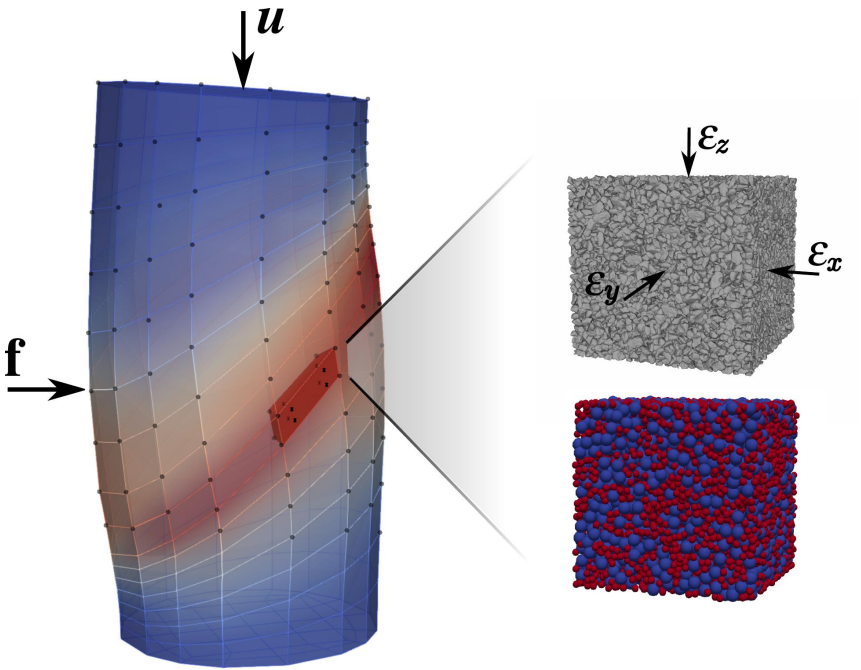


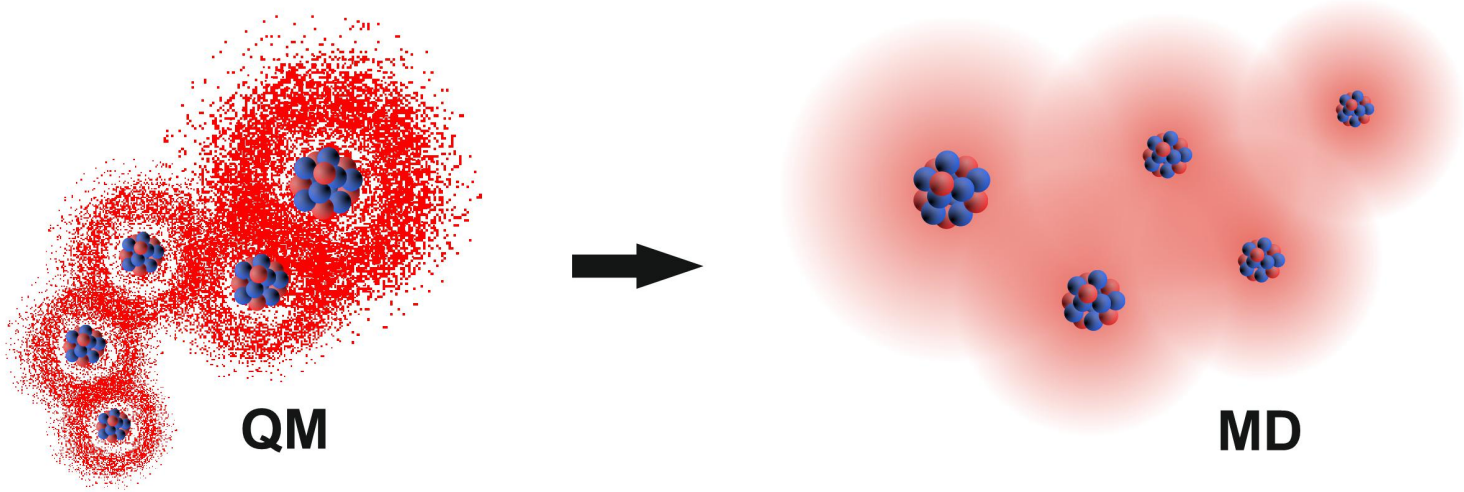
CIVIL-408 Multiscale Modeling in Mechanics

Prof. Kostas Karapiperis

Week 8

From quantum mechanics to atomistics

Quantum mechanics resolves the dynamics of all fundamental particles including electrons surrounding the nuclei. Atomistics take a coarse grained view of the problem, where the electron interactions are condensed out.



