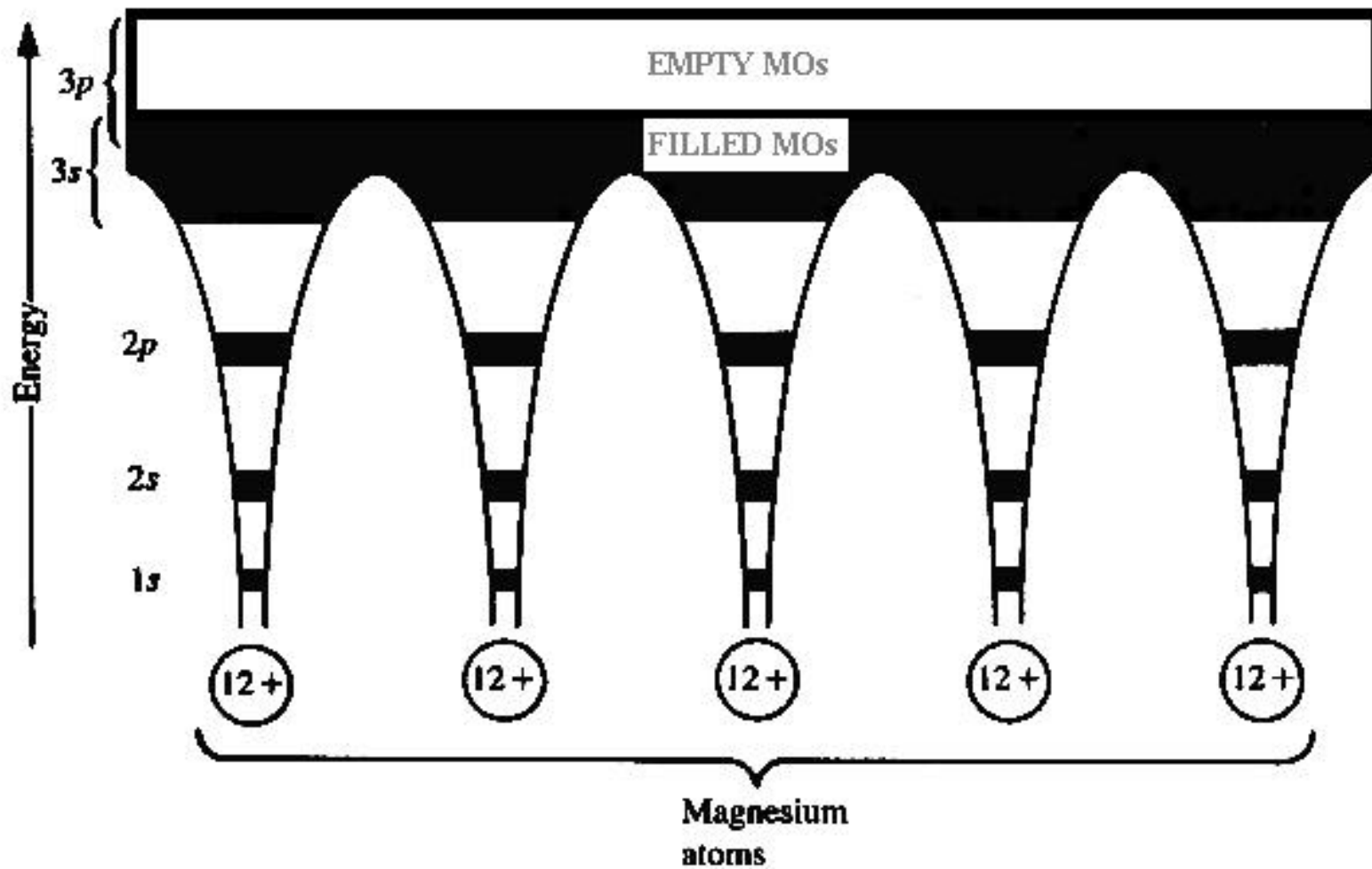


Band Structure of Magnesium



Bonding in Molecular Crystals

- These solids have properties that can be easily understood in terms of the properties of their components: **atoms of the Noble Gas family or neutral molecules.**
- Each molecule retains its identity when undergoing transformation either from the gas to the solid state or from the liquid to the solid state. These various states differ only in the balance between **the intermolecular potential energy and the kinetic energy** of the molecular assembly:
 - low T, low kinetic energy, predominance of the intermolecular attractions leads to the crystalline state.
 - high T, kinetic energy predominates and leads to gas state.

