



# Welcome to CHE 384T: Computational Methods in Materials Science

## Interatomic Potentials

LeSar Ch. 5

# Lecture Outline

Cohesive energy

Types of bonding

Interatomic potentials

- Basic forms

- Lennard-Jones potential

- Mie potential

- Born-Mayer and Morse potentials

Materials considerations

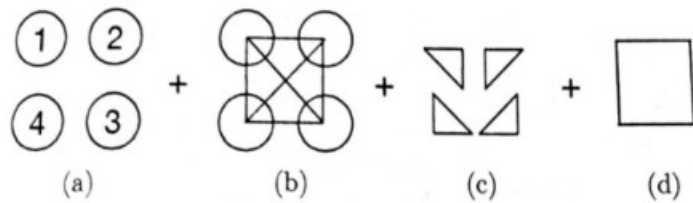
- ionic materials

- metals

- covalent materials

- mixed bonding environments

# Cohesive Energy



$$U = E_{\text{all atoms}}^{\text{total}} - \sum_i^N E_i$$

eok

// } energy isolated atom  
 $\mu_i$

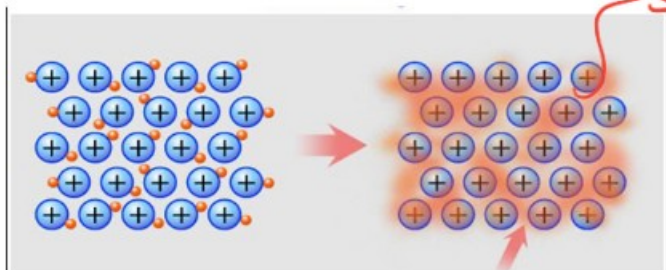
$$U = \underbrace{\sum_{i=1}^N v^{(1)}(\bar{r}_i)}_{\text{external potential}} + \underbrace{\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \phi_{ij}(r_{ij})}_{\text{pair-wise potential}} + \underbrace{\frac{1}{6} \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \lambda^{(3)}(\bar{r}_i, \bar{r}_j, \bar{r}_k)}_{\text{3-body potential}} + \dots$$

# Goals in constructing an interatomic potential

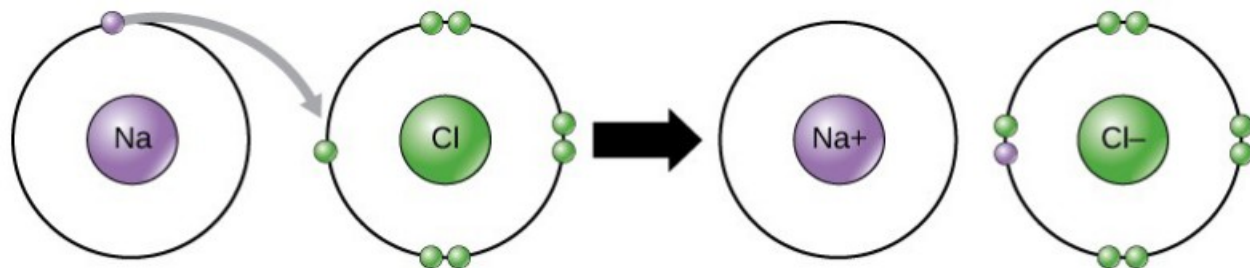
- Define an input and output
  - Input: distance
  - Output: potential
- To create a model that captures how molecules interact with each other
  - Condensed matter exists → must be an attractive component
  - Matter does not collapse on itself → must be a repulse component
- A *semi-quantitative* model can provide some insights on materials behavior
- Re-cast mathematical equations in a form that is conducive to coding

