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

\[
\begin{align*}
\dot{p} & = -\frac{\partial H}{\partial q} \\
\dot{q} & = \frac{\partial H}{\partial p}
\end{align*}
\]

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 \(T\).
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)

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

$$\uparrow$$
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:

$$\text{NO BOUNDARY FORCES } \implies \text{WE ONLY HAVE INTERNAL FORCES}$$

$$\text{NO EXTERNAL FIELDS } \implies \text{TOTAL MOMENTUM } \vec{P} \text{ is CONSERVED}$$

CAN WE STILL USE THE ERGODIC THEOREM?
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 $\overline{P} = \Sigma \overline{p}_i$ is an extensive quantity with $\langle \overline{P} \rangle = 0$ (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 $\overline{P} = 0$ (the relation becomes exact for $V \to \infty$).

Therefore

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

fixing $\overline{P} = 0$.

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