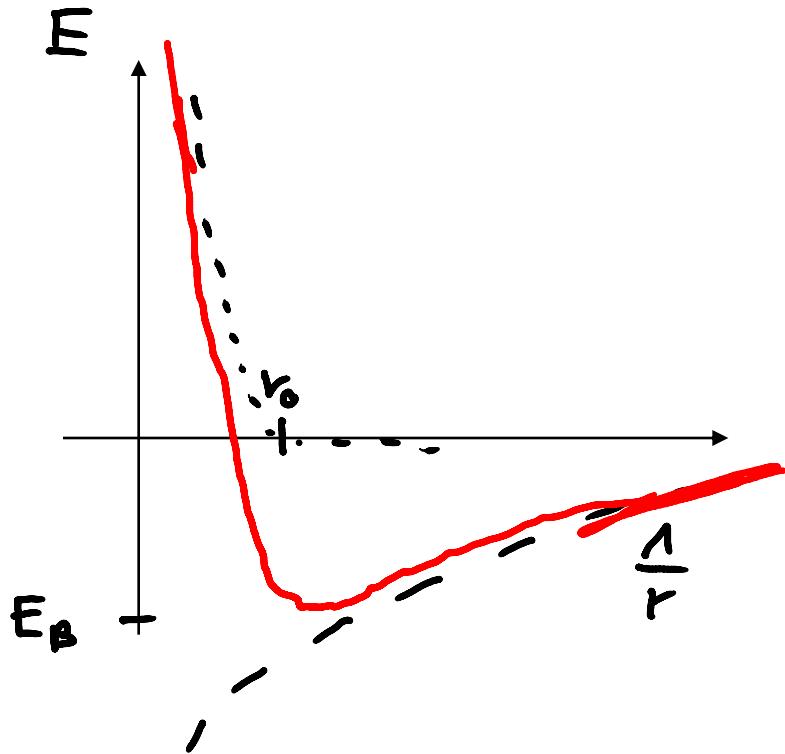


Chapter 01

Atomic interactions and forces

Coulomb and Born-Meyer potential ionic attraction

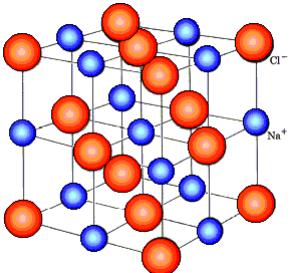


$$E_{\text{attr}} = - \frac{e^2}{4\pi\epsilon_0 r}$$

$$E_{\text{rep}} = B e^{-r/s}$$

How to find B and s ?

- 1) From QM calculation
- 2) From macroscopic experiments using NaCl crystals



How to obtain B and ρ ?

$$E_{\text{attr}} = N \sum_j \frac{\pm e^2}{4\pi\epsilon_0 r_j} = N \frac{e^2}{4\pi\epsilon_0 r_0} \sum_j \frac{\pm 1}{P_j} \quad // r_j = r_0 P_j$$

$\alpha = - \sum_j \frac{\pm 1}{P_j}$ Madelung constant, depends only on structure

$$E = -N \left(\frac{e^2}{4\pi\epsilon_0 r_0} \alpha - Z B e^{-r_0/s} \right) \quad Z \text{ number of next neighbors}$$

$$\left. \frac{dE}{dr} \right|_{r=r_0} = 0 \quad 1^{\text{st}} \text{ Equation to determine } B, s : r_0 \text{ from X-Ray diffraction experiments}$$

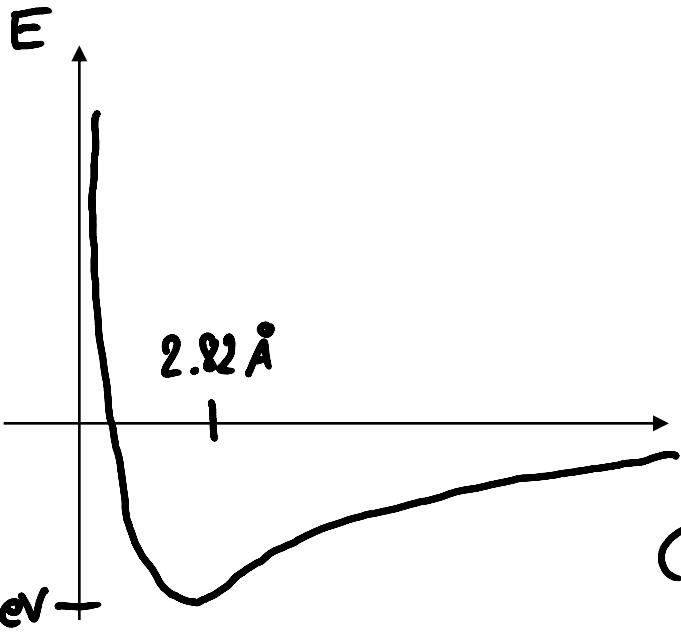
$$dE = -pdV - \frac{dp}{dV} - \frac{d^2E}{dV^2} \quad \frac{1}{\kappa} = -V \frac{dp}{dV} = V \frac{d}{dV} \left(\frac{dE}{dr} \frac{dr}{dV} \right) \Rightarrow 2^{\text{nd}} \text{ Eq.}$$