# Types of interactions

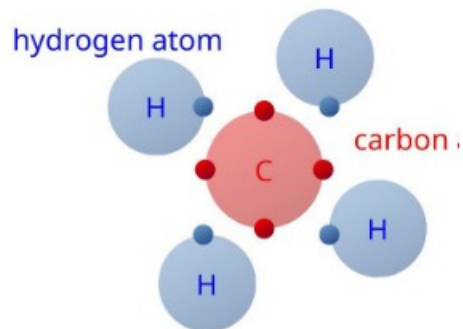
Metallic bonding



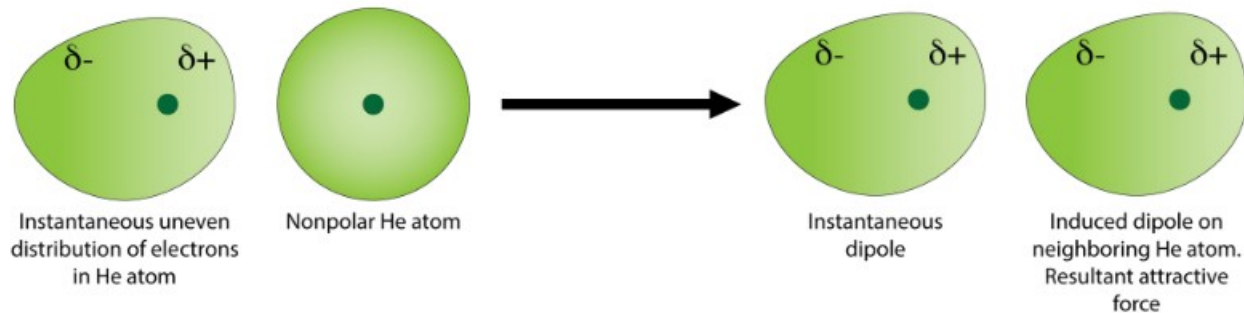
Ionic bonding



Covalent bonding



London dispersion forces



# Periodic trends

$1s^2 2s^1$

$1s^2 2s^2 2p^6 3s^1$

s-block

p-block

1 H Hydrogen																	2 He Helium																												
3 Li Lithium	4 Be Beryllium																	10 Ne Neon																											
11 Na Sodium	12 Mg Magnesium																	18 Ar Argon																											
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton																												
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon																												
55 Cs Caesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon																												
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson																												
<table><tr><td>58 Ce Cerium</td><td>59 Pr Praseodymium</td><td>60 Nd Neodymium</td><td>61 Pm Promethium</td><td>62 Sm Samarium</td><td>63 Eu Europium</td><td>64 Gd Gadolinium</td><td>65 Tb Terbium</td><td>66 Dy Dysprosium</td><td>67 Ho Holmium</td><td>68 Er Erbium</td><td>69 Tm Thulium</td><td>70 Yb Ytterbium</td><td>71 Lu Lutetium</td></tr><tr><td>90 Th Thorium</td><td>91 Pa Protactinium</td><td>92 U Uranium</td><td>93 Np Neptunium</td><td>94 Pu Plutonium</td><td>95 Am Americium</td><td>96 Cm Curium</td><td>97 Bk Berkelium</td><td>98 Cf Californium</td><td>99 Es Einsteinium</td><td>100 Fm Fermium</td><td>101 Md Mendelevium</td><td>102 No Nobelium</td><td>103 Lr Lawrencium</td></tr></table>																		58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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Alkali metals

Alkaline earth metals

Transition metals

Post-transition metals

Metalloids

Reactive nonmetals

Noble gases

Lanthanides

Actinides

Unknown properties

# Trends in the Periodic Table

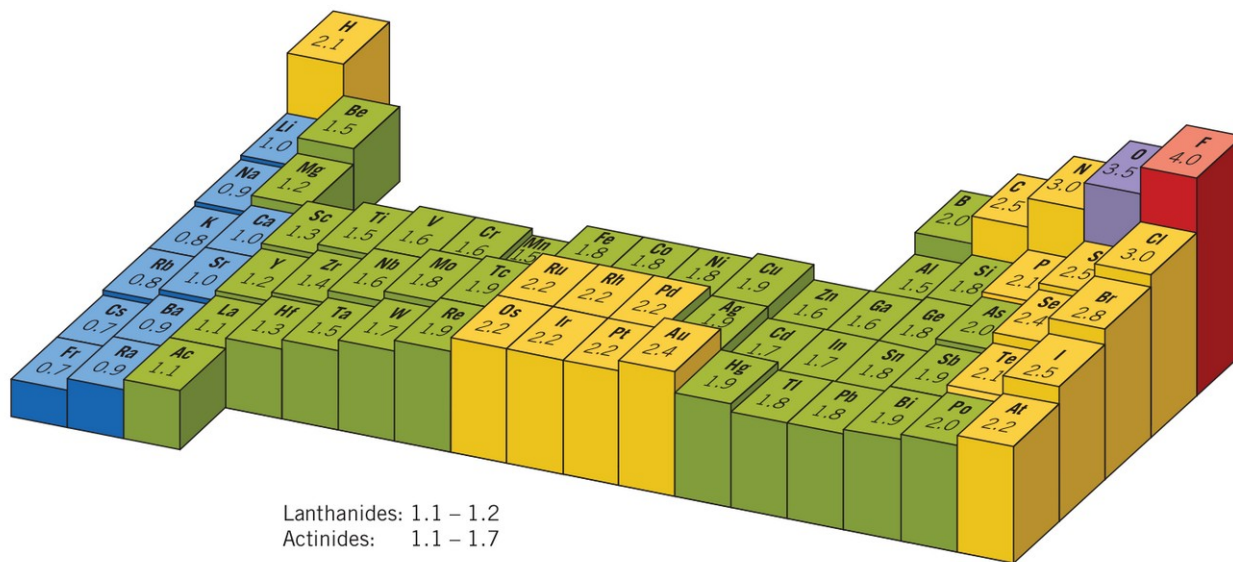
**Electronegativity:** tendency of an atom or a functional group to attract electrons toward itself.

