PERSONAL NOTES

Atomistic Modeling

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2022

Multiscale Computational Mechanics

Multiscale Computational Mechanics.

Atomic Theory Quantum

↓ + $\updownarrow$

Nanoscale Numerical classical.

Methods

fs → ns.

\+

Actual.

Implementation

Hidden: Geared towards Mat. Sci. & Eng.

All models are wrong but some are useful.

Electrical. Conductivity

Strength / Stiffness.

Thermal: Cond.

fracture toughness

} elemental compositions.

Structure property Paradigm.

1. Hall-Petch relation. $\sigma_y \propto \frac{1}{\sqrt{d}}$.

Smaller is stronger
↳ inverse Hall-Petch

Models of Energy.

Module 1: First ~~Principles~~ Methods
QM → HF → DFT.

Module 2: Semi & Empirical Methods
Pair potential i.e., Leonard-Jones
Multibody Potentials.

Module 3: Crystalline solids
"Hard" materials
Elastic & thermal properties.
Statistical Mechanics.

Module 4: Soft ploymers. "Soft"
Fully atomistic MD
Coarse-grain. MD

Module 5: Advanced topics.
- Reactive forcefields
- concurrent multiscaling. - ML.

Feb. 2. Wed.

Module 1: First Principle Method

System description: . No. of particles
. Type of particles.

ICs: positions, velocities.

Interactions. Forces. b/w particles.
Dynamical Eqn. Mathematical form for evolving the system over time.

Classical Mechanics.

$F = ma = \frac{dp}{dt}$ → momentum.
⇓
$p = mv$.

Newton's 2nd law.

Quantum Mechanics

Bonds.
↓
Structure.
Electronic.
Magnetic.
Optical.

Wave-Particle duality.

$p = \frac{h}{\lambda}$ → Planck constant; λ → wave length.
p: momentum (mv).

$h = 6.626 \times 10^{-34}$ J·s.

Given $m = 1kg$, $v = 1 m/s$

$$\lambda = \frac{6.626\times10^{-34}}{?}$$

Postulate a function exists, that capture the systems QM state (positions, time)

→ Wave function $\Psi = \Psi(r, t)$

"Newton's 2nd law for quantum objects"

(First energy model)

Schrödinger's Equation

Time-dependent

$$-\frac{\hbar}{2m}\nabla^2\Psi(r,t) + V(r,t)\Psi(r,t) = i\hbar\frac{\partial\Psi(r,t)}{\partial t}$$

$\frac{h}{2\pi}$ (reduced Planck's const.)

Potential Energy

imaginary unit

Laplace operator.

$$\nabla^2 = \nabla\cdot\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]}_{\text{Hamiltonian}}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

KE

Hamiltonian. $H = T + V$ → PE

C.M. : $T = \frac{p^2}{2m}$

Q.M. $\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$

$$\hat{H}\Psi = E\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Grand state energy

Solve for $\Psi = \psi(r) \cdot f(t)$

ψ: wave function

$f(t)$: $\exp(-i\frac{E}{\hbar}t)$

for each individual particle

→ Time-Independent Schrödinger's Eqn.

$$\hat{H}\Psi(r) = E\Psi(r)$$

Eigenvalue

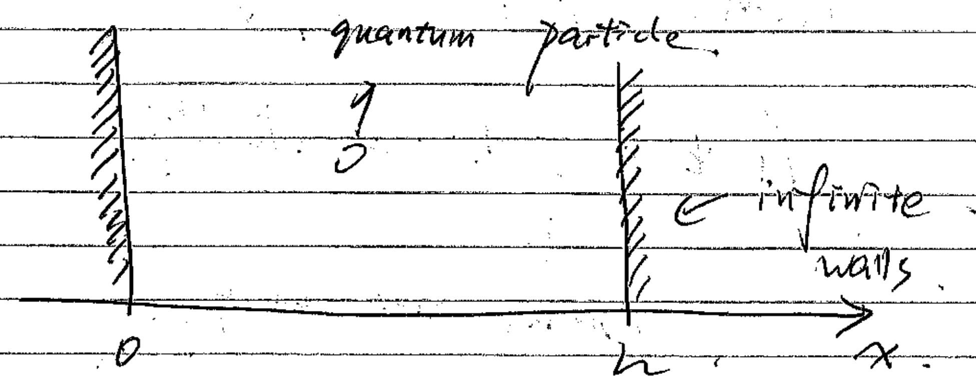
Eigen function

Solution are standing waves:

Physics	Chemistry
Stationary states.	Atomic Orbitals.
Energy eigenstates.	Molecular Orbitals.

Simple Example:

Particle in a box:



$$V(x) = \begin{cases} 0, & \text{if } 0 < x < L \\ \infty, & \text{otherwise} \end{cases}$$

" $\left[-\frac{\hbar^2}{2m}\nabla^2 + \cancel{V}^{\,0}\right]\Psi = E\Psi(x)$

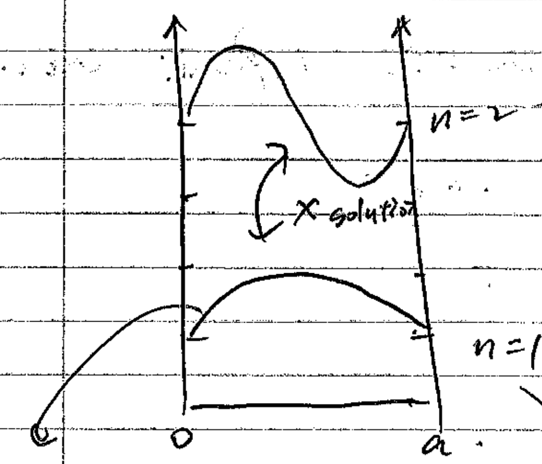
(within the box)

a simple equation: $-\frac{\hbar^2}{2m}\nabla^2\Psi(x) = E\Psi(x)$

BCs: $\Psi(0) = \Psi(L) = 0$.

Solve by inspection, $\Psi(x) = \underbrace{\sqrt{\frac{2}{L}}}_{\text{constant of integration to normalize } |\Psi|^2} \sin\left(\frac{n\pi x}{L}\right)$.

$$E = \frac{n^2\hbar^2\pi^2}{2mL^2}.$$



$E_n I\left(\frac{\hbar^2\pi^2}{2ma^2}\right)$.

→ Energy state are discrete!!!

ground state energy, n=1.

ground state energy, n=1.

Insight into Ψ: Continuous function,

whole system. Square integrable,

Single-valued.

Each "small" ψ, there must be orthogonal (individual particles), with other ψ.

$$\int \psi_i \psi_j \, d\tau = 0, \quad \text{if } i \neq j.$$

Probability of finding an electron somewhere in space must sum to 1:

$\int \psi_i^* \psi_j \, d\tau = 1$, if $i = j$

Must be antisymmetric (Pauli exclusion principle)

$1 \times m \qquad 1 \times 8$

$a \nabla = b$

$\nabla \cdot f = g$

Feb. 4. Fri. 2022.

$\underbrace{\Psi(\underline{r}_1, \underline{r}_2, \cdots \underline{r}_N)}_{\text{N-electrons wave function}}$ > impossible to derive.

$= \underbrace{\psi_1(\underline{r}_1)\, \psi_2(\underline{r}_2) \cdots \psi_N(\underline{r}_N)}_{\text{N-numbers of one-electron wave function}}$

possible

Example : Helium → 2 electrons.

Electron 1 : $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\psi_2)\right]\psi_1 = \varepsilon_1 \psi_1$

2 : $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\psi_1)\right]\psi_2 = \varepsilon_2 \psi_2$

Self-consistent field (SCF)

Guess a solution for both ψ_1 & ψ_2.

Variational principle { $\hat{H}$ & E ←

Solve for ψ_1^{New}, ψ_2^{New} → $\hat{H}^{New}$ agree with $\hat{H}^{*}$

DFT: for a given system,

under given set of conditions.

there exists only one ground state energy

$\delta E = 0$, $\{\psi_i\}$ must be the ground state wave functions.

Quantum Espresso:

- &control: name list.

  scf: self-consistent field.

  prefix: → name of materials.

  tstress output the stress of systems

  tprnfor → print the force.

  pseudo_dir. → directory.

- & System: name list.

  bravy_lattice index.