κ from compression experiments

$$\frac{1}{\kappa} = \frac{1}{18r_0} \left(\frac{6B}{s^2} e^{-r_0/s} - \frac{e^2}{2\pi\epsilon_0 r_0^3} \alpha \right)$$

$$\boxed{\kappa = \frac{1}{V} \frac{dV}{dp}}$$

Coulomb and Born-Meyer potential for NaCl



$$r_0 = 2.82 \text{ \AA}$$

$$\sigma = 0.322 \text{ \AA}$$

$$B = 1030 \text{ eV}$$

$$E_{13} = \frac{e^2}{4\pi\epsilon_0 r_0} \times \left(1 - \frac{\sigma}{r_0}\right)$$

Coulomb energy dominates

$$k_B T = 7.92 \text{ eV} \rightarrow T = 91879 \text{ K}$$

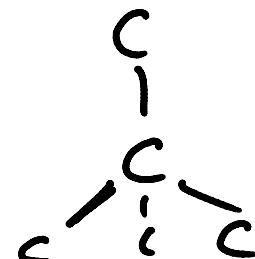
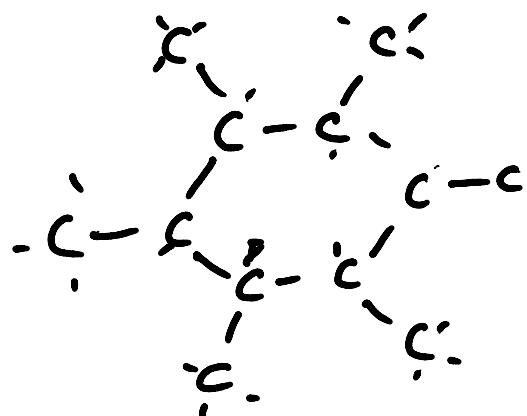
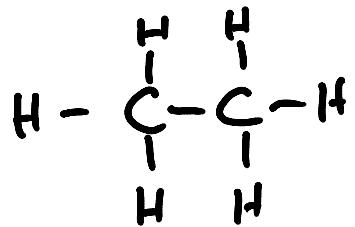
$$T_{\text{melting}} = 1074 \text{ K}$$

$$T_{\text{sublimation}} = 500 \text{ K}$$

Linde mann criterium: Crystal melts when vibrations are
 $\approx 10-15\%$ of r_0

Interatomic potential for covalent bonds

Problem: What is the interaction potential between two carbon atoms in different molecules or materials?



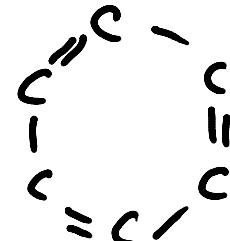
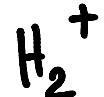
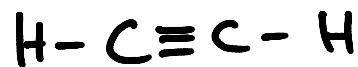
Repulsion : Pauli principle , inner electrons (s-character)

Attraction : Overlap of partially filled orbitals, binding molecular orbitals

$$E = \sum_i V_1(r_i) + \sum_{i < j} V_2(r_i, r_j) + \sum_{i < j < k} V_3(r_i, r_j, r_k) + \dots$$

Bond order

$$N \equiv N$$



$$S = 1,607$$

$$S = 3$$

$$S=1 \quad S=3 \quad S=1$$

$$S = \frac{1}{2}$$

Pauling $S_{ij} = \exp\left(\frac{d_0 - d_{ij}}{b}\right)$ $b = 0.35 \text{ \AA}$