Atoms prefer to have fully (or half) occupied electron shells → energetically stable

**Duet rule:**  $s^2$

**Octet rule:**  $s^2p^6$

**18-electron rule:** transition metals (varies a lot)

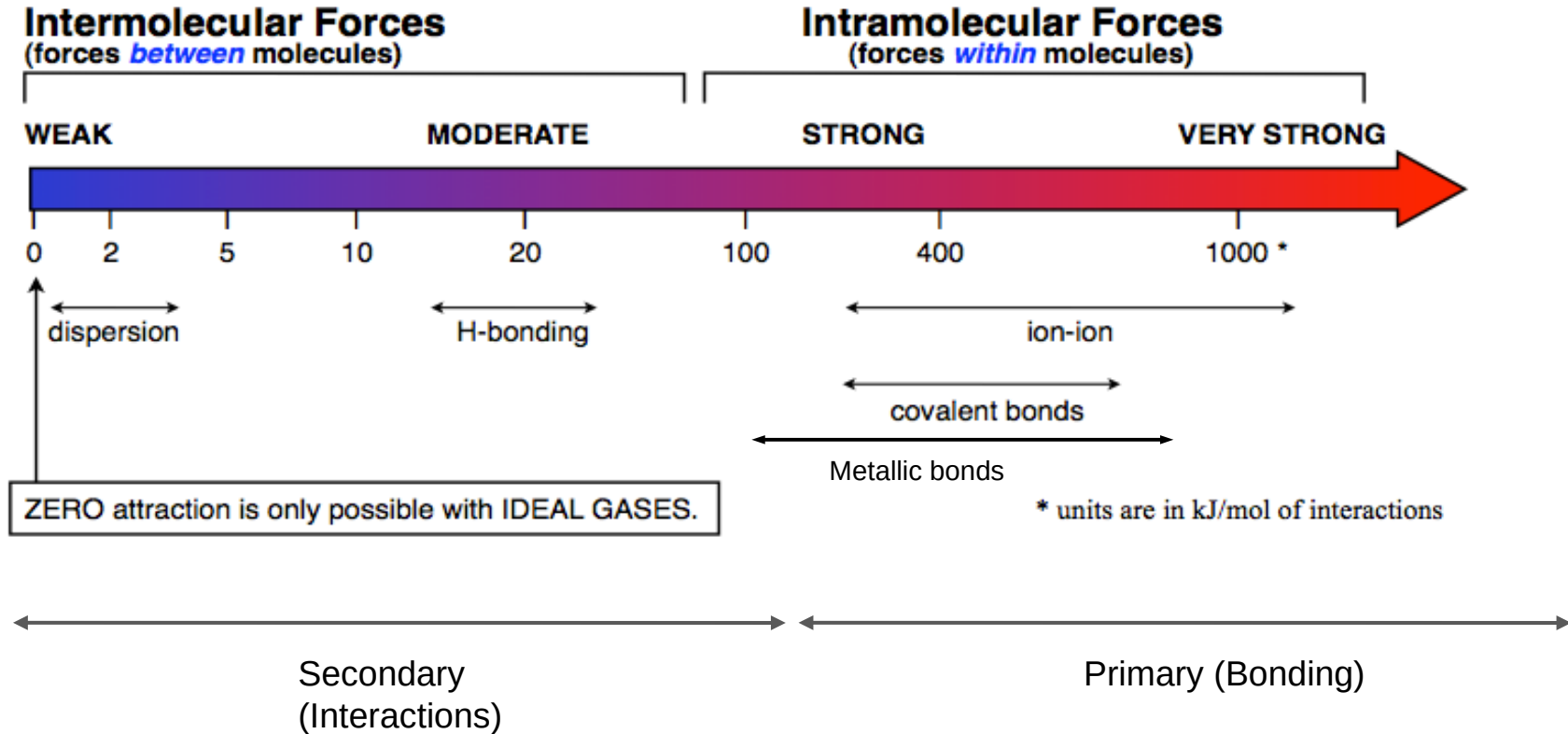


**Figure 2.9** The electronegativity values for the elements.

(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

repulsive

$$\phi_{SR}(\vec{r}) = Ae^{-\alpha r}$$

→ Pauli exclusion principle (QM)

