Welcome to
CHE 384T: Computational Methods in Materials Science

Interatomic Potentials

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Lecture Outline

Cohesive energy

Types of bonding

Interatomic potentials
    Basic forms
    Lennard-Jones potential
    Mie potential
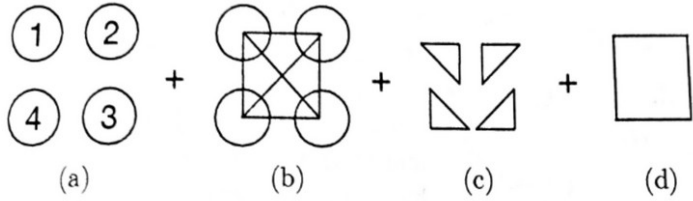   Born-Mayer and Morse potentials

Materials considerations
    ionic materials
    metals
    covalent materials
    mixed bonding environments

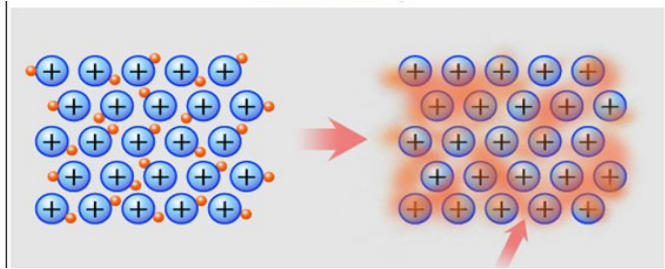# Cohesive Energy

(a) + (b) + (c) + (d)

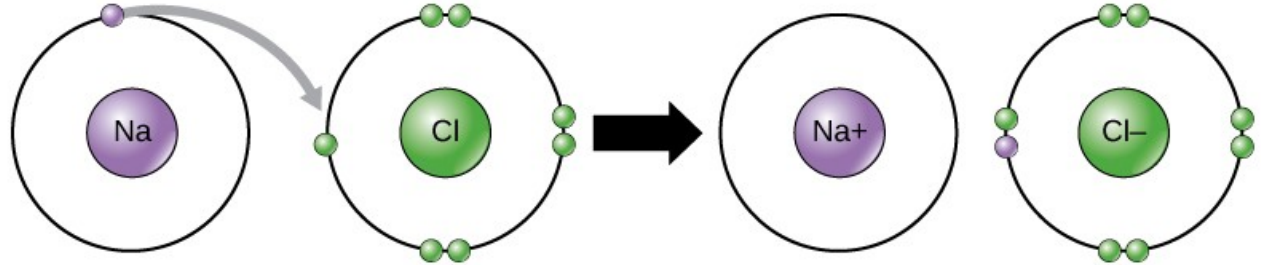# Goals in constructing an interatomic potential

- Define an input and output
    - Input: distance
    - Output: potential

- To create a model that captures how molecules interact with each other
    - Condensed matter exists → must be an attractive component
    - Matter does not collapse on itself → must be a repulse component

- A *semi-quantitative* model can provide some insights on materials behavior

- Re-cast mathematical equations in a form that is conducive to coding
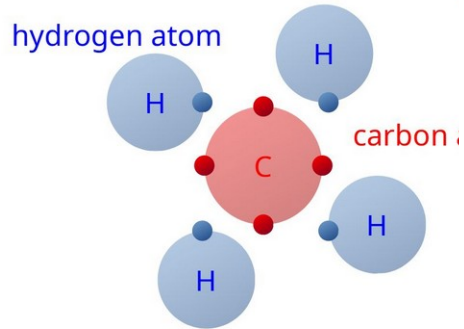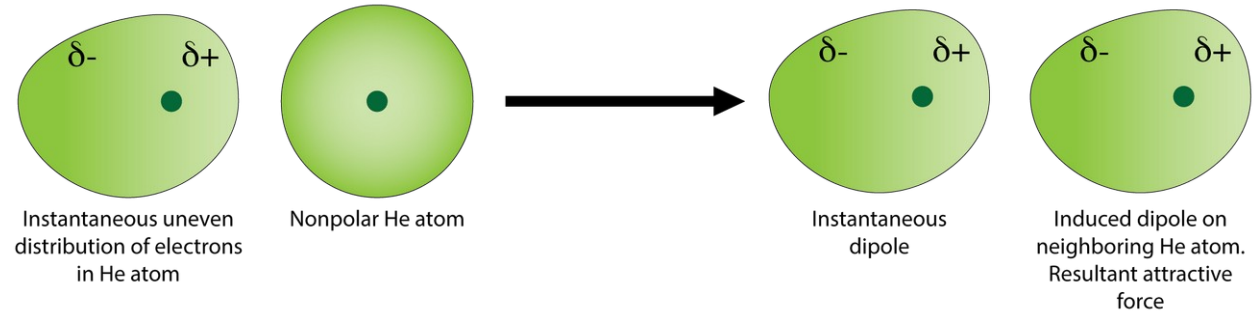
Types of interactions

