

Classical molecular dynamics

Lecture 8

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Outline

- **Born-Oppenheimer approximation**
- **Molecular mechanics**
- **Potentials of interatomic interaction**
- **Energy contributions**
- **Force fields**
- **Molecular dynamics**
 - **Examples**
- **Extend molecular dynamics**
- **Monte-Carlo**

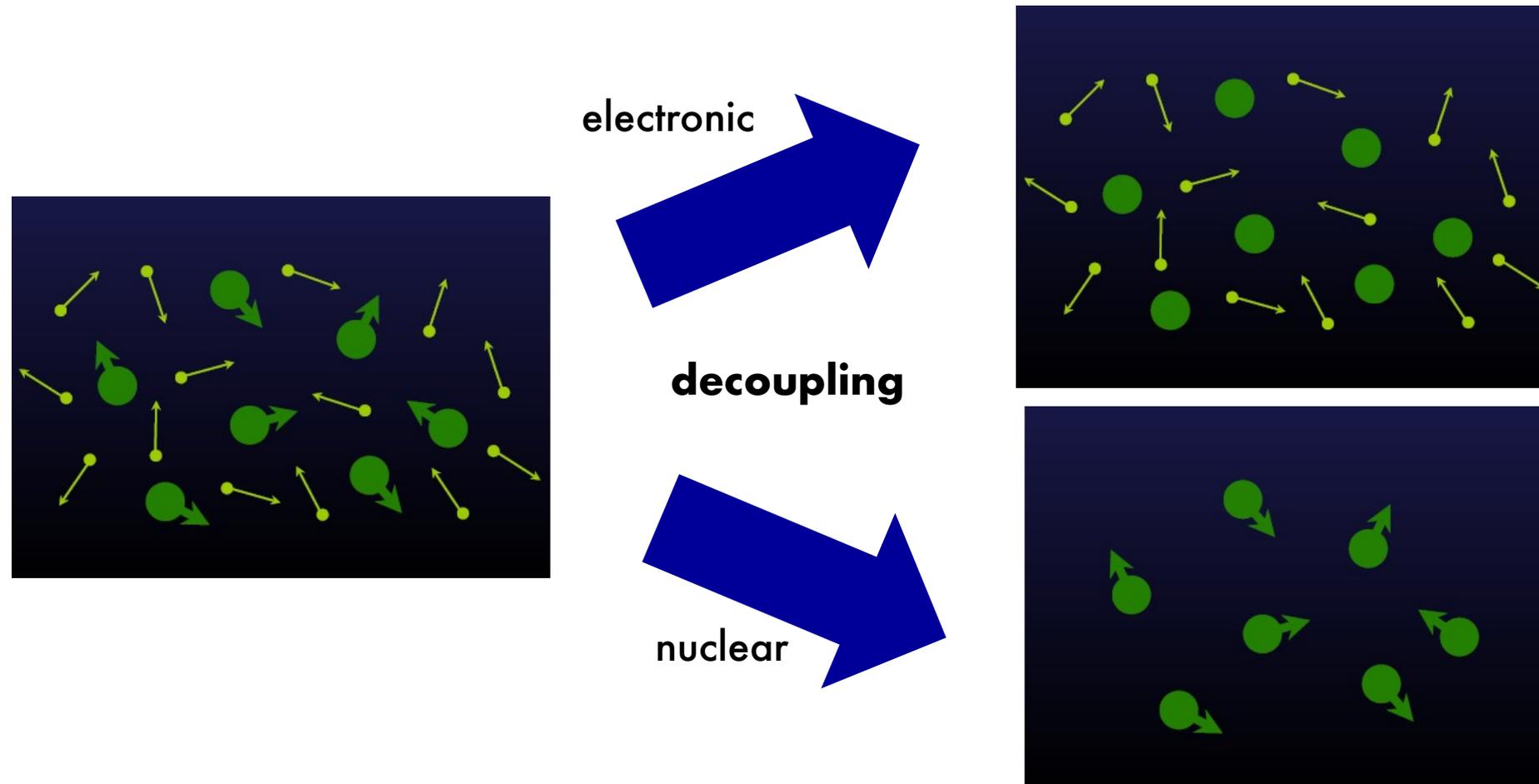
Born-Oppenheimer approximation

- Nuclei are much heavier than electrons
- Nuclei move much slower than electrons
- We can decouple electronic and nuclear motions



Max
Born

Robert
Oppenheimer



Born-Oppenheimer approximation

- Nuclei are much heavier than electrons
- Nuclei move much slower than electrons
- We can decouple electronic and nuclear motions

Hamiltonian

$$\hat{H}\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R}) \quad \rightarrow \quad \hat{H} = \hat{H}_1(\vec{r}) + \hat{H}_2(\vec{R})$$

Separable

$$\psi(\vec{r}, \vec{R}) = \psi_1(\vec{r})\psi_2(\vec{R})$$

$$E = E_1 + E_2$$

Explicitly Hamiltonian

$$\hat{H} = \hat{T}_N(\vec{R}) + \hat{T}_e(\vec{r}) + \hat{V}_{NN}(\vec{R}) + \hat{V}_{eN}(\vec{r}, \vec{R}) + \hat{V}_{ee}(\vec{r})$$

For this case

$$\Psi_T(\vec{r}, \vec{R}) = \Psi_e(\vec{r}, \vec{R})\Psi_N(\vec{R}) \quad \text{Approximately Separable!}$$

$$\hat{H}\Psi_e(\vec{r}, \vec{R})\Psi_N(\vec{R}) = E_{tot}\Psi_e(\vec{r}, \vec{R})\Psi_N(\vec{R})$$

Electronic problem

$$\hat{H}_e = \hat{T}_e(\vec{r}) + \hat{V}_{eN}(\vec{r}, \vec{R}) + \hat{V}_{ee}(\vec{r})$$

$$\left\{ -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{4\pi} \sum_{i,n} \frac{Z_n e^2}{|r_i - R_n|} + \frac{1}{4\pi} \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \right\} \Psi_e(\vec{r}, \vec{R}) = E_{tot} \Psi_e(\vec{r}, \vec{R})$$

Nuclei problem

$$\{\hat{T}_N(\vec{R}) + \hat{E}_e(\vec{R}) + \hat{V}_{NN}(\vec{R})\} \Psi_N(\vec{R}) = E_{tot} \Psi_N(\vec{R})$$

$$\hat{H}_N \Psi_N(\vec{R}) = \left\{ -\sum_n \frac{\hbar^2}{2M} \nabla_n^2 + E_e(\vec{R}) + \frac{1}{4\pi} \frac{1}{2} \sum_{n \neq m} \frac{Z_n Z_m e^2}{|R_n - R_m|} \right\} \Psi_N(\vec{R}) = E_{tot} \Psi_e(\vec{R})$$

The nuclei move in a potential created by the electrons

When molecular mechanics works?

“exactly” in Born-Oppenheimer approximation

Molecular Mechanics is based on several assumptions:

- It treats the electrons around a nucleus and the nucleus itself as a perfect sphere.
- The bonds between molecules are treated as springs.
- Potential functions rely on experimental parameters such as force constants and equilibrium values.
- The potential energy function is the sum of individual functions for bond stretching, angle bending, torsional energies, and non-bonding interactions.

So, we are

- Not interested in electronic properties
- Electronic state remains unchanged
- Electronic dynamics is irrelevant

Think about examples when MM does not work



Challenge is to approximate exact Potential Energy Surface (PES) by interatomic potentials

Grand challenge is to make such potentials transferable

Think about examples when transferability is hardly possible

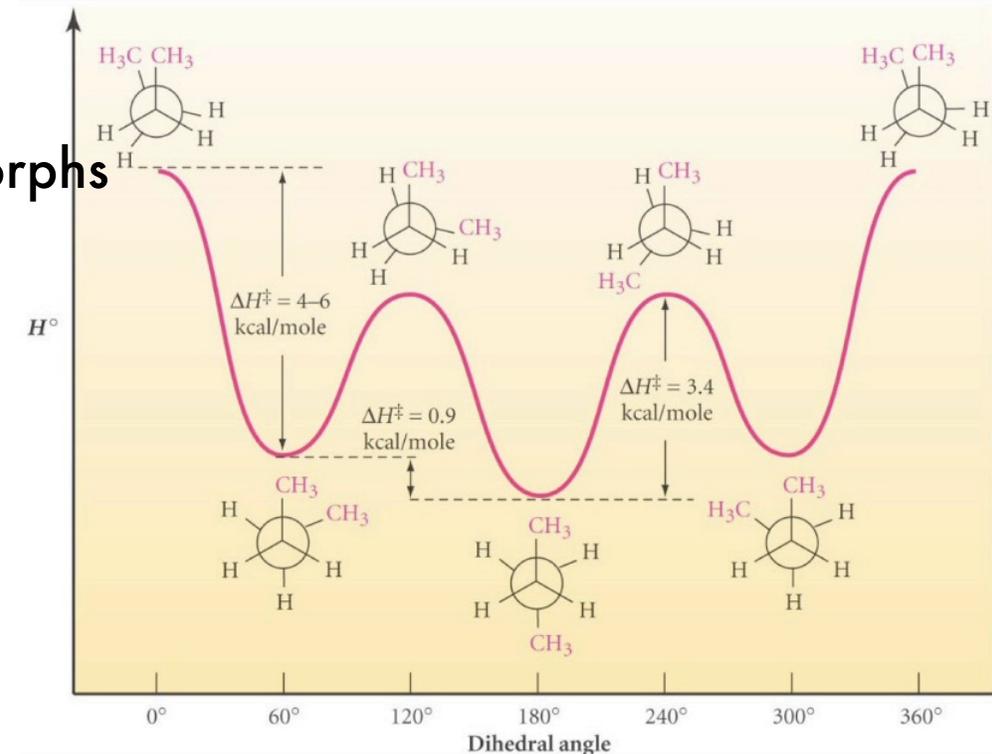


Molecular Mechanics is a computational method that computes the potential energy surface for a particular arrangement of atoms using potential functions that are derived using classical physics.

Molecular Mechanics methods use classical type models (no quantum mechanics) to predict the energy of a system as a function of atomic coordinates, i.e. approximate PES.

Can be used to:

- Optimize geometry (of minima or transition state)
- Calculate relative energies between conformers or polymorphs



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Can be used to:

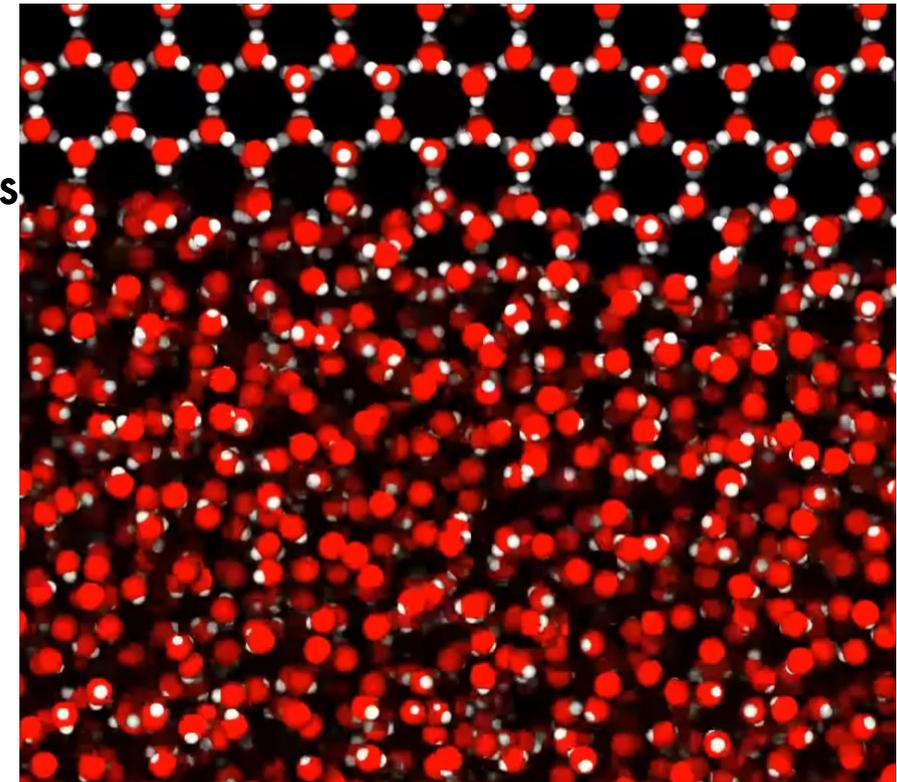
- Optimize geometry (of minima or transition state)
- Calculate relative energies between conformers or polymorphs

But mostly used to:

- Run molecular dynamics
- Sample PES
- Large-scale simulations

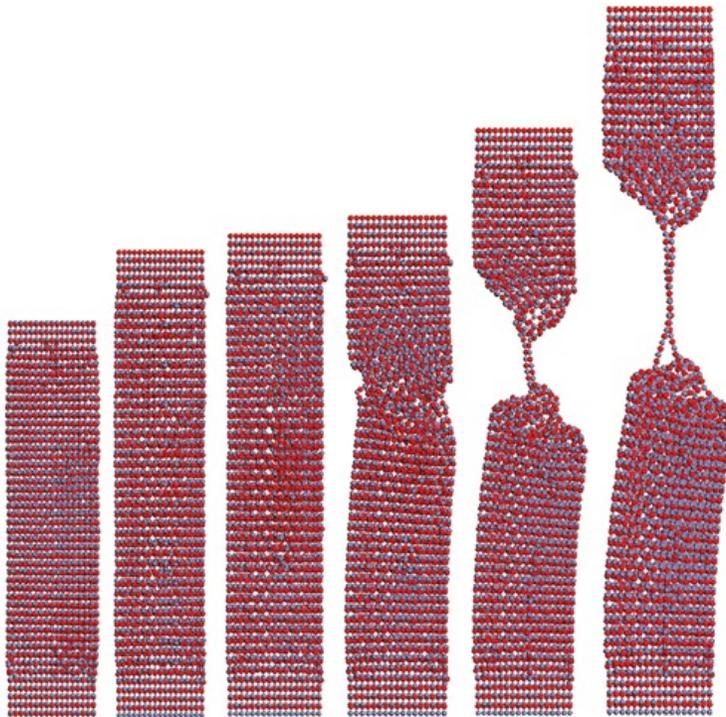
Why can we do it?