Long-range interactions

attractive

→ Coulomb attraction

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$$\phi_{LR}(r) = -\frac{A}{r^6}$$

# Interatomic potentials: Lennard-Jones potential

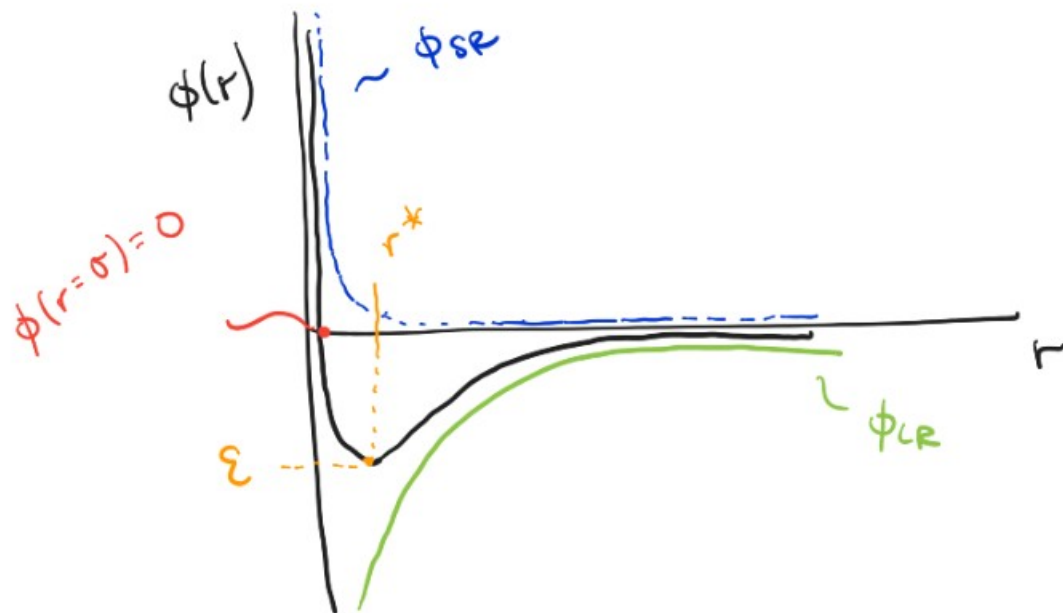
$$\phi(r) = \underbrace{\phi_{SR}(r)}_{\text{repulsive}} + \underbrace{\phi_{LR}(r)}_{\text{attractive}}$$

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

mat'l constants

$r^*$  = equilibrium bond distance

$\phi(r^*) = \epsilon$  binding energy  
aka cohesive energy



# Interatomic potentials: Lennard-Jones potential

Recasting into a more useful form

$$\phi_{LJ}(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$

$$\epsilon = \frac{A^2}{4B}$$

$$\sigma = \left(\frac{B}{A}\right)^{1/6}$$

$$\phi(r=\sigma) = 0$$

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

Scaled/reduced units

$$\phi^* = \phi/\epsilon$$

$$r^* = r/\sigma$$

$$\phi^*(r^*) = 4 \left[ \left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^6 \right]$$

# 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

closed-shell  
noble-gases  
(dispersion forces  
dominate)

not best  
descriptor  
 $\phi_{se} \sim \frac{1}{r^{12}}$

discrepancies  
of Ne  $\rightarrow$   
lighter atom  $\Rightarrow$   
larger zero-point  
motion (QM)

bulk modulus

$$B_o = V \frac{\partial^2 u}{\partial^2 V}$$

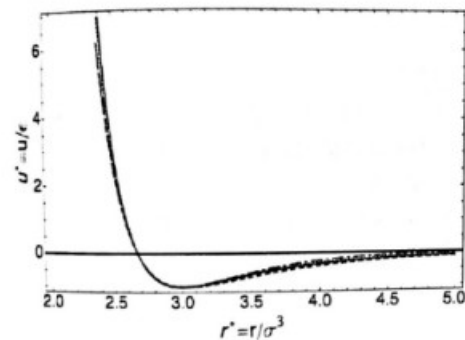
pressure

$$P = - \left( \frac{\partial u}{\partial V} \right) \Big|_{N, T=0K}$$

# Interatomic potentials: other forms

Mie Potential , fitting parameters  $\sigma, \epsilon, \underline{m}, \underline{n}$