Metallic bonding

Ionic bonding

Covalent bonding

hydrogen atom

H

H

carbon

C

H

H

London dispersion forces

| δ- | δ+ | | δ- | δ+ | δ- | δ+ |

Instantaneous uneven
distribution of electrons
in He atom

Nonpolar He atom

Instantaneous
dipole

Induced dipole on
neighboring He atom.
Resultant attractive
force

Periodic trends

Trends in the Periodic Table

Electronegativity: tendency of an atom or a functional group to attract electrons toward itself.

Atoms prefer to have fully (or half) occupied electron electron shells → energetically stable
Duet rule: s^2
Octet rule: s^2p^6
18-electron rule: transition metals (varies a lot)

Lanthanides: 1.1 – 1.2
Actinides: 1.1 – 1.7
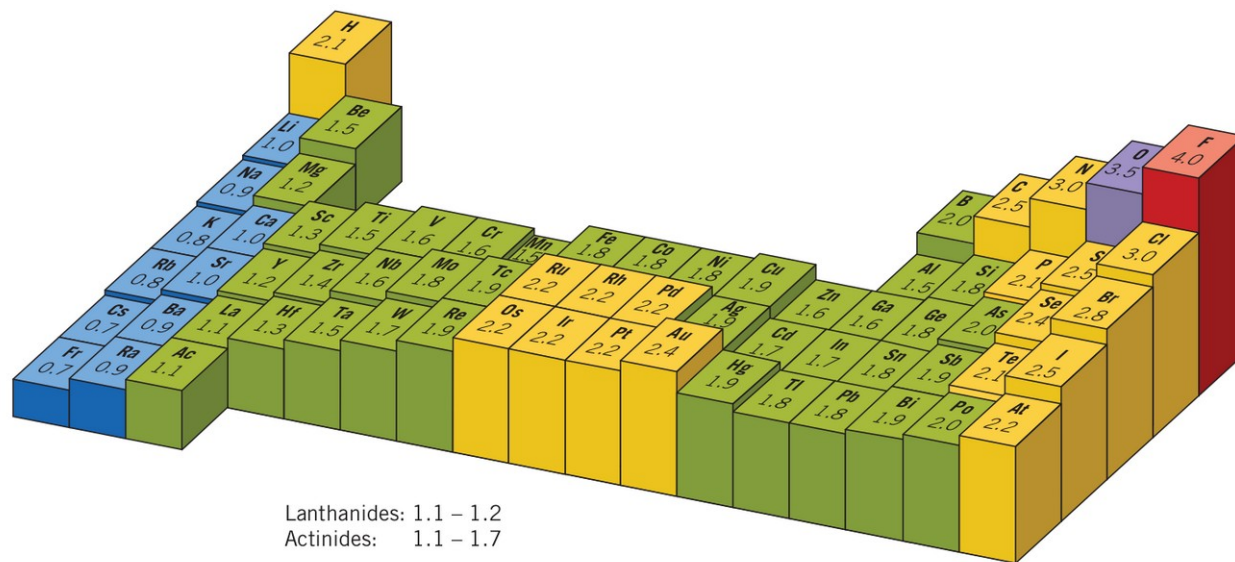
Figure 2.9 The electronegativity values for the elements.
(From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes,* 4th edition, 2004. This material is reproduced with permission of John Wiley & Sons, Inc.)