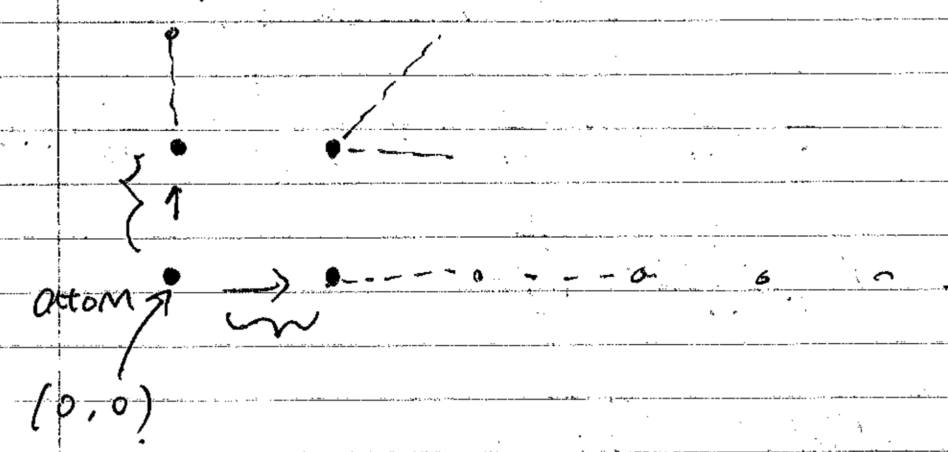
  size of lattice

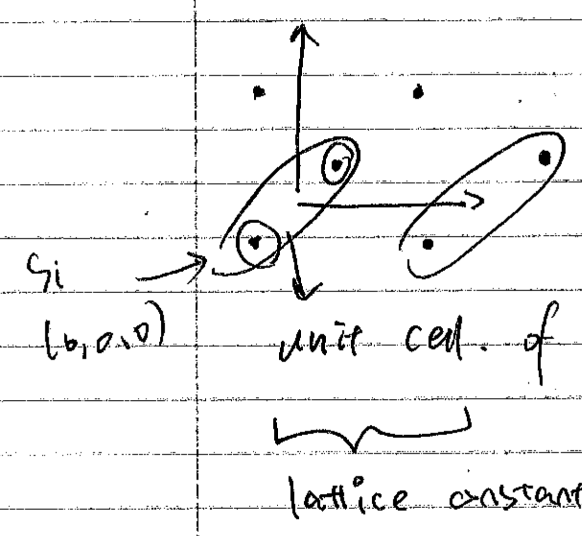
  properties of materials

ATOM SPECIES ↦ card.

specify the card information.

Crystallic materials.





Face-centered cubic

Body-centered cubic.

fixed way

$\boxed{\text{Unit cell} \to \text{Structure}}$

Feb. 9. Wed. 2022.

Example.

10 → electron

2 → Nucleus.

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}$$

$$V(r_{12}) = \frac{q_1 q_2}{r_{12}}$$

$\boxed{7.66}$

VC.

SCF. $\frac{dP}{dt}$

cell. dim 7.62 ~~8.62~~ 9.62

Feb. 16. 2022.

Hartree - Fock approach.

↓

Still computationally costly.

$\Psi(r_1, r_2, \dots r_N) \rightarrow 4N$ variables

$\begin{pmatrix} 3N \text{ spatial} \\ N \text{ spin} \end{pmatrix}$

Recall probability density (electron density) of any pt. in space.

$\rho(r) = |\Psi|^2$

3 vars. x, y, z,

- 1st Hohenberg - Kohn Theorem.

$V_{ext}(r) \rightarrow$ unique functional of $\rho(r)$.

Mathematically.

$$E[\rho(r)] = \overbrace{\underbrace{T[\rho] + V_{ee}[\rho]}_{F[\rho],\ \text{same for any molecule}}}^{\text{universal functional}} + V_{ext}[\rho]$$

V_{ext} ⟹ system - dependent.

$\int V_{ext}(\underline{r})\,\rho(\underline{r})\,d\underline{r}$.

Nucleus - electron interaction.

$-\sum_n \frac{Z_n}{\underline{r}-R}$

How to formulate $E[\rho(\underline{r})]$?

Kohn - Sham 1 electron representation.

$$\rho(\underline{r}) = \sum_{i=1}^{N} |\psi_i(\underline{r}_i)|^2.$$

KS kinetic

Hartree energy

Universal Functional. $F[\rho] = T_s[\rho] + E_H[\rho]$
$+ E_{xc}[\rho]$

Exchange - correlation energy.

$$T_s[\rho] = \sum_{i=1}^{N} \int \psi_i^{*}(\underline{r}) \cdot \left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_i(\underline{r})\,d\underline{r}$$

Corelation: 2 electons with different spins can occupy the same orbital

but not in the same location.

Repulsion to prevent overlap.

KS Eqns.

e-e interactions. Univ. func. F.

$$\Big[\underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V_H(\underline{r}) + V_{xc}(\underline{r})}_{H_{KS}} + V_{ext}(\underline{r})\Big]\psi_i = \varepsilon_i \psi_i(\underline{r}).$$

approximation. pseudo e-n interaction

Recall: Al. pbe ... paw. ... UPF.

Pseudopotential

approximation of V_{xc}. for V_{ext}.

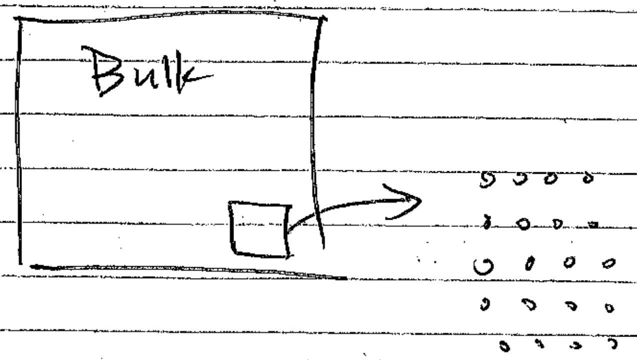
Example: Al, 13 electrons

↑	−2.7 eV
↑↓	−7.8 eV
↑↓ ↑↓ ↑↓	−69.5 eV
↑↓	−105 eV
↑↓ very bottom.	−1512 eV

valence states

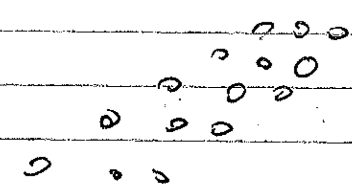
Very stable core state, combine with nuc V_{PP}

Discretization in DFT

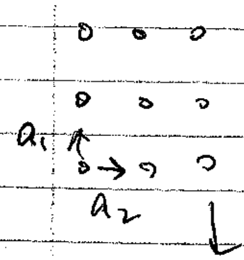


Real lattice space (points)

Fourier Transform.



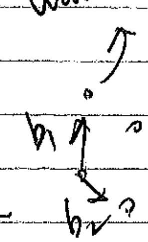
Reciprocal lattice.



Spatial

For 3D,

$$\underline{b}_k = 2\pi \cdot \frac{\underline{a}_l \times \underline{a}_m}{\underline{a}_k \cdot (\underline{a}_l \times \underline{a}_m)}$$



Bloch Theorem

For periodic solids, superpose plane waves to represent orbitals w/ crystal lattice periodicity.

Bloch function

Function w/ same periodicity as crystal lattice.

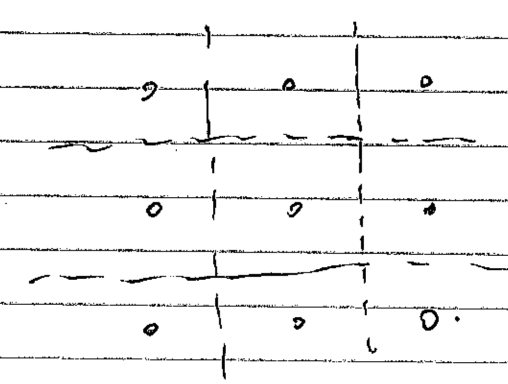
$$\psi_{nk}(\underline{r}) = U_{nk}(\underline{r}) \exp(i\underline{k}\cdot\underline{r})$$

Electron. wavevector

$$U_{nk}(\underline{r}) = \sum_{G} C_{nk}(\underline{G}) \exp(i\underline{G}\cdot\underline{r})$$

$$\sum_{G'} \hat{H}_{GG'}(\underline{k})\, C_{nk}(\underline{G}') = \varepsilon_{nk} \sum_{G} C_{nk}(\underline{G})$$

The 1st Brillouin Zone.



thermo → actual computed.

timestep → [illegible] & [illegible]

$\xi \propto t$

$\propto p$

Lecture 3.

