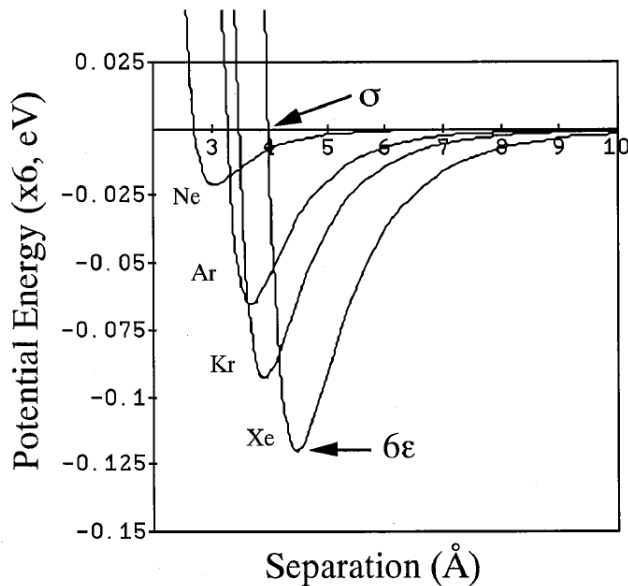




L-J Potential Energy Model (continued)

- The **Lennard-Jones potential** is a model describing the bond energy curves for VDW bonding.
- The L-J potential is more commonly (conveniently) of the form:
$$V_o(\mathbf{r}) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$
 where ε and σ are constants that depend on two bonding atoms.
- These new constants are defined in a more physically significant way. ε is the minimum value of the function or the depth of energy well, thus ε can be taken as a measure of the bond strength.
- σ is the value of r at which $V_o=0$, thus σ can be taken as the size of the repulsive core or the effective diameter of the hard sphere atom (interaction diameter).
- ε and σ parameters can be fitted to reproduce experimental data (Figure below for inert gases) or deduced from results of accurate quantum chemistry/mechanical calculations → Good agreement!

Energy v. Separation for the 6-12 inert gas potentials



- Energy is sum of long range attractive contribution (-) and a short range repulsion (+).
- Since dipole interaction is the origin of the attractive VDW force, bond strength increases with the atomic number, atomic mass (and molecular weight). **Why?**
 - Atoms with larger atomic number have more electrons, separated by a greater distance from the center of the positive charge.
 - This allows for larger dipole moments (more charge is separated over a greater distance) and thus greater interaction energies (stronger VDW bond).
- This accounts for the **first trend** in cohesive energy¹



L-J Potential Energy Model (continued)

- **Second trend**, is shape of molecule: molecules of the same molecular weight have greater bond strengths if they have larger aspect ratios (or less compact) shapes.
- The origin of this trend is that the bonding force is weak and *very short range*, so that electrons on adjacent molecules must get *very close* before the dipolar attractive force provides substantial cohesion.
- Whereas if molecule has a small aspect ratio (or more compact) shape, the electrons on atoms near the center can not contribute to the cohesive/bond force.

- In the overall scheme, cohesive dipolar interactions are present in all solids.
- However, they are usually so weak in comparison to primary bonds, such that they exhibit no more than a few % of the total cohesive energy.
- Thus, we consider VDW interactions to be significant only for crystals we discussed last time: 1) uncharged atoms or molecules without polar bonds, e.g. Ar and F₂, respectively, 2) uncharged molecules with polar bonds, but where the bonded ligands have roughly symmetric arrangement so molecule has no net dipole moment, e.g. CCl₄, alkanes, polyethylene, and 3) layered compounds such as graphite, WS₂, V₂O₅, TiS₂, where VDW plays important role in cohesion.
- This anisotropy (properties vary with direction) in bonding plays a large role in how structure determines properties, e.g. graphite has strong covalent bonding in-plane (C₆ basal planes), but weak VDW out-of-plane. This accounts for graphite's lubricity where interplanar shear occurs.



