Short Lecture:
Structure prediction

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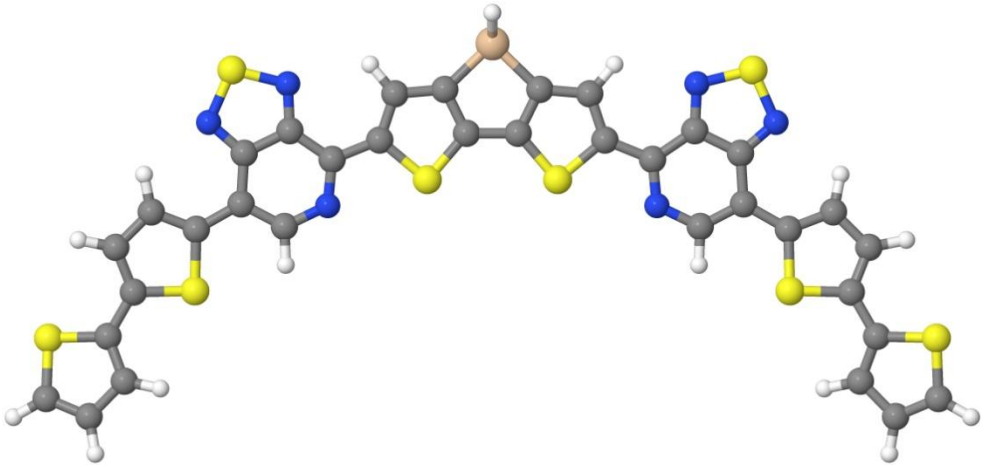
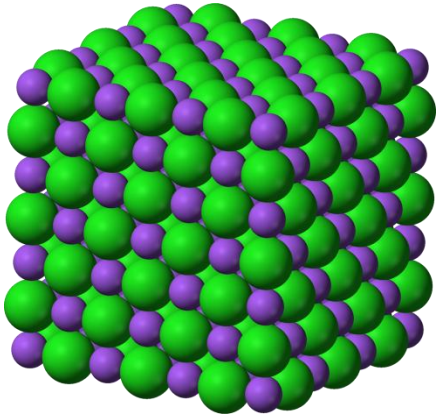
Structure prediction: why it is important





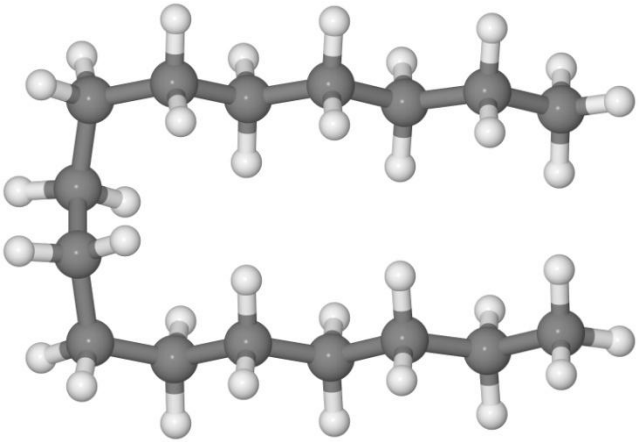
Modeling of any material starts with obtaining initial structure.

Where to get this structure?

- Known from experiment or publications
- Can be found in database
- Can be easily guessed by prototype or chemical rules
- ***Otherwise it must be predicted***

Structure prediction: why it is challenging

Number of conformations/polymorphs grows exponentially with the size of the system



Let's consider polyethylene in the independent rotation approximation: if N is number of C-C-C-C dihedrals and n is average number of dihedrals in gauche conformation then total number of configuration is the binomial coefficient $(2N,n)$. Because n is proportional to N due to thermal fluctuations, number of conformations grows exponentially with N.

In other words,
It is a nontrivial global optimization problem in 3N-dimensional space
(not counting electronic degrees of freedom such as magnetic moments)

Possible approaches

- Enumerative approach
  - Generate all possible/relevant structures at once and calculate energies (if you need only finite number of lowest energy structures)
  - Sample structures randomly using a structure generator (if your ground state is highly degenerate, e.g. for statistical sampling and for frustrated systems)

- Iterative approach
  - "Local" iterations – molecular dynamics (MD) or Monte Carlo runs (the new structure is generated from the previous one)
  - "Global" iterations – modern structure prediction codes (the new structure is generated from all structures generated so far)