Module 2: Molecular Dynamics.

→ Pair potentials.

Born – Oppenheimer Approx.

In Q.M., mass of nuclei >> mass of electrons

Stationary — $\hat{H}\Psi = E\Psi$

In C.M., Dynamic — Average out

Assume classical approx. is adequate,

2nd Energy Model.

$$H(\underset{\sim}{r}, p) = K(p) + V(\underset{\sim}{r})$$

$\underset{\sim}{r}$: coordinates of all particles

p: momenta

$K(p)$: $\underbrace{\frac{p^2}{2m}}_{\text{momentum}}$

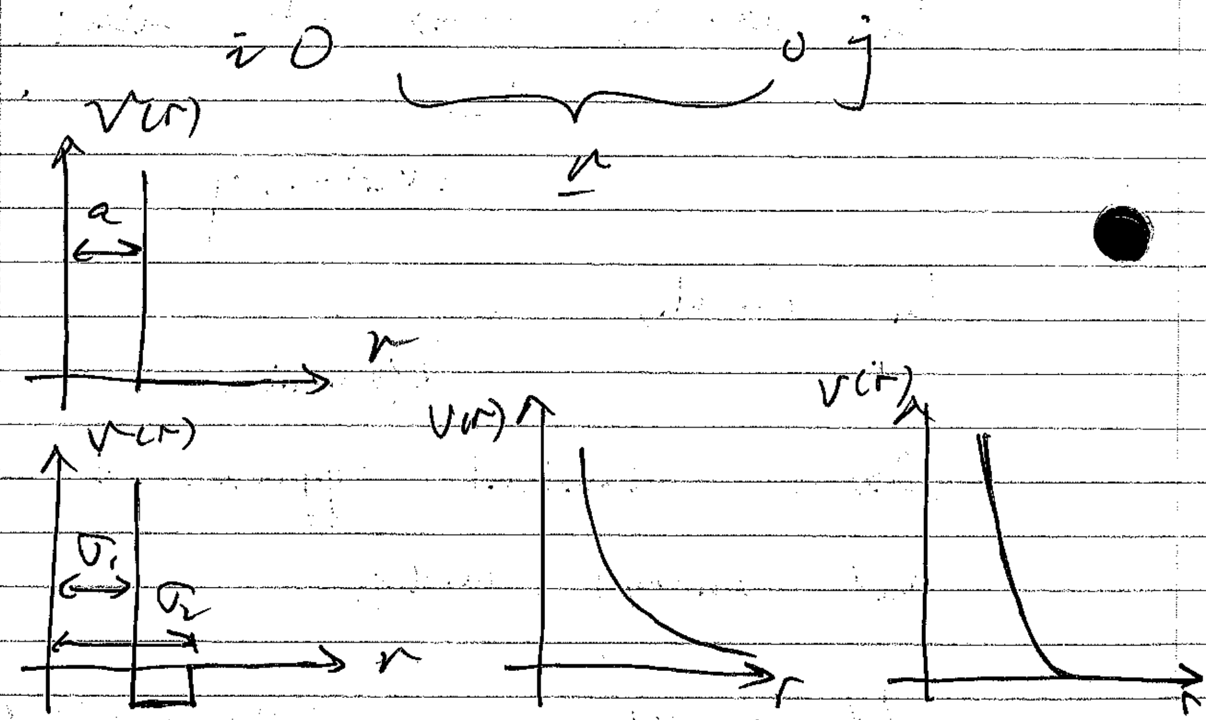
$V(\underset{\sim}{r})$: ? or intractable

$$V(\underset{\sim}{r}) \approx \underbrace{\sum_i V_1(r_i) + \sum_i \sum_{j>i} V_2(r_{ij})}_{V_2^{\text{eff}}} + \underbrace{\cdots}_{\text{comp. expensive}}$$

V_x^{eff} → Density

Lattice constant

Elastic constant.



$V_{LJ}(r_{ij})$ → Lennard-Jones Potentials

$$= 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

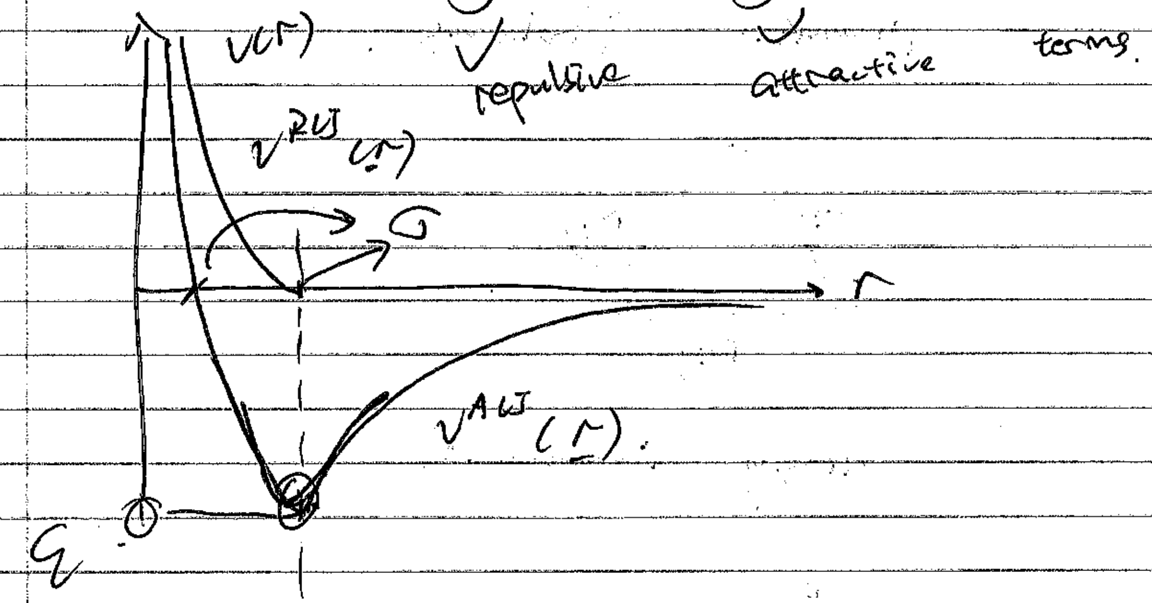
ε → Depth of energy well

σ → Width of EW

$$= \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}$$

Generalized form:

$$V_{LJ} = \underbrace{\frac{A}{r_{ij}^{x}}}_{\text{repulsive}} - \underbrace{\frac{B}{r_{ij}^{y}}}_{\text{attractive}} \text{ terms.}$$



Other forms,

$$V_{Morse} = D_0\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right]$$

$$V_{Buck} = Ae^{-r_{ij}/\rho} - \frac{C}{r_{ij}^{6}}$$

Cross-interactions approx. with mixing rules, ~~Laurence~~

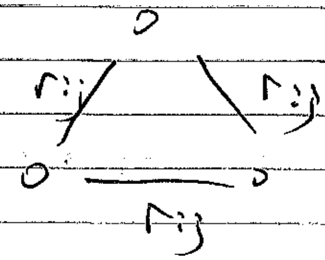
Lorentz-Berthelot mixing rules:

$$\sigma_{\alpha\beta} = \frac{1}{2}[\sigma_\alpha + \sigma_\beta]$$

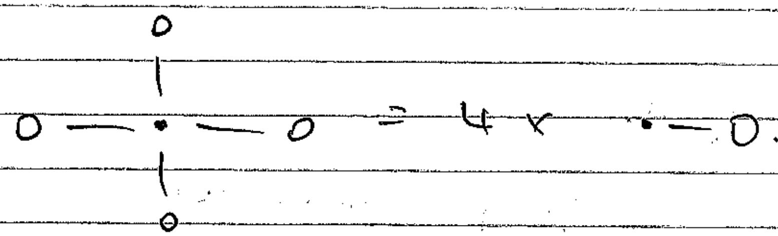
$$\varepsilon_{\alpha\beta} = [\varepsilon_\alpha \varepsilon_\beta]^{1/2}$$

Alder & Wainwright, JCP 1957.