Types of bonding and interactions
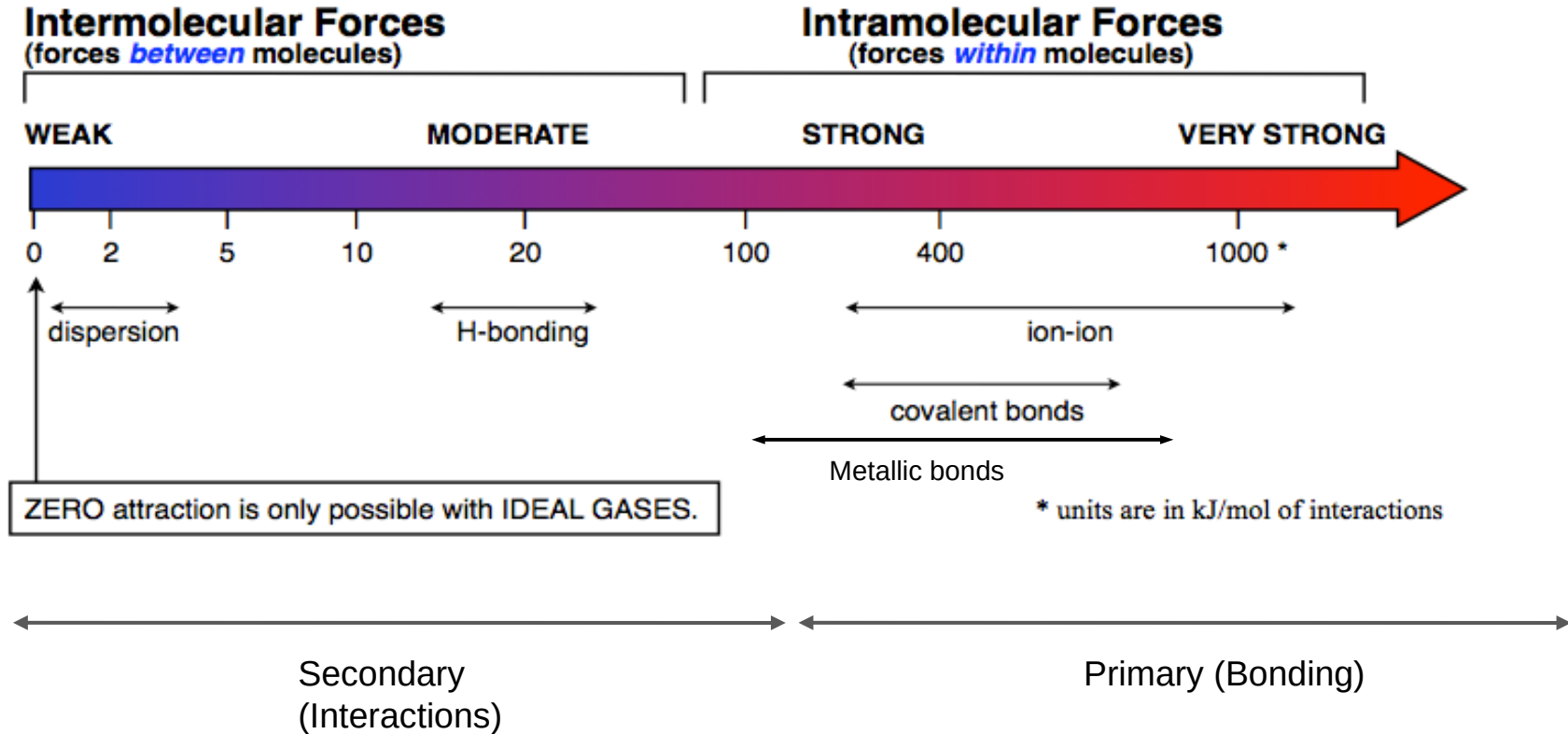
Interatomic potentials: Basic interactions