- Chemical bonding is local
- Number of local structural patterns is limited
- Nonlocal interactions are pairwise

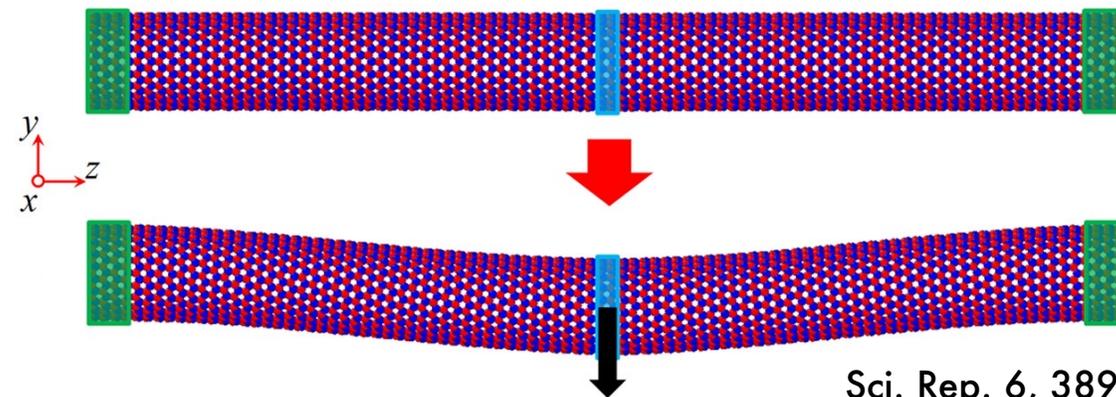


Interatomic potentials are mathematical functions to calculate the potential energy of a system of atoms with given positions in space

Examples of quantitative properties and qualitative phenomena that are explored with interatomic potentials include lattice parameters, surface energies, interfacial energies, adsorption, cohesion, thermal expansion, and elastic and plastic material behavior, as well as chemical reactions



Langmuir 10, 26, 2, 1165-1171 (2010)



Sci. Rep. 6, 38974 (2016)

Interatomic potentials can be divided into several **types**

- Pair potentials
- Force fields
- ML potentials

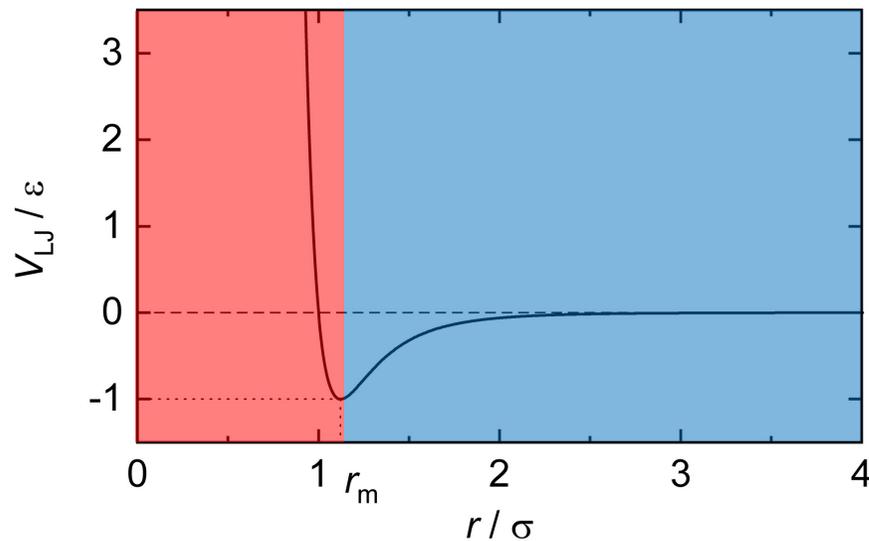
is a function that describes the potential energy of two interacting objects solely as a function of the distance between them

Mostly used for gases, closely packed lattices (metals, ionic crystals), but not for covalent compounds

Lennard-Jones potential

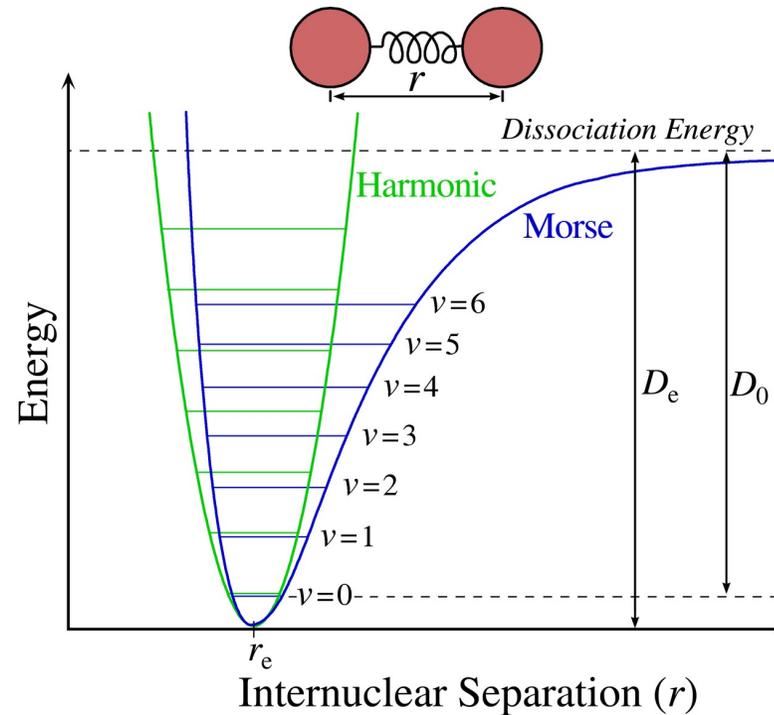
$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

repulsion
attraction



σ is the distance at which the potential energy is 0
 ε is the depth of potential well

Morse potential



$$V_M = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2$$

$$\alpha = \sqrt{\frac{k_e}{2D_3}}$$

k_e is the force constant at the minimum of the well (stiffness of the bond)

D_e is the depth of potential well, α controls the width of the potential

EAM is an approximation describing the energy between atoms and is a type of interatomic potential. The energy is a function of a sum of the separation between an atom and its neighbors.

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij})$$

Embedding energy

Electron cloud contribution

Pair interaction

r_{ij} is the distance between atoms i and j , $\phi_{\alpha\beta}$ is a pair-wise potential function, ρ_β is the contribution to the electron charge density from atom j of type β at the location of atom i , F is an embedding function that represents the energy required to place atom i of type α into the electron cloud.

For a binary alloy, the EAM potential requires seven functions:
three pair-wise interactions (A-A, A-B, B-B),
two embedding functions, and
two electron cloud contribution functions.

Generally, these functions are provided in a tabularized format and interpolated by cubic splines.

a **force field** is a computational method that is used to estimate the forces between atoms within molecules, between molecules, and between atoms in solids

The parameters for a chosen energy function may be derived from experiments in physics and chemistry, calculations in quantum mechanics, or both

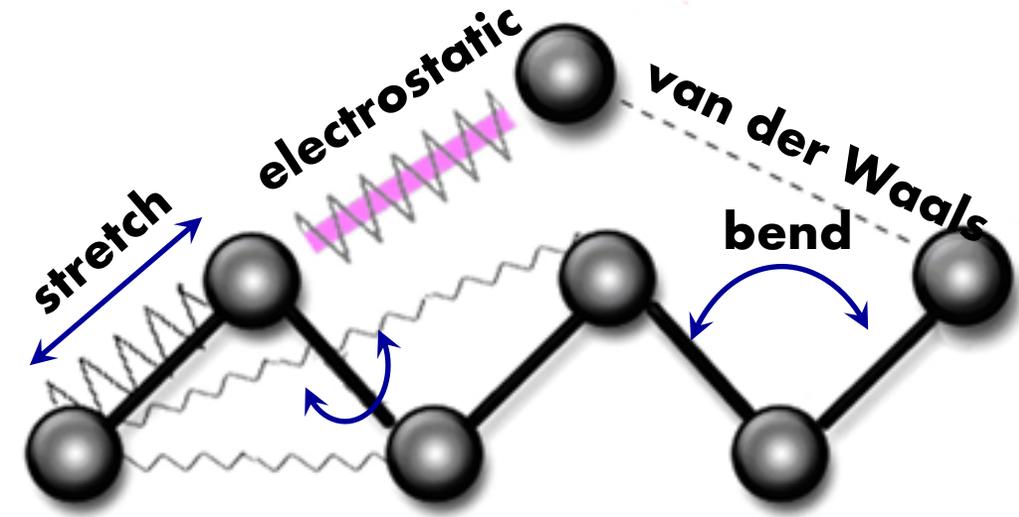
General contributions

- Bonding interactions = stretching + bending + torsion
- Non-bonding interactions = van der Waals + electrostatic
- Cross-terms

$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{el} + E_{cross}$$

Mostly used force fields

- AMBER (Assessment Model Building and Energy Refinement)
- CFF (Consistent Force Field)
- CHARMM (Chemistry at HARvard Molecular Mechanics)
- IFF (Interface Force Field)
- MMFF (Merck Molecular Force Field)
- OPLS (Optimized Potential for Liquid Simulations)
- UFF (Universal Force Field)
- EVB (Empirical valence bond)
- ReaxFF - reactive force field (interatomic potential)



ML potentials

Will be discussed in a separate lecture

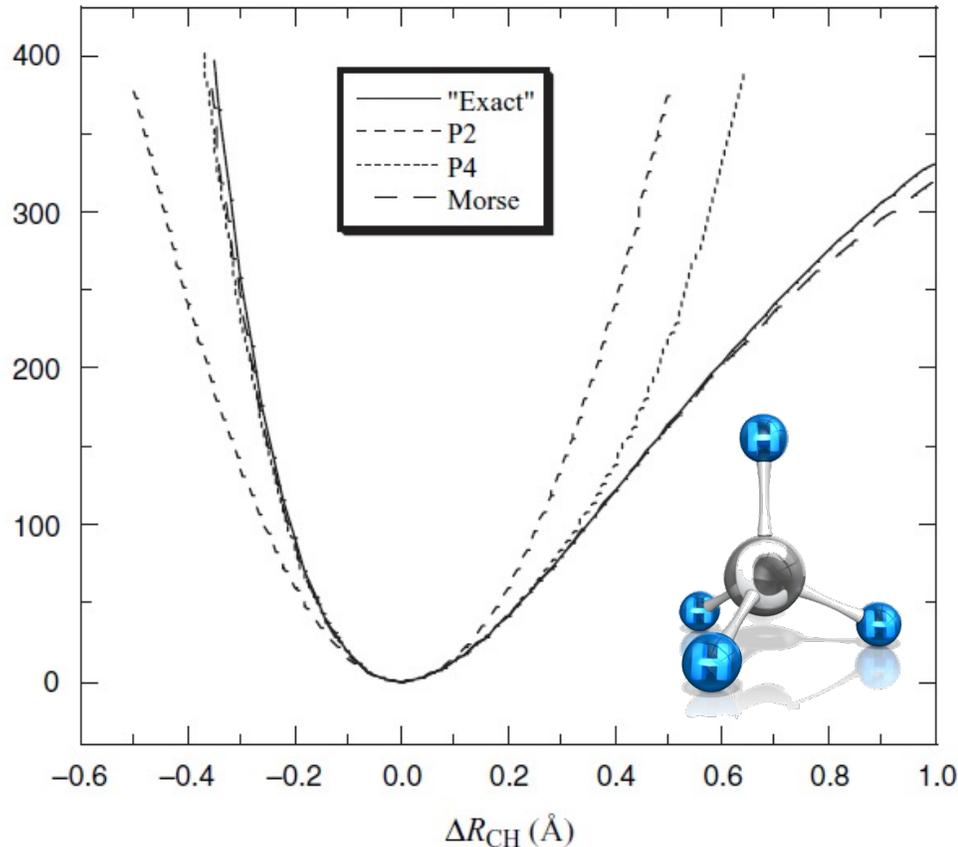
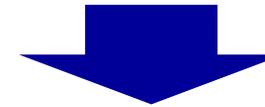
The stretch energy

Start with Taylor expansion of energy $E(R)$ near the minimum

$$E_{str}(R^{ij} - R_0^{ij}) = E(0) + \frac{dE}{dR}(R^{ij} - R_0^{ij}) + \frac{1}{2} \frac{d^2E}{dR^2}(R^{ij} - R_0^{ij})^2$$

Can be set to 0

Vanishes at minimum



$$E_{str}(\Delta R^{ij}) = \underbrace{k_2^{ij}}_{\text{P2 term}} (\Delta R^{ij})^2 + \underbrace{k_3^{ij}}_{\text{P3 term}} (\Delta R^{ij})^3 + \underbrace{k_4^{ij}}_{\text{P4 term}} (\Delta R^{ij})^4 + \dots$$

Alternative forms include Morse potential

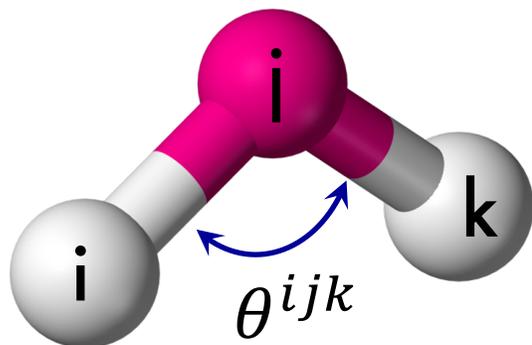
$$E_M(\Delta R^{ij}) = D_e \left(1 - e^{-\alpha \Delta R^{ij}}\right)^2$$

However, numerically friendly polynomial expansion is usually used instead of Morse potential

Every pair of atoms (i,j) requires at least 2 parameters:

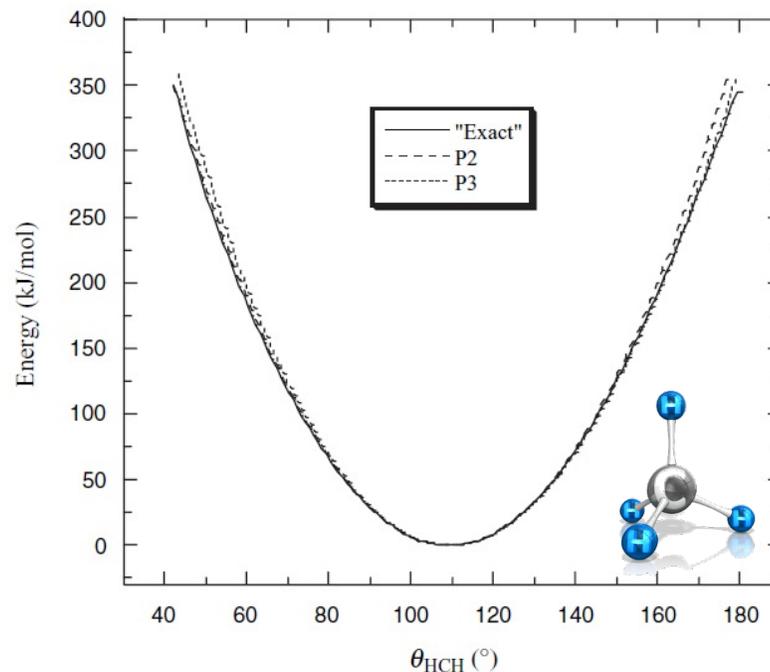
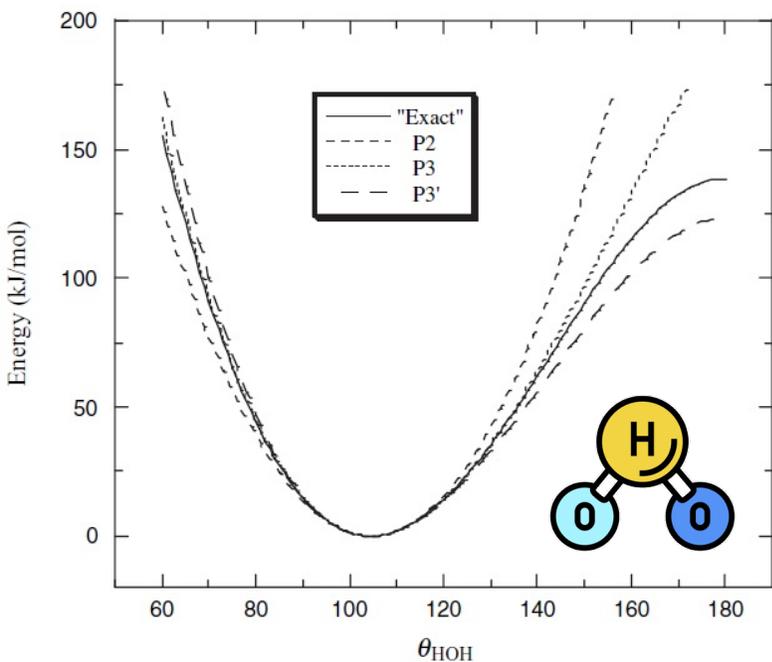
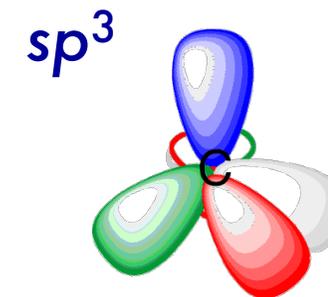
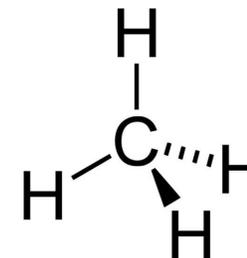
$$k_2^{ij} \text{ and } R_0^{ij}$$

The bending energy



$$E_{bend}(\theta^{ijk} - \theta_0^{ijk}) = k_2^{ijk} (\theta^{ijk} - \theta_0^{ijk})^2$$

Why bending change energy?



