9/7

Last time:

$$\langle f \rangle = \frac{\int f(q,p)\,\rho(q,p;t)\, d^{3N}q\, d^{3N}p}{\int \rho(q,p;t)\, d^{3N}q\, d^{3N}p} \quad (1)$$

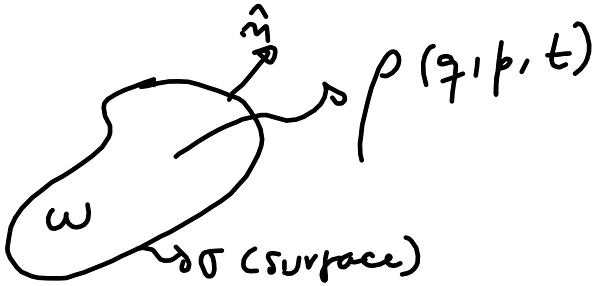
Stationary system:

$$\frac{\partial \rho}{\partial t} = 0 \quad \Rightarrow \quad \rho = \rho(q,p) \text{ but time independent}$$

Stationary $\Rightarrow$ equilibrium $\Rightarrow$ ρ is constant at a fixed point (q,p) (no time dependent).

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

Equilibrium conditions:



We want to see how ρ inside ω changes with time.

volume in phase space

$$\frac{\partial}{\partial t}\int_\omega \rho\, d\omega = -\int_\sigma \underbrace{\rho\, \bar{v}\cdot\hat{n}}_{\text{flux}}\, d\sigma \overset{\text{divergence theorem}}{=} -\int \bar{\nabla}\cdot(\rho\bar{v})\, d\omega =$$

$$\bar{v} = (\dot{q}_i, \dot{p}_i) \qquad = -\int \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}(\rho\,\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\,\dot{p}_i) \right\} d\omega$$

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

Then

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

Since it has to be valid for any ω then:

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

continuity equation

ρ goes through phase space as an incompressible fluid.

$$0 = \frac{\partial \rho}{\partial t} + \bar{\nabla}\cdot(\rho\bar{v}) = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}(\rho \underbrace{\dot{q}_i}_{\frac{\partial H}{\partial p_i}}) + \frac{\partial}{\partial p_i}(\rho \underbrace{\dot{p}_i}_{-\frac{\partial H}{\partial q_i}}) \right\} =$$

$$= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i \right) + \rho \overbrace{\sum_{i=1}^{3N} \left(\underbrace{\frac{\partial \dot{q}_i}{\partial q_i}}_{\partial^2 H/\partial q_i \partial p_i} + \underbrace{\frac{\partial \dot{p}_i}{\partial p_i}}_{= -\frac{\partial^2 H}{\partial p_i \partial q_i}} \right)}^{0}$$

Then

$$0 = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}$$

Define:

$$[\rho, H] = \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right]$$ Poisson's bracket

then

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \Rightarrow \frac{d\rho}{dt} = 0$$ Liouville's theorem.

Equilibrium occurs if $\frac{\partial \rho}{\partial t} = -[\rho, H] = 0$

ρ for a system in equilibrium has to be independent of t and satisfy that $[\rho, H] = 0$.

One way of satisfying $[\rho, H] = 0$ is if

ρ = constant independent of q, p and t.

We can propose a density ρ such that

$$\rho = \begin{cases} \text{constant inside relevant region in phase space (allowed region)} \\ 0 \quad \text{otherwise.} \end{cases}$$

This means that at any time the system with (N, V, E) is uniformly distributed among all its accessible states.

