STUDYING STATISTICAL SYSTEMS USING M.D.

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

$$\begin{cases} \dot{p} = -\dfrac{\partial H}{\partial q} \\ \dot{q} = \dfrac{\partial H}{\partial p} \end{cases} \Rightarrow \quad p(t), q(t) \text{ such that } \begin{array}{l} p(0) = p_0 \\ q(0) = q_0 \end{array}$$

Then, we consider the "temporal average"

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

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)

$$\underbrace{\langle A(p,q) \rangle}_{\text{ensemble average}} = \underbrace{\langle A(p,q) \rangle_{MD,T}}_{\text{temporal average.}} \quad \text{for } T \to \infty$$

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

$$\left.\begin{array}{l}\text{NO BOUNDARY FORCES}\\ \text{NO EXTERNAL FIELDS}\end{array}\right\} \Longrightarrow \text{WE ONLY HAVE INTERNAL FORCES}$$

$$\Downarrow$$

TOTAL MOMENTUM $\vec{P}$ is CONSERVED

CAN WE STILL USE THE ERGODIC THEOREM ?

~~[illegible]~~

Observations

1. For thermodynamics there is a preferred reference system: we consider a gas in a container that <u>DOES NOT MOVE</u>:
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 $\vec{P} = \sum \vec{p}_i$ is an extensive quantity with $\langle \vec{P} \rangle = 0$ (compute it for example in the canonical ensemble). which again reflects the fact that the box does not move.

The assumption in the calculation:

$$\langle A(p,q) \rangle \text{ in the microcanonical ensemble}$$

is dominated by the configurations with $\vec{P} = 0$ (the relation becomes exact for $V \to \infty$).

Therefore

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

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