$$C-C \quad 1.54 \text{ \AA}$$

$$C=C \quad 1.34 \text{ \AA}$$

$$C \equiv C \quad 1.20 \text{ \AA}$$

Bond order, coordination, and periodic table of elements

The more neighbors an atom has, the weaker is each bond

	IA	IIA	IIIB	IVB	VB	VIIB	VIIB	VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	0	
1	H 1.008																He 4.03	
2	Li 6.939	Be 9.012																
3	Na 22.990	Mg 24.312																
4	K 39.102	Ca 40.08	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.69	Cu 65.54	Zn 65.37	Ga 69.72	Ge 72.59	As 74.922	Se 78.96	Br 79.909	Kr 83.80
5	Rb 85.47	Sr 87.62	Y 88.905	Zr 91.22	Nb 92.906	Mo 95.94	Tc (99)	Ru 102.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.40	In 114.82	Sn 118.69	Sb 121.75	Te 127.60	I 126.90	Xe 131.30
6	Cs 132.91	Ba 137.34		Hf 178.49	Ta 180.0	W 183.85	Re 186.2	Os 190.2	Ir 192.2	Pt 195.09	Au 196.97	Hg 200.59	Tl 204.38	Pb 209.17	Bi 208.98	Po (210)	At (210)	Rn (222)
7	Fr (223)	Ra (226)																
			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
			La 138.91	Ce 140.12	Pr 140.91	Nd 144.24	Pm (145)	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.92	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97	
			89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
			Ac (227)	Th (232.04)	Pa (231)	U (238.03)	Np (237)	Pu (242)	Am (243)	Cm (247)	Bk (249)	Cf (251)	Es (254)	Fm (253)	Md (256)	No (253)	Lr (257)	

high coordination
many bonds
closed packed Xtal
metallic

low coordination
single bond
diatomic molecules
covalent

Bond order potential (BOP)

$$E_B = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V_R(r_{ij}) + \beta_{ij} V_A(r_{ij}) \right]$$

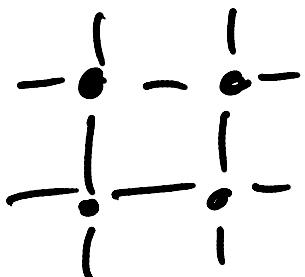
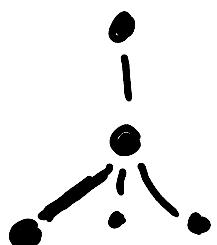
↑ atoms ↑ neighbors

$$V_R = A \exp(-\lambda_1 r_{ij}) \quad V_A = -B \exp(-\lambda_2 r_{ij}) \quad \text{Morse potential}$$

β_{ij} many-body coupling, depends on bond length and angle

Higher coordination Z , weaker bond $\Rightarrow \beta_{ij} \propto Z^{-\delta}$

For $\beta_{ij} \propto Z^{1/2}$ $\Rightarrow E_B$ per atom does not depend on Z



For pure $\beta_{ij} = Z^{-\delta}$ dependence
diamond is equally possible to
"square graphene"

Tersoff BOP for carbon

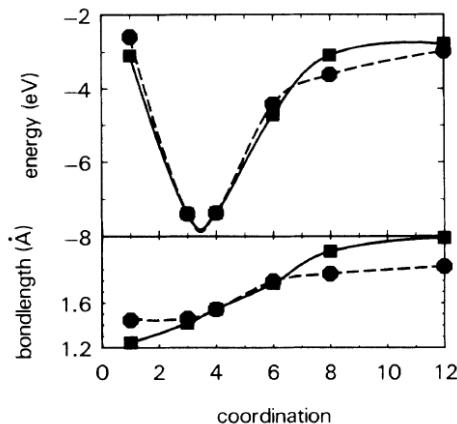
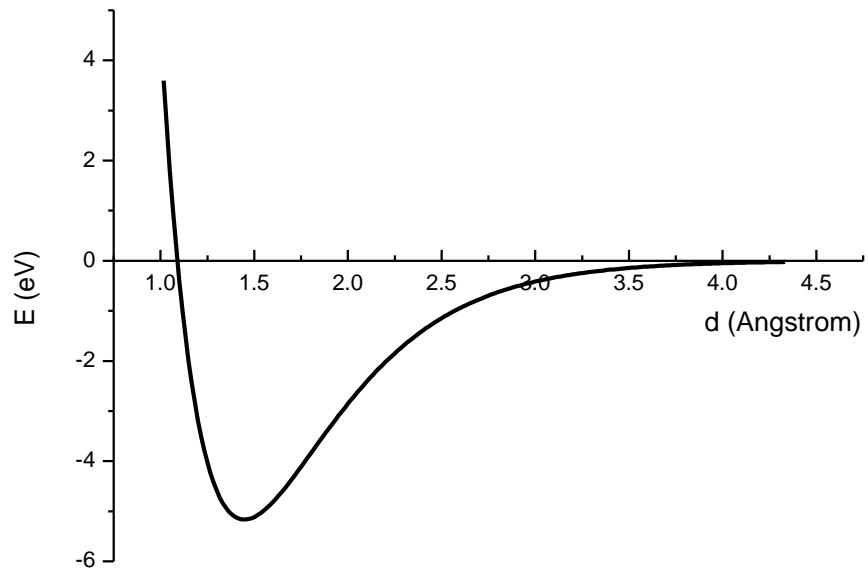