Atomistic simulation

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Atomic **positions**:

$$\boldsymbol{q}(t) = \{\boldsymbol{q}_1(t), \ldots, \boldsymbol{q}_N(t)\}$$

Atomic **momenta**:

$$\boldsymbol{p}(t) = \{\boldsymbol{p}_1(t), \ldots, \boldsymbol{p}_N(t)\}$$

Total **Hamiltonian** of the system:

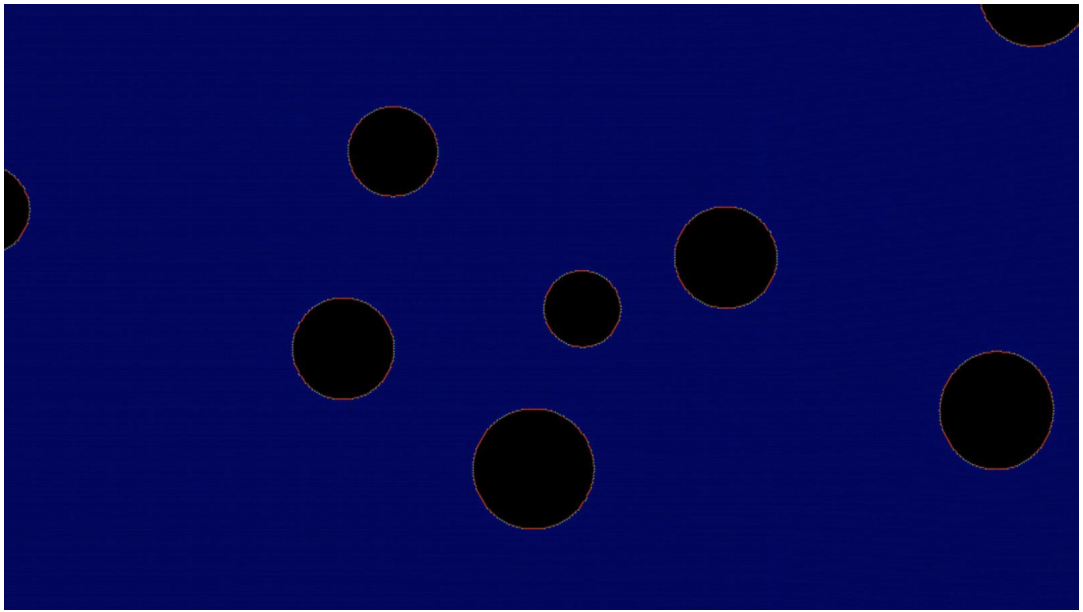
$$\mathcal{H}(\boldsymbol{q}, \boldsymbol{p}) = \sum_{i=1}^{N} \frac{|\boldsymbol{p}_i|^2}{2m_i} + V(\boldsymbol{q})$$

Hamiltonian equations:

$$\dot{\boldsymbol{q}} = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}}, \qquad \dot{\boldsymbol{p}} = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{q}}$$

Equations of motion:

$$m_i \ddot{\boldsymbol{q}}_i = \boldsymbol{f}_i(\boldsymbol{q}) = -\frac{\partial V}{\partial \boldsymbol{q}_i}(\boldsymbol{q})$$



Molecular Statics

Equations of motion (dynamics):

$$m_i \ddot{\boldsymbol{q}}_i = \boldsymbol{f}_i(\boldsymbol{q}) = -\frac{\partial V}{\partial \boldsymbol{q}_i}(\boldsymbol{q})$$

For **molecular statics** (zero temperature), the equations reduce to:

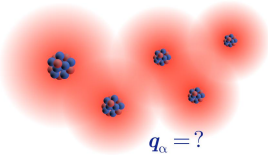
$$\boldsymbol{f}_i(\boldsymbol{q}) = -\frac{\partial V}{\partial \boldsymbol{q}_i}(\boldsymbol{q}) = 0$$

Which amounts to **minimizing the potential energy** of the system

Interatomic potentials

Interatomic potentials and their approximations:

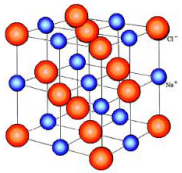
$$V(\boldsymbol{q}) = \sum_{i=1}^{N} V_1(\boldsymbol{q}_i) + \frac{1}{2}\sum_{i\neq j} V_2(\boldsymbol{q}_i, \boldsymbol{q}_j) + \frac{1}{3!}\sum_{i\neq j, i\neq k} V_3(\boldsymbol{q}_i, \boldsymbol{q}_j, \boldsymbol{q}_k) + \dots$$



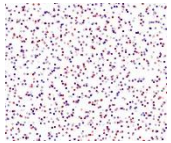
Pair (two-body) potentials:

$$V(\boldsymbol{q}) = \sum_{i\neq j} f(\boldsymbol{q}_i, \boldsymbol{q}_j) = \sum_{i\neq j} f(r_{ij}) \qquad \text{with} \qquad r_{ij} = \|\boldsymbol{q}_i - \boldsymbol{q}_j\|$$

- **Coulomb** (ionic): $V(\boldsymbol{q}) = \dfrac{1}{4\pi\varepsilon_0}\sum_{i\neq j}\dfrac{Q_i Q_j}{r_{ij}}$



- **Lennard-Jones** (ideal gases): $V(r) = -\dfrac{A}{r^n} + \dfrac{B}{r^m}$

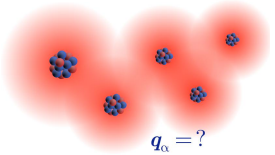


- **Morse** ("simple" metals): $V(r) = D\left[1 - \exp\left(-a(r - r_0)\right)\right]^2$