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

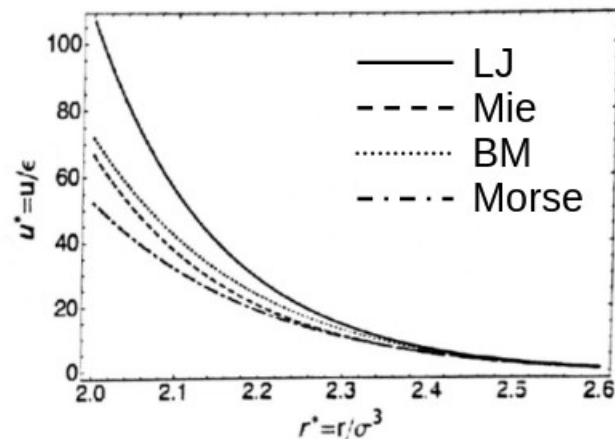


Born-Mayer Potential   
  $\rightarrow$  ionic systems   
  $\hookrightarrow \alpha \Rightarrow$  steepness

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

Morse Potential - metals

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



# 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 Lamé 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

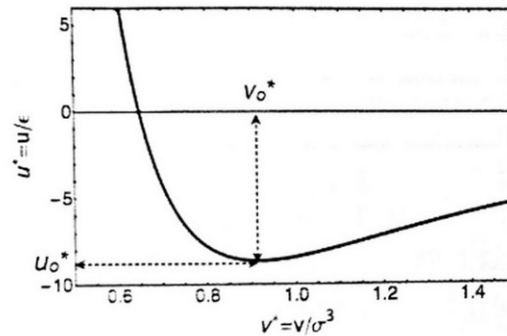
# Interatomic potentials: Lennard-Jones potential

Connection to Thermodynamic quantities

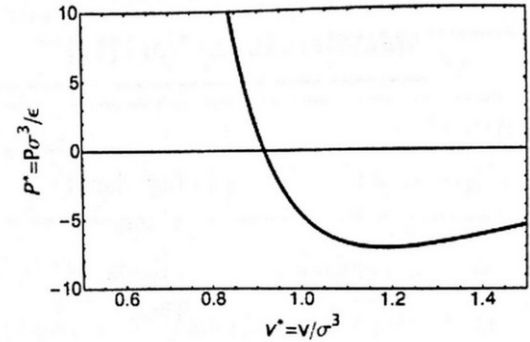
Regardless, can use the simplicity of Lennard-Jones potential to analytically compute some thermodynamic quantities

$$B = V \frac{\partial^2 u}{\partial v^2}$$

$$P = - \frac{\partial u}{\partial V}$$



(a)



(b)

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 proportional 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

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

for FCC  
equil. lattice param  $\sqrt{n} \tilde{r}$   
volume / atom  
cohesive energy / atom  
Bulk modulus

nn-distance

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

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

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

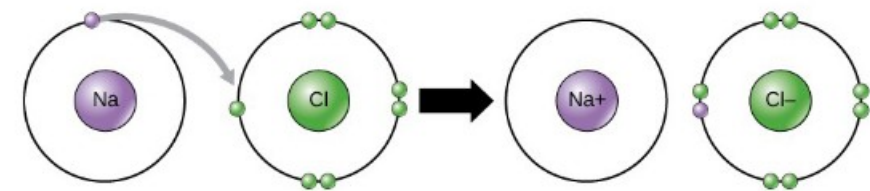
$$B_o = -8 \frac{u_o}{v_o} = 75 \frac{\epsilon}{\sigma^3},$$