Short-range interactions

Long-range interactions

Interatomic potentials: Lennard-Jones potential

Interatomic potentials: Lennard-Jones potential

Recasting into a more useful form

Scaled/reduced units

Interatomic potentials: Lennard-Jones potential

Table 5.2 **Calculated and experimental properties of the rare gas solids.**
Parameters taken from [15]

		Ne	Ar	Kr	Xe
r_o (Å)	Experiment	3.13	3.75	3.99	4.33
	Theory	2.99	3.71	3.98	4.34
u_o (eV/atom)	Experiment	−0.02	−0.08	−0.11	−0.17
	Theory	−0.027	−0.089	−0.120	−0.172
B_o (GPa)	Experiment	1.1	2.7	3.5	3.6
	Theory	1.8	3.2	3.5	3.8

Interatomic potentials: other forms

Mie Potential

$$\phi_{mn}(r) = \frac{\epsilon}{m-n}\left(\frac{m^m}{n^n}\right)^{\frac{1}{m-n}}\left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right]$$
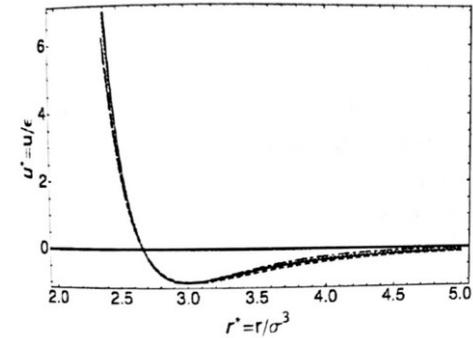
Born-Mayer Potential

$$\phi^{BM}(r) = Ae^{-\alpha r} - \frac{C}{r^6}$$

Morse Potential

$$\phi^M(r) = \epsilon\left[e^{-2\alpha(r-r^*)} - 2e^{-\alpha(r-r^*)}\right]$$

Interatomic potentials: Lennard-Jones potential
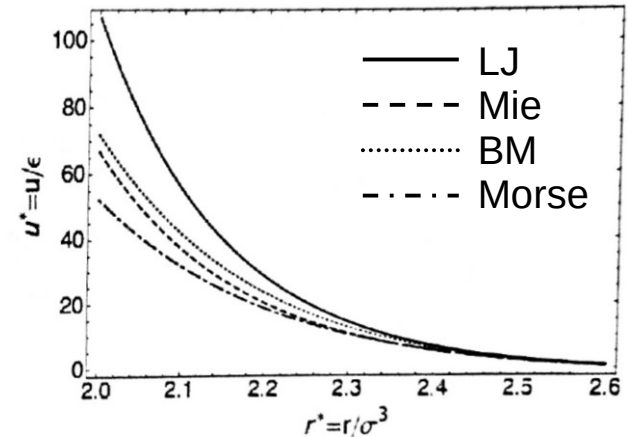
Central-Force potentials

Lennard-Jones potential is an example of a central-force potential

Such potentials will tend to form simple structures, e.g., fcc, bcc

More complex structures require additional thinking

c_{12} and c_{44} are the Lame constant and shear elastic constant

$c_{12} \neq c_{44}$ gives a degree of anisotropy

Table 5.3 Comparison of values for c_{12}/c_{44} for a number of materials. The value from calculations on a Lennard-Jones (LJ) potential are from [267], the data for Ar is from [168], while all other data are from Appendix 1 of [147]

Material	c_{12}/c_{44}
"LJ"	1.00
Ar	1.12
Mo	1.54
Cu	1.94
Au	4.71
NaCl	0.99
Si	0.77
MgO	0.53
diamond	0.16