Interatomic potentials

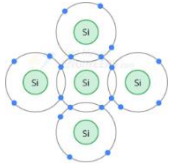
Interatomic potentials and their approximations:

$$V(\boldsymbol{q}) = \sum_{i=1}^{N} V_1(\boldsymbol{q}_i) + \frac{1}{2}\sum_{i\neq j} V_2(\boldsymbol{q}_i, \boldsymbol{q}_j) + \frac{1}{3!}\sum_{i\neq j, i\neq k} V_3(\boldsymbol{q}_i, \boldsymbol{q}_j, \boldsymbol{q}_k) + \dots$$

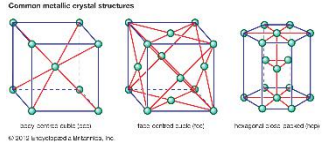


Three-body potentials:

- **Stillinger-Weber** (silicon): $V(\boldsymbol{q}) = \sum_{i,j\in\mathcal{L}} V_2(r_{ij}) + \sum_{i,j,k\in\mathcal{L}} V_3(r_{ij}, r_{ik}, \theta_{ijk})$



- **Embedded Atom Method (EAM)** (metals): $V_i(\boldsymbol{q}) = \frac{1}{2}\sum_{j\in\mathcal{L}} \Phi(r_{ij}) + U(\rho_i) \qquad \rho_i = \sum_{j\in\mathcal{L}} f(r_{ij})$

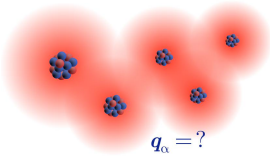


- **Force Field** (organics):

$$V(\boldsymbol{q}) = \sum_{i,j\in\text{bonds}} k_{ij}^{\text{bond}}(r_{ij} - r_{\text{eq.}})^2 + \sum_{i\in\text{angles}} k_i^{\text{angle}}(\theta_i - \theta_{\text{eq.}})^2 + \sum_{i,j\in\text{bonds}} k_i^{\text{dihedral}} f(\phi_i, \theta_i)$$
$$+ \sum_{i,j\in\mathcal{L}} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_{i,j\in\mathcal{L}} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}.$$

Interatomic potentials

All the above potentials are **anharmonic.**



One can always construct a q**uasiharmonic** approximation, through a Taylor expansion:

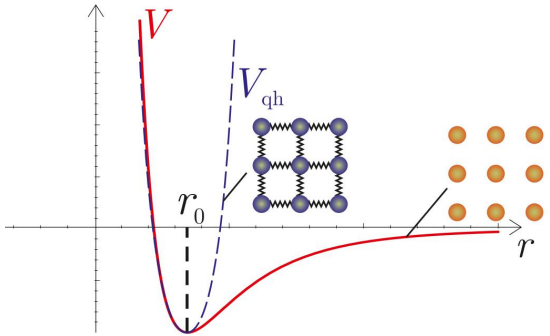
$$V(r) = V(r_0) + \left.\frac{\partial V}{\partial r}\right|_{r_0}(r - r_0) + \frac{1}{2}\left.\frac{\partial^2 V}{\partial r^2}\right|_{r_0}(r - r_0)^2 + \text{h.o.t}$$

By definition the linear term vanishes at equilibrium:

$$V_{qh}(r) \approx V(r_0) + \frac{C}{2}(r - r_0)^2$$

with a **force constant**:

$$C = \left.\frac{\partial^2 V}{\partial r^2}\right|_{r_0} > 0$$



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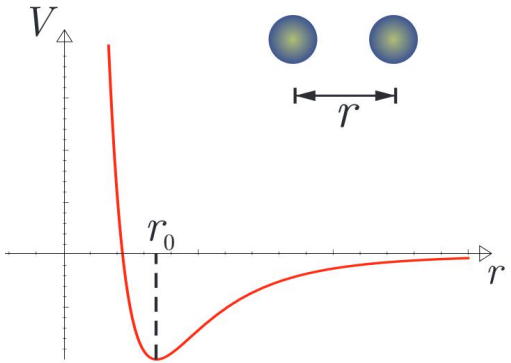
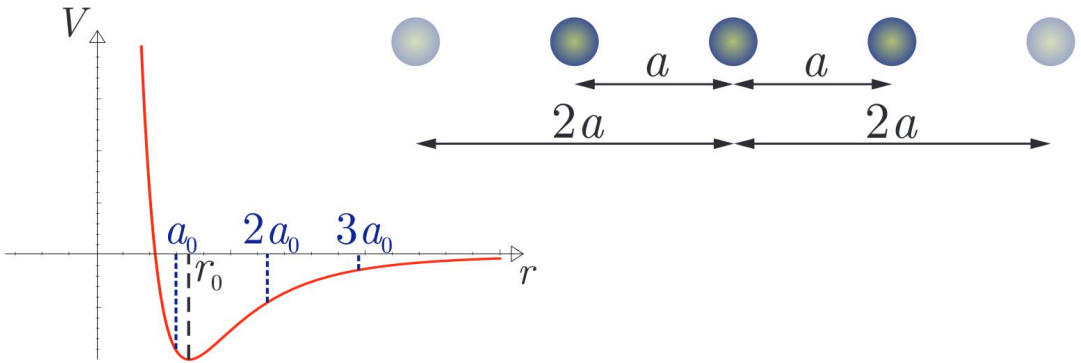
Equilibrium spacing

