Classical Mechanics

Hamiltonian

$$H\left(\{r_i\}, \{p_i\}\right) = \sqrt{r_i(t)} + \sum_{i=1}^{N} \frac{p_i(t)^2}{2m_i}$$

- total energy
- potential energy in terms of position
- kinetic energy in terms of momentum

i denotes atom and position.

Equations of Motion:

$$\dot{r}_i = \frac{\partial H}{\partial p_i}$$

- Velocity
- momentum

- Only few analytic solutions (spring, two masses)
- MD Solve numerical

Time derivative of Hamiltonian:

$$\frac{\partial H}{\partial t} = \sum_{i=1}^{N} \left( \frac{\partial H}{\partial r_i} \dot{r}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right)$$

$$= \sum_{i=1}^{N} \left( \frac{\partial H}{\partial r_i} \frac{\partial H}{\partial p_i} + \frac{\partial H}{\partial p_i} \frac{\partial}{\partial r_i} \right)$$

Hamiltonian does not change time

Total energy conserved:

$$\sum_{i=1}^{N} \dot{r}_i \times \dot{p}_i$$

Linear and angular momentum constant.

Goals: Describe concepts of MD with thermodynamic properties
Structure of MD code:

**Initial conditions**
- \( r_i(0) \) and \( v_i(0) \)

**Calculate the forces at current time**
- \( F_i(t) \) from \( r_i(t) \)

**Integrate equations of motion**
- \( r(t) \rightarrow r(t+\Delta t) \) \& calculate
- \( v(t) \rightarrow v(t+\Delta t) \) \& advance
- \( t \rightarrow t+\Delta t \)

**Save information**

**Done?**  \( \rightarrow \) No

**Yes**
5) Statistical Mechanics.

- Relate microscopic state with macroscopic state.
- Given a thermodynamic state of a material, what are the probabilities of finding the system in various microscopic states?
- Given a microscopic state, what is the corresponding macroscopic state.
- Adiabatic, rigid, impermeable.

\[ N, V, E \]

- \( N \)-atoms
- \( V \)-volume
- \( E \)-Energy

**Question:** What is the probability of finding the state in a given microscopic state?

\[ \sum \psi_i^2 \]

**Example:** 1D harmonic oscillator's potential energy

\[ H = \frac{\mathbf{p}^2}{2m} + \frac{1}{2} k \mathbf{x}^2 \]

\[ \Delta x \Delta p \geq \hbar \]

Hessenberg uncertainty principle.

We then can now define "quantized" states.

Only movements from one box to another can be measured.
Number of states with energy $E$:

$$\mathcal{N}(E) = \frac{1}{\hbar} \int dx dp \, \delta(H(x,p) - E)$$

This counts the amount of squares (states) in my energy curve.

So that it only gives $1$ for energies equal to $H(x,p)$.

Postulate: the probability of the material being in any one state $\mathcal{N}(E,V,N)$ is the same.

What is the probability of subsystem 1 having energy $E_1$ and $E_2$ with $E_2$:

$$P(E_1, E - E_2) = \frac{\mathcal{N}(E,V,N) \times \mathcal{N}(E-E_1, V-V_1, N-N_1)}{\mathcal{N}(E,V,N)}$$

$\mathcal{N} = \# \text{ of microstates with } E_1$.

(1) $\mathcal{N}(E) = \frac{1}{\hbar} \int dx dp \, \delta(H(x,p) - E)$

(2) $\mathcal{N}(E) = \frac{1}{\hbar} \int dx dp \, \delta(H(x,p) - E)$

(3) $\mathcal{N}(E,V,N) = \frac{1}{\hbar^{3N}} \int d^{3N} \mathbf{r} \int d^{3N} \mathbf{p} \, \delta(H(\mathbf{r}, \mathbf{p}) - E)$
\[ P(E_i; E-E_i) = \frac{\lambda_1(E, V, N) \times \lambda_2(E-E_i, V, N, N+i)}{\Lambda(E, V, N)} \]

How do we relate to thermodynamics, because knowing all the possible states does not help.

