

M.D. = MOLECULAR DYNAMICS

Molecular dynamics is defined naturally in the microcanonical ensemble. The total energy is fixed

In the microcanonical ensemble

$$\langle A(p, q) \rangle = \frac{1}{\Omega} \int dp dq A(p, q)$$

↑  
integration on the surface  $H(p, q) = E$ .

The idea:

given a starting point  $(q_0, p_0)$  we consider the Hamiltonian evolution

$$\begin{cases} \dot{p} = -\frac{\partial H}{\partial q} \\ \dot{q} = \frac{\partial H}{\partial p} \end{cases} \Rightarrow p(t), q(t)$$

such that  $p(0) = p_0$   
 $q(0) = q_0$

Then, we consider the "temporal average"

$$\langle A(p, q) \rangle_{\text{MD}, T} = \frac{1}{T} \int_0^T dt A(p(t), q(t))$$

for large  $T$ .

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We would like to relate the ensemble average  $\langle A(p,q) \rangle$  with  $\langle A(p,q) \rangle_{MD,T}$

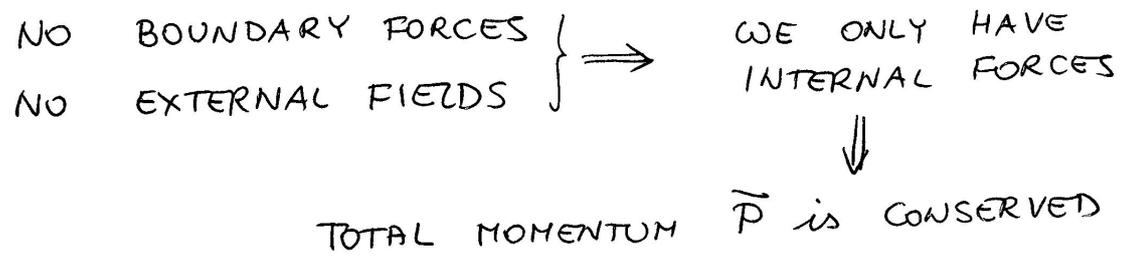
In the absence of additional conserved quantities (the energy is the only conserved quantity) it is conjectured that (ergodic hypothesis)

$$\langle A(p,q) \rangle = \langle A(p,q) \rangle_{MD,T} \text{ for } T \rightarrow \infty$$

$\uparrow$  ensemble average                       $\uparrow$  temporal average.

NOTE:  
T is NOT the temperature  
T is the length of the trajectories

If we use periodic boundary conditions (usual choice) there are no boundary forces and we should therefore consider an additional conserved quantity



CAN WE STILL USE THE ERGODIC THEOREM?

~~THE ANSWER DEPENDS ON THE USABLE~~

## Observations

- ① For thermodynamics there is a preferred reference system: we consider a gas in a container that DOES NOT MOVE:  
The C.M. velocity of the molecules is zero.

The Maxwell distribution of the velocities is of course only valid for a still box.

- ② In statistical mechanics  $\bar{P} = \sum \bar{p}_i$  is an extensive quantity with  $\langle \bar{P} \rangle = 0$  (compute it for example in the canonical ensemble).  
which again reflects the fact that the box does not move.

The assumption in the calculation:

$\langle A(p, q) \rangle$  in the microcanonical ensemble is dominated by the configurations with  $\bar{P} = 0$  (the relation becomes exact for  $V \rightarrow \infty$ ).

Therefore

$$\langle A(p, q) \rangle = \langle A(p, q) \rangle_{MD, T} \text{ for } T \rightarrow \infty \\ \text{fixing } \bar{P} = 0.$$

The starting  $(q_{0i}, p_{0i})$  satisfies  $\sum_i p_{0i} = 0$