Must be accurate in region of few $k_B T$ above the minimum (accessible conformational space)

Problems with $\theta = 180^\circ$, multiple minima, out-of-plane bending

Every triple of atoms (i,j,k) requires 2 parameters:

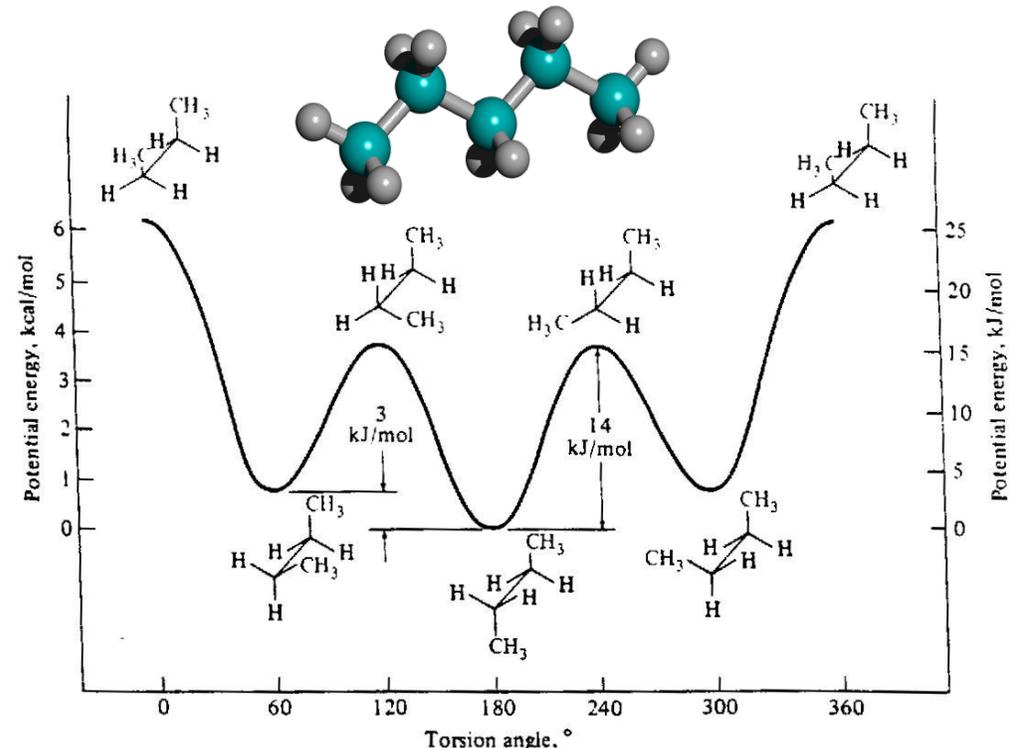
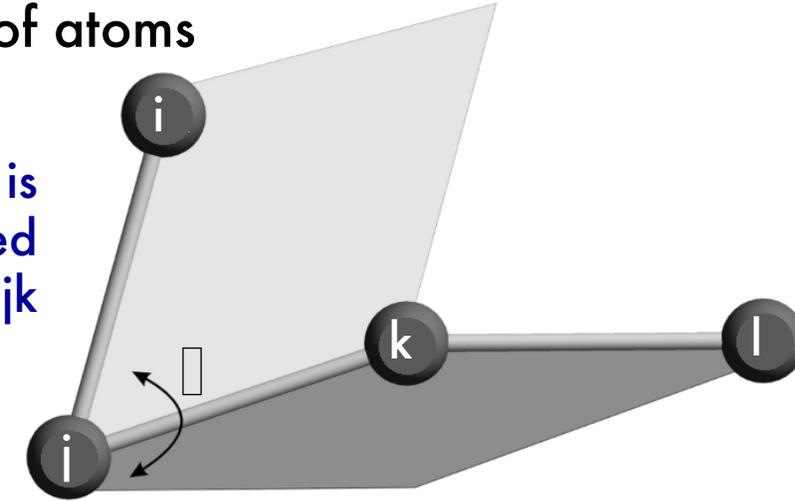
$$k_2^{ij} \text{ and } \theta_0^{ijk}$$

The torsion energy

Torsion energy depends on the dihedral angle between quadruplets of atoms

$$E_{tors}(\omega^{ijkl}) = \frac{1}{2}V_1^{ijkl}(1 + \cos(\omega^{ijkl})) + \frac{1}{2}V_2^{ijkl}(1 - \cos(2\omega^{ijkl})) + \frac{1}{2}V_3^{ijkl}(1 + \cos(3\omega^{ijkl}))$$

Dihedral angle is defined as signed angle between ijk and jkl planes

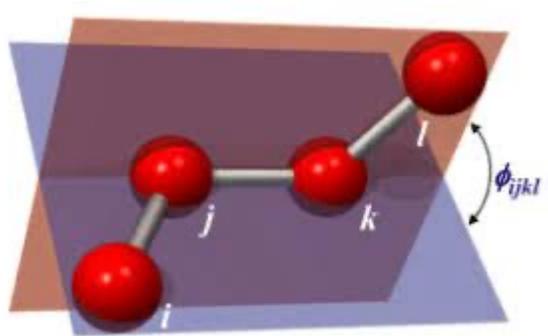


- Dihedral angles are usually flexible and correspond to large-amplitude motions
- Energy scale is 1-2 orders of magnitude smaller than for stretching and bending
- Includes non-bonding interactions
- **Every quadruplet of atoms (i,j,k,l) requires a set of parameters:**

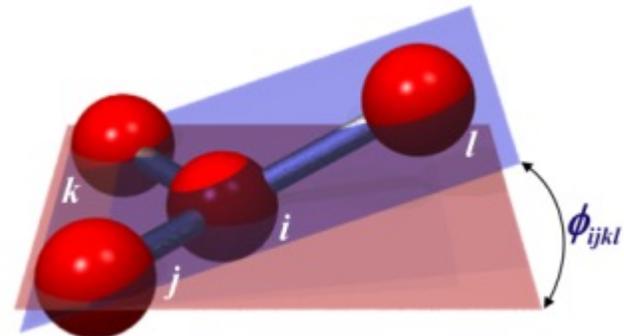
$$V_1^{ijkl}, V_2^{ijkl}, V_3^{ijkl}, \dots$$

Improper torsion

An improper torsion angle is one where the torsion angle is not defined by four angles connected sequentially. It defines improper interactions between quadruplets of atoms



Proper torsion angle

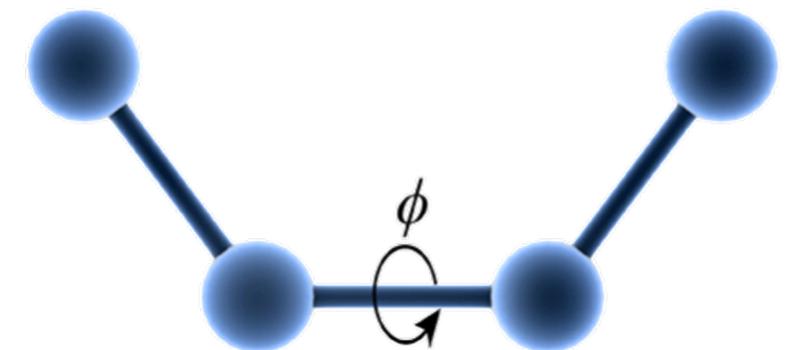


Improper torsion angle

$$E_{imp}(\phi^{ijkl}) = k_{ijkl}(\phi_{ijkl} - \phi_0)^2$$

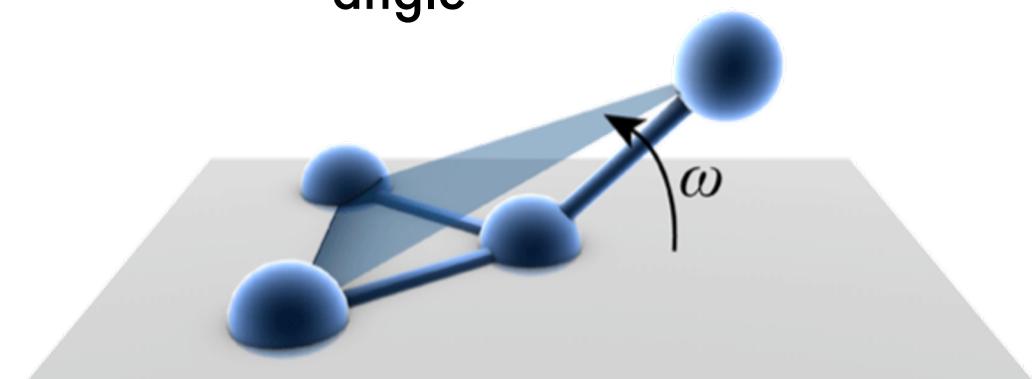
- Correspond to small-amplitude motions, so the harmonic potential is good enough
- Every planar quadruplet of atoms (i,j,k,l) requires only ad single parameter:

$$k_{ijkl}$$



Proper angle

torsion



Improper torsion angle

The van der Waals energy

How many
phenomena/definitions etc. ?
were named after van der
Waals



1910



Johannes
Diderik van der
Waals

The van der Waals energy

- Accounts for all non-electrostatic interaction between non-bonded atoms
- Repulsive at short distance due to **steric interaction** (Pauli exchange)
- Attractive at large distances due to dispersion interaction, **induced dipoles**
- The Lennard-Jones (LJ) potential is commonly used $V_{LJ} = \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$
- For LJ potential every pair of atoms (A,B) requires 2 parameters: ϵ and σ
- To minimize **Some other** number of parameters one use **The Buckingham**
- Usually, **vdW forms** interactions are excluded be

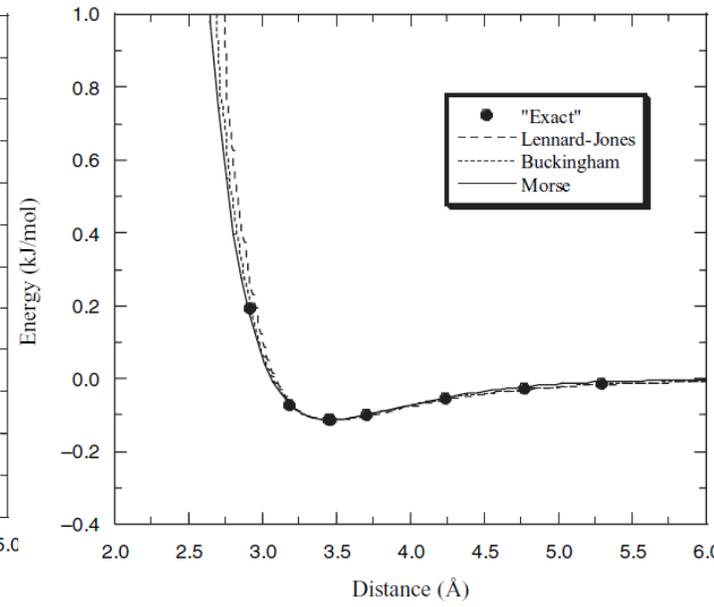
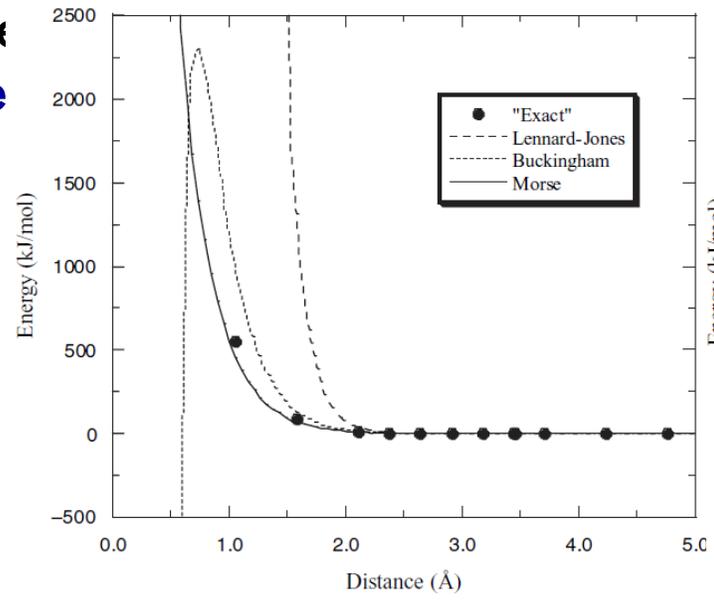


Johannes Diderik van der Waals

$$E_{buck}(r) = \epsilon \left[\frac{\alpha}{\alpha - 6} e^{\alpha(1-r/R_0)} - \frac{\alpha}{\alpha - 6} \left(\frac{R_0}{r} \right)^6 \right]$$

Hydrogen bonding potential

$$E_{H-bond}(r) = \epsilon \left[5 \left(\frac{R_0}{r} \right)^{12} - 6 \left(\frac{R_0}{r} \right)^{10} \right]$$



The electrostatic energy

Strategy 1. Assign atomic charges

Option 1. Calculate molecular electrostatic potential using electronic structure method

$$\phi(\vec{r}) = \sum_n^{N_{nuc}} \frac{Z_n}{|\vec{R}_n - \vec{r}|} - \int \frac{|\Psi(\vec{r}')|^2}{|\vec{r}' - \vec{r}|} d\vec{r}'$$

then minimize error-function

$$ErrF(Q) = \sum_n^{N_{points}} \left(\phi(\vec{r}) - \sum_n^{N_{atoms}} \frac{Q_n(\vec{R}_n)}{|\vec{R}_n - \vec{r}|} \right)^2$$

but result depends on fitting domain

Option 2. Use other quantum chemical charges

Strategy 2. Fit atomic charges

Usually problematic because of ill-conditioned nonlinear optimization problem.