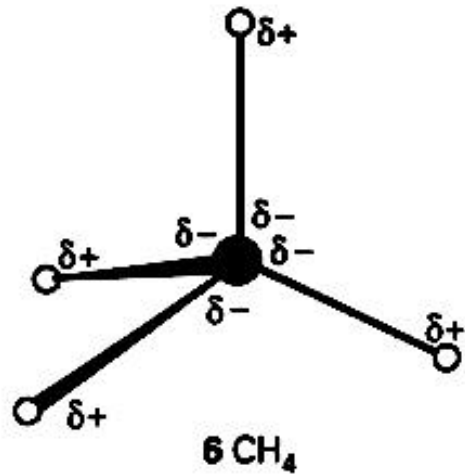
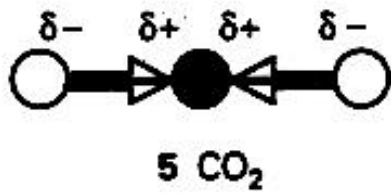
Nature of the Bonding in Molecular Crystals

- The electron distribution is very similar to that of free atoms for Noble Gas elements (He, Ne, Ar, Xe) or to that of free molecules. In all cases, the **components of molecular crystals have filled atomic/molecular orbitals.**
- There is no possibility for further bonding between the components of any molecular crystal.
- The cohesive energy of the crystal is then accounted for by the interactions which exist between neutral molecules or atoms with filled valence orbitals: **Van der Waals Interactions or Dispersion Forces.**

Van der Waals Interactions

- These intermolecular interactions whether attractive or repulsive are all of **electrostatic origin**.
- The attractive interactions between closed shell molecules can have different origins:
 - dipole - dipole interactions
 - dipole - induced dipole interactions
 - induced dipole - induced dipole interactions (dispersion forces)
 - hydrogen bonding
- Note that if one wishes to be rigorous about the estimation of these intermolecular interaction energies, one should consider interactions between **multipoles**.

Multipoles

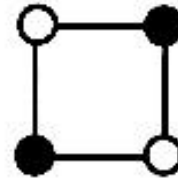


● Monopole

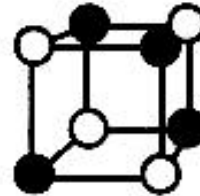
●—○ Dipole



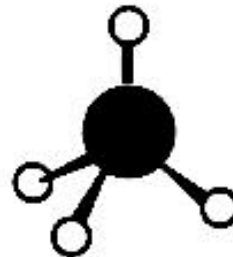
Quadrupole



Quadrupole



Octupole



Octupole

Dipole - Dipole Interactions

- The potential energy of interaction between two polar molecules (dipoles) when the dipoles are parallel is given by:

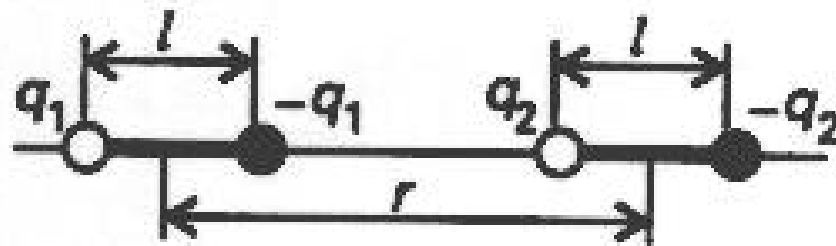
$$V = \frac{\mu_1 \mu_2}{4\pi\epsilon_0} \frac{f}{r^3} \quad f = 1 - 3 \cos^2(\theta)$$

- If the molecules were “freely” rotating then both $\langle f \rangle$ and $\langle V \rangle$ would be zero. However, since the mutual interaction energy depends on the orientation, the molecules are not really freely rotating, when they are in close proximity: The average potential energy for two rotating molecules (i.e. dipoles) is given by:

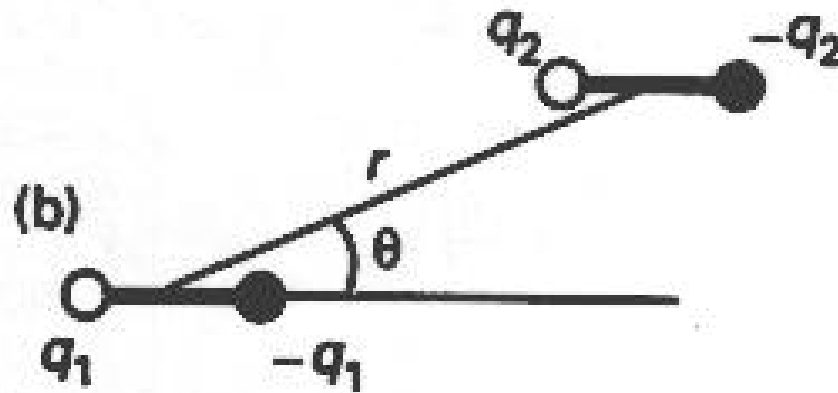
$$V = \frac{-2\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0)^2 kT} \frac{1}{r^6}$$

