Macroscopic Systems

Typical number of molecules in this room $\sim 10^{24}$

In principle, classical mech. can be used to trace the trajectories of each individual particle $\Rightarrow$ not practical, nor useful.

Rather describe such a system in terms of a **macrostate**

In this case, a macrostate is specified by 4 parameters:

Internal energy E
Temperature T
Entropy S
Pressure P
etc., etc.

$\to$ thermodynamic quantities

Given macrostate can correspond to many different microstates

Microstate: collection of particles specified by (p_a, q_a)

$\Rightarrow$ each macrostate will correspond to many microstates

Consider 3 distinct particles → each can have energy $\varepsilon = 0, 1, 2 \dots \infty$

A macrostate can be defined by requiring total energy $E = 3$.

This can be distributed in many possible ways.

$$E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3$$

where ε_i - energy of i

ε_1	ε_2	ε_3	
1	1	1	- 1 state
2	1	0	6 states
2	0	1	
1	2	0	
1	0	2	
0	2	1	
0	1	2	
3	0	0	3 states
0	3	0	
0	0	3	

⟹ Total number of microstates = 10

For a lot of particles in a huge box → the number of microstates can be very large

Ensembles - definitions

- * Stat. Mech. is a framework to assign **probabilities** for a system to be in a microstate for some given macrostate.
- * Use these probabilities to compute averages — identify suitable averages with thermodynamic variables
- * Useful way to think about this is to use the notion of **ensemble**

Ensemble: a collection of a very large number of identical copies of the system.

Example: consider tossing a coin.
aim: to determine the probability of obtaining head or tail.

Alternative: take snapshots of the system at various times ⇒ each shot = member of an ensemble

→ **ensemble**: a very large number of identical copies of a coin ⇒ no. of members = n

Now tossing coins → record ⇒ probability for head $= \lim_{n \to \infty} \frac{N_H}{n}$

where N_H = no. of coins which leads to head

Another example: consider N particles in a box

Ensemble: collection of η such boxes — all identical

Macrostate: total energy E

Microstate: $\vec{P}_i, \vec{x}_i$ $\quad i = 1 \ldots N$

since for a large box these P_i, q_i are continuous variables, introduce

$\rho(P_a, q_a)$ = density of points in the $2Nd$ dimensional phase space

$$P_a : (\vec{P}_i \quad i = 1 \ldots N)$$

$$q_a : (\vec{x}_i \quad i = 1 \ldots N)$$

⇒ Number of members of the ensemble have momenta between $(P_a, P_a + dP_a)$ and positions between $(q_a, q_a + dq_a)$ =

$$= \rho(P_a, q_a)\, d^{Nd}P_a\, d^{Nd}q_a$$

when no. of members $\eta \to \infty$, $\rho(P_a, q_a)$ becomes smooth function

$$\eta = \int d^{Nd}P_a\, d^{Nd}q_a\, \rho(P_a, q_a)$$

Note: ensemble average of any dynamical variable $F(p_a, q_a)$ is

$$\langle F(p,q)\rangle \equiv \frac{\int d^{Nd}p\, d^{Nd}q\; F(p,q)\, \rho(p,q)}{\int d^{Nd}p\, d^{Nd}q\; \rho(p,q)} .$$

Time dependence of $\rho(p,q)$

The phase space density depends on time. Consider region ω in phase space — since each point in phase space moves along its trajectory, new points enter ω and some points in ω move out

No. of members of ensemble in ω $= \int_\omega d^{Nd}p\, d^{Nd}q\; \rho(p,q,t)$

Rate of change of no. of members $= \frac{d}{dt}\int_\omega d^{Nd}p\, d^{Nd}q\; \rho(p,q,t)$

Notation: $y_I = (q_a, p_a)$ $\quad I = 1, 2 \ldots 2Nd$

Velocity vector at a point

$$v_I = \frac{dy_I}{dt}$$

In time dt – no. of points which move out of an element $d\tau_I$ of the boundary of ω

$$= \rho(y,t)\,\frac{dy_I}{dt}\,dt\,d\tau_I$$

* Thus, rate at which points move out of ω is

$$\int d\tau_I\,\rho\,\frac{dy_I}{dt}$$

Stoke's theorem => This is

$$\int d\omega\,\frac{\partial}{\partial y_I}\left(\rho\,\frac{dy_I}{dt}\right)$$

Since there are no "sinks" or "sources" of points in phase space

$$\frac{\partial}{\partial t}\int d\omega\,\rho = -\int d\omega\,\frac{\partial}{\partial y_I}\left(\rho\,\frac{dy_I}{dt}\right)$$

Since this holds for arbitrary ω,

As in a fluid: $$\boxed{\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial y_I}\left(\rho\,\frac{dy_I}{dt}\right) = 0} \Rightarrow \text{eq. of continuity}$$

For a Hamiltonian system the points move according to Hamilton eqs.

$$\dot{p}_a = -\frac{\partial H}{\partial q_a} \; ; \quad \dot{q}_a = \frac{\partial H}{\partial p_a}$$

$$\frac{\partial}{\partial y_I}\left(\rho \frac{dy_I}{dt}\right) = \frac{\partial}{\partial q_a}\left(\rho \frac{dq_a}{dt}\right) + \frac{\partial}{\partial p_a}\left(\rho \frac{dp_a}{dt}\right) =$$