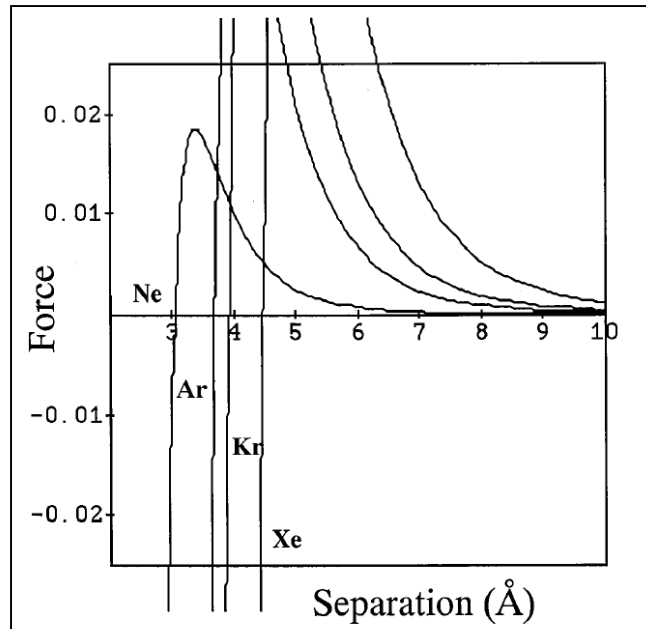
L-J Potential Energy Model (continued)

• To calculate the equilibrium separation (r_o) between two atoms, or in calculating lattice constant, we differentiate eq. (1) to find the minimum of $V_o(r)$:

$$F = -\frac{dV_o}{dr} = 0 = 4\epsilon\sigma^{12} \cdot -12\left(\frac{1}{r}\right)^{13} - 4\epsilon\sigma^6 \cdot -6\left(\frac{1}{r}\right)^7 \quad (2)$$

• Solving for r allows r_o to be determined: $r_o = 2^{1/6}\sigma = 1.12\sigma$ (3) **thus it's the size parameter, σ , that determines r_o .**

• Equivalent to saying the force function, $F(r)$, is the negative of the derivative w.r.t. r of Eq. (1).



• Figure on left for inert gases shows this relationship.

• The first derivative of the interatomic potential energy, with respect to distance, gives the force-displacement curve. The positive forces are attractive and the negative forces are repulsive, and the zero force point is the equilibrium separation (r_o).

• Good agreement (1-2%) between calculated & measured r_o 's.

• The L-J potential is a relatively good approximation and due to its simplicity often used to describe the properties of gases, and to model dispersion and overlap interactions in molecular models. It is particularly accurate for noble gas atoms and is a good approximation at long and short distances for neutral atoms and molecules, layered solids (graphite) and polymers.



L-J Potential Energy Model (continued)

• To calculate the cohesive energy per atom, U' , in eV/atom, we sum the potential energy (V) between each atom and all the other atoms in a crystal. The **interaction energy, U_j** , of the j -th atom with all the other $N-1$ atoms in the crystal is:

$$U_j = \sum_{i=1, i \neq j}^N V(r_i) \quad (4)$$

where r_i is distance to the i -th atom.

• There is a similar term for every atom in the crystal, so the **complete sum, U** , is:

$$U = \frac{1}{2} \sum_{j=1}^N U_j \quad (5)$$

Factor of $\frac{1}{2}$ is included to avoid counting each interaction twice.

• Assuming every atom is indistinguishable, we can **rewrite the complete sum**:

$$U = \frac{1}{2} N U_j \quad (6)$$

• Then the **cohesive energy/atom, U'** is total energy in eq. (6), divided by N :

$$U' = \frac{1}{2} U_j \quad (7)$$

• How do we actually compute U_j , in eq. (4) or eq. (7)?