Note that these interactions are attractive (negative sign of V)

Stationary Parallel Permanent Dipoles



(a)



(b)

Dipole - Induced Dipole Interactions

- A polar molecule of permanent dipole moment μ_1 can induce a dipole μ_2 in a polarizable molecule of polarizability α'_2 . The interaction energy between the permanent and the induced dipoles is given by:

$$V = \frac{-\mu_1^2 \alpha'_2}{\pi \epsilon_0} \frac{1}{r^6}$$

- Note that the dipole - induced dipole interactions are independent of temperature as these interactions are “spontaneous” and the averaging process is not affected by temperature:

Induced Dipole - Induced Dipole Interactions

- Non-polar molecules attract one another because of the interactions between transient instantaneous dipoles that all molecules possess. These transient dipoles arise from the fluctuations in the positions of the electrons in the molecules. As one transient dipole forms, it polarizes a near-by atom/molecule and induces a dipole in that atom/molecule. These two dipoles interact with one another resulting in the potential energy:

$$V = -\frac{2}{3} \alpha'_1 \alpha'_2 \frac{I_1 I_2}{I_1 + I_2} \frac{1}{r^6}$$

where I_1 and I_2 are the ionization energies of the two molecules. These interactions are called **Dispersion** or **London** interactions.

Total Attractive Interactions: Conclusion and Limitations

- The total attractive interaction between rotating molecules is given by the sum of the three interactions which have been discussed above and leads to:

$$V = -\frac{C_6}{r^6}$$

This equation which is widely used is however of limited validity

- ignores higher order multipole interactions
- ignores the fact that in solids the dipoles are usually not rotating
- ignores the fact that pairwise interactions may not be additive

(Axilrod-Teller formula for three-closed shell dispersive interactions shows that three-body interactions account for 10% of the total energy)

Repulsive Potential and Total Interactions

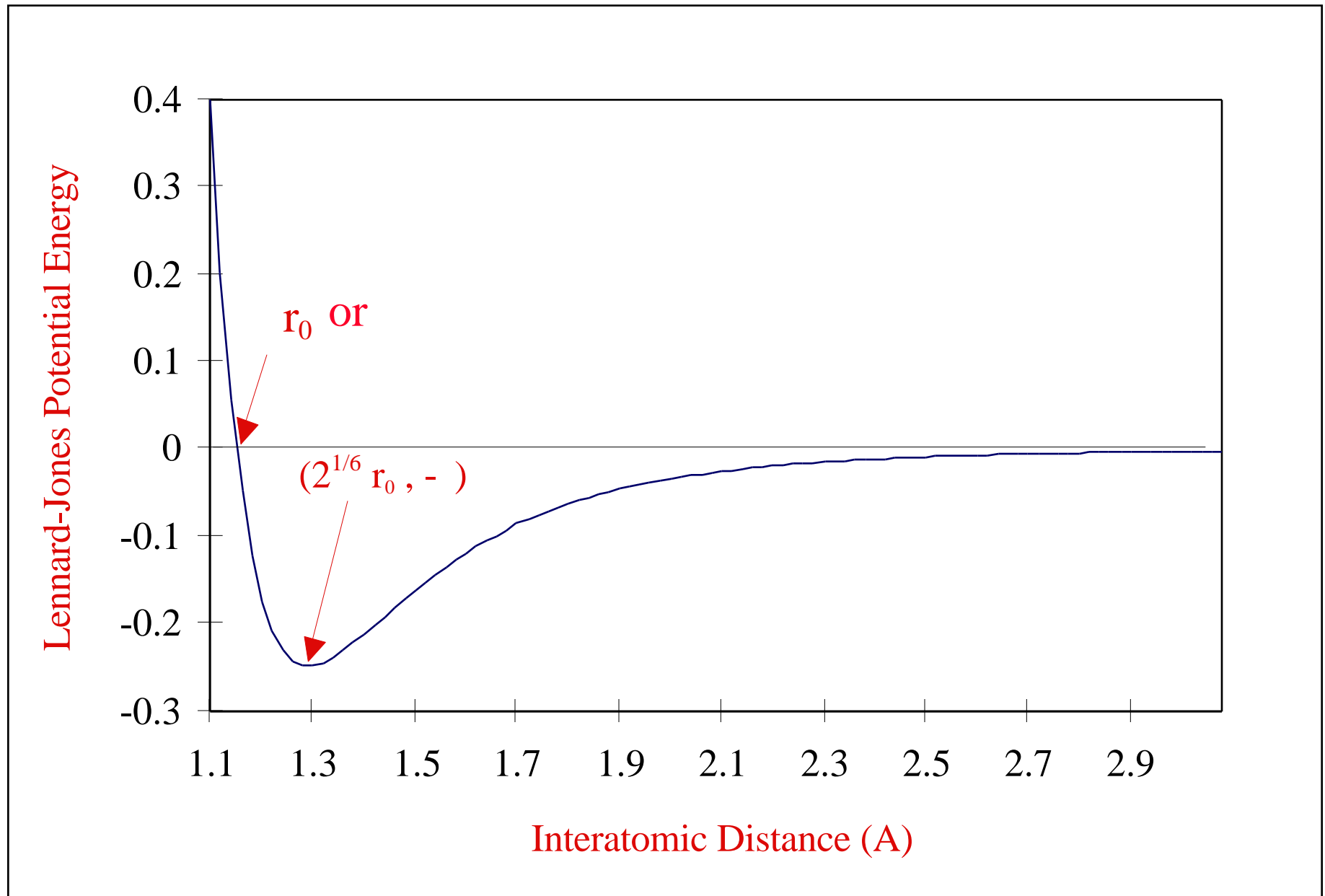
When molecules are squeezed together, the repulsive interactions start to dominate. These repulsions arise from coulombic interactions between on one hand the nuclei and on the other the electrons (Pauli's Principle). These repulsions can only be rigorously modeled through very complex quantum mechanical calculations. They can however be empirically described by a number of empirical models (hard sphere potential, $1/r^n$ ($n>6$)).