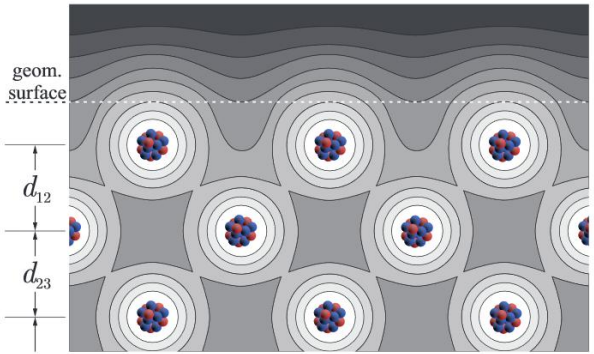


equilibrium spacing between two atoms
= energy minimum

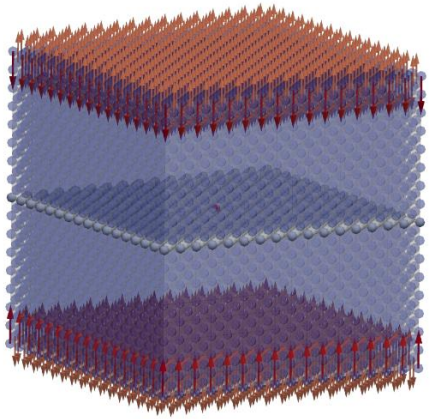


equilibrium spacing in an infinite crystal
= energy minimum

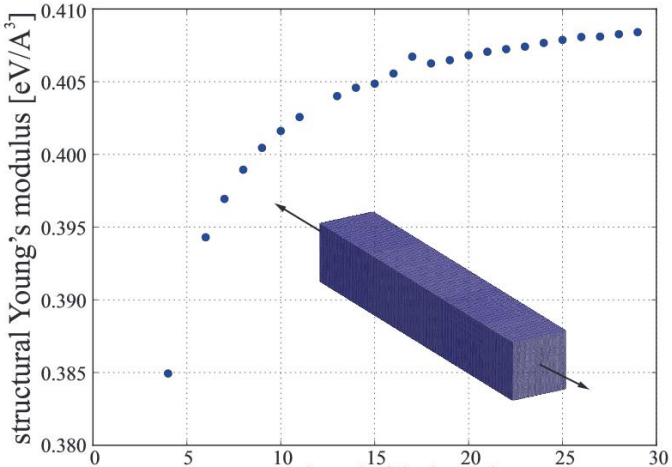
Influence of free surfaces



schematic view of atoms near the
(geometric) surface of a crystal



forces on atoms due to free surfaces
(all atoms at equilibrium spacings)



Cauchy-Born: Effective elastic properties at 0 K

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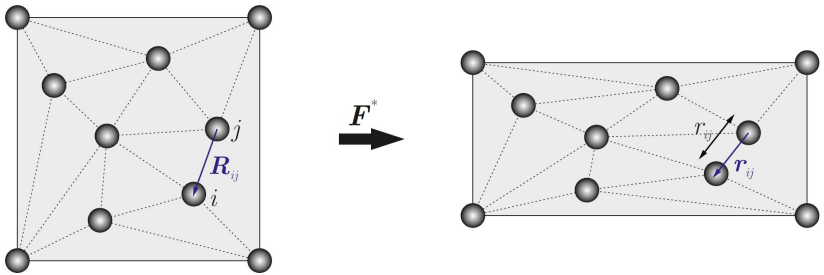
Cauchy-Born rule applied to atoms:

$$\boldsymbol{q}_a = \boldsymbol{F}\boldsymbol{Q}_a, \qquad a = 1, \ldots, N$$



resulting **energy**, **stresses**, **stiffness**:

$$W(\boldsymbol{F}) = \frac{1}{|\Omega|} V(\{\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N\})$$

$$\frac{\partial}{\partial \boldsymbol{F}} = \sum_\alpha \frac{\partial}{\partial \boldsymbol{q}_\alpha} \cdot \frac{\partial \boldsymbol{q}_\alpha}{\partial \boldsymbol{F}}$$

$$\boldsymbol{P}(\boldsymbol{F}) = -\frac{1}{|\Omega|} \sum_{a=1}^{N} \boldsymbol{f}_a(\boldsymbol{q}) \otimes \boldsymbol{Q}_a$$

$$\frac{\partial}{\partial \boldsymbol{F}} = \sum_\alpha \frac{\partial}{\partial \boldsymbol{q}_\alpha} \cdot \frac{\partial \boldsymbol{q}_\alpha}{\partial \boldsymbol{F}}$$

$$\mathbb{C}_{iJkL} = -\frac{1}{|\Omega|} \sum_{a,b=1}^{N} \frac{\partial f_i^a}{\partial q_k^b}(\boldsymbol{q}) Q_J^a Q_L^b$$

