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 $(U = U(x), \partial_t U = 0)$:

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

- $\frac{d}{dt}\mathcal{H}(x,p) = 0$ 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.
$\boldsymbol{\alpha\beta\gamma\delta}$

Formulation of the isothermal-isobaric ensemble In order to get a formulation for the (NPT) ensemble the following steps are carried out:

- Consider the whole system together with the heat bath and the external piston as a NVE ensemble.
  This leads to 10 additional degrees of freedom (9 for the box-matrix entries and one for time scaling) by defining fictious potentials and additional dynamics:
- Use virtual variables for space and time $(\tilde{h}_{i,j}, \gamma)$ and define fictious potentials (U_P, U_T), the so called Parrinello-Rahman barostat and the Nose thermostat. This gives the additional degrees of freedom.
- By this one can define the Parrinello-Rahman-Nose Hamiltonian.
- Transform back to real time (to get equidistant timesteps). By this transformation the system becomes a non-Hamiltonian system.

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.

3 Stress and strain

3.1 Stress $\sigma = \frac{|\vec{F}|}{A}$

- Physical quantity expressing the internal forces that neighbouring particles of a continuous material exert on each other.
- Stress is defined as the average force per unit area that some particle of a body exerts on an adjacent particle. (It is a macroscopic concept.)
- Any strain (deformation) of a solid material generates an internal elastic stress. The relation between mechanical stress, deformation and the rate of change of deformation can be quite complicated.

- The stress state of the material must be described by a tensor (Cauchy stress tensor σ). The stress tensor defines the state of stress at a point inside a material in the deformed placement or configuration. One has the relation $\vec{T} = \sigma \cdot \vec{n}$, where $\vec{T}$ is the stress vector for the plane described by the normal $\vec{n}$.

3.2 Strain $\sigma_{ij} = \sum_{k,l} C_{ijkl}\epsilon_{kl}$

- The strain describes the transformation of a body from a reference configuration to a current configuration. It describes the deformation in terms of relative displacement of particles in the body.
- In a continuous material a deformation field results from a stress field. The relation between stresses and induced strains is expressed by constitutive equations (e.g. Hooke's law).
- The strain tensor ϵ describes what?

3.3 Stress - Strain relation

- Reference state: use matrix h_0 (used to transform virtuel coordinates in real coordinates). A homogeneous distortion is then given by $h_0 \rightsquigarrow h$.
- This creates a displacement u which again yields in a formula for the strain tensor ϵ.
- The coupling of strain and stress is given by "Hooke's law": $\sigma_{ij} = \sum_{kl} C_{ijkl}\epsilon_{kl}$.