FIG. 1. Cohesive energy per atom (eV), and bond length (\AA), plotted vs atomic coordination number, for several real and hypothetical polytypes of carbon: C_2 dimer molecule, graphite, diamond, simple cubic, bcc, and fcc. Squares are experimental values for observed phases, and calculations of Yin and Cohen (Ref. 1) for hypothetical phases. Circles are results of the present model. Lines are spline fits to guide the eye.



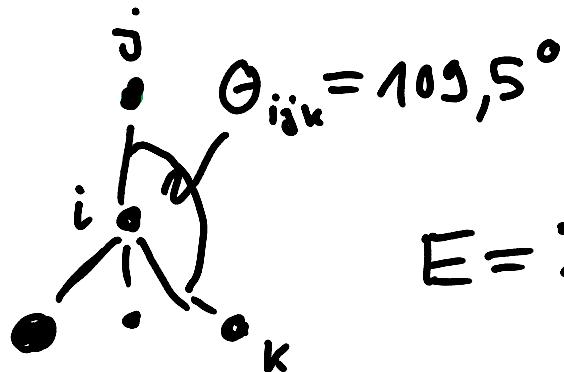
The resulting parameters for carbon are as follows:

$$\begin{aligned} \cancel{A = 1393.6 \text{ eV}, \quad B = 346.74 \text{ eV}, \quad \lambda_1 = 3.4879 \text{ \AA}, \quad \lambda_2} \\ \cancel{= 2.2119 \text{ \AA}}, \quad \beta = 1.572.4 \times 10^{-7}, \quad n = 0.72751, \quad c = 38049, \\ \cancel{d = 4.3484, \quad h = -0.57058, \quad R = 1.95 \text{ \AA}, \quad D = 0.15 \text{ \AA}}. \end{aligned}$$

⇒ Parameters for B_{ij}

Stillinger-Weber potential

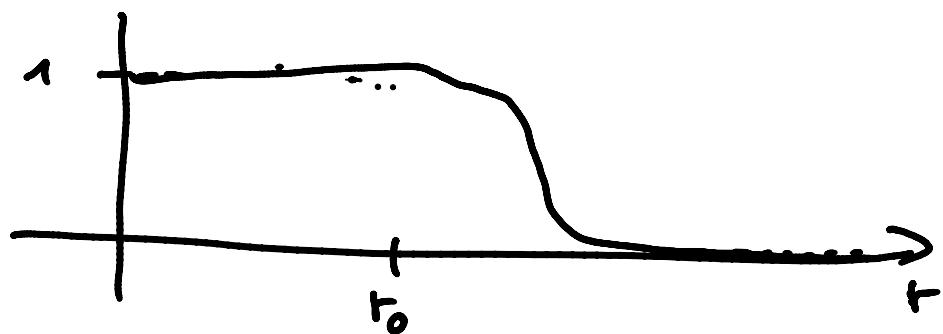
Effective potential for simulation tetrahedral structures.



$$\cos(109,5^\circ) = -\frac{1}{3}$$

$$E = \sum_i \left[\sum_{i < j} V_2(r_i, r_j) + \sum_{i < j < h} g \left(\cos \theta_{ijk} + \frac{1}{3} \right)^2 \right]$$

In all potentials, simulations make use of cut-offs



Taylor expansion of Lennard-Jones potential

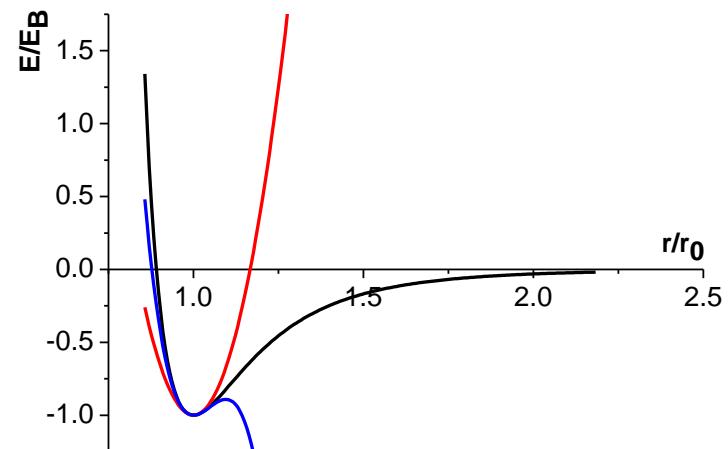
$$E(r) = E(r_0) + \left[\frac{dE}{dr} \right]_{r_0} (r - r_0)$$