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

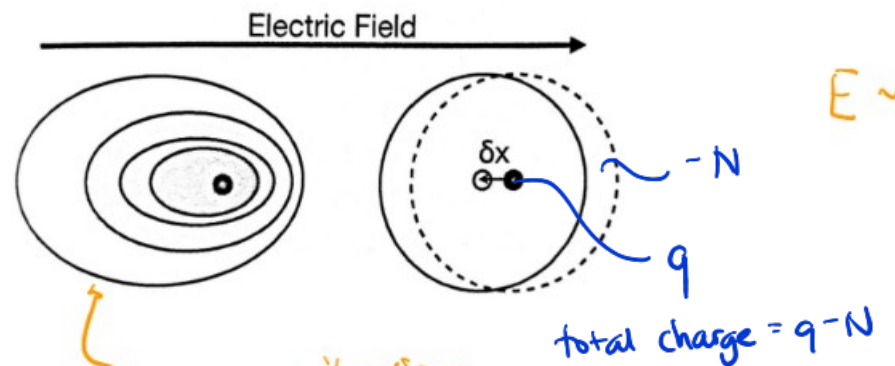
Closed-shell ions with limited charge in interstitial regions



$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left\{ \underbrace{\phi_{ij}(r_{ij})}_{\text{Born-Mayer}} + \underbrace{\frac{k q_i q_j}{r_{ij}}}_{\text{Coulombic attractive nucleus}} \right\}$$

Shell Model

→ harmonic oscillator of  $e^-$  cloud being polarized around (screened) nucleus



$$E \sim \frac{1}{2} k \delta x^2$$

$$k = N^2 / \alpha$$

$$\bar{\mu} = \alpha \bar{E} = -N \delta x \quad \text{polarizability}$$

$$F = k \delta x = -N \bar{E}$$

$$= \frac{N^2}{k} |\bar{E}|$$

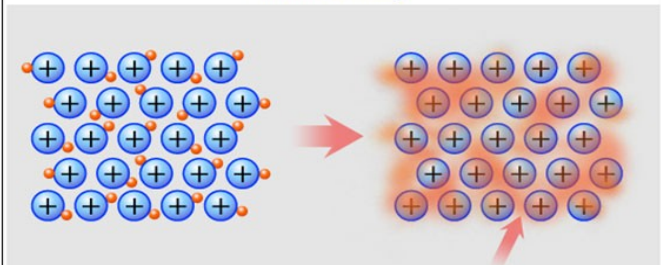
lattice vibrations (e.g. near low-symmetry environment) → defects  
→ drive fluctuations of  $e^-$  cloud  
lead to small finite  $\bar{E}$

• partition Coulomb energy into core+shell, core-cores, shell-shell interactions

# Metallic systems

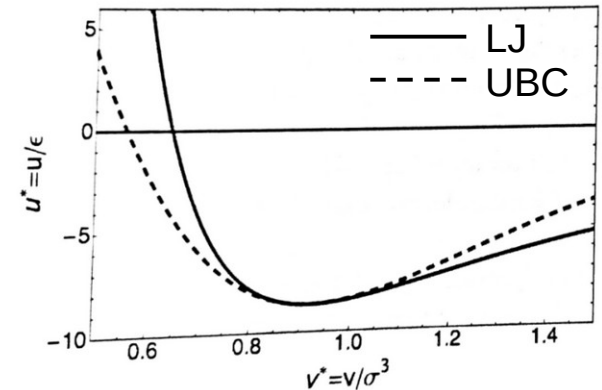
Universal Binding Curve  
↳ empirical

$$u_{\text{UBC}} = u(B, v, E_{\text{sublimation}})$$

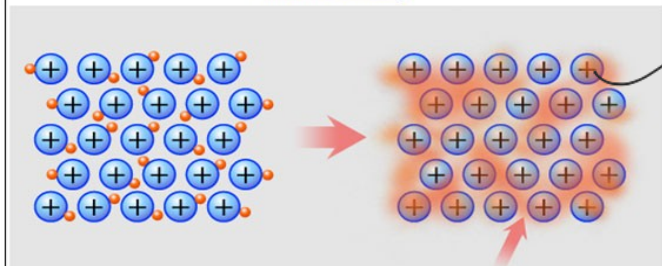


Volume-dependent potential

Universal Binding Curve  
(purely empirical fit to data)