Interatomic potentials: Lennard-Jones potential

Connection to Thermodynamic quantities

Regardless, can use the simplicity of Lennard-Jones potential to analytically compute some thermodynamic quantities
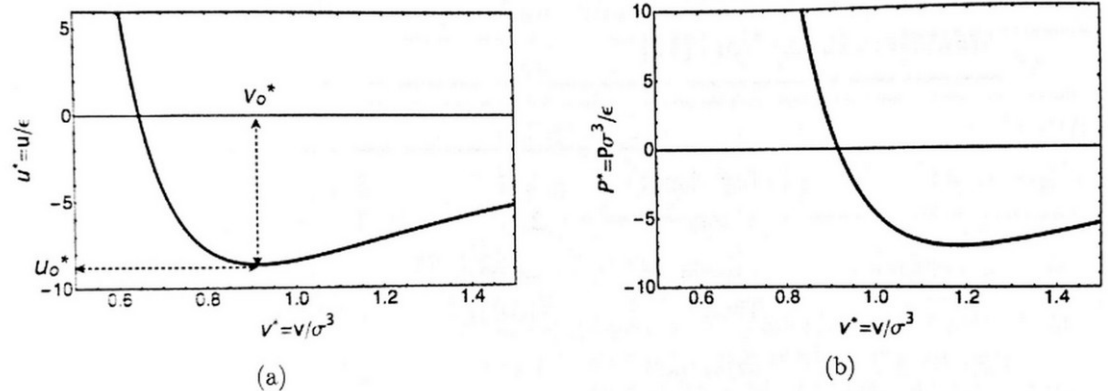

Figure 5.5 (a) Cohesive energy per atom of the Lennard-Jones solid $u^* = u/\epsilon$ as a function of the volume per atom $v^* = v/\sigma^3$, from Eq. (5.39). v_o^* and u_o^* are the equilibrium values from Eq. (5.40). The bulk modulus is proprtional to the curvature of this curve at equilibrium. (b) The pressure for the Lennard-Jones solid at 0 K.

Interatomic potentials: Lennard-Jones potential

Connection to Thermodynamic quantities

For an FCC crystal, rewrite LJ potential in terms of nn distances

$$u(\tilde{r}) = 2\epsilon \left[A_{12} \left(\frac{\sigma}{\tilde{r}} \right)^{12} - A_6 \left(\frac{\sigma}{\tilde{r}} \right)^6 \right]$$

$$r_o = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma = 1.09\,\sigma$$

$$v_o = \left(\frac{2A_{12}}{A_6} \right)^{1/2} \beta\,\sigma^3 = 0.916\,\sigma^3$$

$$u_o = -\frac{\epsilon}{2} \left(\frac{A_6^2}{A_{12}} \right) = -8.6\,\epsilon$$

$$B_o = -8\frac{u_o}{v_o} = 75\frac{\epsilon}{\sigma^3},$$

Table 5.4 Lattice sums (A_n) for cubic crystals. From [161]. $f_1 = 6 + 12(1/\sqrt{2})^n + 8(1/\sqrt{3})^n$, $f_2 = 8 + 6(\sqrt{(3/4)})^n + 12(\sqrt{3/8})^n$, and $f_3 = 12 + 6(1/\sqrt{2})^n + 24(1/\sqrt{3})^n$

| n	Simple cubic	Body-centered cubic	Face-centered cubic
4	16.5323	22.6387	25.3383
5	10.3775	14.7585	16.9675
6	8.4019	12.2533	14.4539
7	7.4670	11.0542	13.3593
8	6.9458	10.3552	12.8019
9	6.6288	9.8945	12.4925
10	6.2461	9.5645	12.3112
11	6.2923	9.3133	12.2009
12	6.2021	9.1142	12.1318
13	6.1406	8.9518	12.0877
14	6.0982	8.8167	12.0590
15	6.0688	8.7030	12.0400
16	6.0483	8.6063	12.0274
17	6.0339	8.5236	12.0198
18	6.0239	8.4525	12.0130
19	6.0168	8.3914	12.0094
$n \geq 20$	f_1	f_2	f_3