$$+ \frac{1}{2} \left[\frac{d^2 E}{dr^2} \right]_{r_0} (r - r_0)^2 + \frac{1}{6} \left[\frac{d^3 E}{dr^3} \right]_{r_0} (r - r_0)^3 + \dots$$

$$E(r) = E_B + a(r - r_0)^2 - b(r - r_0)^3$$

$$a = \frac{1}{2} \left[\frac{d^2 E}{dr^2} \right]_{r_0} > 0 = \frac{1}{2} \left(72 \frac{E_B}{r_0^2} \right)$$

$$b = -\frac{1}{6} \left[\frac{d^3 E}{dr^3} \right]_{r_0} > 0 = \frac{1}{6} \left(1512 \frac{E_B}{r_0^3} \right)$$



Thermal expansion of a crystal I

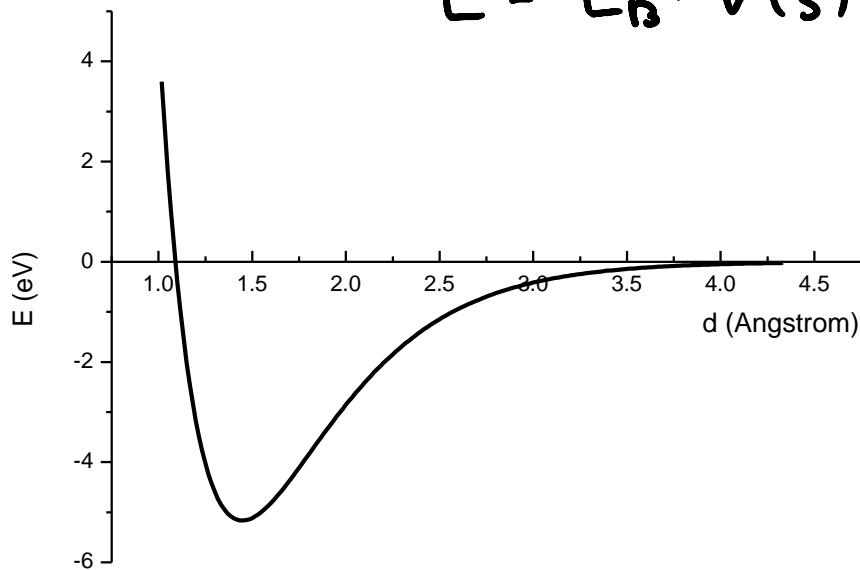
$$s = r - r_0$$

$$\bar{g} = \frac{\int s e^{-\frac{E(s)}{kT}} ds}{\int e^{-\frac{E(s)}{kT}} ds}$$

$$= \frac{\int s e^{-\frac{V(s)}{kT}} ds}{\int e^{-\frac{V(s)}{kT}} ds}$$

Small s approximation

$$E = E_B + V(s)$$



$$e^{-\frac{V(s)}{kT}} = e^{-\frac{as^2 - bs^3}{kT}}$$

$$= e^{-\frac{as^2}{kT}} \left(1 + \frac{bs^3}{kT}\right)$$

Thermal expansion of a crystal II

$$\int_{-\infty}^{\infty} e^{-\frac{as^2}{kT}} \left(s + \frac{bs^4}{kT}\right) ds = \frac{b(kT)^{3/2}}{a^{5/2}} \int_{-\infty}^{\infty} x^4 e^{-x^2} dx = \frac{b(kT)^{3/2}}{a^{5/2}} \frac{3}{4} \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} e^{-\frac{as^2}{kT}} \left(1 + \frac{bs^3}{kT}\right) ds = \frac{(kT)^{1/2}}{a^{1/2}} \sqrt{\pi}$$

$$\bar{s} = \frac{3b k_B}{4a^2} T \quad \text{Linear coefficient of expansion}$$

$$\alpha = \frac{d}{dT} \frac{\overline{r-r_0}}{r_0} = \frac{3k_B b}{4a^2 r_0}$$

If $b=0$ (harmonic approximation) $\Rightarrow \alpha=0$

$$\alpha_{LJ} = \frac{183}{1296} \frac{k_B}{E_B} = 1,2 \times 10^{-3} \frac{1}{k} \quad \text{for Argon}$$