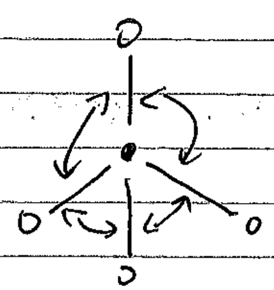
"Potential" Problems.



Energy inaccurate.



Bond coordination, Z.



In metal, $V \propto \sqrt{Z}$

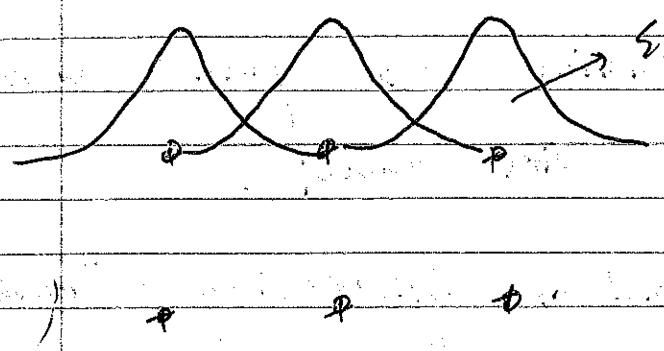
<u>Bloch Theorem.</u>

For periodic solids.

Q.M.: Electrons delocalized over the crystal lattice as plane waves interacting with nuclei.

C.M.: Nucleus interacting / "embedded" within a sea of electrons.

Mar. 2nd, 2022



electron density.

at atom i,

$$\rho_i = \sum_{j \neq i} \rho_j^a(r_{ij})$$

spherically averaged electron density.

embed in the sea of electrons.

Define an embedding function, $G[\rho]$

Such that

$$E_{coh} = \underbrace{\sum_i G_i\left[\sum_{j \neq i} \rho_j^a(r_{ij})\right]}_{\text{Embedding function}} + \underbrace{\frac{1}{2}\sum_{j \neq i} V(r_{ij})}_{\text{pair potential}}$$

Embedded Atom Method (EAM).

Able to reproduce:

Bulk structure.

(SC, BCC, FCC, HCP, ...).

Free surfaces.

Defects & energies.

(Vacancies, interstitials, crack, ...)

NIST Interatomic potential Repo,

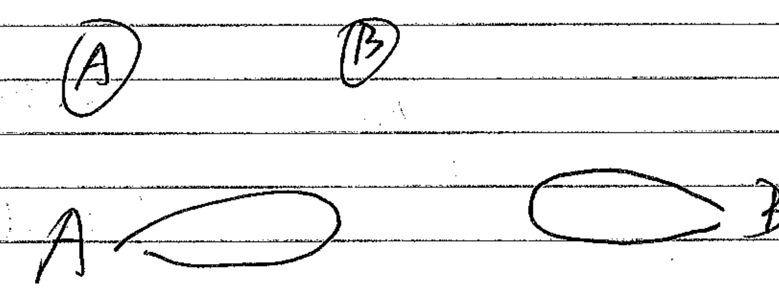
Plimpton, Thompson, MRS Bulletin, 2012.

Good for metals (sea of electrons).

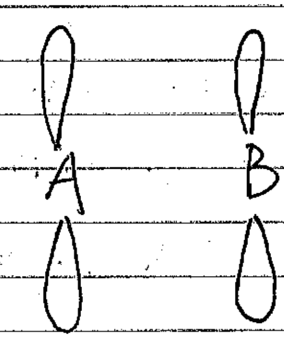
but how about organic molecules

& other molecules w/ directional bonding?

σ - bonds,



π - bond



Tersoff, 1988:

Pair potential form, $E_{ion} = \frac{1}{2}\sum_i \sum_{j\neq i} V(r_{ij})$.

more complicated

$$V_{ij} = f^c(r_{ij})\left[V^R(r_{ij}) + b_{ij} V^A(r_{ij})\right].$$

f^c → cutoff function, going smoothly to zero.

V^R → repulsive

V^A → attractive

b_{ij} → bond order.

$$b_{ij} \propto \frac{1}{\sqrt{Z}}$$

Bond angles.
& distances.
& strength.

Other potentials: Stillinger Weber
COMB, EDIP, AIREBO.

$$H(\underline{r}, \underline{P}) = K(\underline{P}) + \underbrace{V(\underline{r})}$$

we only talk bout this so far.
What can we determine once V is defined.

$$-\nabla V = f_i \longrightarrow \dot{\underline{P}} \longrightarrow \frac{\dot{\underline{P}}}{m_i} \rightarrow \dot{\underline{r}} \rightarrow \underline{r}$$

?

$$\underline{r}_i(t_0) \Rightarrow \underline{r}_i(t_0+\Delta t) \rightarrow \cdots \underline{r}_i(t_0+n\Delta t)$$

<u>Finite difference methods</u>

(Verlet, 1967).

Taylor expansion of $f(x)$ at point a:

$$f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \cdots$$

Let $a = t_0$, $x = t_0 + \Delta t$, $x - a = \Delta t$

$$\underline{r}_i(t_0+\Delta t) = \underline{r}_i(t_0) + \dot{\underline{r}}_i(t_0)\Delta t + \frac{1}{2}\ddot{\underline{r}}(t_0)\Delta t^2 + \cdots$$

$$\underline{r}_i(t_0-\Delta t) = \underline{r}_i(t_0) - \dot{\underline{r}}_i(t_0)\Delta t + \frac{1}{2}\ddot{\underline{r}}_i(t_0)\Delta t^2 + \ldots$$

Simplifying ① + ② :

$$\underline{r}_i(t_0+\Delta t) + \underline{r}_i(t_0-\Delta t) = 2\underline{r}_i(t_0) + \ddot{\underline{r}}_i(t_0)\Delta t^2 + O(\Delta t^4).$$

$$\underline{r}_i(t_0+\Delta t) = \underbrace{\underbrace{2\underline{r}_i(t_0)}_{\text{current}} - \underbrace{\underline{r}_i(t_0-\Delta t)}_{\text{previous}}}_{\text{large}} + \underbrace{\underbrace{\ddot{\underline{r}}_i(t_0)}_{\text{acceleration of current}}\Delta t^2}_{\text{small}}.$$

$$\dot{\underline{r}}_i(t_0) = \frac{\underline{r}_i(t_0+\Delta t) - \underline{r}(t_0-\Delta t)}{2\Delta t}$$

Position error $O(\Delta t^4)$

Velocity error $O(\Delta t^2)$ ⇒ known only when $\underline{r}_i(t_0+\Delta t)$ is known

Leap-frog Verlet

$$\dot{\underline{r}}_i(t_0+\tfrac{1}{2}\Delta t) = \dot{\underline{r}}_i(t_0-\tfrac{1}{2}\Delta t) + \ddot{\underline{r}}_i(t_0)\Delta t.$$

$$\underline{r}_i(t_0+\Delta t) = \underline{r}_i(t_0) + \dot{\underline{r}}_i(t_0+\tfrac{1}{2}\Delta t)\Delta t.$$

$$\dot{\underline{r}}_i(t_0) = \frac{1}{2}\left[\dot{\underline{r}}_i(t_0+\tfrac{1}{2}\Delta t) + \dot{\underline{r}}_i(t_0-\tfrac{1}{2}\Delta t)\right]$$

Remove arithm ...

Velocity Verlet

① $$\underline{r}_i(t_0+\Delta t) = \underline{r}_i(t_0) + \dot{\underline{r}}_i(t_0)\Delta t + \frac{1}{2}\ddot{\underline{r}}_i(t_0)\Delta t^2$$

$$\dot{\underline{r}}_i(t_0+\Delta t) = \dot{\underline{r}}_i(t_0) + \frac{1}{2}\Delta t\left[\ddot{\underline{r}}_i(t_0) + \ddot{\underline{r}}_i(t_0+\Delta t)\right]$$

② $$\dot{\underline{r}}_i(t_0+\tfrac{1}{2}\Delta t) = \dot{\underline{r}}_i(t_0) + \frac{1}{2}\ddot{\underline{r}}_i(t_0)\Delta t.$$

③ $$\dot{\underline{r}}_i(t_0+\Delta t) = \dot{\underline{r}}_i(t_0+\tfrac{1}{2}\Delta t) + \frac{1}{2}\ddot{\underline{r}}_i(t_0+\Delta t)\Delta t$$

MD simulations.