# Metallic systems



local  $\rho(\vec{r}) \rightarrow$  slowly varies across material

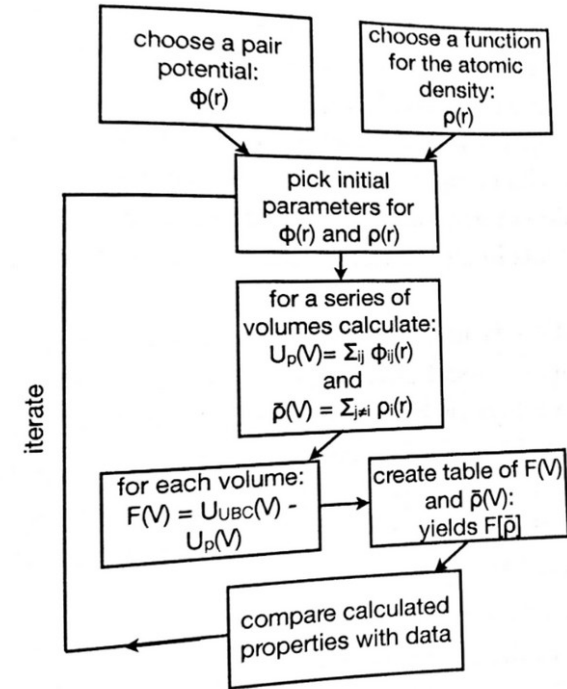
Embedded-atom Model - sums of local  $e^-$  density  
inspired by DFT

$$U = \sum_i F_i \left[ \sum_{j \neq i} f_{ij}(r_{ij}) \right] + \frac{1}{2} \sum_i \sum_j \phi_{ij}(r_{ij})$$

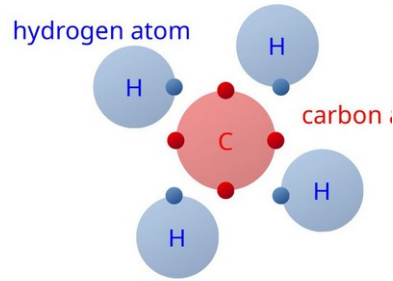
functional  
non-linear many-body interactions

pair-potential

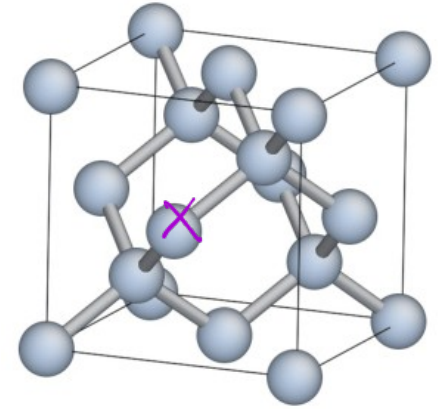
approx. local  $e^-$  density, dep. on  $r_{ij}$



# Covalent systems



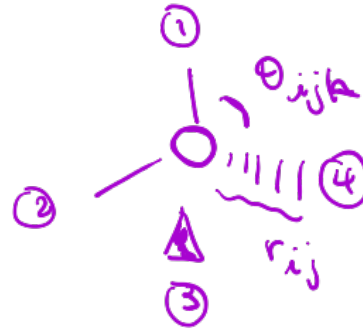
directional bonding interactions  
anisotropic interactions



Angular-dependent potentials

Stillinger-Weber potential

$$\vec{r}_{ij} \cdot \vec{r}_{ik} = 2 r_{ij} r_{ik} \cos \theta_{ijk}$$



~ limited to tetrahedral

Bond-order potentials

$$U = \sum_i E_i$$

$$E_i = \frac{1}{2} \sum_{j=1}^{z_i} \left[ a e^{-\alpha r} - \frac{C}{z_i^{1/2}} e^{-\beta r} \right]$$

use to tune strength of bond

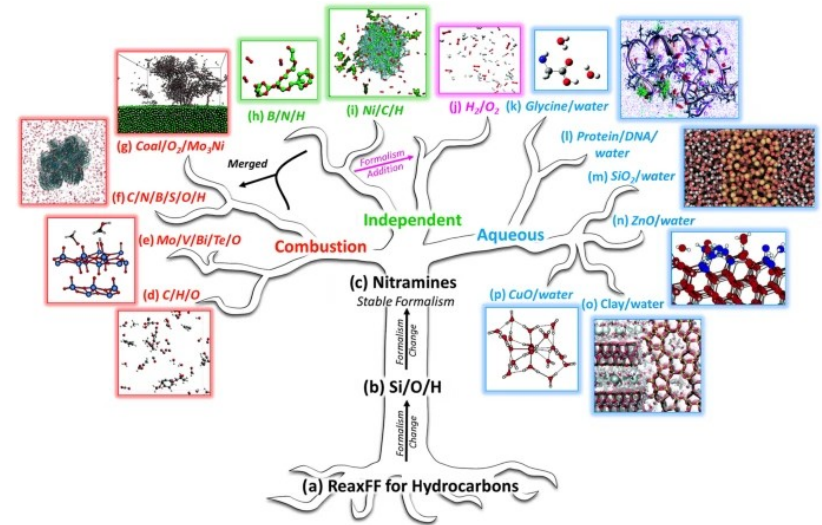
$b = C Z^{1/2}$   
bond-order parameter

$Z \rightarrow \# \text{ nn}$

# Mixed bonding systems

Reactive force potentials

Reax FF



npj Comput Mater 2, 15011 (2016).