Ionic systems

Closed-shell ions with limited charge in interstitial regions
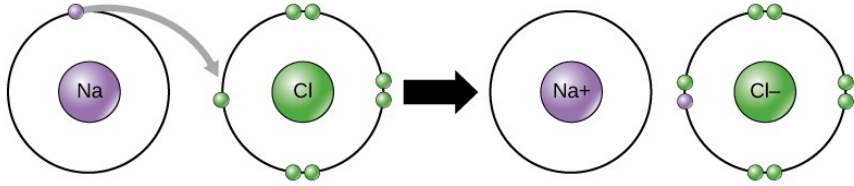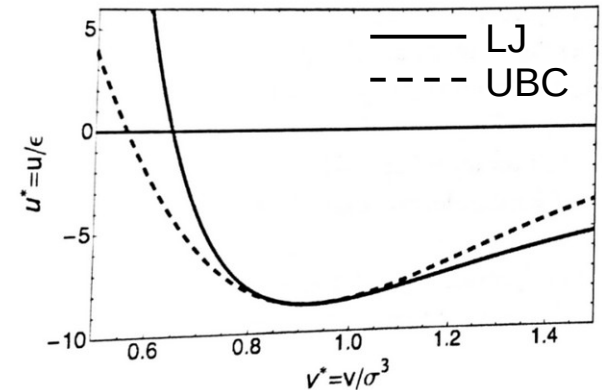

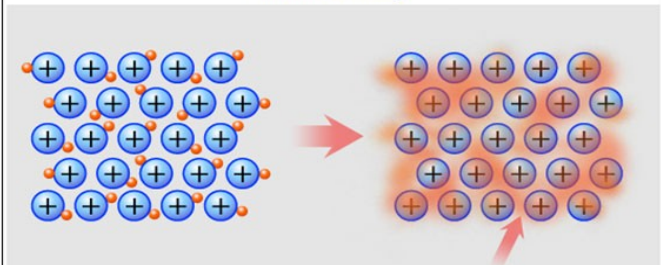
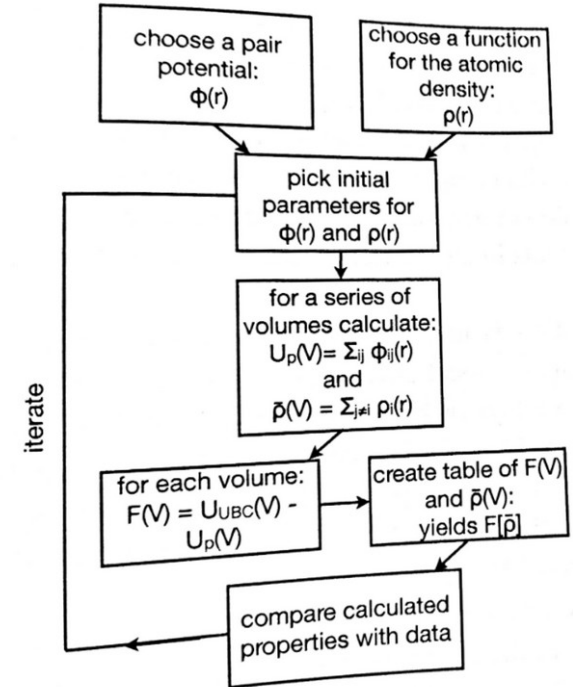Shell Model
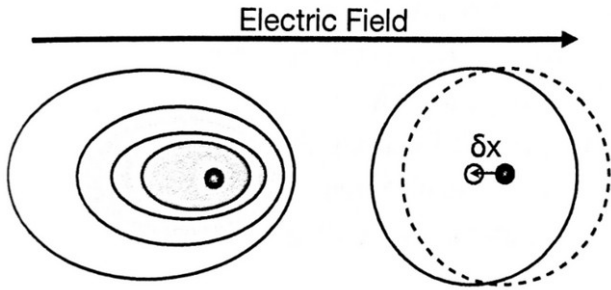
Metallic systems
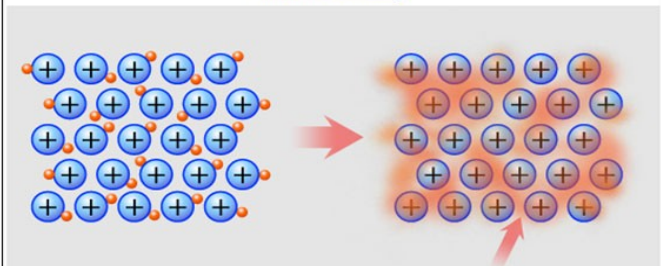
Volume-dependent potential