Some of the most widely used are the $V_{\text{rep}}(r) = 1/r^{12}$ potential and the more meaningful $\exp(-B.r)$ repulsive potential.

Under these conditions, combination of attractive and repulsive potentials leads to the **Lennard-Jones** and the **exp-6** potentials:

$$V = 4\epsilon \left[\frac{r_0^{12}}{r^{12}} - \frac{r_0^6}{r^6} \right] \quad V = A.\exp(-B.r) - \frac{C_6}{r^6}$$

Lennard-Jones Potential Energy Curve



Lattice Structure of Molecular Crystals

- Since the dispersion forces are associated with instantaneous fluctuating dipole moments of individual atoms, they are weak and only instantaneously directional. The absence of directionality leads to the crystallization of atoms with filled valence orbitals and spherical symmetry (noble gas atoms) in **close-packed structures** (fcc and hcp).
- Molecular crystals of diatomic or larger molecules are rarely found to be close-packed and crystallize in structures that maximize **1)** the solid-state density and **2)** the cohesive energy

Equilibrium Lattice Constants and Lattice Energy of Noble Gas Crystals

- The cohesive energy of an inert gas molecular crystal is obtained by summing the Lennard-Jones potential over all pairs of atoms in the crystal. If there are N atoms in a given crystal, then the cohesive energy is:

$$U_{\text{tot}} = \frac{1}{2} N (4\epsilon) \sum_{j \neq i} \left[\left(\frac{\sigma}{p_{ij} R} \right)^{12} - \left(\frac{\sigma}{p_{ij} R} \right)^6 \right]$$

where $p_{ij} R$ is the distance between atoms i and j , expressed in terms of the nearest neighbor distance, R .

- For the fcc structure:

$$\sum_{j \neq i} \frac{1}{p_{ij}^{12}} = 12.13188 \quad \sum_{j \neq i} \frac{1}{p_{ij}^6} = 14.45392$$

- For the hcp structure:

$$\sum_{j \neq i} \frac{1}{r_{ij}^{12}} = 12.13229$$

$$\sum_{j \neq i} \frac{1}{r_{ij}^6} = 14.45489$$

- The equilibrium value of R (denoted R_0) is obtained by minimizing U_{tot} with respect to R:

$$\frac{dU}{dR} = 0 = -2N\epsilon \left[(12)(12.13) \frac{\sigma^{12}}{R^{13}} - (6)(14.45) \frac{\sigma^6}{R^7} \right]$$

which leads to $R_0 / \sigma = 1.09$. Experimental values for this ratio are 1.14, 1.11, 1.10 and 1.09 for Ne, Ar, Kr, Xe respectively.

- The cohesive energy of inert gas crystals at absolute zero and zero pressure is then: $U_{\text{tot}}(R_0) = -(2.15)(4N \epsilon)$
Quantum mechanical corrections reduce the binding by 28, 10, 6 and 4% for Ne, Ar, Kr and Xe, respectively and allow experimental and calculated values to agree within 1 to 7%.

