1}{\sqrt{L_x L_y L_z}} e^{i\vec{k}_n \cdot \vec{r}} \quad \text{with} \quad \frac{\hbar^2 \vec{k}_n^2}{2m} = \epsilon$$

From the boundary condition we get

$$\frac{1}{\sqrt{L_x L_y L_z}} e^{i(k_n^x L_x + k_n^y L_y + k_n^z L_z)} = \frac{1}{\sqrt{L_x L_y L_z}} e^{i k_n^x L_x} e^{i(k_n^y L_y + k_n^z L_z)}$$

$$\Rightarrow 1 = e^{i k_n^x L_x} \Rightarrow k_x L_x = 2\pi n$$

$$k_x^n = \frac{2\pi n_x}{L_x}$$

$$k_y^n = \frac{2\pi n_y}{L_y}$$

$$k_z^n = \frac{2\pi n_z}{L_z}$$

In each direction we notice that the difference between consecutive quantum numbers n_i is

$$\Delta k_i^n = \frac{2\pi}{L_i} \Delta n_i$$

so the volume in k space of small variations between states is

$$\rho(\vec{k}) = \frac{L_x}{2\pi} \frac{L_y}{2\pi} \frac{L_z}{2\pi} = \frac{L_x L_y L_z}{(2\pi)^3} = \frac{V}{(2\pi)^3} \quad \text{density of states in } k \text{ space}$$

For a free particle $\vec{p} = \hbar \vec{k}$

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

Let's say we want to calculate a quantity that is better defined in the energy domain.

$$\Phi = \int g(\epsilon) \rho(\epsilon) d\epsilon$$

↳ number of states in the energy range $\{\epsilon, \epsilon + d\epsilon\}$

The same quantity can be calculated by considering all possible states in k -space

$$\Phi = \int \underbrace{g(\epsilon)}_{\text{function of } k} \underbrace{\rho(\vec{k})}_{V/(2\pi)^3} d^3k \rightarrow k^2 d\Omega_k dk$$

but ~~g(\epsilon)~~

$\epsilon(\vec{p}) = \frac{p^2}{2m}$ does not depend on direction

$$d\epsilon = \frac{2p dp}{2m} = \frac{p dp}{m} \quad k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

$$= 4\pi \frac{V}{(2\pi)^3} \int g(\epsilon) k^2 dk = \frac{V}{2\pi^2} \int g(\epsilon) k \frac{m d\epsilon}{\hbar^2}$$

$$\Phi = \int g(\epsilon) \underbrace{\frac{V m}{2\pi^2 \hbar^3} (2m\epsilon)^{1/2}}_{\rho(\epsilon)} d\epsilon$$

$\rho(\epsilon) \equiv$ density of states

For an ideal non-interacting quantum gas

$$\mathcal{E} = \frac{\hbar^2 \vec{k}^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

If we consider that in equilibrium the system is isotropic

$$\frac{\langle n_x^2 \rangle}{L_x^2} = \frac{\langle n_y^2 \rangle}{L_y^2} = \frac{\langle n_z^2 \rangle}{L_z^2}$$

the average of the square of the momentum squared is the same in all directions

$$\langle \mathcal{E} \rangle = \frac{3\hbar^2 \pi^2}{2m} \frac{\langle n_x^2 \rangle}{L_x^2}$$

$$\frac{\langle n_x^2 \rangle}{L_x^2} = \frac{2m \langle \mathcal{E} \rangle}{3\hbar^2 \pi^2}$$

Varying the size of the box in x

$$\frac{\partial \langle \mathcal{E} \rangle}{\partial L_x} = - \frac{\hbar^2 \pi^2}{2m} \frac{2 \langle n_x^2 \rangle}{L_x^3} = - \frac{2}{L_x} \underbrace{\frac{\hbar^2 \pi^2}{2m} \frac{\langle n_x^2 \rangle}{L_x^2}}_{\frac{\langle \mathcal{E} \rangle}{3}}$$

$$= - \frac{2}{3L_x} \langle \mathcal{E} \rangle$$

If the system is isolated $dQ=0$

$$d\mathcal{E} = dW = -P_y L_z dL_x$$

$$\frac{d\mathcal{E}}{dL_x} = -P_y L_z$$

$$\frac{-2}{3L_x} \langle \mathcal{E} \rangle = -P_y L_z$$

$$PV = \frac{2}{3} \langle \mathcal{E} \rangle$$

$$H(q_i, p_i) = \sum_i \frac{p_i^2}{2m} + \sum_i U(q_i) + \frac{1}{2} \sum_{i \neq j} U(q_i, p_i)$$

Hamilton's equations

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i$$

We then define a phase space by the set of coordinates (q_i, p_i)

microstate $\rightarrow (q_i(t), p_i(t))$

Obs: A trajectory in phase-space cannot self intersect (unless the system is cyclic)

\rightarrow deterministic \Rightarrow the microstate is uniquely defined

Time evolution

$$q'_i = q_i + \dot{q}_i dt = q_i + \frac{\partial H}{\partial p_i} dt$$

$$p'_i = p_i + \dot{p}_i dt = p_i - \frac{\partial H}{\partial q_i} dt$$

vector quantity

$$\begin{pmatrix} q'_i \\ p'_i \end{pmatrix} = \begin{pmatrix} q_i \\ p_i \end{pmatrix} + \begin{pmatrix} \dot{q}_i \\ \dot{p}_i \end{pmatrix} dt$$