• We use simplest approximation, i.e., since VDW forces are very weak, the nearest neighbor shells will significantly contribute to cohesive energy. Thus, we only need to compute the sum over the nearest neighbors. For our previous example, all inert gases have face-centered cubic (FCC) lattice, so **cohesive energy/atom** is:

$$U' = \frac{1}{2} \sum_{i=1}^{12} V(r_i) \quad \text{or} \quad U' = \frac{1}{2} N \cdot V(r) \quad (8)$$

• For all 12 neighbors (N), $V(r_i) = V(r_o) = -\epsilon$. Substitute into eq.(8), **cohesive energy/atom**:

$$U' = -6\epsilon \quad (9)$$

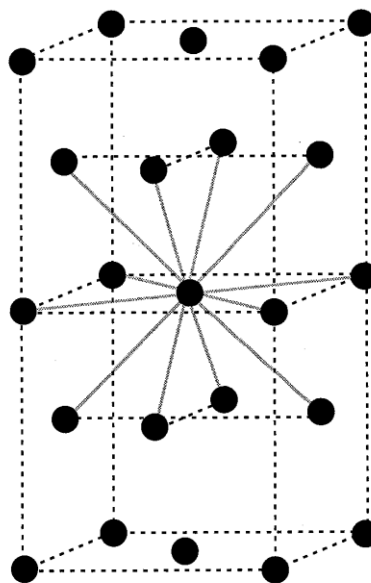
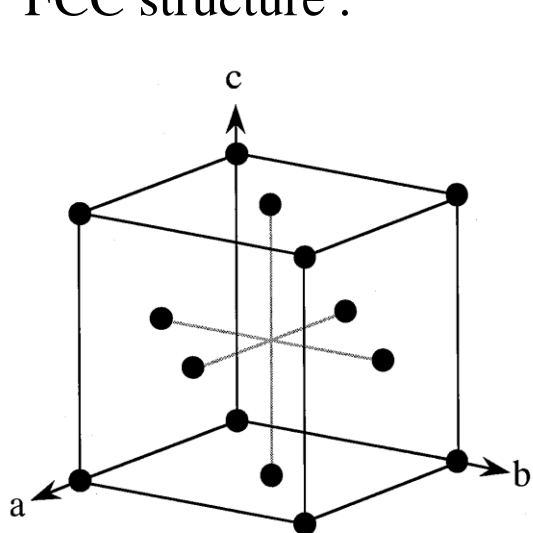
• We can also calculate this U'

• This approximation slightly underestimates the measured cohesive energy, since we have ignored all additional interactions (long range) with atoms outside of the nearest neighbor shell.

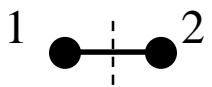
Recall FCC lattice

nearest neighbors (N) or coordination number (CN) is 12:

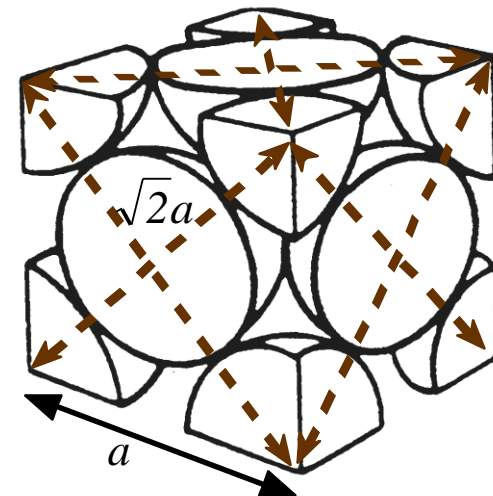
FCC structure :



The extended cubic F lattice (2 unit cells stacked along y-axis)

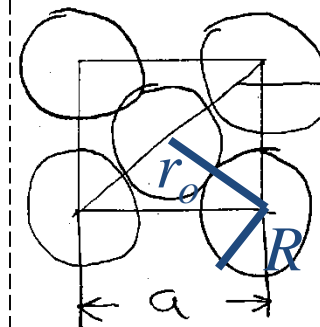


Pair energy (each atom's contribution),
each atom is partitioned



Close-packed directions:

$$\text{length} = 4R = \sqrt{2} a$$



$$\sqrt{2}a = 4R$$

$$a = 2\sqrt{2}R$$

$$2R = r_o$$

$$a = \sqrt{2}r_o$$

- This is a cubic face (F) center Bravais lattice.
- Lattice + basis vectors = crystal structure.
- 12-fold coordination of each lattice point (same atom) is identical.