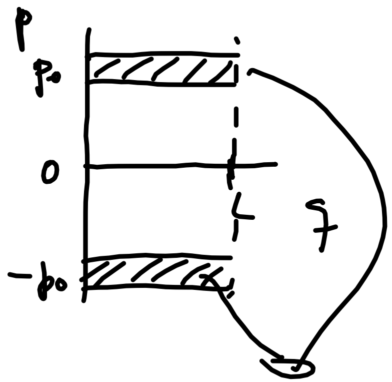
This means that now

$$\boxed{\langle f \rangle} \overset{①}{=} \frac{\rho \int' f(q,p)\, d^{3N}q\, d^{3N}p}{\rho \int' d^{3N}q\, d^{3N}p} \equiv \frac{\int' f\, d\omega}{\int d\omega} = \boxed{\frac{\int' f\, d\omega}{\omega}}$$

$$\int' d\omega = \int_{\text{over accessible regions in phase space}}$$

$$d\omega \equiv d^{3N}q\, d^{3N}p.$$

An ensemble with constant ρ in the allowed regions is called the microcanonical ensemble.



allowed ω

1 particle Volume L in 1D

$$E_0 - \frac{\Delta}{2} < E < E_0 + \frac{\Delta}{2}$$

$$E = \frac{p^2}{2m} \Rightarrow p = \pm\sqrt{2mE}$$

the integrals go $\int_0^L dq$ and $\int_{-p_0-\frac{\Delta'}{2}}^{-p_0+\frac{\Delta'}{2}} dp + \int_{p_0-\frac{\Delta'}{2}}^{p_0+\frac{\Delta'}{2}} dp$

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

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

We will later see that

$$\rho(q,p) \propto e^{-\frac{H(q,p)}{kT}}$$

is the natural form for $\rho(H(q,p))$.

This is the form of ρ that will characterize the canonical ensemble where T rather than E is fixed.

Microcanonical ensemble:

Macrostate defined by N, V, E (E interval really)

$\left(E_0 - \frac{\Delta}{2} \leq E \leq E_0 + \frac{\Delta}{2}\right)$

Then the accessible states, i.e. the compatible microstates, lie in a hypershell in the hypervolume.

The shell is defined by

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

$$\omega = \int' d\omega \equiv \int' d^{3N}q \, d^{3N}p \qquad \omega = \omega(N, V, E, \Delta)$$

total volume allowed in phase space.

$$\rho(q,p) = \begin{cases} \text{constant if (2) is satisfied.} \\ 0 \quad \text{otherwise.} \end{cases}$$

The average value of f over the allowed space is considered equivalent to the time average for the observable in one single member of the ensemble:

$$\langle f \rangle = \frac{1}{\omega} \int f \, d\omega = \langle f \rangle_{\text{time averaged}}$$

Ergodicity is implied. Each point (each member of the ensemble) is supposed to visit all phase space after a long enough time.

How do we relate ρ and ω to the entropy?

We need to be able to count the number of states inside ω.

We know that Γ, the number of states in ω has to be proportional to ω since ρ is constant

$\therefore \; \Gamma \propto \omega \quad \Rightarrow \quad \Gamma = \dfrac{\omega}{\omega_0} \qquad c = \dfrac{1}{\omega_0}$

ω_0 : "arbitrary" volume in phase space that contains 1 microstate.

ω_0 is not arbitrary in quantum mechanics as we will see.

Then

$$S = k \ln \Gamma = k \ln (\omega/\omega_0)$$

Units of ω_0 : $[\omega_0] = [q_i][p_i] = m^{3N} \left(kg \frac{m}{s}\right)^{3N} =$

$$= \underbrace{\left(\frac{kg\,m^2}{s}\right)}_{\text{angular momentum.}}{}^{3N}$$

Examples:

Find ω_0 for a classical ideal gas:

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

$$V = L^3$$

$$\underset{\substack{\text{total volume}\\\text{of allowed}\\\text{phase space}}}{\omega} = \int^{1}\cdots\int^{1} d^{3N}q\, d^{3N}p = \underbrace{\int_0^L\cdots\int_0^L d^{3N}q}_{V^N} \underbrace{\int_{E-\frac{1}{2}\Delta \le E \le E+\frac{1}{2}\Delta} d^{3N}p}_{\substack{\text{Volume of}\\\text{hypersphere shell}}} =$$

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

See Section 1.4 where the volume of the shell is calculated.

Also Γ, the number of states inside the shell was also calculated in 1.4 using quantum states. It was found that

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

if a classical aproximation is used h is replaced by h_0.

Now

$$\frac{1}{\omega_0} = \frac{\Gamma}{\omega} = \frac{1}{h^{3N}}$$

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

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