1 The basics

- Hamilton's equation of motion:

$$\dot{x} = \nabla_p \mathcal{H}(x, p) \qquad \dot{p} = \nabla_x \mathcal{H}(x, p)$$

- Hamiltonian $\mathcal{H}$ with conservative potential U $(U = U(x), \partial_t U = 0)$:

$$\mathcal{H}(x, p) = \frac{1}{2} \sum_{i=1}^{N} \frac{p_i^T p_i}{m_i} + U(x_1, \dots, x_N) = E_{kin} + E_{pot}$$

- $\frac{d}{dt}\mathcal{H}(x, p) = 0$ microcanonical ensemble.

2 The ensembles

A statistical ensemble is an idealization consisting of a large number of virtual copies (sometimes infinitely many) of a system, considered all at once, each of which represents a possible state that the real system might be in. In other words, a statistical ensemble is a probability distribution for the state of the system.

2.1 The microcanonical ensemble (NVE)

Statistical ensemble that is used to represent the possible states of a mechanical system which has an exactly specified total energy.

- isolated system: energy remains constant
- Number, Volume, Energy are constant
- the microcanonical ensemble is defined by assigning an equal probability to every microstate whose energy falls within a range centered at E.

2.2 The canonical ensemble (NVT)

Statistical ensemble that is used to represent the possible states of a mechanical system which is in thermal equilibrium with a heat bath.

- energy can vary
- Number, Volume, Temperature remain constant
- the canonical ensemble assigns a probability P to each microstate given by the following exponential: $P = \exp(\frac{A-E}{kT})$.

2.3 The isothermal-isobaric ensemble (NPT)

Statistical ensemble that is used to represent the possible states of a mechanical system which maintains constant temperature and constant pressure.

2.4 The grand canonical ensemble (μVT)

Statistical ensemble that is used to represent the possible states of a mechanical system of particles that is being maintained in thermodynamic equilibrium (thermal and chemical) with a reservoir.

- can exchange energy and particles
- chemical potential μ, Volume, Temperature are constant.