Positions of atoms.

$r(t)$, $\dot{r}(t)$, $\ddot{r}(t)$,

Sampling from ensembles.

Statistical Mechanics

Material Properties

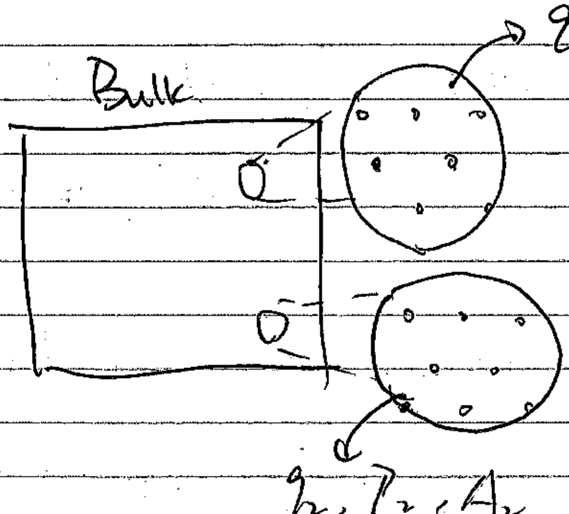
- Thermodynamics

(Pressure (P), C_v, S, G, λ, α, σ, T)

- State.

(gas, liquid, solid)

Bulk



Multiple possible microscopic states.

For each states, assuming N-atoms,

6N dimensions for each states.

(3N spatial, 3N momenta).

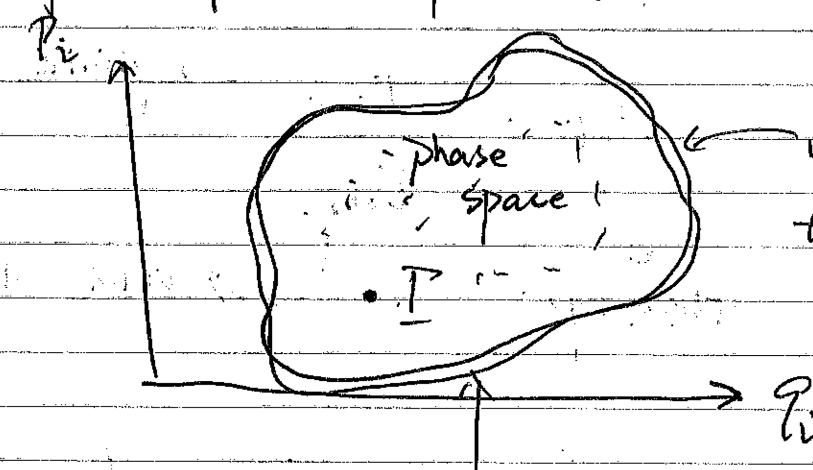
For each state, define

$q_i \Rightarrow$ Generalized coordinate

$\hookrightarrow$ index for each state

$P_i \Rightarrow$ Generalized momenta.

Define phase space



where defines the boundary.

Bulk properties define thermodynamics constraints (N, V, T, ...)

Generalized pt. in phase space Γ (Gamma)

Evolve w/ time $\Gamma(t)$

Macroscopic properties: observed experimentally. $A_{obs} = \langle A(\Gamma(t)) \rangle$

time-average.

Ideally. $A_{obs} = \lim_{t_{obs} \to \infty} \frac{1}{t_{obs}} \int_0^{t_{obs}} A(\Gamma(t))$

if t_{obs} is continuous.

Practically, in MD simulations.

$\Delta t = \frac{t_{obs}}{\tau_{obs}}$ → finite time

Δt → timestep

τ_{obs} → total number of steps.

$A_{obs} = \langle A(\Gamma(t)) \rangle = \frac{1}{\tau_{obs}} \sum_{\tau=1}^{\tau_{obs}} A(\Gamma(t))$

MD samples $\underbrace{\text{collections of } \Gamma}_{\text{Ensembles}}$.

Microcanonical (NVE).

loosen the constraints

↓

canonical (NVT).

Grand canonical (μVT)

↓

chemical potential.

e.g. concentration

Isobaric-Isothermal (NPT)

Is $A_{obs} = \frac{1}{M}(A_1 + A_2 + \dots A_m)$?

No!

MD samples collections of Γ.

distributed by probability density. $\rho(\Gamma)$

Each ensemble / constraints determines

$\rho(\Gamma)$, i.e. ρ_{NVT}, ρ_{NVE}, ...,

generally ρ_{ens}.

$$\rho_{ens}(\Gamma) = \frac{W_{ens}(\Gamma)}{\sum_{\Gamma} W_{ens}(\Gamma)} = \frac{W_{ens}(\Gamma)}{Q_{ens}}$$

(Z, Ω).

partition function, accessible phase space

⇒ (See Sethna, Statistical Mech.)

Thermodynamic potential, $\Psi_{ens} = -\ln Q_{ens}$

Min. at thermodynamic equil.

Mar. 16, 2022 Wed.

Partition function

Q_{ens} → determine many properties.

$$A_{obs} = \langle A \rangle_{ens} = \frac{\sum_{\Gamma} W_{ens}(\Gamma) A(\Gamma)}{\sum_{\Gamma} W_{ens}(\Gamma)}$$

Examples:

Internal Energy $\langle E \rangle = -\frac{\partial}{\partial \beta}(\ln Q_{NVT})$

beta, $\frac{1}{k_B T}$

Boltzmann constant.

Heat capacity.

$$C_V = \frac{1}{N} \frac{\partial \langle E \rangle}{\partial T}$$

$$= \frac{1}{k_B T^2} \frac{\partial^2}{\partial \beta^2} (\ln Q_{NVT}).$$

How to generate $\bar{c}$ correct ensemble in MD? $\Gamma(\tau) \to \Gamma(\tau+1)$.

Newtonian EOM. ⇒ NVE, i.e. ρ_{NVE}

NVE → fix ... nve

⇓

velocity verlet algorithm

$H = K + V$

LJ, EAM, ...

Modify EOM → P_{NVT}, P_{NPT}, ...

⇓

"fix ... nvt"

Nosé – Hoover thermostat → (Nosé, JCP 1984, Hoover, PRA 1985)

"fix ... langevin"

Langevin thermostat

Berendsen / Andersen

Example Nosé – Hoover (NVT)

Introduce extra DOFs, s, to simulate heat bath.

$$H(p, q, P_s, s) = \sum_i \frac{P_i^2}{2 m s^2} + \frac{1}{2}\sum_{i \neq j} V(r_{ij})$$

$$+ \frac{P_s^2}{2Q} + g k_B T \ln s.$$

extra DOFs from heat bath.

particle momentum in the heat bath.

effective mass.

degree of freedoms.

See Tildesley, Comp. Sim. Liquids.

How to get thermodynamic avg. of some property, $\langle A \rangle$?

> Toda, Kubo, Saito, Outline of Stat. Mech.

Generally, $\langle A \cdot \frac{\partial H}{\partial q_k} \rangle = k_B T \langle \frac{\partial A}{\partial q_k} \rangle$.

... Lots of Math.

$\langle P_k \cdot \frac{\partial H}{\partial P_k} \rangle = k_B T$, for some coordinate (small) k.

$P_k \cdot \frac{\partial K}{\partial P_k}$

For one single atom i,

$$K = \frac{|\underline{P}_i|^2}{2m_i}, \quad \frac{\partial K}{\partial P_i} = \frac{P_i}{m_i}$$

For N - atoms.

$$\left\langle \sum_{i=1}^{N} \underline{P}_i \cdot \frac{\underline{P}_i}{m} \right\rangle = \left\langle \sum_{i=1}^{N} \frac{|\underline{P}_i|^2}{m_i} \right\rangle = 3N k_B T$$

$$\langle K \rangle = \frac{3}{2} N k_B T = 3N \cdot \underbrace{\frac{1}{2} k_B T}$$

Each DOF contribute $\frac{1}{2} k_B T$ to K.

At any timestep, $T = \frac{2}{3Nk_B} K$

$$= \frac{1}{3Nk_B} \sum_{i=1}^{N} \frac{|\underline{P}_i|^2}{m_i}$$

$$P_i = m_i v_i.$$

" Velocity ... create 300.00 ... gaussian".

Generally, $\left\langle A \frac{\partial H}{\partial q_k} \right\rangle = k_B T \left\langle \frac{\partial A}{\partial q_k} \right\rangle$.