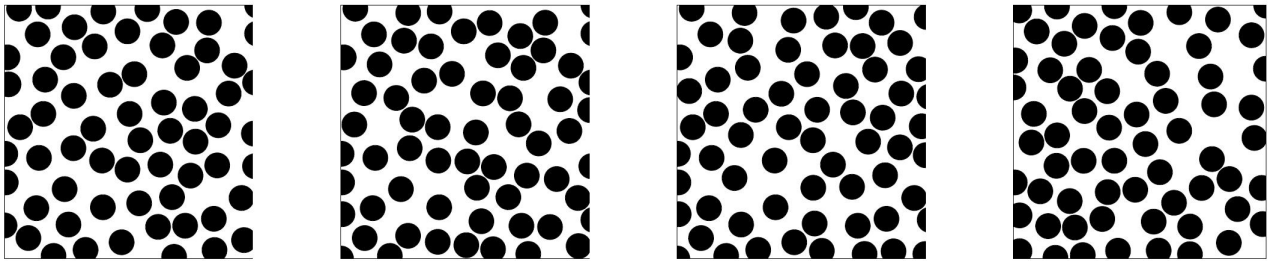
e.g., **EAM potential**: $V_i(\boldsymbol{q}) = \frac{1}{2} \sum_{j \in \mathcal{L}} \Phi(r_{ij}) + U(\rho_i) \qquad \rho_i = \sum_{j \in \mathcal{L}} f(r_{ij})$

$$c_{ijkl} = \frac{1}{|\Omega|} \left\{ U''(\rho) \left[\sum_{\alpha \in \mathcal{L}} f'(r^\alpha) \frac{r_i^\alpha r_j^\alpha}{r^\alpha} \right] \left[\sum_{\beta \in \mathcal{L}} f'(r^\beta) \frac{r_k^\beta r_l^\beta}{r^\beta} \right] \right.$$
$$\left. + \sum_{\alpha \in \mathcal{L}} \left[\left(\left(U'(\rho) f''(r^\alpha) + \frac{1}{2} \Phi''(r^\alpha) \right) - \frac{1}{r^\alpha} \left(U'(\rho) f'(r^\alpha) + \frac{1}{2} \Phi'(r^\alpha) \right) \right) \frac{r_i^\alpha r_j^\alpha r_k^\alpha r_l^\alpha}{(r^\alpha)^2} \right] \right\}$$

Statistical Mechanics - Micro and macrostates

Ensemble and realizations:

- Recall realizations containing the same volume fraction of particles:



macrostate: volume fraction v of the black phase
microstates: geometric realizations above

- When the locations $\boldsymbol{q}$ of all particles are known, we can uniquely calculate the macrostate: $v = v(\boldsymbol{q})$
- More generally, all realizations $(\boldsymbol{p},\boldsymbol{q})$ complying with the same macrostate $\mathcal{A}$ form an **ensemble**.
- In atomistics, typical macrostates are **energy**, **temperature**, **pressure**.

Statistical Mechanics - Averages

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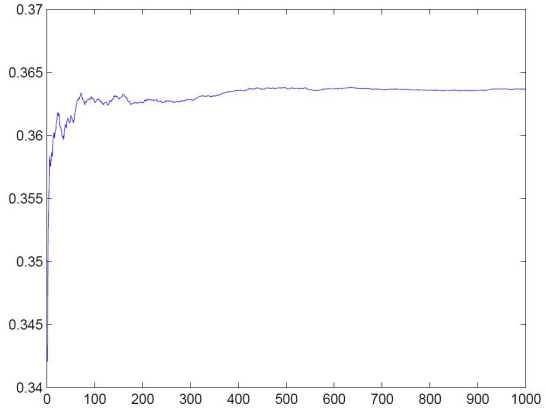
Macrostates are best averaged over time to remove fluctuations:

$$\mathcal{A}(t) = \frac{1}{\Delta t}\int_{t}^{t+\Delta t} A\left(\boldsymbol{q}(\tau), \boldsymbol{p}(\tau)\right)\ \mathrm{d}\tau$$

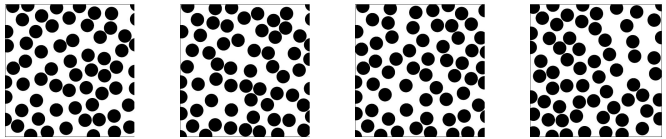


Equilibrium implies

$$\overline{\mathcal{A}} = \lim_{\Delta t\to\infty}\frac{1}{\Delta t}\int_{t}^{t+\Delta t} A\left(\boldsymbol{q}(\tau), \boldsymbol{p}(\tau)\right)\ \mathrm{d}\tau$$

If we introduce an ensemble of fixed macrostate *B* (e.g., temperature), we may run many simulations with different ICs to find **all those realizations compliant with *B***, over which we average:

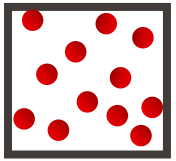
$$\frac{1}{n}\sum_{\alpha=1}^{n}\mathcal{A}_{\mathcal{B}}(\boldsymbol{p}_\alpha, \boldsymbol{q}_\alpha)$$



For example, we may fix the temperature (*B* = temperature) and evaluate the average energy of the system (*A* = energy).