Let's then say we want to integrate over the phase space

$$dq_i dp_i$$

If we want to perform this integral at a time dt later

$$dq'_i dp'_i$$

$$\Rightarrow dq_i dp_i = \underbrace{\left| \frac{\partial(q_i, p_i)}{\partial(q'_i, p'_i)} \right|}_{\text{determinant of the Jacobian}} dq'_i dp'_i$$

determinant of the Jacobian

$$\frac{\partial(q_i', p_i')}{\partial(q_i, p_i)} = \begin{pmatrix} \frac{\partial q_i'}{\partial q_i} & \frac{\partial q_i'}{\partial p_i} \\ \frac{\partial p_i'}{\partial q_i} & \frac{\partial p_i'}{\partial p_i} \end{pmatrix} = \begin{pmatrix} 1 + \frac{\partial^2 H}{\partial p_i \partial q_i} dt & \frac{\partial^2 H}{\partial p_i^2} dt \\ -\frac{\partial^2 H}{\partial q_i^2} dt & 1 - \frac{\partial^2 H}{\partial p_i \partial q_i} dt \end{pmatrix}$$

$$J(t) = \left| \frac{\partial(q_i', p_i')}{\partial(q_i, p_i)} \right| = 1 - \left(\frac{\partial^2 H}{\partial p_i \partial q_i} dt \right)^2 + \frac{\partial^2 H}{\partial p_i^2} dt \frac{\partial^2 H}{\partial q_i^2} dt = 1 + O(dt^2)$$

to order dt the Jacobian is independent of time

$$\frac{dJ(t)}{dt} = 0$$

$$J = 1$$

$$\prod_i dq_i dp_i = \prod_i dq_i' dp_i'$$

The volume in phase-space
is constant

Liouville's theorem.

Density

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A microstate is defined as a set of particles in a set of coordinates in phase space $\{\vec{r}_i, \vec{p}_i\}$

A macrostate will be an average of microstates.

We then define the probability of observing a particular microstate

$$\mathcal{D}(\vec{r}_i, \vec{p}_i, t) \quad \text{at } t=0 \quad \mathcal{D}(\vec{r}_i, \vec{p}_i, t=0) = \mathcal{D}_0(\vec{r}_i, \vec{p}_i)$$

If we integrate over the entire phase space we must get 1

$$\Rightarrow \int \prod_{i=1}^N d^3\vec{p}_i d^3\vec{r}_i \mathcal{D}(\vec{r}_i, \vec{p}_i) = \int d\Gamma \mathcal{D}_0(\vec{r}_i, \vec{p}_i)$$

$$\text{where } d\Gamma = C \prod_{i=1}^N d^3\vec{p}_i d^3\vec{r}_i$$

in principle, an arbitrary constant

The same is valid for any time t

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considering the conservation of probability

$$\mathcal{D}(q(t+dt), p(t+dt), t+dt) dq' dp' = \mathcal{D}(q(t), p(t), t) dq dp$$

From Liouville's theorem

$$dq' dp' = dq dp$$

Taylor expanding the LHS

$$\mathcal{D}(q(t+dt), p(t+dt), t+dt) dq' = \mathcal{D}(q(t), p(t), t) + \frac{\partial \mathcal{D}}{\partial q} \frac{\partial q}{\partial t} dt + \frac{\partial \mathcal{D}}{\partial p} \frac{\partial p}{\partial t} dt + \frac{\partial \mathcal{D}}{\partial t} dt$$

$$\Rightarrow \underbrace{\left\{ \frac{\partial \mathcal{D}}{\partial q} \dot{q} + \frac{\partial \mathcal{D}}{\partial p} \dot{p} + \frac{\partial \mathcal{D}}{\partial t} \right\}}_{=0} dt = 0 \quad \leftarrow \text{arbitrary}$$

This means that $\frac{d\mathcal{D}}{dt} = 0$

For N particles with components $\alpha \equiv \{x, y, z\}$

$$\sum_{i\alpha} \left(\frac{\partial \mathcal{D}}{\partial \dot{q}_{i\alpha}} \dot{q}_{i\alpha} + \frac{\partial \mathcal{D}}{\partial \dot{p}_{i\alpha}} \dot{p}_{i\alpha} \right) + \frac{\partial \mathcal{D}}{\partial t}$$

\uparrow $\frac{\partial H}{\partial p_{i\alpha}}$ \uparrow $-\frac{\partial H}{\partial q_{i\alpha}}$

$$\{H, \mathcal{D}\} + \frac{\partial \mathcal{D}}{\partial t}$$

where $\{H, \mathcal{D}\} = \sum_{i\alpha} \left(\frac{\partial H}{\partial p_{i\alpha}} \frac{\partial \mathcal{D}}{\partial q_{i\alpha}} - \frac{\partial H}{\partial q_{i\alpha}} \frac{\partial \mathcal{D}}{\partial p_{i\alpha}} \right)$

Poisson bracket

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For a general dynamical variable

$$\frac{dA}{dt} = \{H, A\} + \frac{\partial A}{\partial t}$$

and

$$\langle A \rangle(t) = \int dx \mathcal{D}(x(t), t) A(x) = \int dx \rho_0(x) A(x(t), t)$$