... math ...

$$\left\langle q_k \frac{\partial H}{\partial q_k} \right\rangle = k_B T.$$

For N- atoms, $\left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \nabla_{\underline{r}_i} V \right\rangle$

$$= - \left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \underline{f}_i^{tot} \right\rangle.$$

$$= 3N \cdot k_B T.$$

Clausius virial theorem.

$$\frac{1}{3} \left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \underline{f}_i^{tot} \right\rangle = - N k_B T. \rightarrow ①$$

$$\underline{f}_i^{tot} = \underline{f}_i^{ext} + \underline{f}_i^{int}$$

$$\frac{1}{3} \left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \left(\underline{f}_i^{ext} + \underline{f}_i^{int} \right) \right\rangle = - N k_B T.$$

$\hookrightarrow$ define external pressure:

$$\frac{1}{3} \left\langle \sum_{i=1}^{N} \underline{r}_i \cdot \underline{f}_i^{ext} \right\rangle = - PV \rightarrow ②$$

$V \rightarrow$ volume. e.g. piston / walls

Internal "pressure", a.k.a. "Virial",

$$\frac{1}{3}\sum_{i=1}^{N} r_i \cdot f_i^{int} = W \quad \cdots ③$$

②, ③, → ①:

$$PV = Nk_BT + \langle W \rangle.$$

At any timestep, the instantaneous pressure

$$P_{ins} = \rho k_B T^{ins} + \underbrace{\frac{W}{V}}_{\text{volume}}$$

Mar. 23, 2022. Wed.

Stat. mech.

- Ergodicity.
- Sampling phase space

→ Two fundamental methods ~~to~~ sample phase space.

1. MD simulation → Generate trajectory that moves state by state.

   $A_{obs} = \langle A \rangle_{time}$

2. Monte - Carlo (MC)

   - "Shooting darts" → Randomly generate system at various points in phase space

   $A_{obs} = \langle A \rangle_{ens}$

$$A_{obs} = \langle A \rangle_{time} = \langle A \rangle_{ens}$$

To ensure, need a property called "ergodicity".

Non-ergodic vs. poor sampling

Enhance Sampling:

Replica Exchange MD.

Meta dynamics

Module 4

— Soft Materials.

⇒ Restricting to "polymers"

many parts.

- Monomers
- Viscoelasticity.
- Anisotropy.
- Gels / Hydrogels
- Long chains
- crosslinks

— PE. PP. PVA.
PET. Acrylic.
PMMA.

PE $[CH_2-CH_2]_n$ PVC $[CH_2-CH(Cl)]$

Chemical interactions in polymers.

- Covalent bonds. • Hydrogen bonds (NH ⋮ O)
- vdW interactions.
  (Non-directional, nonpolar, isotropic)
- Electrostatic (+ or − charged).

Unique properties of polymers

- Viscoelasticity. • Entanglements.
- Thermal, electrical, optical, ...

Surprisingly simple pairwise functions:

$V_{total} = V_{covalent} + V_{elec} + V_{vdW}$.

Mar. 13. 2022. Wed.

Simple pairwise functions

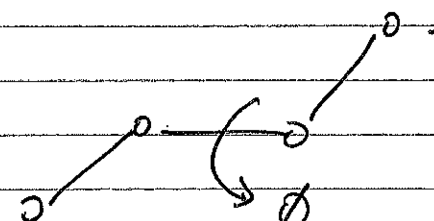
$$U_{total} = \underbrace{V_{covalent}} + V_{elec} + U_{vdw}$$

- Bond o—o $\frac{k_b}{2}(r_{ij})^2$

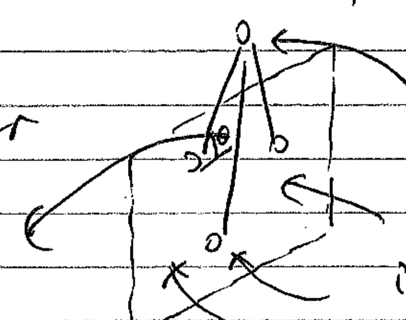
bond_style harmonic.

- Angle $\frac{k_\theta}{2}(\theta_{ij})^2$

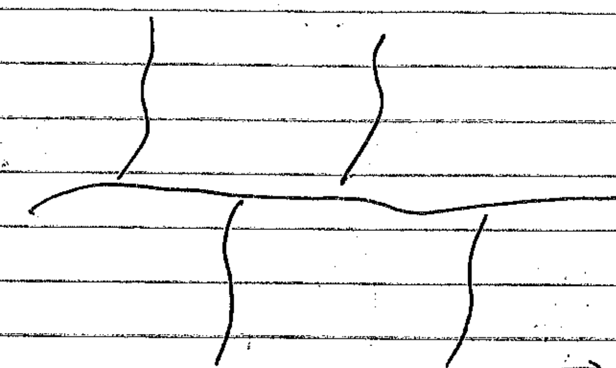
- Dihedrals $\frac{k_\phi}{2}(1+\cos(n\phi-\phi_0))$



- Improper $\frac{k_\psi}{2}(\psi-\psi_0)^2$



- Polymeric Isomerism.



V_{elec} : $\frac{q_i q_j}{\varepsilon r_{ij}}$

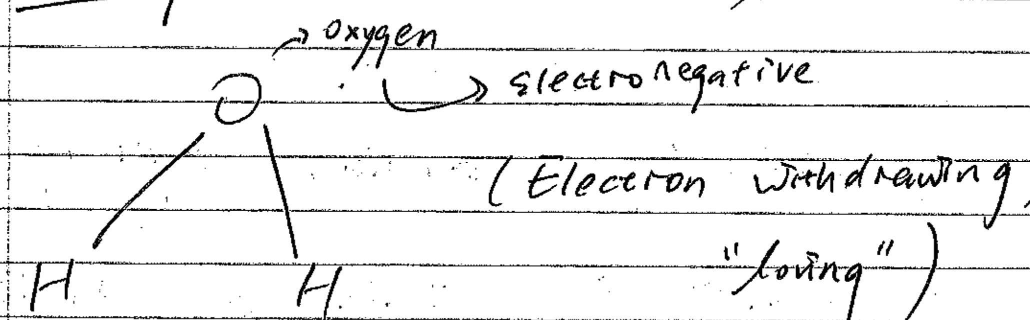
$q_i q_j$ → particle charge

ε → permitivity

Ions : Ca^{2+}, Na^+, Cl^-, ...
(Integer charges)

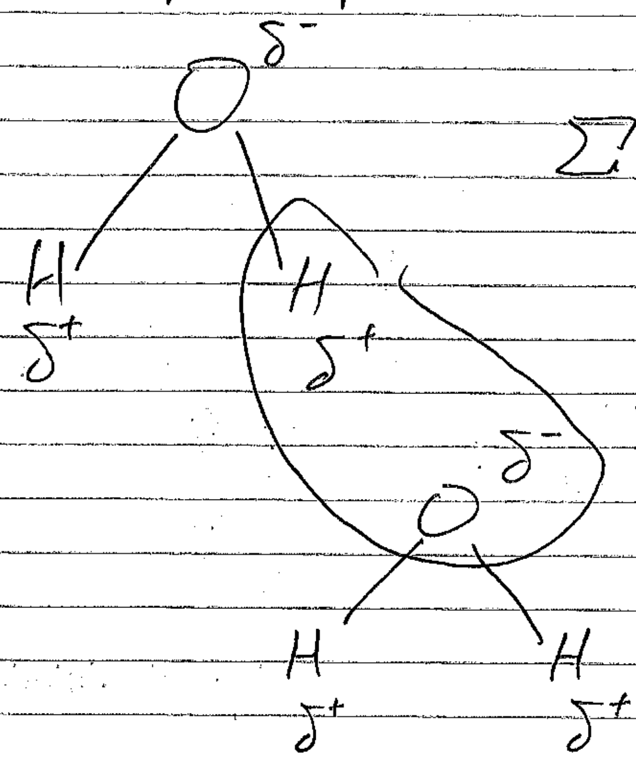
partial charges :

Example Water (H_2O)



Overall charge of H_2O = 0

$\sum_i \delta^+ = \sum_i \delta^-$



$\frac{q_i q_j}{\Sigma r_{ij}}$

LJ: 12-6, 9-6, ⇒ V_{vdw}.