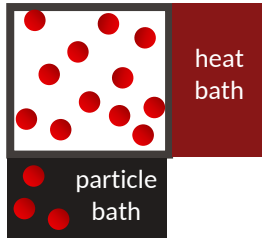
Atomistic ensembles

- The **microcanonical ensemble** (NVE-ensemble) describes an isolated system with constant energy E, constant particle number N and constant volume V, therefore we refer to this as the NVE-ensemble.



- The **canonical ensemble** (NVT-ensemble) describes a system in contact with a heat bath, i.e. in constant temperature, besides constant particle number N and constant volume V.

- The **grand canonical ensemble** (μVT-ensemble) is an extension of the canonical ensemble and describes a system in contact with both heat and particle baths, i.e. constant temperature, volume and chemical potential μ.



Note: There are *further ensembles* (e.g., *NpT*)

The statistical probabilisty distribution

If we wait infinitely long, the system will have visited every accessible state (**ergodicity**).

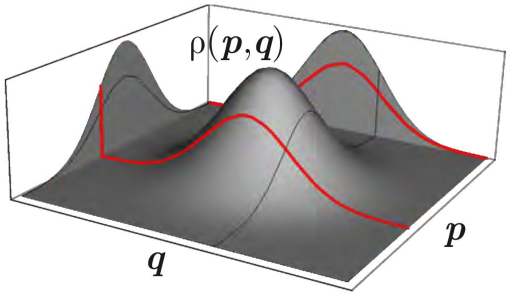
$$\langle \mathcal{A} \rangle \approx \frac{1}{n} \sum_{i=1}^{n} \mathcal{A}(\boldsymbol{q}_n, \boldsymbol{p}_n)$$

introduce a **probability distribution** (*probability density*):

$$\int_{\Gamma} \rho(\boldsymbol{q}, \boldsymbol{p}) \, \mathrm{d}\boldsymbol{p} \, \mathrm{d}\boldsymbol{q} = 1$$

such that

$$\boxed{\langle \mathcal{A} \rangle = \int_{\Gamma} A(\boldsymbol{q}, \boldsymbol{p}) \, \rho(\boldsymbol{q}, \boldsymbol{p}) \, \mathrm{d}\boldsymbol{p} \, \mathrm{d}\boldsymbol{q}}$$



The probability distribution may depend on any *fixed macrostates*.
It therefore varies between ensembles.

Zero-temperature Atomistic simulation

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Atomic **positions**:

$$\boldsymbol{q}(t) = \{\boldsymbol{q}_1(t), \dots, \boldsymbol{q}_N(t)\}$$

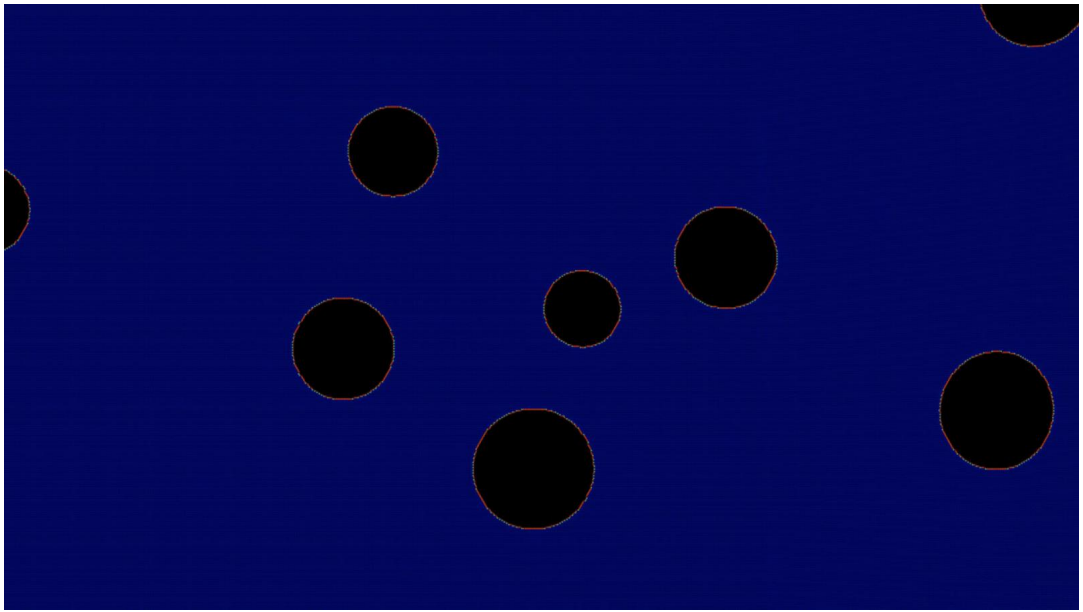
Total **Hamiltonian** of the system:

$$\mathcal{H}(\boldsymbol{q}, \boldsymbol{p}) = \sum_{i=1}^{N} \frac{|\boldsymbol{p}_i|^2}{2m_i} + V(\boldsymbol{q})$$