Strategy 3. Assign bond dipoles

How? Using experimental data or electronic structure methods

Strategy 4. Use multipoles and polarizabilities

Example: Effective Fragment Potential (EFP) best for molecules in a liquid

(Ann. Rev. Phys. Chem. 64, 553, 2013)

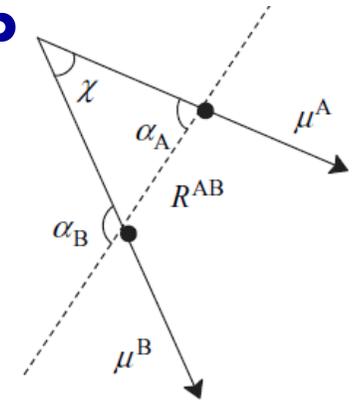
Point-charge interaction:

$$E_{el}(R^{AB}) = \frac{Q^A Q^B}{\epsilon R^{AB}}$$

Dipole-dipole interaction:

$$E_{el}(R^{AB}) = \frac{\mu^A \mu^B}{\epsilon (R^{AB})^3} (\cos \chi - 3 \cos \alpha_A \cos \alpha_B)$$

Coulomb



$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{el} + E_{cross}$$

The various terms in the total energy are not independent, and cross-terms should be considered

$$u_i(\vec{x}) = u_i(0) + \sum_j x_j \left(\frac{\partial u_i}{\partial x_j} \right)_0 + \sum_{k \leq j} \sum_j x_j x_k \left(\frac{\partial^2 u_i}{\partial x_j \partial x_k} \right)_0$$

For example, stretching-bending:

$$E_{str/bend} = k^{ABC} (\theta^{ABC} - \theta_0^{ABC}) [(R^{AB} - R_0^{AB}) - (R^{BC} - R_0^{BC})]$$

Other terms

$$E_{str/str} = k^{ABC} (R^{AB} - R_0^{AB})(R^{BC} - R_0^{BC})$$

$$E_{bend/bend} = k^{ABCD} (\theta^{ABC} - \theta_0^{ABC})(\theta^{BCD} - \theta_0^{BCD})$$

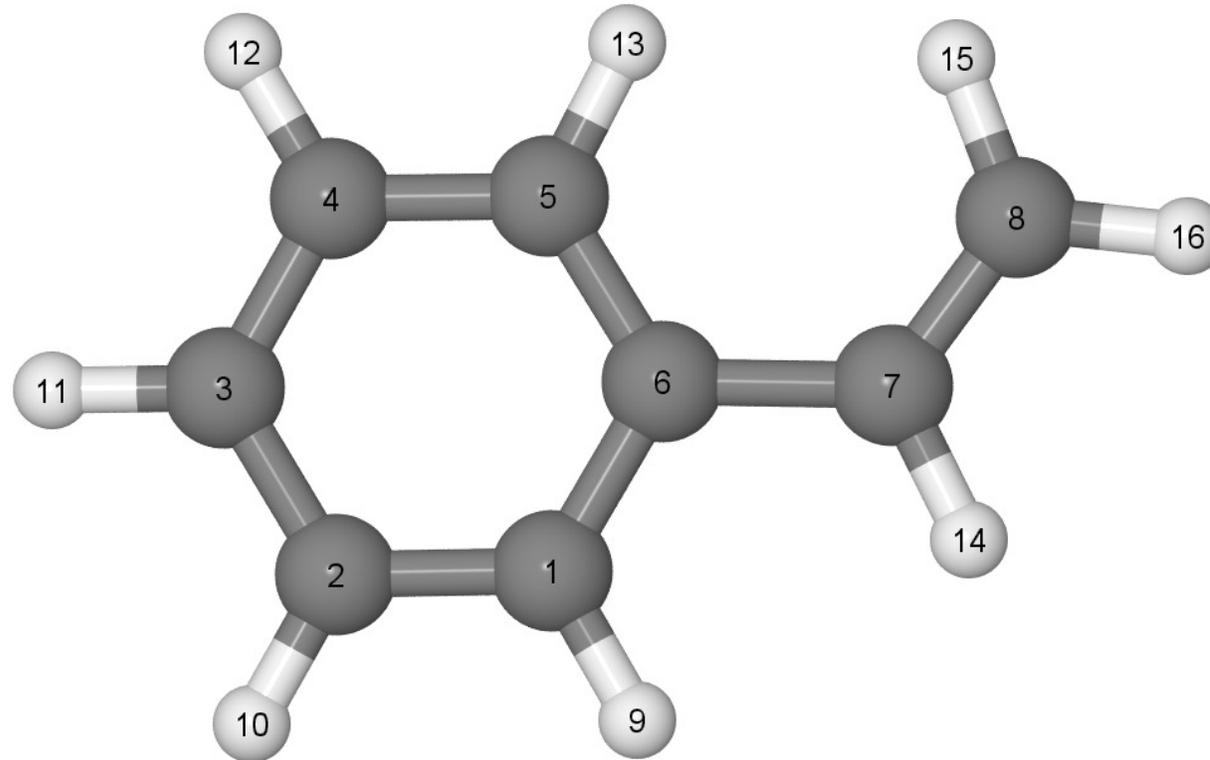
$$E_{str/tors} = k^{ABCD} (R^{AB} - R_0^{AB}) \cos(n\omega^{ABCD})$$

$$E_{bend/tors} = k^{ABCD} (\theta^{ABC} - \theta_0^{ABC}) \cos(n\omega^{ABCD})$$

$$E_{bend/tors/bend} = k^{ABCD} (\theta^{ABC} - \theta_0^{ABC})(\theta^{BCD} - \theta_0^{BCD}) \cos(n\omega^{ABCD})$$

Cross-terms are rarely used because of problems with their parametrization

Illustrate all elements of a force field using this molecule:



MM2 force field

Type	Symbol	Description	Type	Symbol	Description
1	C	sp ³ -carbon	28	H	enol or amide
2	C	sp ² -carbon, alkene	48	H	ammonium
3	C	sp ² -carbon, carbonyl, imine	36	D	deuterium
4	C	sp-carbon	20	lp	lone pair
22	C	cyclopropane	15	S	sulfide (R ₂ S)
29	C·	radical	16	S ⁺	sulfonium (R ₃ S ⁺)
30	C ⁺	carbocation	17	S	sulfoxide (R ₂ SO)
38	C	sp ² -carbon, cyclopropene	18	S	sulfone (R ₂ SO ₂)
50	C	sp ² -carbon, aromatic	42	S	sp ² -sulfur, thiophene
56	C	sp ³ -carbon, cyclobutane	11	F	fluoride
57	C	sp ² -carbon, cyclobutene	12	Cl	chloride
58	C	carbonyl, cyclobutanone	13	Br	bromide
67	C	carbonyl, cyclopropanone	14	I	iodide
68	C	carbonyl, ketene	26	B	boron, trigonal
71	C	ketonium carbon	27	B	boron, tetrahedral
8	N	sp ³ -nitrogen	19	Si	silane
9	N	sp ² -nitrogen, amide	25	P	phosphine
10	N	sp-nitrogen	60	P	phosphor, pentavalent
37	N	azo or pyridine (-N=)	51	He	helium
39	N ⁺	sp ³ -nitrogen, ammonium	52	Ne	neon
40	N	sp ² -nitrogen, pyrrole	53	Ar	argon
43	N	azoxy (-N=N-O)	54	Kr	krypton
45	N	azide, central atom	55	Xe	xenon
46	N	nitro (-NO ₂)	31	Ge	germanium
72	N	imine, oxime (=N-)	32	Sn	tin
6	O	sp ³ -oxygen	33	Pb	lead
7	O	sp ² -oxygen, carbonyl	34	Se	selenium
41	O	sp ² -oxygen, furan	35	Te	tellurium
47	O ⁻	carboxylate	59	Mg	magnesium
49	O	epoxy	61	Fe	iron (II)
69	O	amine oxide	62	Fe	iron (III)
70	O	ketonium oxygen	63	Ni	nickel (II)
5	H	hydrogen, except on N or O	64	Ni	nickel (III)
21	H	alcohol (OH)	65	Co	cobalt (II)
23	H	amine (NH)	66	Co	cobalt (III)
24	H	carboxyl (COOH)			

MM2 force field

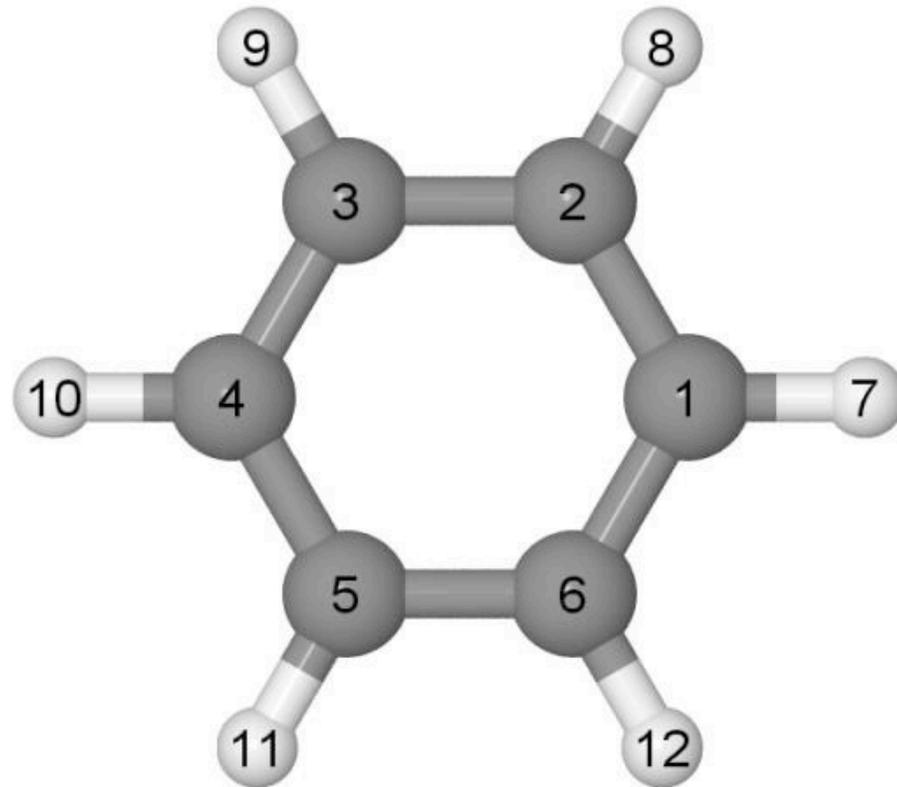
- Each of the 71 atom types has two van der Waals parameters, ϵ^A and R^A , giving **142** parameters
- There are approximately $1/2 \times 30 \times 30 = 450$ different E_{str} terms, each requiring at least two parameters ϵ^{AB} and R^{AB} , for a total of at least **900** parameters
- There are approximately $1/2 \times 30 \times 30 \times 30 = 13500$ different E_{bend} terms, each requiring at least two parameters ϵ^{ABC} and R^{ABC} , for a total of at least **27000** parameters
- There are approximately $1/2 \times 30 \times 30 \times 30 \times 30 = 405000$ different E_{tors} terms, each requiring at least three parameters ϵ^{ABCD} , R^{ABCD} , and γ^{ABCD} , for a total of at least **1215000** parameters
- Cross-terms may add another million possible parameters

Table 2.3 Comparison of possible and actual number of MM2(91) parameters

Term	Estimated number of parameters	Actual number of parameters
E_{vdw}	142	142
E_{str}	900	290
E_{bend}	27000	824
E_{tors}	1215000	2466

Reduce number of parameters

- Assign atomic charges (e.g. from DFT) instead of fitting them
- Use element-wise LJ parametrization instead of pair-wise
- Group atom types into **atom classes** for bonded interactions
- Omit unnecessary dihedral and minimize number of improper



Parametrization

How to do it? Define functional form, objective function, and fit parameters

$$ErrF(parameters) = \sum_i^{data} weight_i \cdot (reference\ value - calculated\ value)_i^2$$

1) How to choose **functional form**:

- The choice is not unique and depends on material, scales, and goals
- Linear optimization is preferable
- Systematic improvement of accuracy is challenging for non-ML potentials

2) What are **reference values**:

- Experimental data (vibrational frequencies, X-ray structures, heats of formation) were commonly used in past, but they are often incomplete and have large error bars (especially lab-to-lab and batch-to-batch variations)
- Today high-throughput DFT calculations are used, including semi-automated parametrization routines (e.g. AMBER-DFT or ML-potentials)

3) How to define and generate **fitting (training) dataset**:

- The dataset must be representative (cover required part of PES with proper weights) and suitable for fitting (confidence intervals for all parameters must be reasonable, parameter dependencies must be resolved)

Parametrization is a difficult process requiring good knowledge of underlying physical phenomena/interactions, chemical intuition, use of experimental data and utilization of electronic structure codes

Various types of potentials

Different classes of materials require different approaches:

- Simple metals (Al – yes, Pu – no) – embedded-atom (EAM)
- Ionic solids (NaCl) – embedded-ion model
- Complex bonding – charge optimized many body potential (COMB)
- Tetrahedral semiconductors/insulators (Si, SiO₂) – Tersoff potentials
- Water – TIP3/4/5P models
- π -conjugated molecules – MM3 force field + Huckel model
- Biomolecules – well parameterized AMBER, CHARMM, GROMOS with residue-based parametrization (proteins) and united atoms
- Attempts to make universal force field for molecules – OPLS, UFF, DREIDING
- Polarizable force- DRUDE, AMOEBA
- Chemical reactions – reactive force (ReaxFF)

Different states of the same molecule require different values of parameters

Anion, cation, excited singlet S₁, etc

Fitting-friendly parametrization (allow for black-box fitting and systematic improvement by ML approaches):

$$E = \sum_i E(\text{local geometry of } i^{\text{th}} \text{ atom}) + E_{\text{long-range}}$$

Computational efficiency

- Make no mistake: molecular mechanics is MUCH faster compared to any electronic structure model based on quantum mechanics!
- Evaluation of the non-bonded energy is the most time-consuming step growing $\sim N^2$
- Can be reduced to $\sim N$ using cut-off distances or advanced summation techniques

Table 2.6 Number of terms for each energy contribution in $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$

n	N_{atoms}	E_{str}	E_{bend}	E_{tors}	E_{vdw}
10	32	31 (5%)	30 (10%)	81 (14%)	405 (70%)
20	62	61 (3%)	60 (6%)	171 (8%)	1710 (83%)
50	152	151 (1%)	300 (3%)	441 (4%)	11 025 (93%)
100	302	301 (1%)	600 (1%)	891 (2%)	44 550 (96%)
	N	$(N - 1)$	$2(N - 2)$	$3(N - 5)$	$\frac{1}{2}N(N - 1) - 3N + 5$

Benchmarks by LAMMPS

Potential	System	# Atoms	Timestep	Neighs/atom	Memory	CPU	LJ Ratio
<u>Granular</u>	chute flow	32000	0.0001 tau	7.2	33 Mb	2.08e-7	0.26x
<u>FENE bead/spring</u>	polymer melt	32000	0.012 tau	9.7	8.4 Mb	2.86e-7	0.36x
<u>Lennard-Jones</u>	LJ liquid	32000	0.005 tau	76.9	12 Mb	8.01e-7	1.0x
<u>DPD</u>	pure solvent	32000	0.04 tau	41.3	9.4 Mb	1.22e-6	1.53x
<u>EAM</u>	bulk Cu	32000	5 fmsec	75.5	13 Mb	1.87e-6	2.34x
<u>REBO</u>	polyethylene	32640	0.5 fmsec	149	33 Mb	3.18e-6	3.97x
<u>Stillinger-Weber</u>	bulk Si	32000	1 fmsec	30.0	11 Mb	3.28e-6	4.10x
<u>Tersoff</u>	bulk Si	32000	1 fmsec	16.6	9.2 Mb	3.74e-6	4.67x
<u>ADP</u>	bulk Ni	32000	5 fmsec	83.6	25 Mb	5.58e-6	6.97x
<u>EIM</u>	crystalline NaCl	32000	0.5 fmsec	98.9	14 Mb	5.60e-6	6.99x
<u>Peridynamics</u>	glass fracture	32000	22.2 nsec	422	144 Mb	7.46e-6	9.31x
<u>SPC/E</u>	liquid water	36000	2 fmsec	700	86 Mb	8.77e-6	11.0x
<u>CHARMM + PPPM</u>	solvated protein	32000	2 fmsec	376	124 Mb	1.13e-5	14.1x
<u>MEAM</u>	bulk Ni	32000	5 fmsec	48.8	54 Mb	1.32e-5	16.5x
<u>Gay-Berne</u>	ellipsoid mixture	32768	0.002 tau	140	21 Mb	2.20e-5	27.5x
<u>BOP</u>	bulk CdTe	32000	1 fmsec	4.4	74 Mb	2.51e-5	31.3x
<u>AIREBO</u>	polyethylene	32640	0.5 fmsec	681	101 Mb	3.25e-5	40.6x
<u>ReaxFF/C</u>	PETN crystal	32480	0.1 fmsec	667	976 Mb	1.09e-4	136x
<u>COMB</u>	crystalline SiO2	32400	0.2 fmsec	572	85 Mb	2.00e-4	250x
<u>eFF</u>	H plasma	32000	0.001 fmsec	5066	365 Mb	2.16e-4	270x
<u>ReaxFF</u>	PETN crystal	16240	0.1 fmsec	667	425 Mb	2.84e-4	354x
<u>VASP/small</u>	water	192/512	0.3 fmsec	N/A	320 procs	26.2	17.7e6
<u>VASP/medium</u>	CO2	192/1024	0.8 fmsec	N/A	384 procs	252	170e6
<u>VASP/large</u>	Xe	432/3456	2.0 fmsec	N/A	384 procs	1344	908e6

- Blind use of empirical potentials is very dangerous and can lead to errors.
- Well-parameterized potentials can give more accurate geometries and relative energies than low-level QM methods
- Often FF are bound to specific MD code (AMBER, CHARMM etc.) so that parameters are not easily transferable between codes.