Universal Binding Curve
(purely empirical fit to data)

Metallic systems

Embedded-atom Model

choose a pair potential: $\Phi(r)$

choose a function for the atomic density: $\rho(r)$

pick initial parameters for $\Phi(r)$ and $\rho(r)$

for a series of volumes calculate:
$U_P(V) = \Sigma_{ij} \, \Phi_{ij}(r)$
and
$\bar{\rho}(V) = \Sigma_{j \neq i} \, \rho_i(r)$

for each volume:
$F(V) = U_{UBC}(V) - U_P(V)$

create table of $F(V)$ and $\bar{\rho}(V)$: yields $F[\bar{\rho}]$

compare calculated properties with data
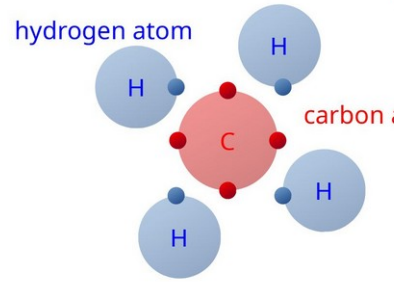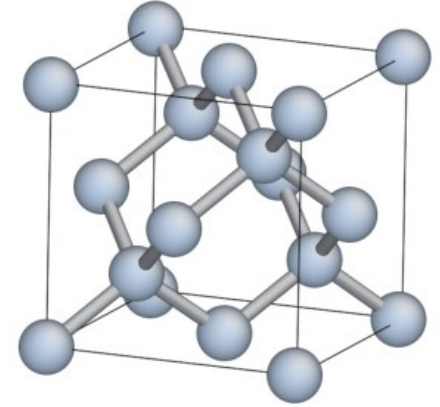
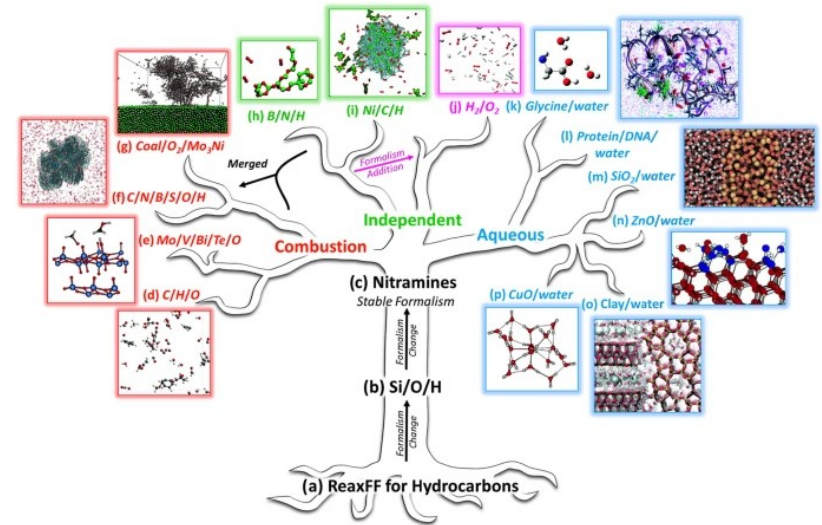iterate

Covalent systems

Angular-dependent potentials

Bond-order potentials

Mixed bonding systems

Reactive force potentials

npj Comput Mater 2, 15011 (2016).