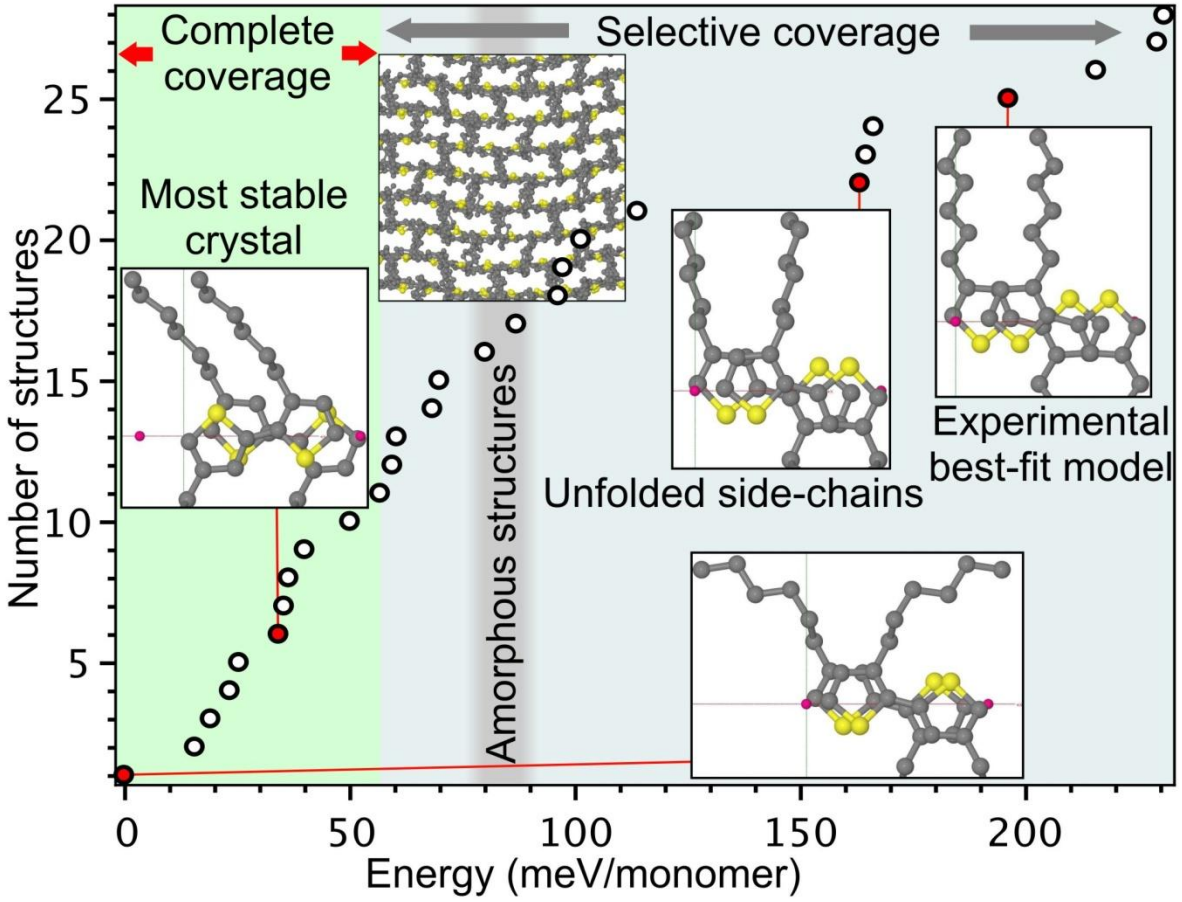
In all cases you must create ***structure generator***

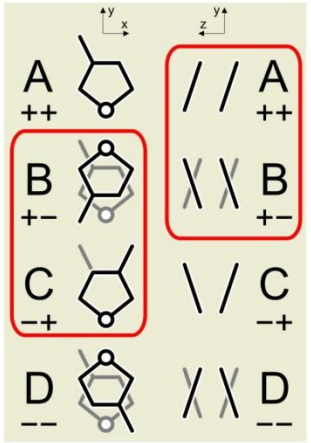
Enumerative search of global minimum

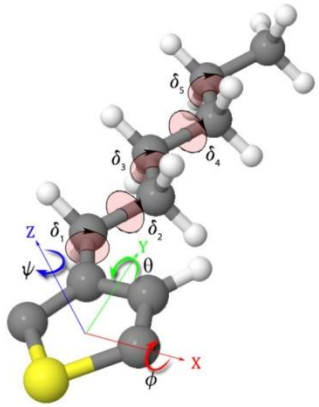
Works well when the search space is practically countable, e.g.

- using library/database of structures
- finite number of flexible degrees of freedom

Example: J Phys Chem C 122, 9141 (2018) pdf







Structure sampling

Works well if you need only a statistical sampling, i.e. missing the lowest-energy structures is not critical.

Commonly used to generate initial structure for MD:

- A good starting point is liquid/gas/solution phase of the material (most of MD codes have tools to generate such structure)
- For molecular systems, initial structure must have correct topology (bonds)

Modern structure prediction codes

- Usually use combinations of various approaches (multiple generators)
- Use evolutionary algorithms to iteratively improve set of structures used to generate the next iteration
- Provide more-or-less black box solution
- Limited to not-very-complex systems (e.g. very efficient for ternary compounds with tens of atoms in unit cell)

Examples:

- USPEX – we use it at Skoltech
- GRACE – one of the best for molecular crystals
- CALYPSO, XtalOpt, other codes

Individual studies

- USPEX tutorial
- See recommended reading on this class web-page