- 1) Choose the **functional form** of empirical potentials:
 - define atom types;
 - decide on type of potentials and number of parameters (e.g. not all dihedral angles are usually needed, parametrization of LJ interactions can be chosen element-wise or pair-wise)
 - which parameters are fitted, and which are assigned (e.g. often it is bad idea to fit charges in force fields, for intramolecular dynamics LJ parameters can be assigned from generic tables)
- 2) Force fields require **topology** – define it
- 3) Provide initial parametrization
(from generic force field like OPLS or from DFT calculations)
- 4) Parametrize

- Solve Newton's equation of motion for N classical particles (3N coupled equations)
- For now, let limit ourselves by natural NVE ensemble
- The force depends on positions only (not velocities)
- Each particle is allowed to interact simultaneously with every other particle and can experience an additional external potential
- A single point in a 6N-dimensional phase space (p,r) represents our dynamical system

Our dimensionality: N particles, 3N-dim

vectors

- Coordinates
- Velocities
- Momenta
- Accelerations
- Potential energy
- Kinetic energy
- Forces
- Particle masses

$$\vec{r} = \vec{q} = (x_1, y_1, z_1, x_2, \dots)$$

$$v = d\vec{r}/dt$$

$$\vec{p} = m\vec{v}$$

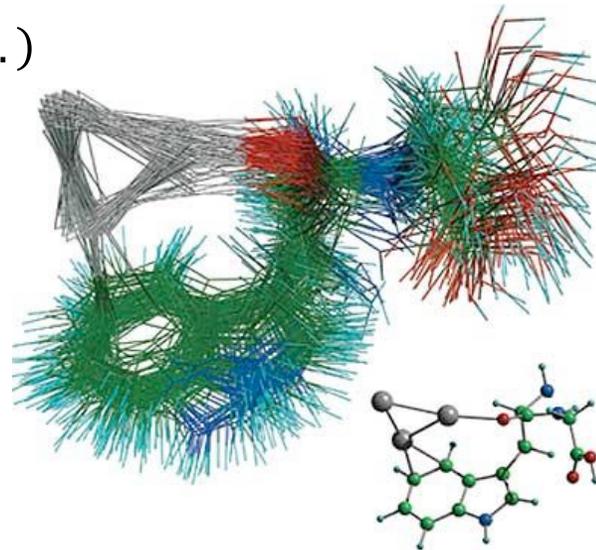
$$\vec{a} = d\vec{v}/dt$$

$$V(\vec{r})$$

$$K(\vec{p}) = \sum \frac{1}{2} m \vec{v}_i^2$$

$$\vec{F}(\vec{p}) = d\vec{V}/d\vec{r}$$

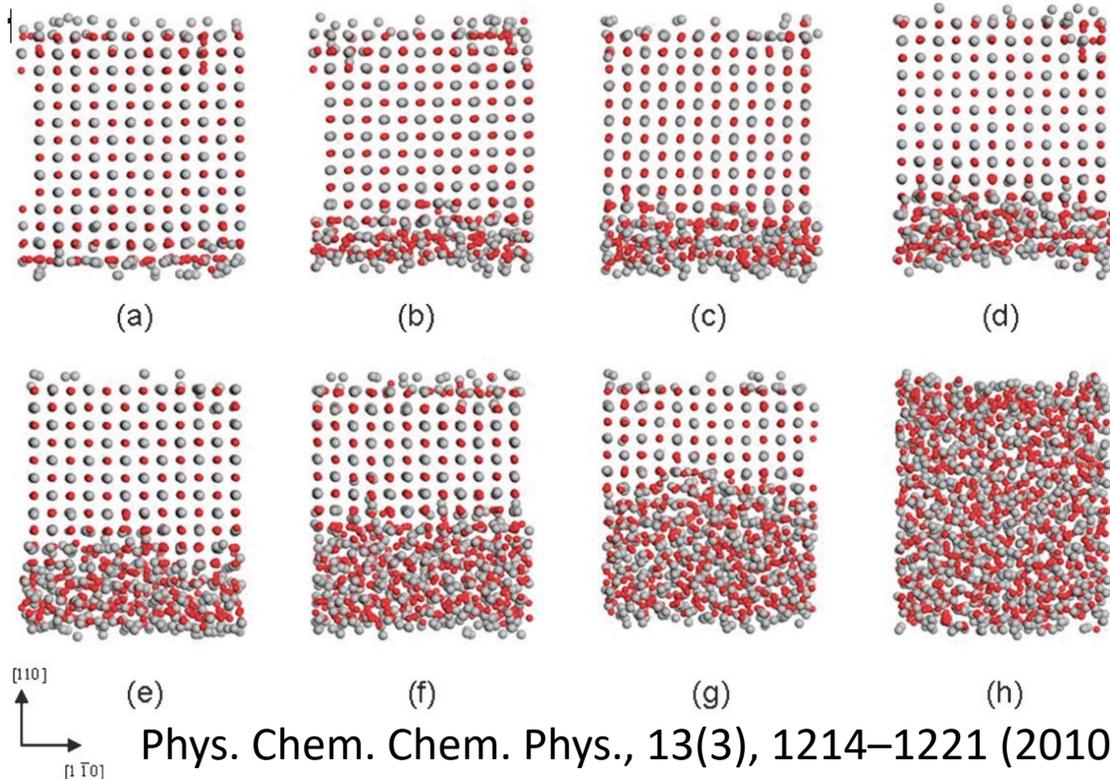
$$m_i$$



$$\vec{F} = m\vec{a}$$
$$E_{tot} = \sum_{i=1}^N \frac{1}{2} m \vec{v}_i^2 + V(\vec{r})$$
$$-\frac{dV}{d\vec{r}} = m \frac{d^2\vec{r}}{dt^2}$$

Ensemble of possible structures of a tryptophan-glycine-silver cluster cation complex, obtained by superimposing the configurations sampled from MD trajectory simulation
Phys Rev Lett 101, 213001 (2008)

- **Initialize:** select position and velocities
- **Propagate:** compute all forces, and then determine new positions
- **Equilibrate:** let the system reach equilibrium for a given thermodynamic ensemble (NVE, NPT etc.)
- **Sample (average):** accumulate long enough



Phys. Chem. Chem. Phys., 13(3), 1214–1221 (2010)

Algorithm

Give particles initial positions

$r_0 = r(t = 0)$, velocities $v_0 = v(t = 0)$

Calculate and store energy $E_0 = E(t = 0)$
and other quantities at $t = 0$

Choose short timestep Δt (typical 0,1-1 fs)

Set forces $F(t)$ and accelerations $a(t)$

Move particles,
i.e. compute $r(t + \Delta t)$ and $v(t + \Delta t)$

Move time forward $t = t + \Delta t$

Calculate and store energy $E(t)$
and other quantities at t

Repeat

Selecting initial positions:

- Interconnection topology should agree with chemical structure
- Avoid short distances – huge energy penalty ($\sim 1/r^{12}$ for Lenard-Jones)
- Avoid highly non-equilibrium conditions

Selecting initial velocities

- Start with $v=0$, then allow to equilibrate/thermalize with an increase of temperature OR
- Start with some distribution (e.g. Maxwell-Boltzmann distribution)

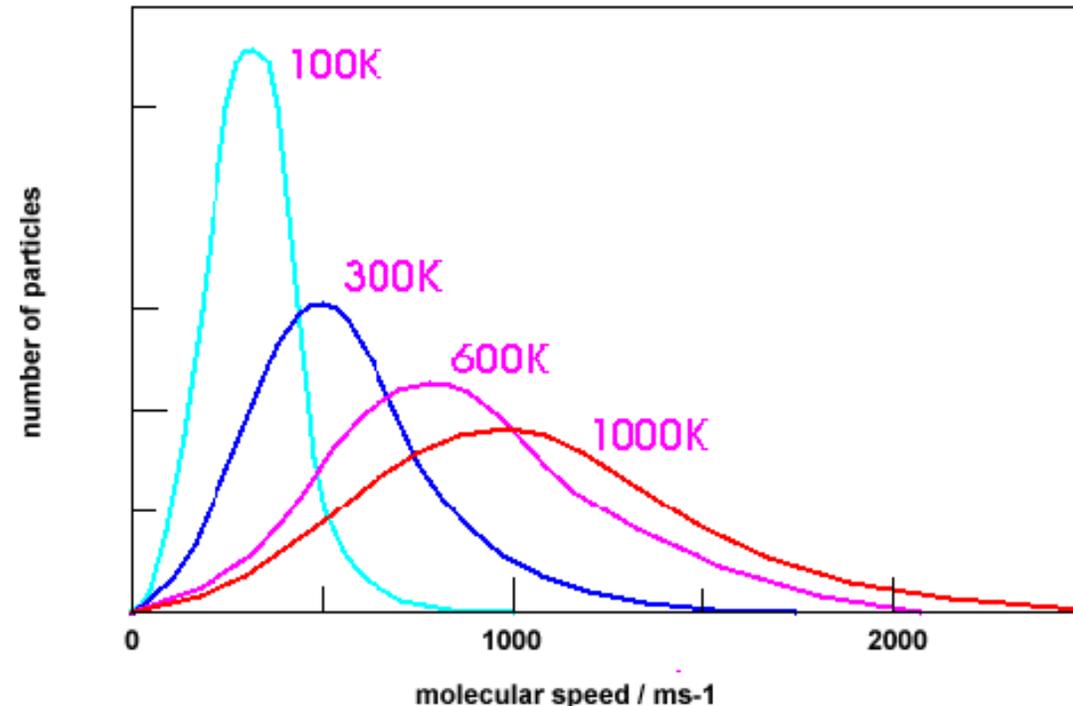
$$f(v) = \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$

$$\frac{dN}{N} = f(v)dv$$

$$v_p = \sqrt{\frac{2k_B T}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$



Verlet type integration (typical accuracy up to $O(t^4)$): Most common in the MD land!

Simple to calculate, well preserves the energy along the trajectory (i.e. time-reversible)

As usual, start with Taylor expansion

$$\vec{r}_{i+1} = \vec{r}_i + \frac{d\vec{r}}{dt}(\Delta t) + \frac{1}{2} \frac{d^2\vec{r}}{dt^2}(\Delta t)^2 + \frac{1}{6} \frac{d^3\vec{r}}{dt^3}(\Delta t)^3 + \dots$$

or $\vec{r}_{i+1} = \vec{r}_i + \vec{v}_i(\Delta t) + \frac{1}{2} \vec{a}_i(\Delta t)^2 + \frac{1}{6} \vec{b}_i(\Delta t)^3 + \dots$ **and** $\vec{r}_{i-1} = \vec{r}_i - \vec{v}_i(\Delta t) + \frac{1}{2} \vec{a}_i(\Delta t)^2 - \frac{1}{6} \vec{b}_i(\Delta t)^3 + \dots$

The original Verlet

$$\vec{r}_{i+1} = (2\vec{r}_i - \vec{r}_{i-1}) + \vec{a}_i(\Delta t)^2 + \dots$$

$$\vec{a}_i = \frac{\vec{F}_i}{m_i} = -\frac{1}{m_i} \frac{dV}{d\vec{r}_i}$$

To initiate $\vec{r}_{-1} = \vec{r}_0 - \vec{v}_0 \Delta t$

Note $\vec{v}(t) = [\vec{r}(t) - \vec{r}(t - \Delta t)] / \Delta t$ (velocities)

are not necessary but useful. Also is a large difference! Require 9N variables for storage for $i=1, \dots, N$ (compact!)

The leap-frog Verlet

$$\vec{r}_{i+1} = \vec{r}_i + \vec{v}_{i+\frac{1}{2}} \Delta t$$

$$\vec{v}_{i+\frac{1}{2}} = \vec{v}_{i-\frac{1}{2}} + \vec{a}_i \Delta t$$

$$\vec{a}_i = \frac{\vec{F}_i}{m_i} = -\frac{1}{m_i} \frac{dV}{d\vec{r}_i}$$

To initiate $\vec{r}_{-1} = \vec{r}_0 - \vec{v}_0 \Delta t$

Note velocities $\vec{v}_{i+\frac{1}{2}}$ 'leap' over coordinates half-step. Explicit velocities is a plus. But and are out of phase

The Velocity Verlet

$$\vec{r}_{i+1} = \vec{r}_i + \vec{v}_i \Delta t + \frac{1}{2} \vec{a}_i \Delta t^2$$

$$\vec{v}_{i+1} = \vec{v}_i + \frac{1}{2} \{ \vec{a}_i + \vec{a}_{i+1} \} \Delta t$$

$$\vec{a}_i = \frac{\vec{F}_i}{m_i} = -\frac{1}{m_i} \frac{dV}{d\vec{r}_i}$$

To initiate $\vec{r}_{-1} = \vec{r}_0 - \vec{v}_0 \Delta t$

Best numerical performance and compact storage make this method of choice for MD codes!

NVE (microcanonical) ensemble is natural: energy is conserved being redistributed along potential and kinetic parts along the trajectory

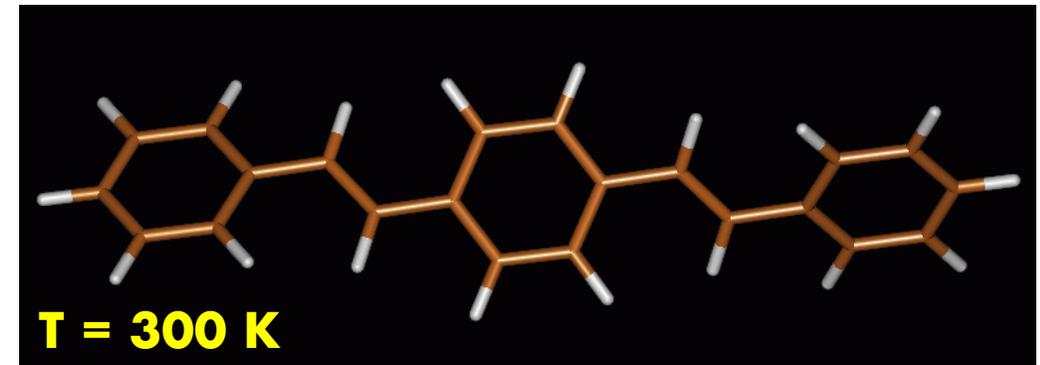
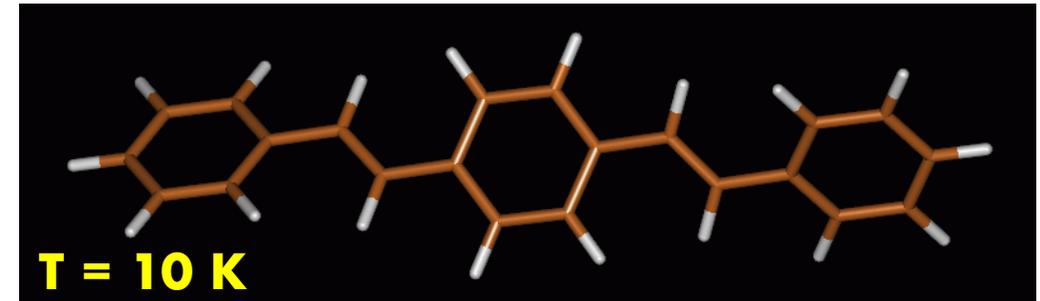
What about NVT (canonical) ensemble? Need thermostat (e.g. Anderson, Nose-Hoover, Berendsen, Langevin etc.) allowing an exchange of the energy with a bath (e.g. solvent, buffer-gas)

Langevin equation of motion

$$m \frac{d^2 \vec{r}}{dt^2} = -\zeta \frac{\partial \vec{r}}{\partial t} + \vec{F}_{intra} + \vec{F}_{random}$$

Compared to the standard Newton's equation we have new terms:

- 1) $\zeta \vec{v}$ - friction term with a friction coefficient ($\sim 2\text{ps}^{-1}$), which removes energy from the system
- 2) \vec{F}_{random} - random force associated with the temperature, which balances energy from the system



Molecular dynamics with coupling to an external bath

H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola,^{a)} and J. R. Haak
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(Received 30 April 1984; accepted 27 June 1984)

In molecular dynamics (MD) simulations the need often arises to maintain such parameters as temperature or pressure rather than energy and volume, or to impose gradients for studying transport properties in nonequilibrium MD. A method is described to realize coupling to an external bath with constant temperature or pressure with adjustable time constants for the coupling. The method is easily extendable to other variables and to gradients, and can be applied also to polyatomic molecules involving internal constraints. The influence of coupling time constants on dynamical variables is evaluated. A leap-frog algorithm is presented for the general case involving constraints with coupling to both a constant temperature and a constant pressure bath.

J. Chem. Phys. **81** (8), 15 October 1984

Thermostat

$$\sum_i \frac{|\vec{p}_i|^2}{m_i} = 3Nk_B T$$

Barostat

$$\sum_i \left(\frac{|\vec{p}_i|^2}{m_i} + \sum_{j>i} \vec{r}_{ij} \vec{F}_{ij} \right) = 3pV$$

Rescale velocities by λ and coordinates (or unit cell) by μ , where

$$\lambda^2 = 1 + \gamma \Delta t \left(\frac{T_0}{T} - 1 \right), \quad \mu^3 = 1 - \beta \Delta t (p_0 - p),$$

Advanced thermostat, barostat, and integrator see in program manuals

LAMMPS users see `fix nvt/npt/nph` command

Simulation of indentation of nanometer-thick carbon membranes by using classical MD with Tersoff potential (direct simulation of experimental setup)

Lonsdaleite Films with Nanometer Thickness

Alexander G. Kvashnin^{*,†,‡} and Pavel B. Sorokin^{†,‡,||}

[†]Technological Institute of Superhard and Novel Carbon Materials, 7a Centralnaya Street, Troitsk, Moscow 142190, Russian Federation

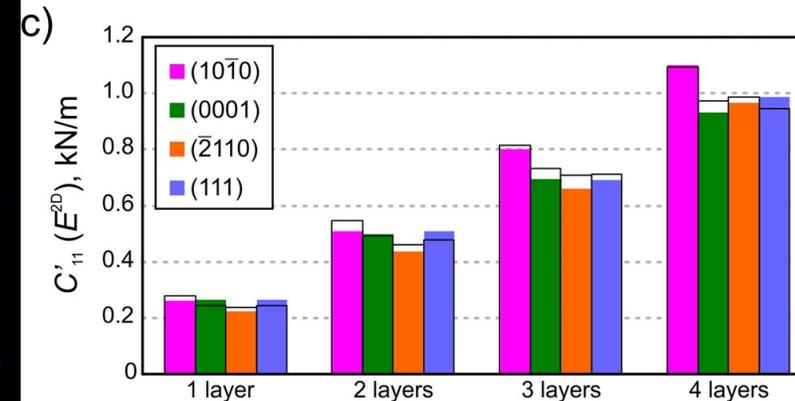
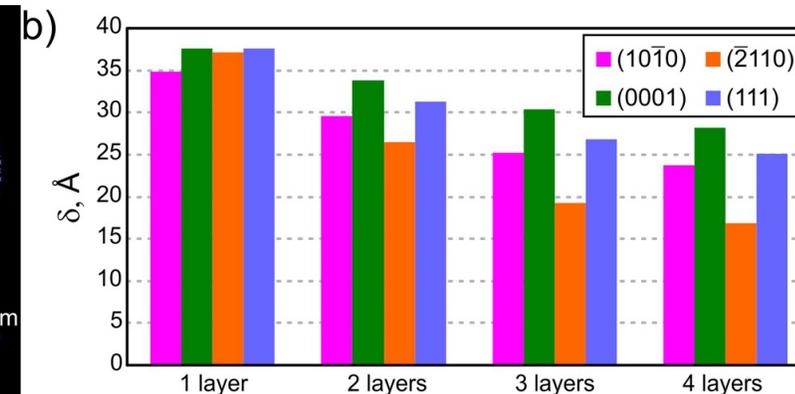
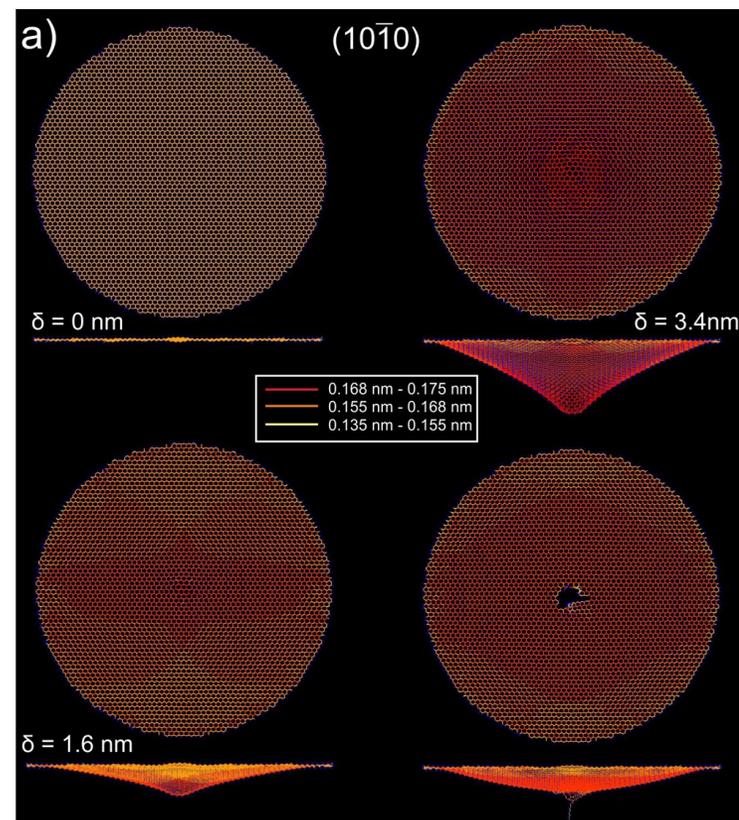
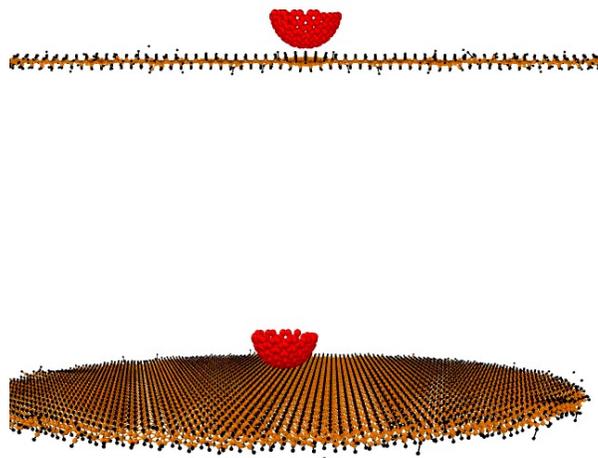
[‡]Moscow Institute of Physics and Technology, 9 Institutsky lane, Dolgoprudny 141700, Russian Federation

^{||}National University of Science and Technology "MISIS", Leninsky Avenue 4, Moscow 119049, Russian Federation

✉ Cite this: *J. Phys. Chem. Lett.* 2014, 5, 3, 541–548

Publication Date: January 24, 2014

<https://doi.org/10.1021/jz402528q>



Nanohardness from First Principles with Active Learning on Atomic Environments

Evgeny V. Podryabinkin,* Alexander G. Kvashnin, Milad Asgarpour, Igor I. Maslenikov, Danila A. Ovsyannikov, Pavel B. Sorokin, Mikhail Yu Popov, and Alexander V. Shapeev

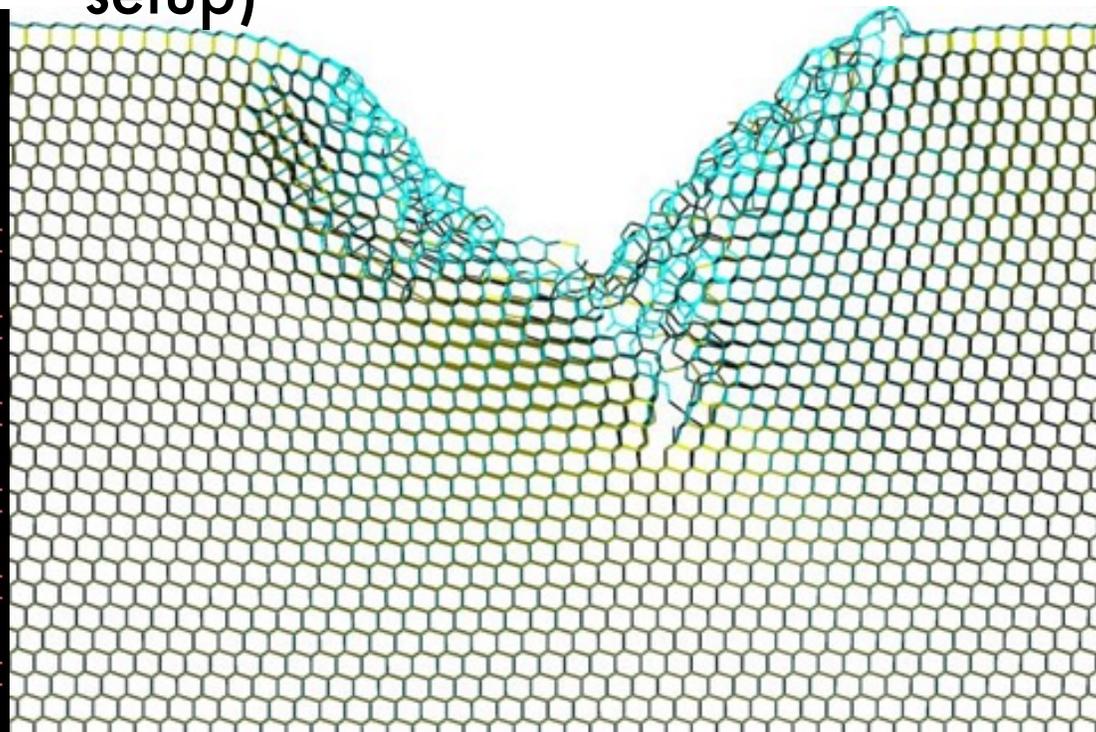
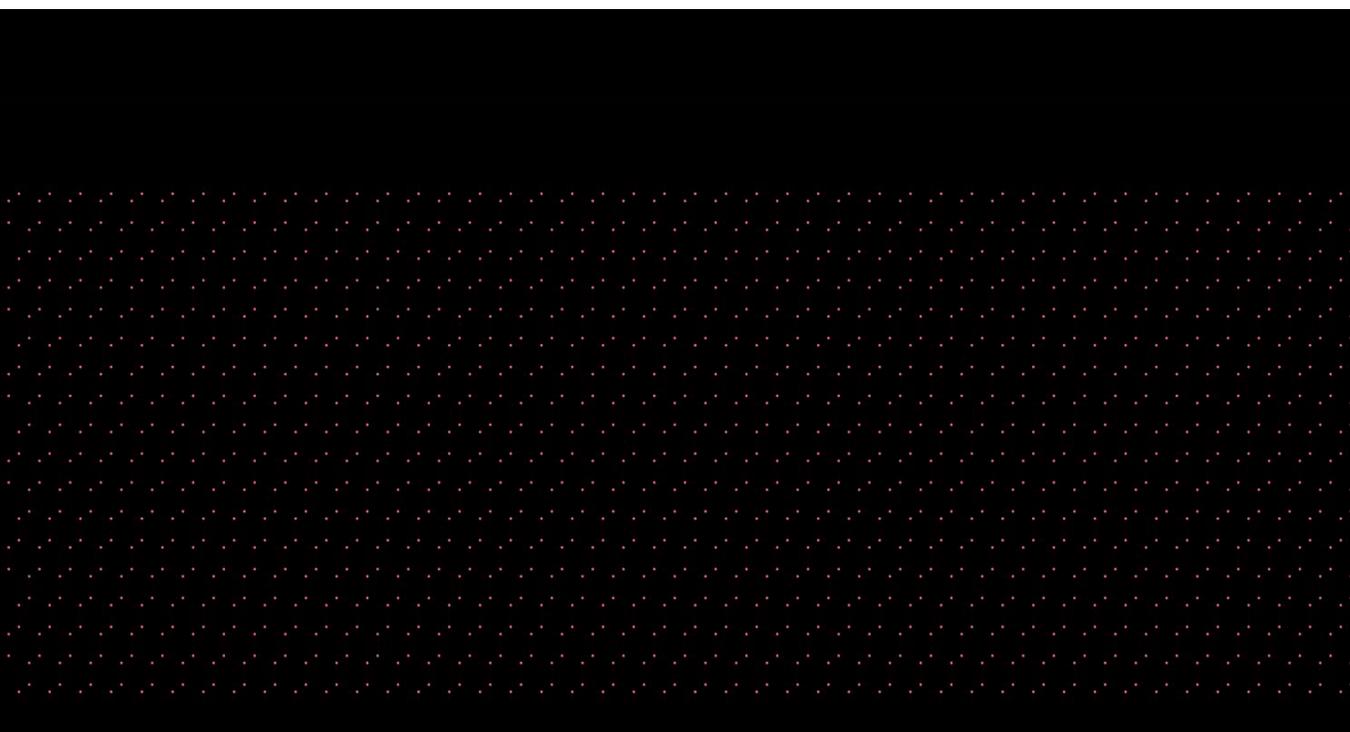
Cite This: <https://doi.org/10.1021/acs.jctc.1c00783>

 Read Online

Example 2

ML potential

Simulation of nanoindentation of materials by using ML potentials via direct measurements of forces and imprints from the indenter (direct simulation of experimental setup)

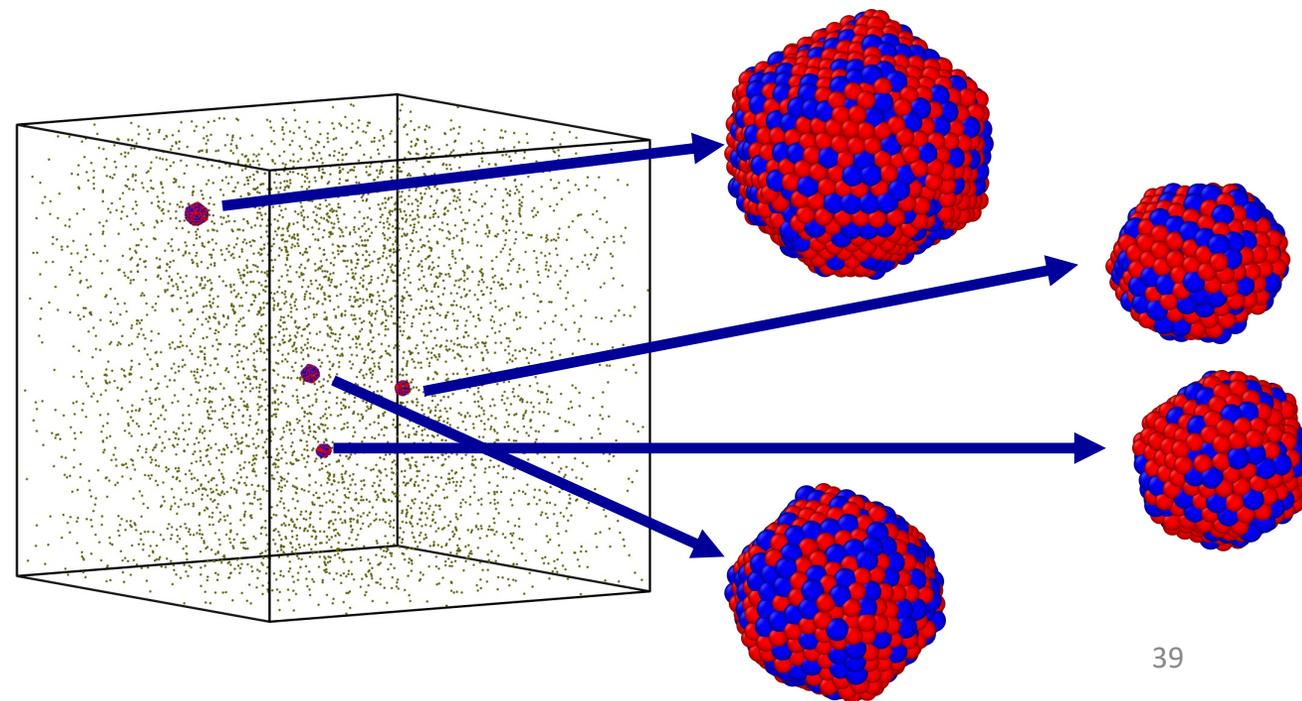
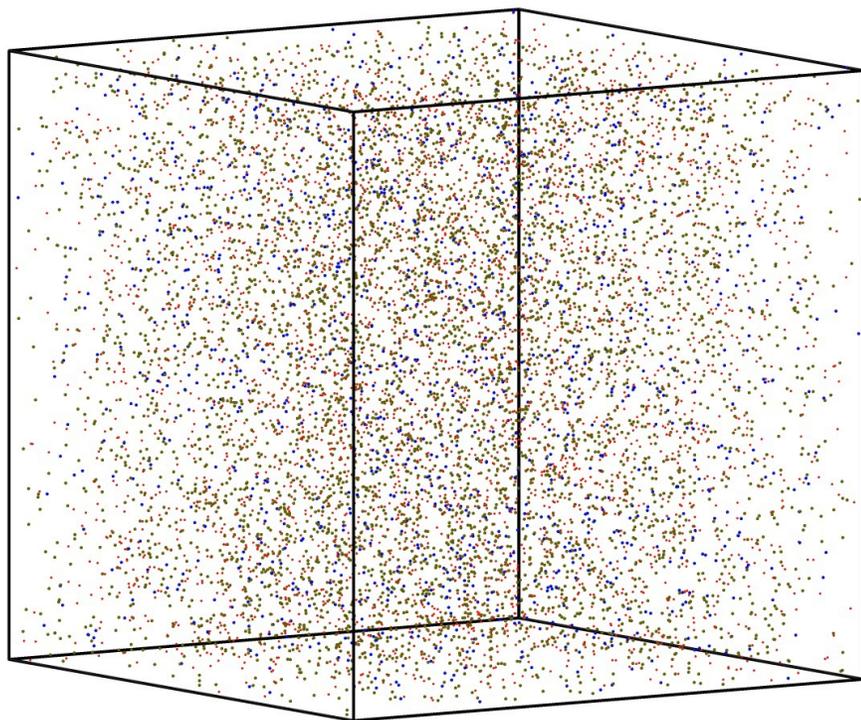


Cu–Au nanoparticles produced by the aggregation of gas-phase metal atoms for CO oxidation

Ilya V. Chepkasov¹ | Viktor S. Baidyshev² | Artem A. Golubnichiy² | Ivan S. Zamulin² | Alexander G. Kvashnin¹ | Sergey M. Kozlov³ 

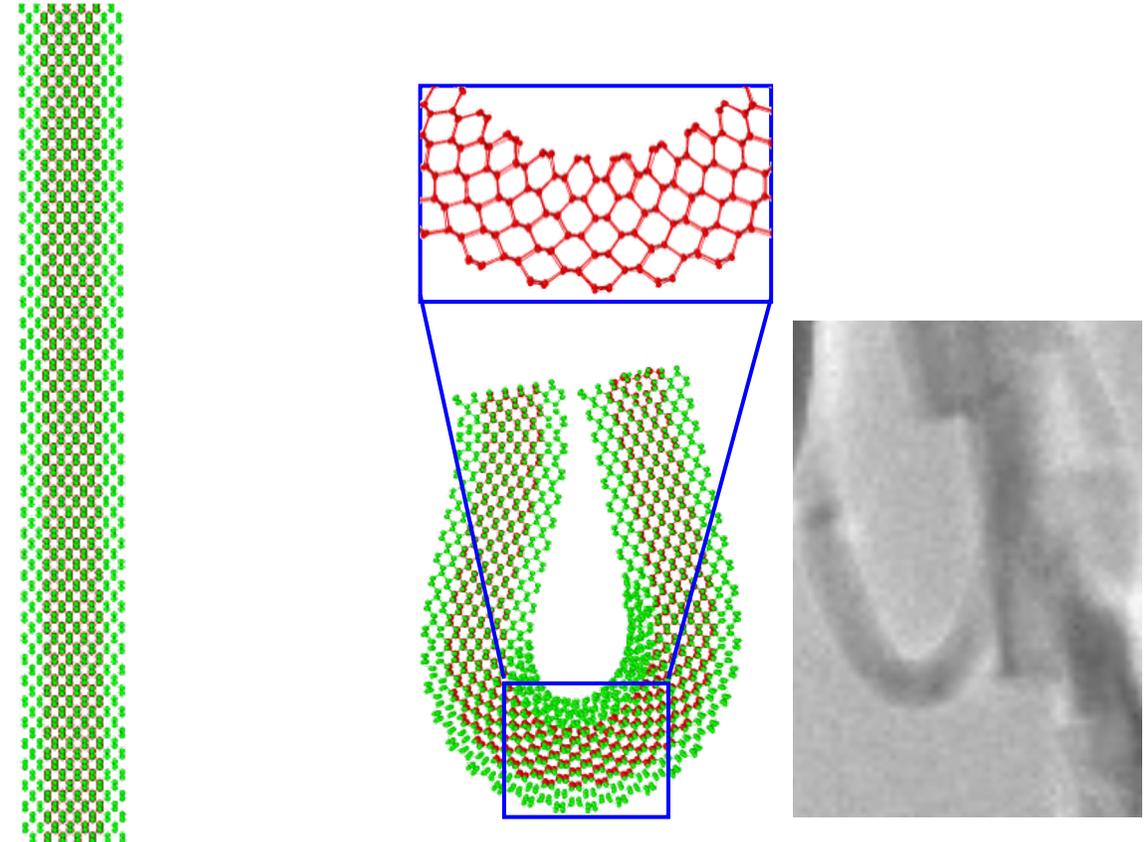
EAM potential

Molecular dynamics to simulate the PVD synthesis of Cu–Au nanoalloys through the non-isothermal aggregation of Cu and Au atoms at a 3:1 ratio in the Ar atmosphere to obtain realistic structures of Cu–Au nanoparticles



Mechanical, Electrical, and Crystallographic Property Dynamics of Bent and Strained Ge/Si Core–Shell Nanowires As Revealed by *in situ* Transmission Electron Microscopy

Chao Zhang,^{*,†} Dmitry G. Kvashnin,^{‡,⊥} Laure Bourgeois,[§] Joseph F. S. Fernando,[†] Konstantin Firestein,[†] Pavel B. Sorokin,^{‡,⊥} Naoki Fukata,^{||} and Dmitri Golberg^{*,†,||}

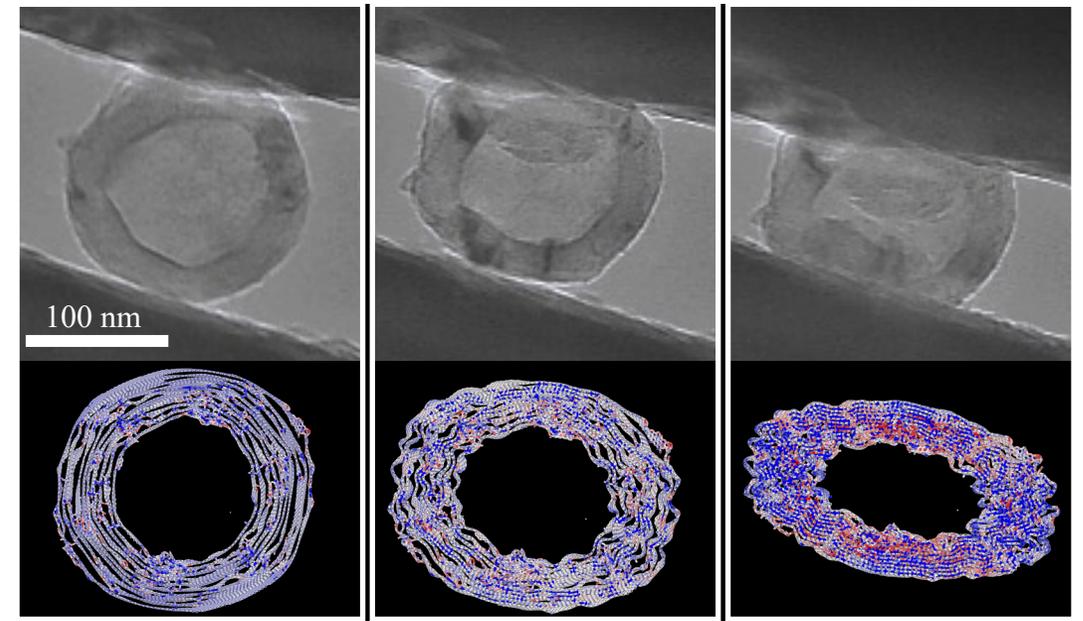


Tersoff many-body potential

Nanoscale, 10, 8099 (2018)

Compressive properties of hollow BN nanoparticles: theoretical modeling and testing using a high-resolution transmission electron microscope

Konstantin L. Firestein,^{id *a,b} Dmitry G. Kvashnin,^{id a} Andrey M. Kovalskii,^a Zakhar I. Popov,^{id a} Pavel B. Sorokin,^{id *a,c} Dmitri V. Golberg^{id b,d} and Dmitri V. Shtansky^{id *a}



Nanoscale



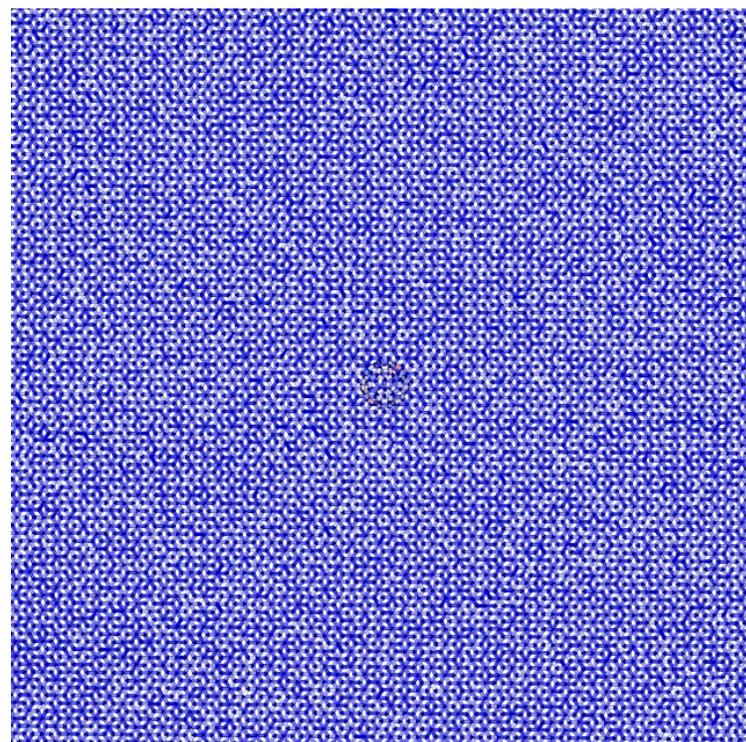
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Cite this: *Nanoscale*, 2018, 10, 14499

Nanostructuring few-layer graphene films with swift heavy ions for electronic application: tuning of electronic and transport properties†

N. A. Nebogatikova,¹ I. V. Antonova,¹ S. V. Erohin,² D. G. Kvashnin,³
A. Olejniczak,⁴ V. A. Volodin,⁵ A. V. Skuratov,⁶
A. V. Krashennnikov,⁷ P. B. Sorokin⁸ and L. A. Chernozatonskii⁹

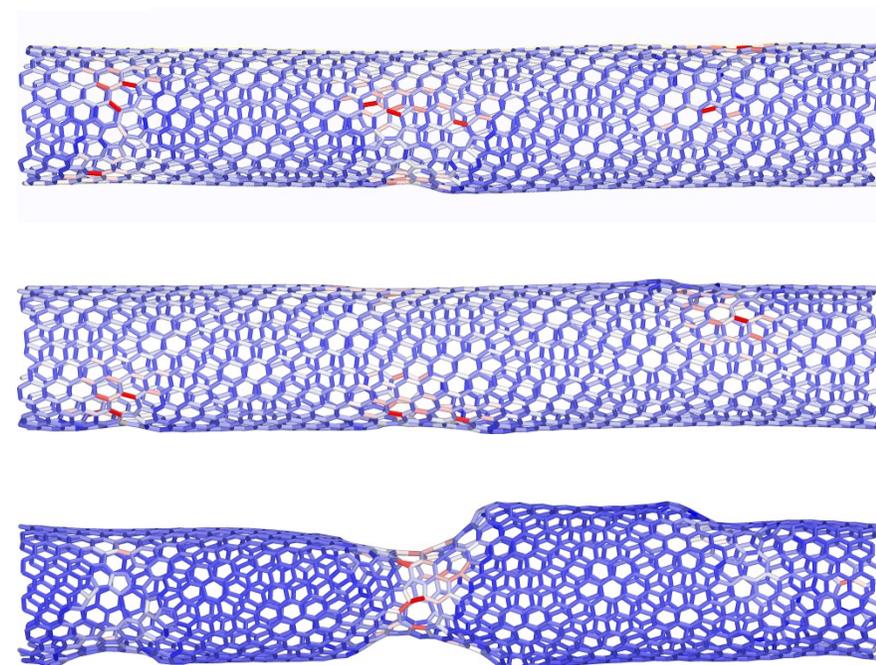


Application of classical potentials and MD simulations to describe irradiation and changes of structure of carbon nanomaterials

Tersoff many-body Semiconductor nanochannels in metallic carbon nanotubes by thermomechanical chirality alteration

Dai-Ming Tang^{1*}, Sergey V. Erohin², Dmitry G. Kvashnin^{2,3}, Victor A. Demin³, Ovidiu Cretu⁴, Song Jiang⁵, Lili Zhang⁵, Peng-Xiang Hou⁵, Guohai Chen⁶, Don N. Futaba⁶, Yongjia Zheng⁷, Rong Xiang⁷, Xin Zhou¹, Feng-Chun Hsia¹, Naoyuki Kawamoto⁴, Masanori Mitome¹, Yoshihiro Nemoto⁸, Fumihiko Uesugi⁸, Masaki Takeguchi⁸, Shigeo Maruyama⁷, Hui-Ming Cheng^{5,9,10}, Yoshio Bando^{11,12}, Chang Liu^{5*}, Pavel B. Sorokin^{2,13*}, Dmitri Golberg^{1,14*}

Tang *et al.*, *Science* **374**, 1616–1620 (2021)

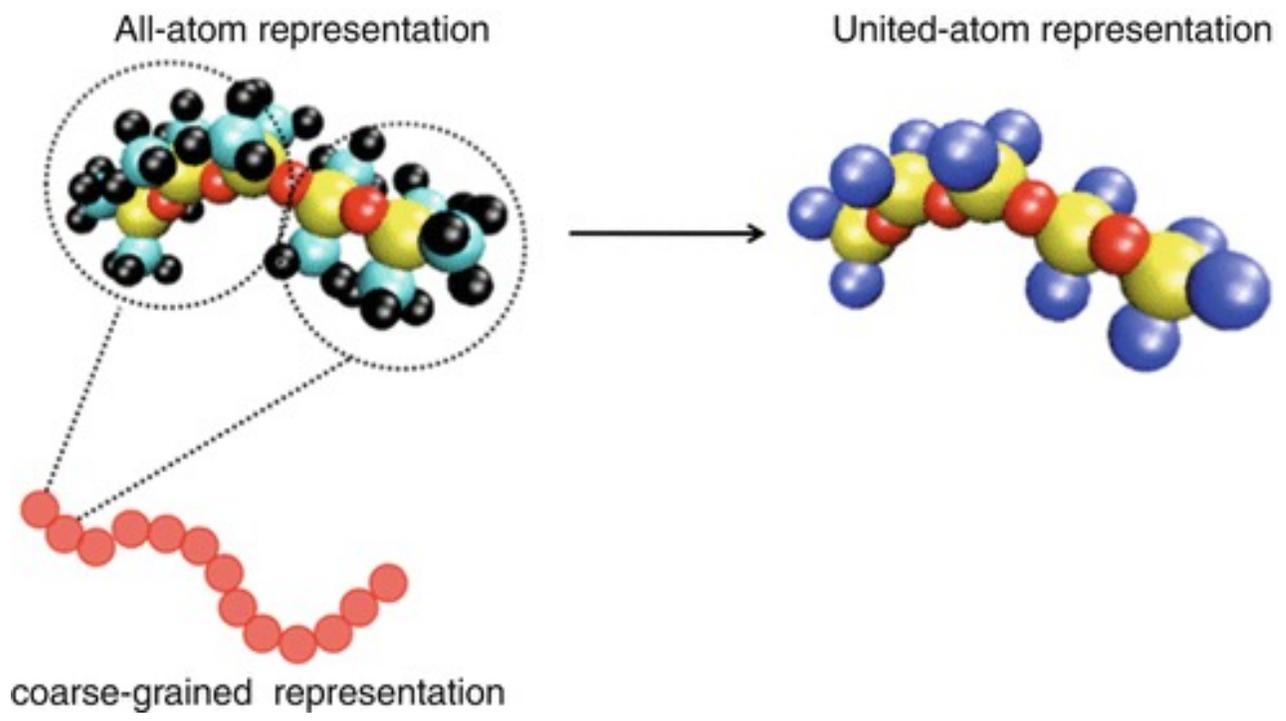


Aim is to simulate the behavior of complex systems using their coarse-grained (simplified) representation.

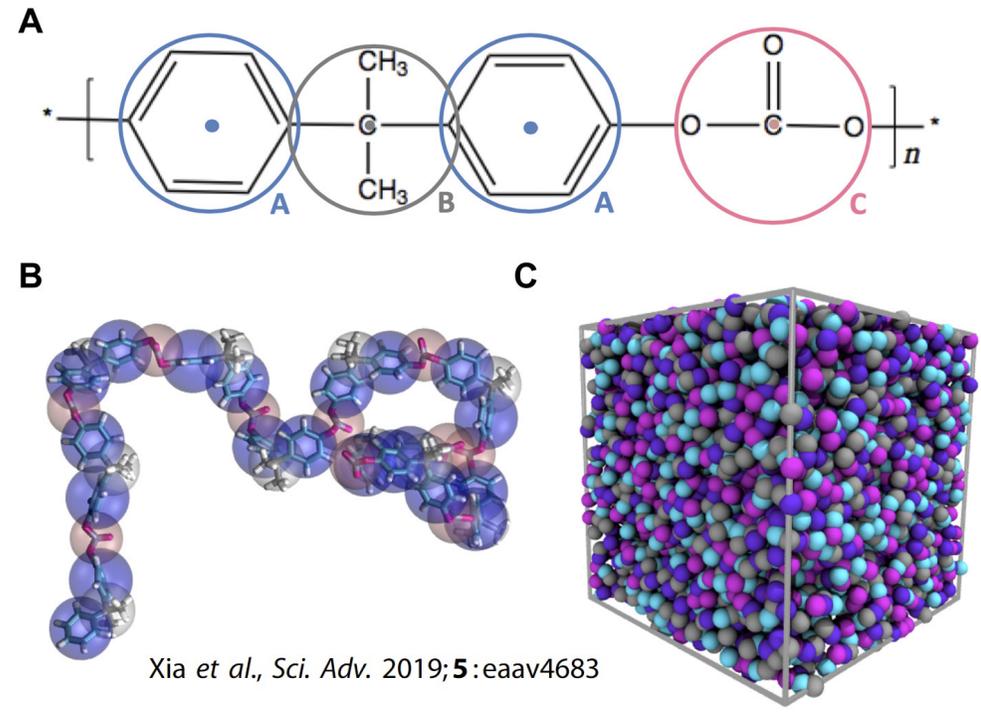
Coarse-grained models are widely used for molecular modeling of biomolecules at various granularity levels.

Idea is to simulate coarse grained model, then get back to all-atom description to refine local geometry.

Multiscale coarse-grained (CG)



Bisphenol-A polycarbonate chemical structure and the corresponding CG



Statistical mechanics

Thermodynamics variables: volume (V), pressure (p), temperature (T). Number of particles (N), energy (E), chemical potential (μ)

Statistical mechanics: connection between properties of a microscopic system and a macroscopic sample

Ensemble: collection of microscopic states consistent with thermodynamic boundary conditions; defined by 3 variables (NVT) or (NVE) or (NPT) or (μVT)

Boltzmann probability: relative probability to be in a state with an energy E at a temperature T and is proportional to $\exp(-E/k_B T)$

Partition function is a key quantity in statistical mechanics, a normalization factor for the Boltzmann probability distribution:

$$Q = \sum_i^{\infty} e^{-E_i/k_B T} = \int e^{-E(\vec{r}, \vec{p})/k_B T} d\vec{r} d\vec{p}$$

Everything can be expressed through Q , e.g., for a canonical ensemble (NVT)

- **Internal energy**

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

- **Enthalpy**

$$H = U + PV = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

- **Entropy**

$$S = \frac{U - A}{T} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B T \ln Q$$

- **Gibbs free energy**

$$G = H - TS = k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T - k_B T \ln Q$$

- **Helmholtz free energy** $A = U - TS = -k_B T \ln Q$

Thermodynamic ensembles

Microcanonical (NVE): Newtonian system ($N = \text{const}$) in box ($V = \text{const}$) with elastic walls (or PBC)

Canonical (NVT): Newtonian system ($N = \text{const}$) in box ($V = \text{const}$) with non-elastic walls (walls are equilibrated with $T = \text{const}$ - thermostat)

Isothermal-isobaric (NPT): Newtonian system ($N = \text{const}$) in box with varying volume (keeping $P = \text{const}$ - barostat) and non-elastic walls (keeping $T = \text{const}$ - thermostat)

Grand-canonical (μVT): Open system (number of particles is not conserved but their energy in the reservoir is fixed at μ)

Constants in different ensembles, and corresponding equilibrium states

N	P	V	T	E	μ	Acronym	Equilibrium	Name
×		×	×			NVT	A has minimum	Canonical
×		×		×		NVE	S has maximum	Micro-canonical
×	×		×			NPT	G has minimum	Isothermal-isobaric
		×	×		×	$VE\mu$	(PV) has maximum	Grand canonical

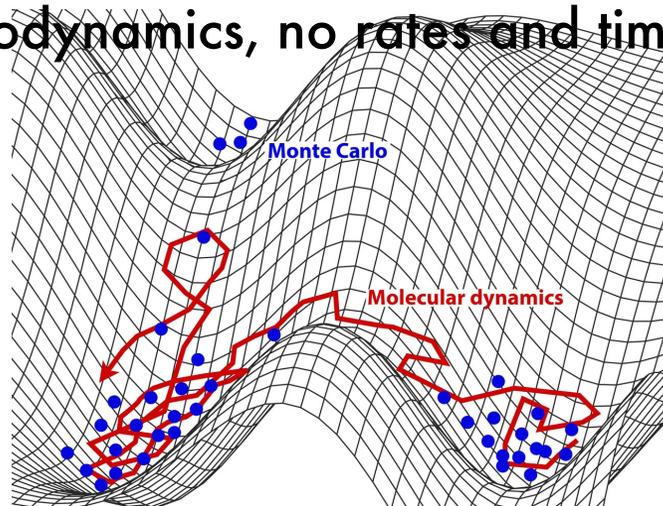
At what number of particles $NVE = NVT$?

Ergodicity: Time-average of a property can be replaced by a suitable average over collection of possible microscopic states (**ensemble average**)

Given a potential energy surface $E_p(r)$, what are the possible modeling routes for generating ensembles?

Molecular dynamics (MD): propagate Newton's equation of motion, analyze trajectories – generally gives rates and time constants

Monte-Carlo (MC): 'flip a coin' statistical approach
(T is an essential component) – gives information on the thermodynamics, no rates and time scales



Differences between Monte Carlo and molecular dynamics methods

Property	MC	MD
Basic information needed	Energy	Gradient
Particles moved in each step	One	All
Coordinates	Any	Cartesian
Constraints	Easy	Difficult
Atomic velocities	No	Yes
Time dimension	No	Yes
Deterministic	No	(Yes)
Sampling	Non-physical	Physical
Natural ensemble	NVT	NVE

Replace strategy

“first pick, then weight” with

“first weight, the pick”

by penalizing states with high energy by a Boltzmann factor $\exp(-\Delta E/k_B T)$

How?

Say on $(i-1)$ step, the energy of accepted configuration is E_{i-1}

on i^{th} step, the energy of new configuration is E_i

Case 1: $E_i < E_{i-1}$: Good! We are going lower, accept i

Case 2: $E_i > E_{i-1}$: We are going higher, calculate $\exp(-\Delta E/k_B T) = \exp(-(E_i - E_{i-1})/k_B T)$, pick a random number ξ from $[0, 1]$

If $\xi > \exp(-\Delta E/k_B T)$ reject it

If $\xi < \exp(-\Delta E/k_B T)$ accept it

**Metropolis (+Fermi, Ulam, von Neuman)**

Monte-Carlo (1952): “walks” through phase space (Markov chain of states) visiting each state with proper probability (in the infinite time limit)

Algorithm

Generate trial configuration q_1 , its energy $E_1 = E(q_1)$ and store the desired property $A_1 = A(q_1)$

For $i = 2, \dots, M$ do

Perturb the system, get new configurations

Calculate energy of q_i : $E_i = E(q_i)$

Test E_i vs E_{i-1} for acceptance

If rejected, discard q_i

If accepted, calculate and store $A_i = A(q_i)$

If $i < M$

Calculate $\langle A(M) \rangle = \frac{1}{M} \sum_{i=1}^M A_i$

1) The natural Monte-Carlo ensemble is (NVT)

2) The “Devil is in details”: the art of running a MC calculation lies in defining the perturbation step(s)

If the steps are very small, then volume of phase space sampled will increase only slowly over time, and it is computationally expensive. If the steps are too large, then the rejection rate will grow so high that again resources will be wasted by an inefficient phase space.

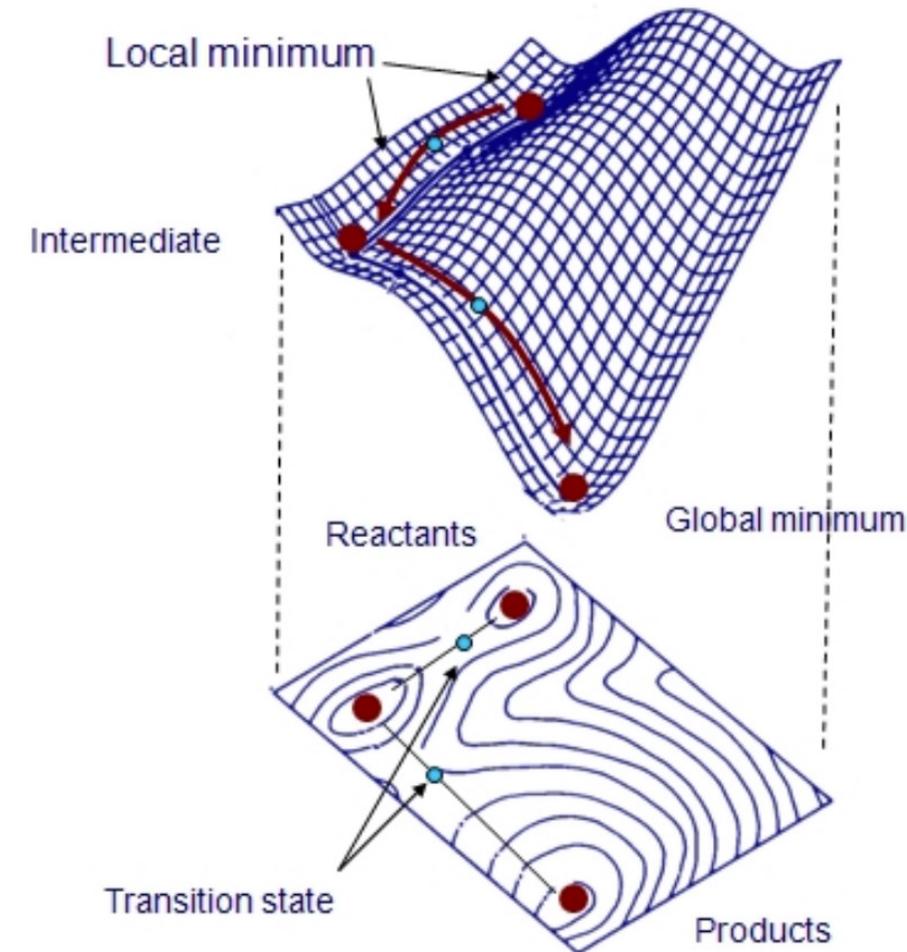
3) Monitoring convergence of $\langle A(M) \rangle$ and possibly $\langle E(M) \rangle$ with M is necessary

This will tell you a lot about convergence rate and possible transitions to a different PES valley

4) Multiple Mc variations were developed, including different ensembles, annealing (varying T) algorithms, simulating timescales.

For example, (NPT) isothermal-isobaric ensemble, G (Gibbs free energy) at min (frequent in experimental conditions)

$$\Delta E \rightarrow \Delta E + P\Delta V - Nk_B T \ln(1 + \Delta V/V)$$



Example of PES

Thank!