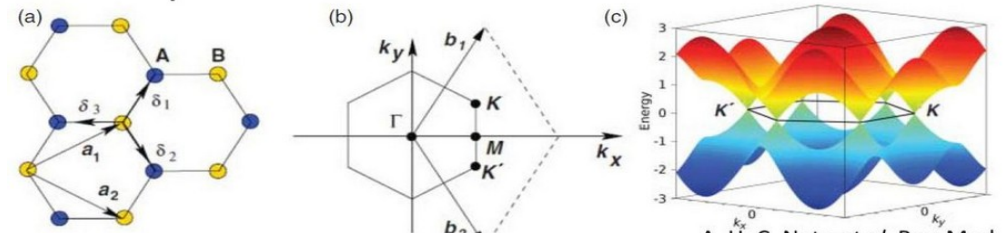
Tight-binding Method

↳ approx to QM

① develop Hamiltonian  
KE, PE

② solve eigenvalues (energies)  
eigenvectors (wavefunctions)

## Graphene



Tight binding Hamiltonian with only NN hopping:

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

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

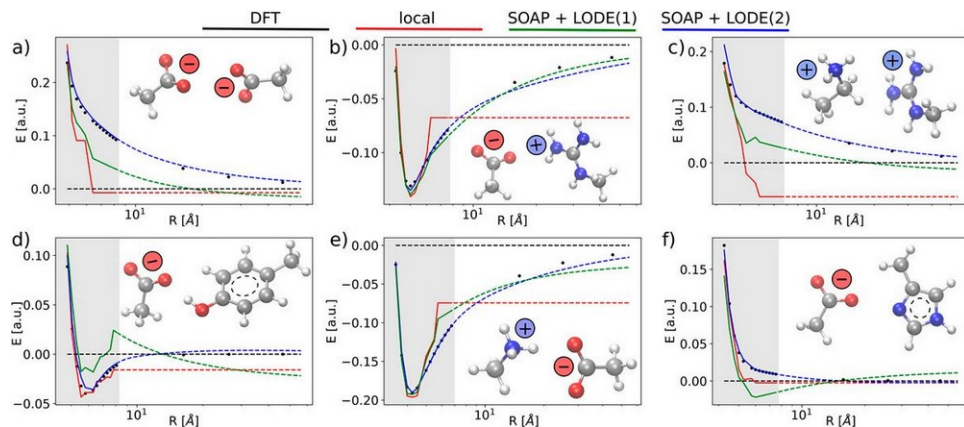


# ML for interatomic potentials

*Ab initio* methods are still quite limited in terms of the length and time scales accessible

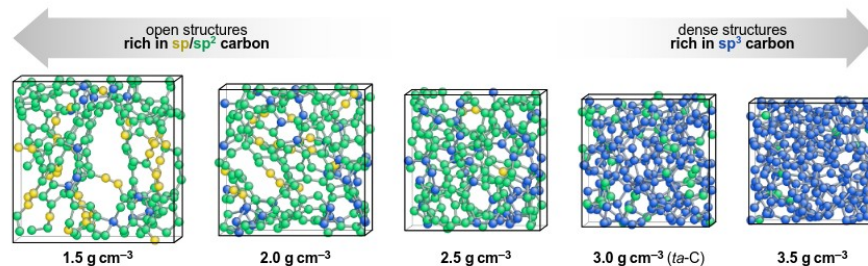
Current area of research: fit interatomic potentials to first-principles (usually DFT) data

Incorporating long-range interactions



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

Modeling amorphous systems



Phys. Rev. B 95, 094203 (2017)

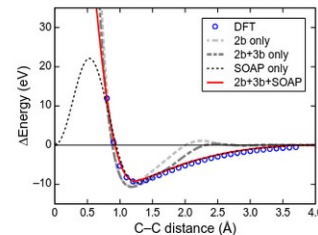


FIG. 2. Potential-energy scans for an isolated carbon dimer. This plot, with DFT data as reference (blue), allows us to assess the use of different structural descriptors: all three combined are needed for a high-quality fit (see text).