L-J Potential Energy Model (continued)

•To correct errors from our neglect of long range interactions, we start by expressing all of the interatomic distances, r_i , as multiples of the shortest one, r_o .

•Thus eq. (8) becomes:
$$U' = \frac{1}{2} \sum_{i=1}^N V(\rho_i r_o) \quad (10)$$
 therefore determining **cohesive energy/atom:**
$$U' = 2\varepsilon \left[\sum_{i=1}^N \left(\frac{\sigma}{\rho_i r} \right)^{12} - \sum_{i=1}^N \left(\frac{\sigma}{\rho_i r} \right)^6 \right] \quad (11)$$

 ρ is a dimensionless parameter dependent on crystal structure (values are tabulated much like the Madelung constants)

amounts to evaluating the sums:
$$A_{12} = \sum_{i=1}^N (1/\rho_i)^{12} \quad A_6 = \sum_{i=1}^N (1/\rho_i)^6 \quad (12)$$
 Note: these sums are the same for isostructural crystals

•Minimizing eq. (11) to find equilibrium separation (r_o) results in:
$$r_o = \left(2 \frac{A_{12}}{A_6} \right)^{1/6} \sigma \quad (13)$$

•Note eq. (13) is similar to eq. (3) except the A_{12} and A_6 terms, since we are now including long-range interactions.

•For FCC crystal structure, $A_{12}=12.13$ and $A_6=14.45$, thus $r_o=1.09\sigma$, which differs from the nearest neighbor estimate we calculated in eq. (3), $r_o=1.12\sigma$, by only 3%.

•When the corrected value for U' is computed using new value for r_o & eq.(11):
$$U' = -8.6\varepsilon \quad (14)$$



L-J Potential Energy Model (continued)

- The differences between the values computed using the N.N. and L.R. interaction models are summarized:

parameter	nearest neighbor (N.N.)	long range (L.R.)	difference
r_0	1.12σ	1.09σ	3%
U'	-6ϵ	-8.6ϵ	30%

- What this means for FCC structures in terms of U' is 12 N.N. only contribute 70% of the total cohesive energy, and final 30% is supplied by the rest of crystal (next N.N. and so on.....).
- Relatively good agreement between measured and calculated parameters for inert gases.
- The L-J pair potential model has been successfully used to describe bonding in other systems.
- For example, the interaction between different segments on polymers: one LJ particle may represent a single atom on the chain (*explicit atom model*), a CH_2 segment (*united atom model*), or segment consisting of several CH_2 units (*coarse-grained model*). The united atom model has been shown to successfully reproduce explicit atom results for polymer melts.



An example of the significance of L-J Potential Model

- While the L-J pair potential, eq. (1), is intended as a physical model for VDW bonds, it is often extended empirically to model other types of crystals by adjusting the constants σ and ϵ .
- Assuming that regardless of physical mechanism governing interactions among atoms, the total energy of the system can be treated as sum of attractive and repulsive pair-wise contributions.
- Constants σ and ϵ are chosen such that pair-wise potentials reproduce known properties with accuracy.
- Empirical models constructed in this way can then be used to compute physical properties that are difficult, tedious or impossible to measure by experiment. While quantitative accuracy can not be expected, the relative energies computed from such models are often qualitatively meaningful and instructive.

• For example, a L-J model for Cu (FCC metal) was used to compute the surface energy/unit area (γ) as a function of surface normal. The surface energy can be defined as the work required for the creation of a unit area of surface. Creating new surfaces requires bond breaking. For a surface with a unit cell that contains N atoms in an area A , the γ is:

where U' is bulk potential energy/atom, V_o is the L-J potential defined in eq. (1) and r_{ij} is distance between i^{th} and j^{th} atom. Creating a surface breaks symmetry of the lattice so positions do not have same environment, thus need to compute sum over atom pairs.

$$\gamma = \frac{NU' \sum_i \sum_{j>1} V_o(r_{ij})}{A} \quad (15)$$

• Anisotropic γ is proportional to # bonds broken/area:

