Cohesive Energy of Secondary Bonds

- Substances held together by VDW bonds include 3 groups: 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 (shown), V₂O₅, TiS₂, where VDW plays important role in cohesion between atomic sheets (e.g., WS₂ hexagonal basal planes).

- Two main factors that affect the strength of bonding, or **cohesive energy**, the energy required to dismantle the components and separate them until there is no longer any interaction, of a material are 1) **molecular weight** & 2) **molecular shape**.

1) For melting points, as the cohesive energy increases more thermal energy is required to melt the material, so melting point is higher.

- MP and cohesive energy increases with the number of electrons or atomic number.
For **alkanes**, the molecular weight is proportional to number of electrons.

These solids are held together by VDW bonds and the strength of this force increases with MW, thus higher MP.

2) **Molecules with larger aspect ratios are bound with greater strength.**
- For example, the strength of the VDW bonds in the **isomers of pentane**, as indicated by their BP, varies with their molecular shape:
- **Each has same MW and number of electrons, thus change in cohesive energy (as measured by their BP) must be due to difference in molecular shape or configuration.**
- **Linear** n-pentane is more strongly bound than nearly **spherical** neopentane.
- **Larger aspect ratios** form stronger intermolecular bonds, i.e. the **linear** configuration, in comparison to the more compact (**spherical**) geometry, allows more of the electrons in each molecule to be in a close proximity with electrons in the adjacent molecules, thus they can interact more strongly.
Physical Model for the VDW Bond

• In all bonds the attractive force that holds atoms together is electrostatic.
• Since VDW bonds form between uncharged, closed-shell species, the electrostatic attraction must be dipolar in origin.

Origin of molecular attraction and repulsion:
• Recall temporary induced dipoles are random fluctuations of the electron density around an otherwise spherical atom/molecule that can create transient or temporary dipoles.
• The strength of the electric field around a dipole is proportional to the dipole moment and inversely proportional to the cube of the distance, \( r \), from the center of the dipole.
• The dipolar field created by one temporary dipole is thus able to “induce” a dipole in a neighboring atom by polarizing its electron density.
• The magnitude of the induced dipole moment is proportional to the temporary field and thus decreases with \( r^{-3} \).
• The interaction (attractive) energy is between the two dipoles is the product of two dipole moments divided by \( r^3 \), so it varies as \( r^{-6} \).
• This attractive dipolar energy between uncharged species is what causes inert gases to condense.
• Because of the \( r^{-6} \) dependence, this attraction is weak and acts only at relatively short ranges.
• Thus solids held together by VDW bonds usually have low melting points.
• As previously discussed for the attractive force in primary bonds, the attractive VDW force brings atoms together until the electron distributions (or clouds) on adjacent atoms begin to overlap. This creates a repulsive force.

• When the repulsion becomes strong enough to compensate the attraction, an equilibrium separation \( r_o \) is established.

• Thus, as the electron densities of the two atoms begin to overlap, electrons associated with the first atom have a tendency to occupy states on the second atom that are already occupied and vice versa.

• To prevent multiply occupancy, electrons must be promoted to higher energy states at a significant cost of energy.

• This interaction is strongly repulsive at short separations, but decreases rapidly at large separations.

• To summarize, neutral atoms and molecules are subject to two distinct forces in the limit of large distance and short distance: an attractive VDW force, or dispersion force, at long ranges, and a repulsion force, at short ranges, the result of overlapping electron orbitals, referred to as Pauli repulsion.
The attractive dipolar and repulsive short-range forces have been incorporated into a model known as Lennard-Jones model or “6-12” potential model.

The potential energy between two atoms, $V_o$, (pair potential) as a function of separation, $r$, is

$$V_o (r) = \frac{-A}{r^6} + \frac{B}{r^{12}}$$

where $A$ and $B$ are positive constants for attraction and repulsion, respectively.

This potential satisfies our requirements, since it shows an attractive $r^{-6}$ character and a strong, short-range repulsion $r^{-12}$.

Exponent of 12 was chosen for computational simplicity, in practice any exponent greater than 8 gives about the same result.

Ex: Calculate bond length ($r_o$) and bond energy ($V_o$) for Argon given $A$ and $B$ are $10.37 \times 10^{-78}$ J·m$^6$ and $16.16 \times 10^{-135}$ J·m$^{12}$, respectively.

The qualitative effect of the function described above is shown schematically in Figure ➞

When atoms are separated by distances $\gg d_o$ there is only weak attractive interaction ($d_A$).

Attraction increases as they get closer ($d_B$) and at point of contact ($d_C$), attraction is max. Attraction diminishes and repel each other at $d_D$.