Benefits

- Comp. cheap.
- Applicable to atoms (tunable)
- Scale up easily.
- Well-defined bonding topology.
- Easier to optimize the algorithm.

NAMD, GROMACS, CHARMM, AMBER, ...

- Library of fragments.

Mix & match parameters, OPLS,

CGenFF, Amber GenFF

Limitations:

- Bond breaking → bonds are unbreakable.
- Complex library for atom typing

Apr. 20, 2022, Wed

- Coarse-graining.

Class I (empirical, simpler formulations)

- CHARMM.
- OPLS.
- AMBER
- GROMOS

Class II (QM fitting; complex formulating)

- Consistent forcefield family.

– CFF
– PCFF
– CVFF
– COMPASS (only commercially, most modern)

- DREIDING, • VFF

DFT → ~~EAM / Tersoff~~ → CHARMM / PCFF

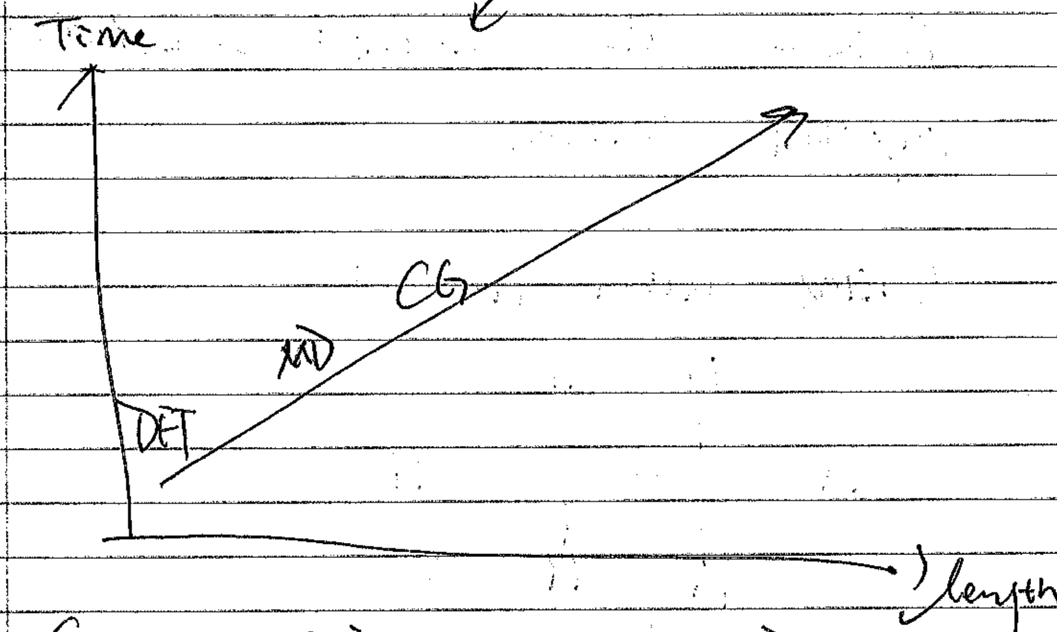
↑

QM.

$\underbrace{\text{EAM / Tersoff}}_{0.3\ fs}$ $\underbrace{\text{CHARMM / PCFF}}_{2fs-4fs}$

Not moving → Dynamic.

Electrons → Atoms → Molecules.



Coarse-graining → why?

Take advantage of repeating units:

DNA → single nucleotide

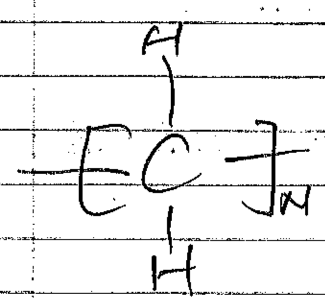
Proteins → Amino acid

Crystalline materials

↓

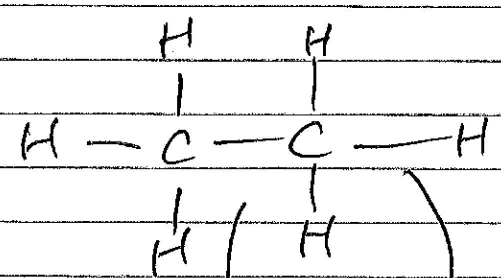
Single unit.

Water, H_2O → 1 bead combines H_2O.



Reduced order models: Considering only important features.

United atom model:



→ Vibration timescales are very different.

CH (3000 cm^{-1})

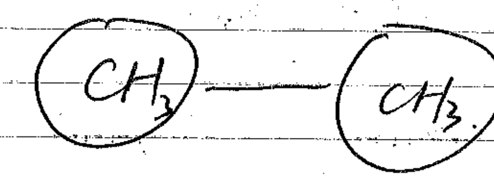
C–C (1200 cm^{-1})

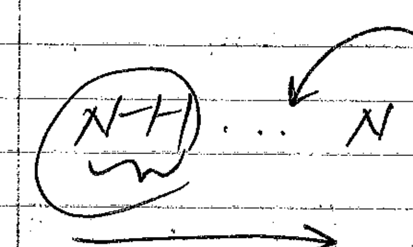
Merge CH into a single "bead".

increase mass

change partial charges

OPLS-UA, CHARMM → Hydrogen mass repartitioning.





CG Models: → Physics-based.

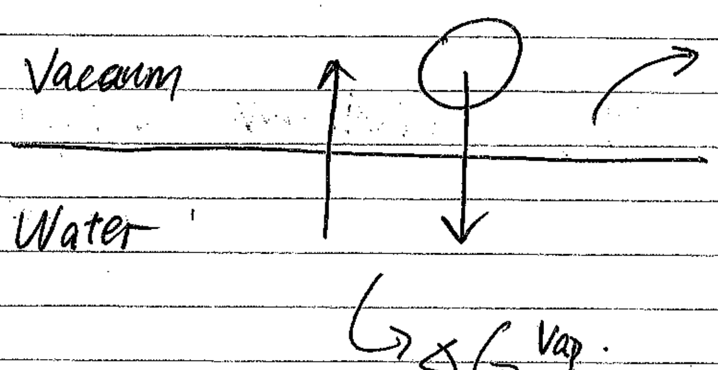
→ knowledge-based.

→ Structure-based.

①: Physics-based Models

MARTINI → 4-to-1 mapping.

Parameterize the non-bonded interactions using partitioning free energy.



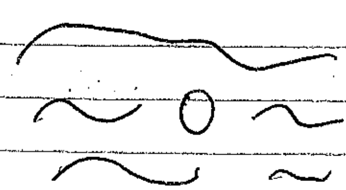
$\Delta G^{Hyd} = k_B T \ln\left(\frac{\rho_{vacuum}}{\rho_{wat}}\right)$

ΔG^{Vap}.

Vacuum / Water / Organic solvents (hexadecane, chloroform, ...).

Bonded interactions: Fit to actual distributions of representative basis set of structures, e.g. proteins from PDB.

∘ Dissipative Particle Dynamics — viscosity



Particle in fluid media — anti-thermostat

$$F_i^{tot} = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right)$$

↗ Remove KE.

F_{ij}^R : collisions w/ media

Add kinetic energy.

F_{ij}^C : Purely repulsive, beads tend to spread evenly, e.g. diffusion.

$$\Rightarrow A_{ij}\left(1 - \frac{r_{ij}}{r_c}\right)\frac{\vec{r}_{ij}}{r_{ij}}$$

chemical identity

For chemically different beads, Flory-Huggins parameter, χ^{AB} & $(A_{ij}^{AB} - A_{ij}^{AA})$

$$A_{ij}^{AA} = A_{ij}^{BB}$$

Tie beads together w/ springs,

Simple harmonic spring: $V = kx^2$

FENE (Finitely extensible nonlinear elastic)

$$V_{FENE} = -0.5KR_0^2 \ln\left[1-\left(\frac{r_{ij}}{R_0}\right)^2\right] \underbrace{+ 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \varepsilon}_{\text{repulsive}}$$

attractive interaction.

repulsive

Boltzmann inversion.

For canonical ensemble, (NVT) & generalized coordinate q, Probability distribution of q obeys Boltzmann distribution.

$$P(q) = \frac{\exp[-\beta V(q)]}{\underbrace{\int \exp[-\beta V(q)]dq}_{\text{partition function.}}}$$

$\frac{1}{k_B T}$

potential

partition function.

