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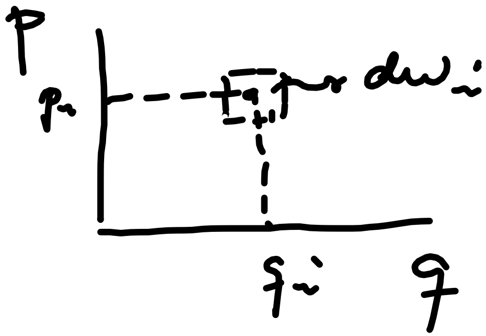
Density Function:

$$\rho(q,p,t) \equiv \rho(\{q_i\},\{p_i\},t)$$

# of representative points in $d\omega$

$$\rho(q,p,t)\,d\omega = \lim_{N\to\infty} \frac{dN(p,q,t)}{N}$$

total # of microstates



$\rho(q,p,t)$ gives the number of microstates in $d\omega$

ρ provides a weight that allows to evaluate averages in the ensemble:

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

In general $\langle f \rangle = \langle f \rangle(t)$.

Notice that $\int$ goes over ALL phase space but $\rho(q,p,t)$ may be zero in some regions.

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Stationary system:

$\frac{\partial \rho}{\partial t} = 0 \Rightarrow \rho$ independent of t.

then $\rho \equiv \rho(q, p)$

if $\frac{\partial \rho}{\partial t} = 0 \Rightarrow \langle f \rangle$ is time independent for an stationary system.

A thermodynamic system is in equilibrium if $\langle f \rangle$ is independent of t for all f's. Then this happens if $\frac{\partial \rho}{\partial t} = 0$.

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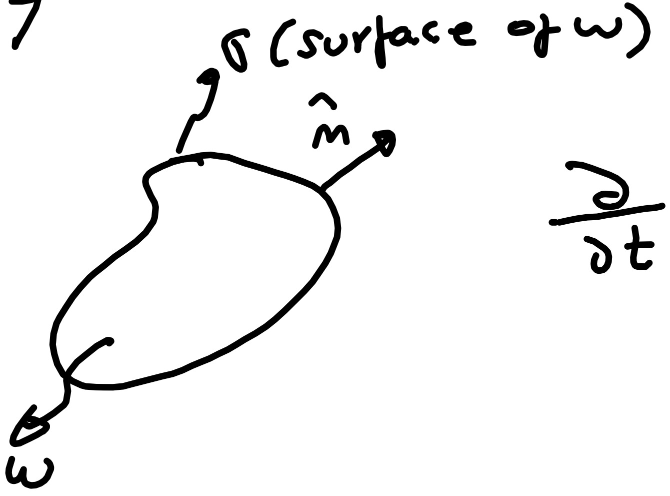
Equilibrium conditions:



$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega$$

rate of change of the total number of points (microstates) inside volume ω)

ω is the volume in phase space of a macrostate. (Defined by E, total energy).
(and also by N and V)

It contains many microstates

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The flux of points (microstates) across the surface σ is given by:

$$\int_\sigma \rho\, \bar{v}\cdot\hat{n}\, d\sigma = \int \bar{\nabla}(\rho\bar{v})\, dw$$

divergence theorem

$$\bar{v} = (\dot{q}_i, \dot{p}_i)$$

in 3D $\bar{\nabla}\cdot\bar{p} = \frac{\partial p_x}{\partial x} + \frac{\partial p_y}{\partial y} + \frac{\partial p_z}{\partial z}$

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

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The volume ω may move in phase space as a function of time but all the points inside ω at time t_0 will continue to be in ω at time t_f. There are no sources nor sinks for microstates. Then:

$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega = -\int_{\omega} \bar{\nabla}(\rho \bar{v})\, d\omega$$

Then

$$\int_{\omega} \left\{ \frac{\partial \rho}{\partial t} + \bar{\nabla}(\rho \bar{v}) \right\} d\omega = 0 \qquad (1)$$

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Since ⓪ has to be independent of ω then

$$\frac{\partial \rho}{\partial t} + \bar{\nabla}(\rho \bar{v}) = 0 \quad (2)$$

continuity equation for the points in ω.

replacing $\bar{\nabla}(\rho\bar{v})$ by expression in (*):

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

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

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

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

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} + \frac{\partial \rho}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right)\right\} + $$
$$+ \rho \sum_{i=1}^{3N} \left\{ \underbrace{\frac{\partial^2 H}{\partial q_i \partial p_i} + \left[-\frac{\partial^2 H}{\partial p_i \partial q_i}\right]}_{0} \right\} = 0$$

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

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

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Let's define:

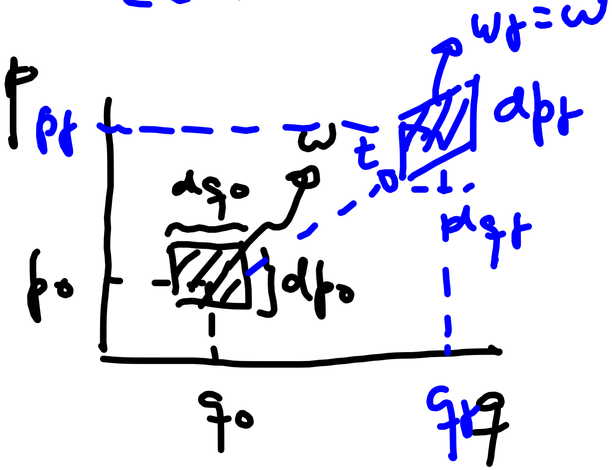
$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

total time derivative

partial time derivative

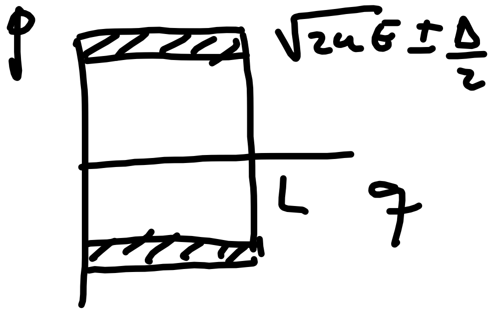
Liouville's theorem.