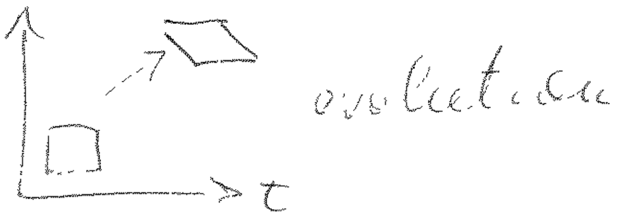
$$= \frac{\partial}{\partial q_a}\left(\rho \frac{\partial H}{\partial p_a}\right) - \frac{\partial}{\partial p_a}\left(\rho \frac{\partial H}{\partial q_a}\right) =$$

$$= \frac{\partial \rho}{\partial q_a} \cdot \frac{\partial H}{\partial p_a} + \rho \cancel{\frac{\partial^2 H}{\partial q_a \partial p_a}} - \frac{\partial \rho}{\partial p_a} \frac{\partial H}{\partial q_a} - \rho \cancel{\frac{\partial^2 H}{\partial p_a \partial q_a}}$$

using $\frac{\partial}{\partial p_a} \frac{\partial}{\partial q_a} H = \frac{\partial}{\partial q_a} \frac{\partial}{\partial p_a} H \Rightarrow$

$$\Rightarrow \frac{\partial}{\partial y_I}\left(\rho \frac{dy_I}{dt}\right) = \frac{\partial \rho}{\partial q_a} \frac{\partial H}{\partial p_a} - \frac{\partial \rho}{\partial p_a} \frac{\partial H}{\partial q_a} = \{\rho, H\}_{PB}$$

Thus, $\boxed{\frac{\partial \rho}{\partial t} + \{\rho, H\}_{PB} = 0}$ Liouville's theorem



Alternative Path to Louisville eq.

Rate at which the no. of representative points in Ω increases with time is

$$\frac{\partial}{\partial t}\int_{\Omega} \rho \, d\Omega \qquad (1)$$

where $d\Omega = dp^{3N} dq^{3N}$

The **net** rate of the flow out of Ω (across σ) is

$$\int \rho (\vec{v}\cdot\hat{n})\, d\sigma$$ where $\hat{n}$ - normal to σ

using div (Gauss theorem): $\int_V (\vec{\nabla}\cdot\vec{F})\, dV = \oint_S \vec{F}\cdot\hat{n}\, ds$

$$\int \rho (\vec{v}\cdot\hat{n})\, d\sigma = \int \underbrace{\mathrm{div}}_{\vec{\nabla}\cdot}(\rho\vec{v})\, d\Omega \qquad (3a)$$

where $$\mathrm{div}(\rho\vec{v}) = \sum_{i=1}^{3N}\left\{\frac{\partial}{\partial q_i}(\rho\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right\} \qquad (3b)$$

Because no sources/sinks in phase space, eqs. (1) + (3a):

$$\frac{\partial}{\partial t}\int_{\Omega}\rho\, d\Omega = -\int_{\Omega}\mathrm{div}(\rho\vec{v})\, d\Omega$$

$$\to \int_{\Omega}\left\{\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\vec{v})\right\} d\Omega = 0 \qquad (6)$$

Necessary & sufficient condition for (6) → 0 is

$$\boxed{\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\vec{v}) = 0} \quad \text{- eq. of continuity} \qquad (7)$$

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From (3b) + (7):

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\underbrace{\dot{q}_i}_{\partial H/\partial p} + \frac{\partial \rho}{\partial p_i}\underbrace{\dot{p}_i}_{-\partial H/\partial q}\right) + \rho \overbrace{\sum_{i=1}^{3N}\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right)}^{=0} = 0 \qquad (8)$$

In eq. 8, the last parenthesis → 0, from Hamiltonian eqs. of motion:

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i, p_i)}{\partial q_i \partial p_i} \equiv \frac{\partial^2 H(q_i, p_i)}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$$

Since $\rho \equiv \rho(q_i, p_i, t)$, the remaining terms in (8) can be combined to form the total time derivative of ρ:

$$\boxed{\underbrace{\frac{d\rho}{dt}}_{\text{convective derivative}} = \frac{\partial \rho}{\partial t} + \underbrace{[\rho, H]}_{\text{Poisson brackets}} = 0 \qquad (10)}$$

eq. (10) → Liouville theorem (1838)

In comoving system of reference, the local density ρ = const.

⇒ ρ in phase space behaves as incompress. fluid! ⇒ Note difference between $\frac{\partial \rho}{\partial t} = 0$ and $\frac{d\rho}{dt} = 0$!

ρ changes because of 2 reasons (i.e. at p, q):

(a) ρ itself is explicitly t-dependent

(b) p, q are t-dependent

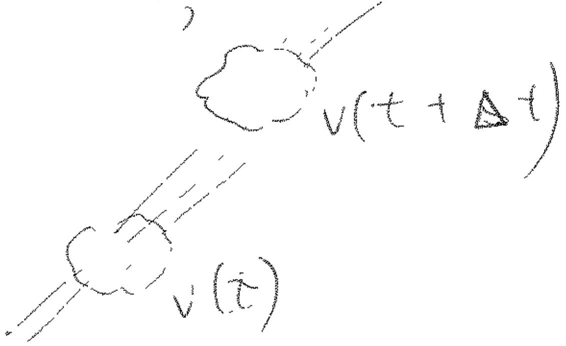
Thus, if $\vec{X}=(p,q)$:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial x^I}{\partial t}\frac{\partial \rho}{\partial x_I}$$

Meaning of $d\rho/dt$:

$$\frac{d\rho}{dt} = \lim_{t \to 0} \frac{\rho(\vec{x}+\delta\vec{x}; t+\Delta t) - \rho(\vec{x},t)}{\Delta t}$$

So, over Δt: $\vec{x} \to \vec{x} + \Delta\vec{x}$



⟸ Tracing a given volume of a phase space