Equations of motion:

$$m_i \ddot{\boldsymbol{q}}_i = \boldsymbol{f}_i(\boldsymbol{q}) = -\frac{\partial V}{\partial \boldsymbol{q}_i}(\boldsymbol{q})$$

Solve numerically $\boldsymbol{q}(t)$ using explicit time integration



Algorithmic realization - Velocity Verlet scheme

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(i) start with $t^0 = 0$ and known $\boldsymbol{q}_i^0$ and $\boldsymbol{v}_i^0 = \boldsymbol{p}_i^0/m$

(ii) $\boldsymbol{f}_i^0 = -\partial\mathcal{V}/\partial\boldsymbol{q}_i(\boldsymbol{q}^0)$

(iii) $\boldsymbol{a}_i^0 = \boldsymbol{f}_i^0/m_i$

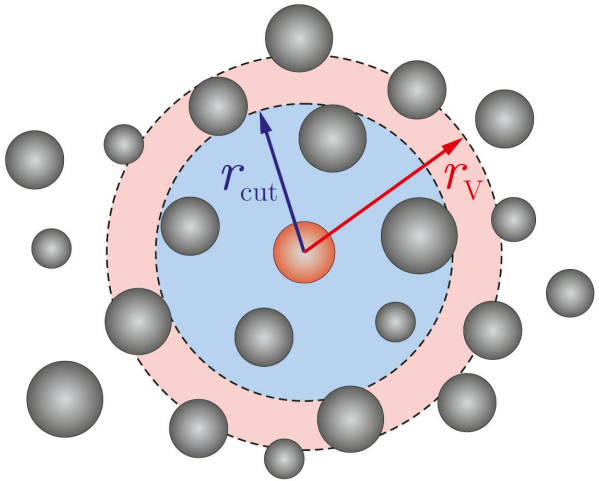
(iv) while $t \leq t_{\text{end}}$:

$$\boldsymbol{q}_i^{\alpha+1} = \boldsymbol{q}_i^\alpha + \boldsymbol{v}_i^\alpha \Delta t + \boldsymbol{f}_i^\alpha \Delta t^2/2m_i$$

$$\boldsymbol{f}_i^{\alpha+1} = -\partial\mathcal{V}/\partial\boldsymbol{q}_i(\boldsymbol{q}^{\alpha+1})$$

$$\boldsymbol{a}_i^{\alpha+1} = \boldsymbol{f}_i^{\alpha+1}/m_i$$

$$\boldsymbol{v}_i^{\alpha+1} = \boldsymbol{v}_i^\alpha + \Delta t(\boldsymbol{a}_i^\alpha + \boldsymbol{a}_i^{\alpha+1})/2$$



all atoms within the
Verlet radius are considered

Some classical thermodynamic results

Some classical **thermodynamics** and the link to phase-space quantities:

$$U = \langle \mathcal{H} \rangle$$ (note: for an isolated system *E* =*U*)

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad \text{and} \quad T = \frac{1}{\partial S / \partial E}$$

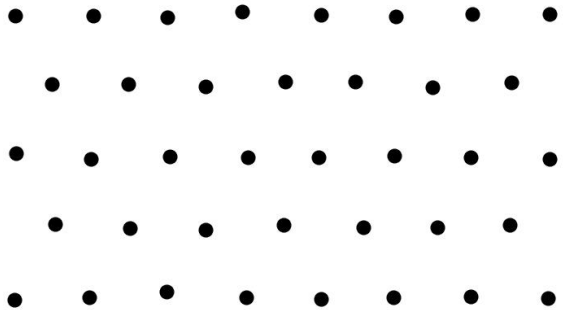
$$S(E) = k_B \ln V_R(E)$$

After a lot of math, one arrives at these relations:

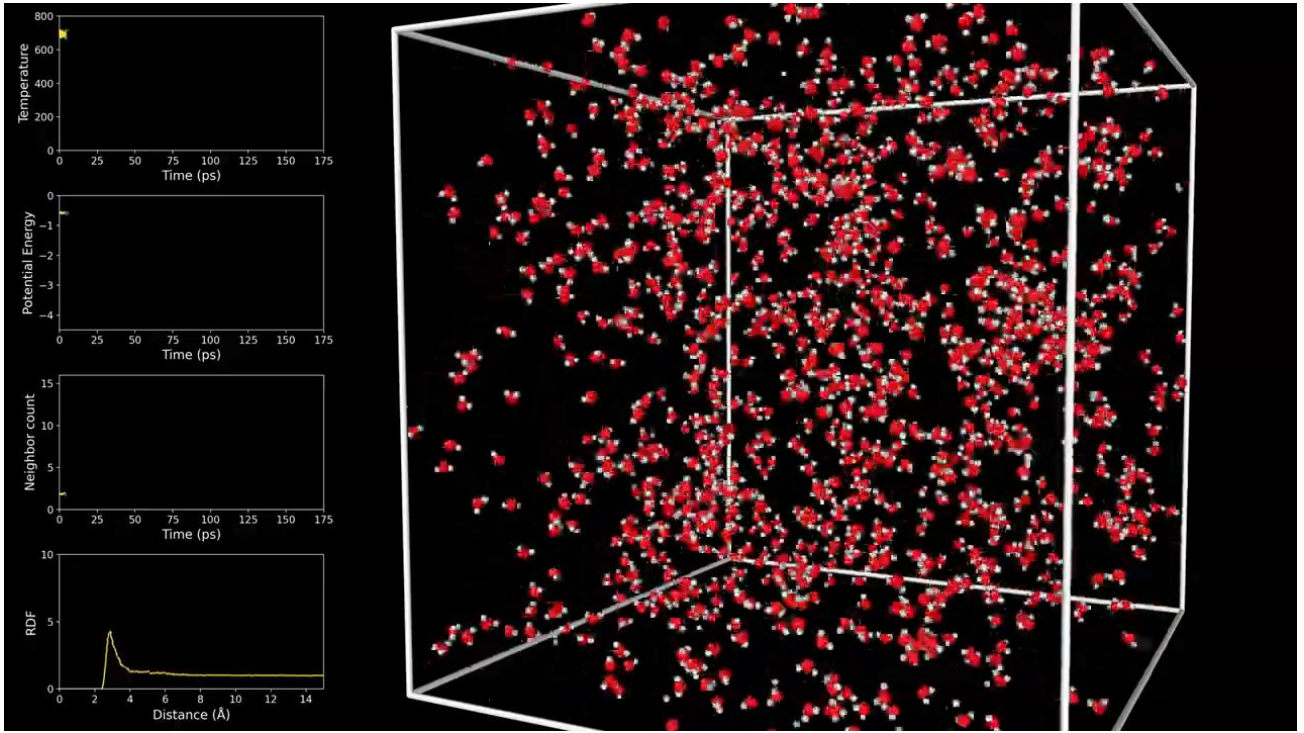
$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = \frac{1}{2} k_B T$$ (*equipartition theorem*)

$$T = \frac{2\langle \mathcal{K}_{\text{vibr.}} \rangle}{3N k_B}$$

$$\boldsymbol{\sigma} = -\frac{1}{|\Omega|} \sum_{a=1}^{N} \left\langle \frac{\boldsymbol{p}_a \otimes \boldsymbol{p}_a}{2m_a} + \boldsymbol{f}_a \otimes \boldsymbol{q}_a \right\rangle$$ (*virial stress tensor*)



Temperature as thermal vibrations



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The canonical ensemble - Enforcing temperature

Recall the **definition of temperature**:

$$T(t^\alpha) = \frac{2}{3Nk_B}\sum_{i=1}^{N}\frac{m_i}{2}\left\|\delta\boldsymbol{v}_i^\alpha\right\|^2 \qquad \text{with} \quad \delta\boldsymbol{v}_i^\alpha = \boldsymbol{v}_i(t^\alpha) - \boldsymbol{P}(t^\alpha)/m_i \qquad \boldsymbol{P} = \textstyle\sum_i m_i\boldsymbol{v}_i$$

Imposing an **initial temperature** onto an atomic ensemble:

1. assign random velocities to all atoms
2. $\boldsymbol{v}_i^0 \leftarrow \boldsymbol{v}_i^0 - \dfrac{\boldsymbol{P}^0}{M}$ with $M = \displaystyle\sum_{i=1}^{N} m_i$ and calculate T^0
3. $\boldsymbol{v}_i^0 \leftarrow \sqrt{\dfrac{T_{\text{ini}}}{T^0}}\boldsymbol{v}_i^0$

Verify:

$$\frac{2}{3Nk_B}\sum_{i=1}^{N}\frac{m_i}{2}\left\|\delta\boldsymbol{v}_i^0\right\|^2 = \frac{2}{3Nk_B}\sum_{i=1}^{N}\frac{m_i}{2}\frac{T_{\text{ini}}}{T^0}\left\|\boldsymbol{v}_i^0\right\|^2 = \frac{T_{\text{ini}}}{T^0}\frac{2}{3Nk_B}\sum_{i=1}^{N}\frac{m_i}{2}\left\|\boldsymbol{v}_i^0\right\|^2 = T_{\text{ini}}$$

The canonical ensemble - Maintaining temperature

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The **thermostat** modifies the equations of motion to maintain a constant temperature:

Langevin thermostat:

$$m_i\ddot{\boldsymbol{q}}_i = \boldsymbol{f}_i - \gamma_i m_i \dot{\boldsymbol{q}}_i + \boldsymbol{g}_i(t)$$

random, time-varying force (Brownian motion)

damping

Nosé-Hover thermostat:

$$m_i\ddot{\boldsymbol{q}}_i = \boldsymbol{f}_i - \gamma m_i \dot{\boldsymbol{q}}_i,$$

non-constant drag aims to drive the system to the enforced temperature

$$\dot{\gamma} = \frac{1}{M}\left(\sum_{i=1}^{N}\frac{\|\boldsymbol{p}_i\|^2}{m_i} - 3Nk_BT\right)$$

Discussion

That's what I prepared for you today.

What would you like to discuss?

Reading for next class:

Multiscale Modeling, D. M. Kochmann

Chapters 17, 18