Take the log, so that states can be additive (intensive)

\[ \ln P(E_i; E-E_i) = \ln \lambda_1(E, V, N) + \ln \lambda_2(E-E_i, V, N, N+i) + C \]

\[ \sum_i E_i = E \]

\[ \frac{\partial}{\partial E_i} \ln \lambda_1(E, V, N) = 0 \]

\[ \frac{\partial}{\partial E_i} \ln \lambda_2(E-E_i, V, N, N+i) = 0 \]

Temperature \[ \frac{\partial S}{\partial T} = \frac{1}{T} \] so \[ T = \frac{1}{\partial S/\partial T} \]

Vibrational calculus

Maximize \[ \frac{\partial}{\partial E} \ln \Lambda(E, V, N) \]

Equilibrium

\[ P_i(E_i; E-E_i) = 0 \]

Condition for equilibrium:

\[ \frac{\partial}{\partial E_i} \ln \lambda_1(E, V, N) + \frac{\partial}{\partial E_i} \ln \lambda_2(E-E_i, V, N, N+i) = 0 \]

So that \[ S = k \ln \Lambda(E, V, N) \] in units.

\[ \frac{\partial}{\partial E} \ln \Lambda(E, V, N) \]
Pressure at equilibrium:
\[ \frac{\partial S(E,V,N)}{\partial V} = -\frac{P}{T} \]

Moles at equilibrium:
\[ \frac{\partial S(E,V,N)}{\partial N} = \frac{U}{N} \]

Vieanna Boltzmann's grade:

Canonical ensemble

E + E_bath = E_{tot} = constant.

Microscopic \( (\rho, P_c) \) state \( \rho \in \mathbb{W} / \text{energy} \)

\[ \rightarrow \text{E system} \]

Since \( E < E_{tot} \) we expand \( \log N_{\text{bath}} \) around \( E_{tot} \)

\[ \ln P(\rho, P_c) = \ln N_{\text{bath}}(E_{tot}) - \frac{\partial \ln N_{\text{bath}}}{\partial E} . E \]

Taylor expansion of \( \log \)

\[ P(\rho, P_c) = \epsilon^{-\beta H(\rho, P_c)} \]

\[ \frac{\mu}{\epsilon} e^{-\beta H(\rho, P_c)} \]

Maxwell-Boltzmann distribution.

\[ \text{Partition function:} \]

\[ Z(\rho, N, V, T) = \sum_{\text{microstate}} e^{-\beta H(\rho, P_c)} \]

\[ Z(V, T) = \sum_{\text{microstate}} e^{-\beta H(\rho, P_c)} \]
\[ \ln Z(\text{NVT}) = \ln Z(\text{NVE}) - \frac{E}{kT} = F(\text{NVT}) \]

\[ \ln Z(\text{NVT}) = S - \frac{E}{kT} \]

\[ -kT \ln Z(\text{NVT}) = E - ST = F \quad \text{Helmholtz free energy.} \]

\[ Z(\text{NVT}) \rightarrow \text{is a microscopic variable.} \]

Consider atomic position and momenta quantity (any property)

\[ A \in \{ \phi_i \} \]

equilibrium average of that is

\[ \langle A \rangle = \sum_{\text{micro}} A P_{\text{micro}} = \frac{\sum A(\phi_i) e^{-\beta H(\phi_i, p_i)}}{\sum e^{-\beta H(\phi_i, p_i)}} \]

Maxwell

Boltzmann

when you measure property \( A \) in an experiment or MD

\[ \frac{1}{2} \int dt A(\phi_i, p_i(t)) \quad \text{time average.} \]

at equilibrium ensemble and temporal averages are equal.
Consider a variable which appears squared in the Hamiltonian.\(^9\)

\[
H(\mathbf{r}, \mathbf{p}) = \lambda \rho_i \lambda \rho_i + V(\mathbf{r}(t)) + \sum_{i=2}^{3n} \frac{\mathbf{p}_i(t)^2}{2m_i}
\]

\[
= \lambda \rho_i \lambda \rho_i + H' - \frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{kT}
\]

\[
\langle \lambda \rho_{i}^{2} \rangle = \frac{\int d^{3n} \rho \int d^{3n} \rho \lambda \rho_{i}^{2} e^{-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{kT}}}{\int d^{3n} \rho \int d^{3n} \rho e^{-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{kT}}}
\]

\[
= \frac{\int d\mathbf{p}_i \lambda \rho_{i}^{2} e^{-\frac{\lambda \rho_{i}^{2}}{kT}}}{\int d\mathbf{p}_i e^{-\frac{\lambda \rho_{i}^{2}}{kT}}}
\]

**Usual.**

*Change of variable.* \[
\frac{\lambda \rho_{i}^{2}}{kT} = x^2 \quad dp_i = \frac{kT}{\lambda} dx
\]

\[
\langle \lambda \rho_{i}^{2} \rangle = \frac{(kT)^2}{\lambda} \int dx x^2 e^{-x^2} = \frac{1}{2} kT
\]

\[
\frac{kT}{\lambda} \int dx e^{-x^2}
\]
Probability distributions:

Micro canonical (NVE)  Canonical (NVT)  Isothermal/Isobaric (NPT)

P(r, p) = \frac{1}{\mathcal{Z}_{\text{EVM}}}  P(r, \varepsilon) = \frac{e^{-\beta H(r, p)}}{\mathcal{Z}(\text{TVN})}  P(r, \varepsilon, V) = \frac{e^{-\beta H(r, \varepsilon, V)}}{\mathcal{Z}_P(\text{TPN})}

\mathcal{Z}(\text{TVN}) = \sum \delta(E - H(r, p, \varepsilon))_{\text{micro}}

\mathcal{Z}_P(\text{TPN}) = \sum \delta(E - pV)_{\text{micro}}

Partition functions
Normalization of distribution

Free energies (atomistic → macroscopic Heisenberg)

S = k \log \mathcal{Z}(\text{EVM})  \quad F(\text{TVN}) = -kT \log \mathcal{Z}  \quad G(\text{TPN}) = -kT \ln \mathcal{Z}_P

Equation of energy:

H(r, p, \varepsilon) = \lambda p_i^2 + V(r, \varepsilon) + \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} = \lambda p_i^2 + H_i

Out of equilibrium energy contribution:

\langle \lambda p_i^2 \rangle = \frac{\int d^3\rho \int d^3\rho' \lambda p_i^2 e^{-H(r, p, \varepsilon)/kT}}{\int d^3\rho \int d^3\rho' e^{-H(r, p, \varepsilon)/kT}}

\langle \lambda p_i^2 \rangle = \frac{\int d^3\rho \int d^3\rho' \lambda p_i^2 e^{-H(r, p, \varepsilon)/kT}}{\int d^3\rho \int d^3\rho' e^{H_i/kT}} = \frac{\int d^3\rho \int d^3\rho' \lambda p_i^2 e^{H_i/kT}}{\int d^3\rho e^{-\lambda p_i^2 / kT}}

\langle \lambda p_i^2 \rangle = \frac{1}{2} \frac{kT}{kT}

Factor out variables which don't contribute.

\equiv \frac{1}{2} kT any squared term contributes.
Equipartition of energy: Any degree of freedom that appears squared in Hamiltonian contributes $\frac{1}{2} k T$ of energy.

This means in the case of kinetic energy in $H = \lambda \frac{1}{2m} \text{ all atoms will have } \frac{1}{2} k T$ at equilibrium.

MD temperature

$\langle k \rangle = \frac{3N}{2} k T$ - 3 dimensions will contribute.

Most cases center of mass of motion is set to zero at time zero.

$\langle k \rangle = \frac{3N-3}{2} k T$ \quad $\frac{p^2}{2m} = \frac{1}{2} k x^2$

kinetic energy.

Often angular momentum is zero

$\langle k \rangle = \frac{3N-6}{2} k T$

Temperature is related to the average kinetic energy.

$K(t) = \frac{N_{eff} k T(t)}{2}$
Fluctuations from equilibrium are also related to materials properties.

\[
\langle \delta A^2 \rangle = \frac{1}{2} \int_0^\infty [A(t) - A(t')]^2 dt' = \langle A^2 \rangle - \langle A \rangle^2
\]

Specific heat:

\[
C_v = \frac{\delta E}{\delta T} \bigg|_{\text{NVT}} \quad \text{or} \quad \langle \delta H^2 \rangle_{\text{NVT}} = kT^2 C_v
\]

Compressibility:

\[
\beta_v = \frac{1}{V} \frac{\delta V}{\delta P} \bigg|_{\text{NVT}} \quad \langle \delta V^2 \rangle_{\text{NVT}} = k \langle V^2 \rangle + \beta T
\]

Quantum effects. When does classical mechanics fail? Stop working.