Multipole Interactions

Interaction Type	Distance Dependence of potential energy	Typical Energy	Comment
Ion - Ion	$1/r$	250 kJ/mol	Only between Ions
Ion - Dipole	$1/r^2$	15 kJ/mol	
Dipole - Dipole	$1/r^3$	2 kJ/mol	Stationary Polar Molecules
Dipole - Dipole	$1/r^6$	0.3 kJ/mol	Rotating Polar Molecules
London Dispersion	$1/r^6$	2 kJ/mol	Between All Types of Molecules

Bonding in Ionic Crystals

- Ionic crystals are made up of positive ions (cations) and negative ions (anions). The electronic configuration of all ions in simple ionic crystals is characterized by **closed electronic shells**, imparting them a nearly-spherical symmetry.
- In contrast to molecular crystals, it is quite easy to calculate the cohesive energy of ionic crystals through a **summation of all Coulombic interactions between like and unlike charges** (neglect weaker Van der Waals interactions, which contribute only 1 to 2 percents of the total cohesive energy).
- The structure of ionic crystals is such that each ion is surrounded by a shell of ions of opposite charge. The number of nearest ions is referred to as the coordination number, z . The crystal structure is given by **whatever arrangement gives rise to the largest cohesive energy**.

- **M - X Salts:**
 - **Cesium Chloride** $Z = 8$ (Cesium halides)
 - **Rock salt:** $Z = 6$ (AgF, AgBr, AgCl, Alkaline earth oxides and sulfides, Li, Na, K, Rb halides)
 - **Zinc Blende** $Z = 4$ (BeS, BeSe, BeTe, CdS, ZnTe, ZnS)
 - **Wurtzite** $Z = 4$ (BeO, MgTe, CdS, ZnTe, ZnS)
- **M - X₂ Salts**
 - **Rutile** (TiO₂)
 - **Fluorite** (CaF₂)
- **M₂ - X Salts**
 - **Antirutile**
 - **Antifluorite**

Bonding Energy in Ionic Crystals

- The pair potential energy between two ions is given by the Born-Mayer potential:

$$U_{ij} = \lambda \cdot \exp \left[\frac{-R}{\rho} - \frac{q^2}{4\pi\epsilon_0 R} \right] \quad \text{for nearest neighbors}$$

$$U_{ij} = \pm \frac{1}{p_{ij}} \frac{q^2}{4\pi\epsilon_0 R} \quad \text{for non-nearest neighbors}$$

- The total energy is obtained by summation of the pair potentials over all pairs of ions. Note here that each ion has a charge of magnitude q and has z nearest neighbors:

$$U_{\text{tot}} = \sum_{i,j} U_{ij} = N z \lambda \cdot \exp \left[\frac{-R}{\rho} - \frac{\alpha q^2}{4\pi\epsilon_0 R} \right]$$

$$\alpha = \sum_{i,j} \frac{\pm 1}{p_{ij}} \quad \text{Madelung Constant}$$

- At equilibrium separation, $dU_{\text{tot}}/dR = 0$ so that:

$$-\frac{Nz\lambda}{\rho} \exp \frac{-R}{\rho} + \frac{N\alpha q^2}{4\pi\epsilon_0 R^2} = 0$$

which leads to the knowledge of R_0 in terms of λ , ρ and z .

- The total lattice energy of the crystal having $2N$ ions, U_{tot} , is then given by:

$$U_{\text{tot}} = -\frac{N\alpha q^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{\rho}{R_0} \right)$$

Note that ρ is of the order of $0.1R_0$ so the repulsive interactions are extremely short range interactions.

- Typical values of the Madelung constant are listed below based on unit charges and on the nearest neighbor distance.

Structure

Sodium Chloride, NaCl	1.747565
Cesium Chloride, CsCl	1.762675
Zinc Blende, ZnS (cubic)	1.6381

Summary of the Characteristics of the Different Types of Solids

Type of Solid	Molecular	Atomic Network	Metallic Network	Ionic
Structural Unit	Molecule	Atom	Atom	Ion
Bonding Type	Dipole-Dipole, London dispersion forces	Highly directional covalent bonds	Non directional covalent bonds with delocalized electrons	Electrostatic
Typical Property	Soft Low T _m Insulator	Hard High T _m Insulator	Wide Range of Hardness Wide Range of T _m Conductor	Hard High T _m Insulator
Examples	Ice Dry Ice	Diamond Graphite	Silver Iron	Sodium Chloride