The microstates inside ω travel in time like an incompressible fluid.



The shape of ω may change but its volume stays the same.

Example: particle in a box!



The shaded regions are W the volume that contains the allowed microstates compatible with a given energy

$$E = \frac{p^2}{2m}$$

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Then $\frac{d\rho}{dt} = 0$ is always valid

while $\frac{\partial \rho}{\partial t} = 0$ is valid only if the system is in equilibrium.

Both are simultaneously valid if $[\rho, H] = 0$.

When can $[\rho, H]$ be zero?

1) If ρ is independent of q_i and p_i in addition to being independent of t.

Then $\rho(q,p,t) = \begin{cases} \text{constant inside } \omega \\ 0 \text{ everywhere else.} \end{cases}$

$\therefore$ at any time the system will be uniformly distributed over <u>all</u> the accessible states (microstates). All the microstates in a macrostate are equally likely.

This is equivalent to the equal probability postulate for a system with energy $E \pm \Delta E$.

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Under these conditions:

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

$$= \frac{1}{\omega} \int f(q,p)\, d\omega$$

volume of relevant phase space.

The ensemble with a given (N, V, E) which has equal probability of being in any accessible microstate is called the microcanonical ensemble.

Microcanonical Ensemble: $\rho(q, p) = \text{constant}$.

Notice that $[\rho, H] = 0$ can also be satisfied if $\rho(q, p) = \rho[H(p, q)]$

since $[\rho, H] = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$

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

We will see that the most natural form for $\rho(q, p)$ will be $\rho(q, p) \propto e^{-\frac{H(p, q)}{kT}}$

Microcanonical Ensemble.

Macrostates defined by : (N, V, E)

The accessible microstates lie in an hypershell in phase space.

$$E - \frac{1}{2}\Delta \leq H(q,p) \leq E + \frac{1}{2}\Delta \quad (1)$$

accessible states.

$$\omega = \int d\omega = \int' d^{3N}q \, d^{3N}p$$

$$\rho(q,p) = \begin{cases} \text{constant if } (1) \\ 0 \text{ otherwise} \end{cases}$$

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$\langle f \rangle$ is obtained either from a time average of a single system or from an ensemble average at a single time.

Both are equivalent.

Ergodicity: assumption that each point in phase space visits all the allowed space after a long enough time.

Minimum volume element in phase space:
(volume in phase space associated to one single microstate).

Microstates are uniformly distributed in ω.

Then $\Gamma \propto \omega$ $\qquad \Gamma$: total number of microstates.

$$\Gamma = \frac{\omega}{\omega_0}$$

$\frac{1}{\omega_0}$: proportionality constant

ω_0 : volume per microstate.

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$$w_0 = \frac{w}{\Gamma}$$

Notice that knowing w_0 we obtain

$$S = k \ln \Gamma = k \ln(w/w_0)$$

Units of w_0

$$[w_0] = [q_i]^{3N}[p_i]^{3N} = m^{3N}\left(kg\frac{m}{s}\right)^{3N} =$$

$$= \left(\frac{kg\, m^2}{s}\right)^{3N}$$

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Finding ω_0: classical ideal gas.

N particles, V $\qquad E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \qquad 0 \le q_i \le L$

$V = L^3$

$$\omega = \int' \cdots \int' d^{3N}q \, d^{3N}p = \underbrace{\int_0^L \cdots \int_0^L d^{3N}q}_{L^{3N} = V^N} \underbrace{\int \cdots \int d^{3N}p}_{E - \frac{1}{2}\Delta \le E \le E + \frac{1}{2}\Delta} =$$

$$= V^N \int \cdots \int d^{3N}y \qquad y_i^2 = \frac{p_i^2}{2m}$$

$$2m(E - \tfrac{1}{2}\Delta) \le \sum_i y_i^2 \le 2m(E + \tfrac{1}{2}\Delta)$$

(Volume between 2 hyperspheres of radius $\sqrt{2m(E \pm \frac{\Delta}{2})}$

If $\Delta << E \Rightarrow$ vol. shell $= \underbrace{\Delta \left(\frac{m}{2E}\right)^{1/2}}_{\text{shell thickness}} \underbrace{\left\{ \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} (2mE)^{\frac{3N-1}{2}} \right\}}_{\text{volume of sphere of radius } \sqrt{2mE} \text{ in } 3N \text{ dimensions}}$

Then

$$\omega \simeq V^N \Delta (2mE)^{\frac{3N-1}{2}} \sqrt{\frac{m}{2E}} \frac{2\pi^{\frac{3N}{2}}}{\left[\frac{3N}{2}-1\right]!} =$$

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

We found before that for the ideal gas:

$$\Gamma = \left(\frac{V}{h^3}\right)^N \frac{3N}{2} \frac{(2m\bar{E})^{3N/2}}{E\left(\frac{3N}{2}\right)!}\Delta$$

# of microstates in the hypershell.

Then

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

$$\sim \frac{1}{h^{3N}}$$

$$\therefore \quad \omega_0 = h^{3N} = h^{\mathcal{N}}$$

$\mathcal{N}$: # of degrees of freedom.

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