Q_{NVT} (or Z).

Once $P(q)$ is known/measured, then by inversion,

$$V(q) = -k_B T \ln[P(Q_{NT})]$$

$$\begin{array}{ccccc} V_{tot} = V_{bond} & + V_{angle} & \cdots\cdots & + V_{nonbonded} \\ \downarrow & \downarrow & & \downarrow \\ P_{bond} & P_{angle} & \cdots\cdots & P_r \end{array}$$

Procedure is iterative ⇒ Iterative BI

$$V_{i+1}(q) = V_i(q) - \alpha k_B T \ln\left(\frac{g_i}{g_{target}}\right)$$

Scaling factor

If $g_i = g_{target}$, $\ln 1 = 0$.

Interpretation of timescales

Less "friction" between beads:

Sampling time vs. effective time.

1μs total s. time ← 30fs timestep ⇒ 4-fold faster in terms of "real" dyn-

Sequential multiscaling

→ finer – train – coarser approach.

Computational load vs. details

(Chemical / Physics / structural).

Concurrent Multiscaling:

Introduce finer details back,

e.g. chemistry into MD,

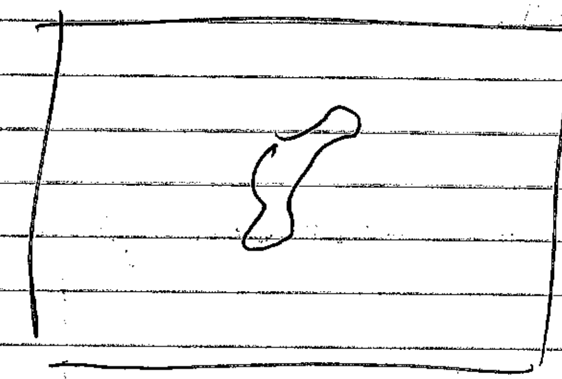
MD into FEM,

ReaxFF: Highly accurate bond-order potential.

Chenoweth et al., JPCA, 2008

load vs detail

(concurrent multiscaling).



· Many applications...

in concurrent multiscaling, we care about information passing:

- embed atomic region in a larger continuum (FEM) region.

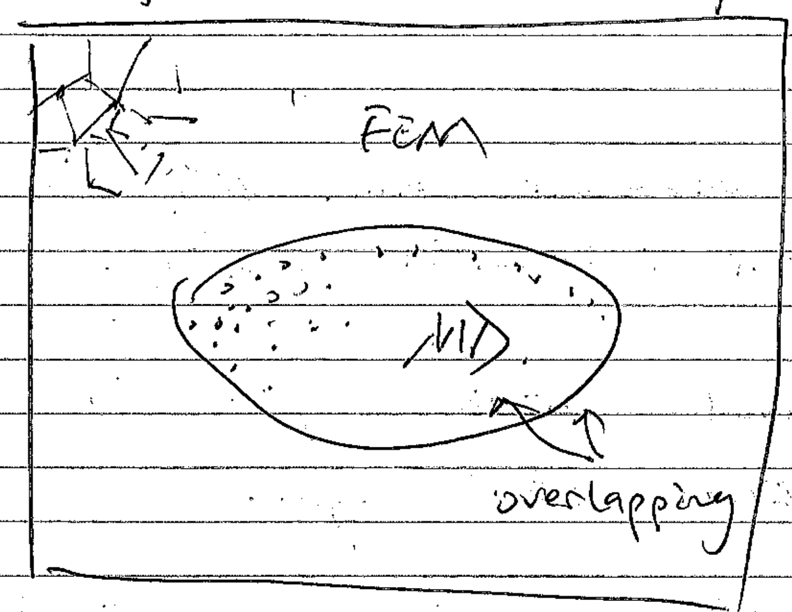
there's a miss match of properties in both regions.

Property	Atomistic	Finite Element.
~~temperature~~	Velocity	Thermodynamics.
Displacement.	Atomic coordinates	Nodal displacement
Forces.	Derivative of Potential energy. discrete point forces.	Distributed forces.

Need "handshaking". i.e. transfer of information.

Mixed Hamiltonian.

Atom-to-continuum package.



Ω - whole domain.

$\Omega_{FEM} \rightarrow FE$

$\Omega_{MD} \rightarrow$ Set of atoms. $\mathcal{A}$

$T \rightarrow BC_s$

Vector: $\vec{X}$

- Ref. coord. of any given point in Ω.

Example of 1D heat trans. (lab).

In Ω_{FEM}, Fourier heat law,

$$\rho \cdot C_p \cdot \dot{T}(\vec{X}, t) = \nabla \cdot K \nabla T(\vec{X}, t)$$

ρ → Density. C_p → Specific heat. K → Thermal conductivity. $T(\vec{X}, t)$ → temp. field.

In Ω_{MD}, Recall $\frac{3}{2} n_a \cdot k_B T = \langle \sum_{\alpha \in \mathcal{A}} \frac{1}{2} m_\alpha |V_\alpha|^2 \rangle$

$T_\alpha \equiv \frac{1}{3k_B} m_\alpha |\vec{V}_\alpha|^2$

α → Atom index

Generally, for an integrable function, $g(\vec{X})$, over Ω

$$\int_{\Omega} g(\vec{x})\, dV = \underbrace{\int_{\Omega_{MD}} g(\vec{x})\, dV + \int_{\Omega_{FEM}} g(\vec{x})\, dV}_{\sum_{\alpha \in A} g_\alpha \Delta V_\alpha}$$

↳ sum over atoms.

For an interpolated temp. field,

$$T^h(\vec{x}, t) = \sum_{I \in N} N_I(\vec{x})\, \theta_I(t).$$

Temp. DoF on I.

Some node I

set of all nodes in Ω

shape func

Given T_α & θ_I, minimize squared difference.

$$\int_{\Omega} [T(\vec{x}) - T^h(\vec{x})]^2\, dV$$

Combine all prior eqns & solving via variations.

... lots of math. ...

For all I,

$$\sum_{J \in M} \left(\sum_{\alpha \in A} N_{I\alpha} N_{J\alpha} \Delta V_\alpha \right) \theta_J$$

$$= \sum_{\alpha \in A} N_{I\alpha} \Delta V_\alpha T_\alpha$$

↳ set of nodes w/ shape function, intersecting Ω_{MD}.

FE → atoms, introduce "force",

$$m_\alpha \dot{\vec{V}}_\alpha = \vec{f}^{MD}_\alpha + \vec{f}^\lambda$$

$$\vec{f}^\lambda = -\frac{m_\alpha}{2} \lambda_\alpha \vec{V}_\alpha$$

$$\lambda_\alpha(t) = \sum_{I \in M} N_{I\alpha} \lambda_I(t)$$

Course Wrap-Up.

- Models of energy.

LJ. EAM, AIREBO, Tersoff.

Schrodinger → pseudopotentials

Reaxff, Martini.

Harmonic → Bonds, Angle.

Coulombic potential.

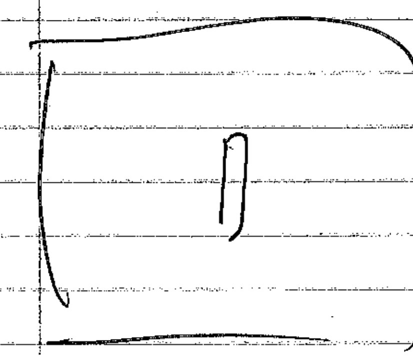
symmetry → defect / box

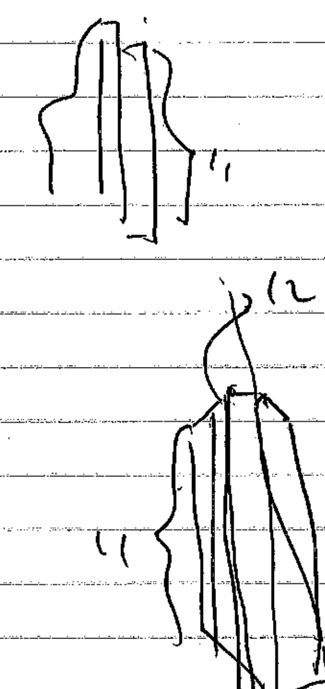
1. PBC verification ⟹ Problem
   yield stress
   stress strain   animation

2. length of crack

3. thermal.

Ce





AIREBO → tuned [illegible] for graphene