Note: Antisymmetric thermal expansion.

Debye temperature indicates when MD breaks down.

\[ kT \gg \hbar \omega \quad \text{classical} \]

\[ kT \ll \hbar \omega \quad \text{quantum regime} \]
How to Integrate Equations

 discretization

\[ \frac{1}{\tau_i} = \frac{p_i}{m_i} = \frac{r_i(t) - r_i(t)}{\Delta t} \]

\[ \dot{r}_i = \frac{p_i}{m_i} = F_i = \frac{p_i(t+\Delta t) - p_i(t)}{\Delta t} \]

\[ \vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \frac{p_i(t)}{m_i} \Delta t \]

1st order taylor expansion

(Awful) not good stability

Euler method

Verlet algorithm: Taylor expansion of position w/ bin.

3rd order

\[ \vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t) \Delta t + \frac{1}{2} \vec{a}_i(t) \Delta t^2 + \frac{1}{6} \vec{a}_i(t) \Delta t^3 + O(\Delta t^4) \]

\[ \vec{r}_i(t-\Delta t) = \vec{r}_i(t) - \vec{v}_i(t) \Delta t + \frac{1}{2} \vec{a}_i(t) \Delta t^2 + \frac{1}{6} \vec{a}_i(t) \Delta t^3 + O(\Delta t^4) \]

Sum two equation:

4th order

\[ \vec{r}_i(t+\Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t-\Delta t) + \vec{a}_i(t) \Delta t^2 + O(\Delta t^4) \]

Acceleration (from force)

\[ \vec{a}_i(t) \]

have to store

old position

in memory

Velocity Verlet:

Leap for Verlet: different positions of time w/ velocity.
Verlet algorithm: features and advantages
- Exactly time reversible
- Symplectic – conserves volume in phase space
- No long-term energy drifts
- Trajectory stays very close to the constant energy hypersurface of phase space. Remember: $S = k \log \Lambda (eV)$

Simple molecule: $H_2 + e^- \rightarrow \text{Molecule}$

Wave functions as linear combinations:
$$\psi_{\text{sym}}(\vec{r}) = \frac{1}{\sqrt{2}} (\psi_1(\vec{r}) + \psi_2(\vec{r}))$$
$$\psi_{\text{asym}}(\vec{r}) = \frac{1}{\sqrt{2}} (\psi_1(\vec{r}) - \psi_2(\vec{r}))$$

- K.E good
- P.E bad
- Bonding

- K.E not so good
- P.E good
- Anti-bonding

How do you calculate the force?

Interatomic potentials: Ab initio electronic structure methods,
- Hartree-Fock, Density Functional Theory
- Quantum Monte Carlo
  - Very accurate but computationally intensive
  - 100s-1000s atoms
Interatomic potentials:
\[ V(r_i) = V_{\text{core/lin}}(r_i) + V_{\text{elect}}(r_i) + V_{\text{vdw}}(r_i) \]

Parameterize to describe specific materials.
Ab initio data

**Tool-kit**

**Pair-wise potentials**

\[ V(r_{ij}) = \sum_{i \neq j} \phi(|r_i - r_j|) \]

- **Lennard-Jones (6-12)**
  \[ \phi_{LJ}(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]
  - 2 parameters: distance \( \sigma \), energy \( \varepsilon \)
  - Repulsion
  - Attraction

- **Exponential-6**
  \[ \phi_{\text{exp-6}}(r) = \varepsilon \left( e^{-3r} - A r^{-6} \right) \]

- **Morse**
  \[ \phi_{\text{Morse}}(r) = 4\varepsilon \left[ \exp\left( \gamma \left( 1 - \frac{r}{r_0} \right) \right) \right] - 2\exp\left( \frac{\gamma}{2} \left( 1 - \frac{r}{r_0} \right) \right) \]

- L-J and Morse (3 parameters)
- Distance
- Energy
- Curvature
- Bond stiffness
- Elastic moduli
Two-Body Potential

Pair-wise Interactions

\[ E(r) = \sum_{i<j} \phi(r_{ij}) \]