Tight-binding Method

Graphene

Tight binding Hamiltonian with only NN hopping:

$$\hat{H} = -t \sum_{<i,j>} a_i^\dagger b_j + a_j^\dagger b_i$$

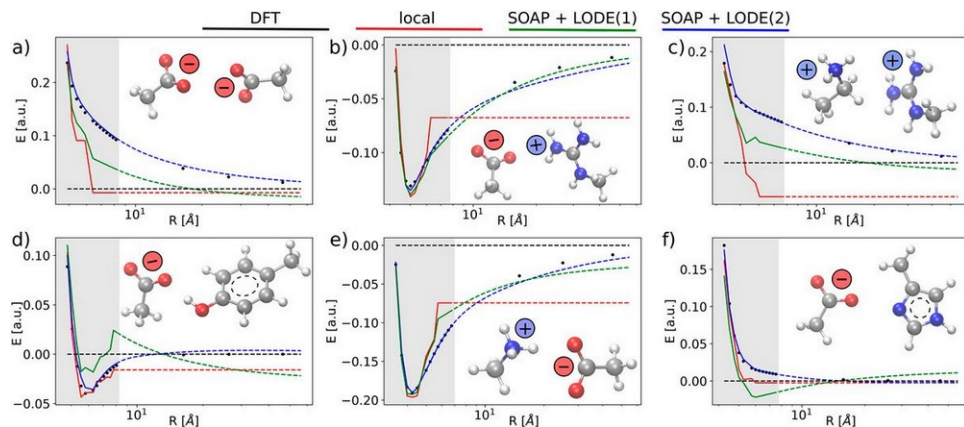A. H. C. Neto *et al.* Rev. Mod. Phys. **81** 109 (2009)
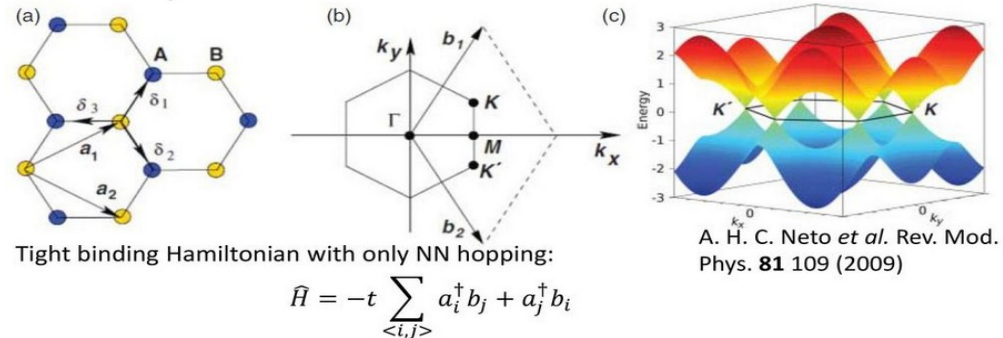
ML for interatomic potentials

Ab initio methods are still quite limited in terms of the length and time scales accessible
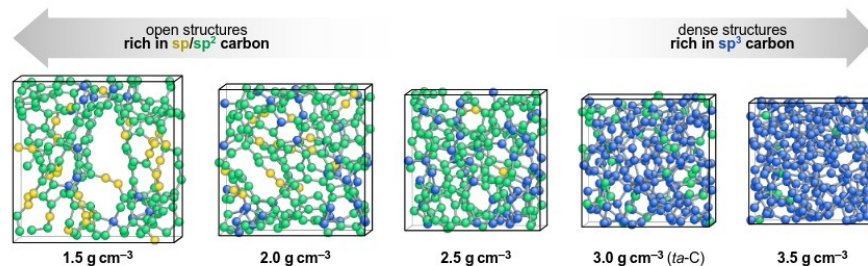
Current area of research: fit interatomic potentials to first-principles (usually DFT) data

Incorporating long-range interactions

J. Chem. Phys. 151, 204105 (2019)

Modeling amorphous systems
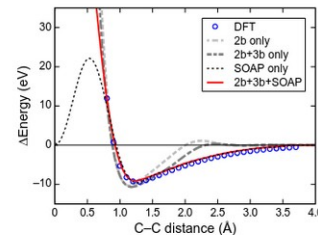

Phys. Rev. B 95, 094203 (2017)

FIG. 2. Potential-energy scans for an isolated carbon dimer. This plot, with DFT data as reference (blue), allows us to assess the use of different structural descriptors: all three combined are needed for a high-quality fit (see text).