Interaction is independent of other atoms

\( \square \)

Vacancy energy in perfect crystal

\( E_{\text{ext}} = \frac{1}{2} N zE_0 \)

Interaction between atoms

Create a vacancy

\[ E_{\text{vac}}(N-1) = E_{\text{vac}} \]

\[ = E_{\text{vac}}(N-1) - \frac{N-1}{N} E_{\text{ext}}(N) \]

\[ = \frac{1}{2} N zE_0 - 2E_0 - \frac{1}{2} (N-1) zE_0 \]

\[ = -\frac{1}{2} zE_0 \]

Vacancy is equal to chemical energy.

Metals \( E_{\text{vac}} \approx \frac{1}{3} E_{\text{con}} \)
Interatomic Potentials II

Many-Body effects (Embedded atom model)

\[ V = \sum_{i} \phi (r_i) + \sum_{j=1}^{N} \mathbf{f} (\mathbf{r}_i) \]

Embedding energy depends on atoms around it

Electronic density on atom i

Accurate description for:
- Environment dependence of bonding in metals (Vacancy and surfaces)
- Elastic constants and plastic deformation
- Phase transformation (melting & solid-solid)

Not accurate for:
- Highly directional bonding

Diamond, wurtzite, zincblende

Directional, covalent bonding
- Gold, aluminum, platinum, FCC

\[ \mathbf{f} (\mathbf{r}_i) = \sum_{j} \mathbf{f}_2 (r_{ij}) + \sum_{j,k} \mathbf{f}_3 (r_{ij}, r_{jk}) \]

\[ f_2 (r_{ij}) = \sum_{a} A (Br - r_{ij} r_{a}^2) \exp (ra) r_{ij} \]

Silicon Potentials
- Stillinger, Weber
- 1985
In accounts for which atom makes bond angles, and configuration of bond angle.

\[
\cos \theta = \frac{1}{3} \quad \text{ideal for bond.}
\]

Interatomic Potentials of Molecular Materials (Polymer).

\[
V(\{x, y, z\}) = V_{\text{cov}}(\{x, y, z\}) + V_{\text{elect}}(\{x, y, z\}) + V_{\text{vdW}}(\{x, y, z\}).
\]

No void wall for \(3 \text{A} \) bonded atoms.

1-3 atoms (separated by 2 covalent bonds)

\[
\frac{\sqrt{3}}{2} \quad \text{some 1.}
\]

Non-bond interactions: Electrostatics

Electrostatic energy (point charge).

\[
V_{\text{elect}} = \text{Cunit} \times \frac{\bar{q}_i \bar{q}_j}{r_{ij}}
\]

Coulomb relation

How to assign charges

"Formal charge O"  \[\text{electronic structure}\]

* Dipole moment polarization
Coulomb Interaction decays slowly.

\[ V_{\text{elec}} = \text{const} \frac{\varepsilon_0}{r_{ij}} \]

Conditionally convergent.

(periodic boundary conditions infinite system).

- results depend on summation of terms
- results depend on arrangement of surface

Need to use special sum techniques and boundary conditions
- Ewald method (part of sum in real space, part of sum in reciprocal space, Fourier space)
- Particle mesh Ewald and others

\[ \rightarrow \text{ de Leeuw 1980 Paper.} \]

Not point like charges.

\[ \rightarrow \text{shielded Coulomb.} \]
Covalent Interactions

Bond stretch \( \phi_{\text{Bond}}(r) = \sum \frac{1}{2} k_{ij} (r - r_{ij}^\text{eq})^2 \)

Angle bending

\[ \phi_{\text{angle}}(\theta) = \sum \frac{1}{2} k_{ij,k} (\theta - \theta_{ij,k}^\text{eq})^2 \]

\[ = \frac{1}{2} k_{ij,k} \left( \frac{\cos \theta - \cos \theta_{ij,k}^\text{eq}}{\sin^2 \theta_{ij,k}^\text{eq}} \right)^2 \]

Torsion bending (dihedral angles)

\[ \phi_{\text{torsions}}(\phi) = k_{ij,k} \left[ 1 - \cos (\phi_{ij,k} - \phi_{ij,k}^\text{eq}) \right] \]