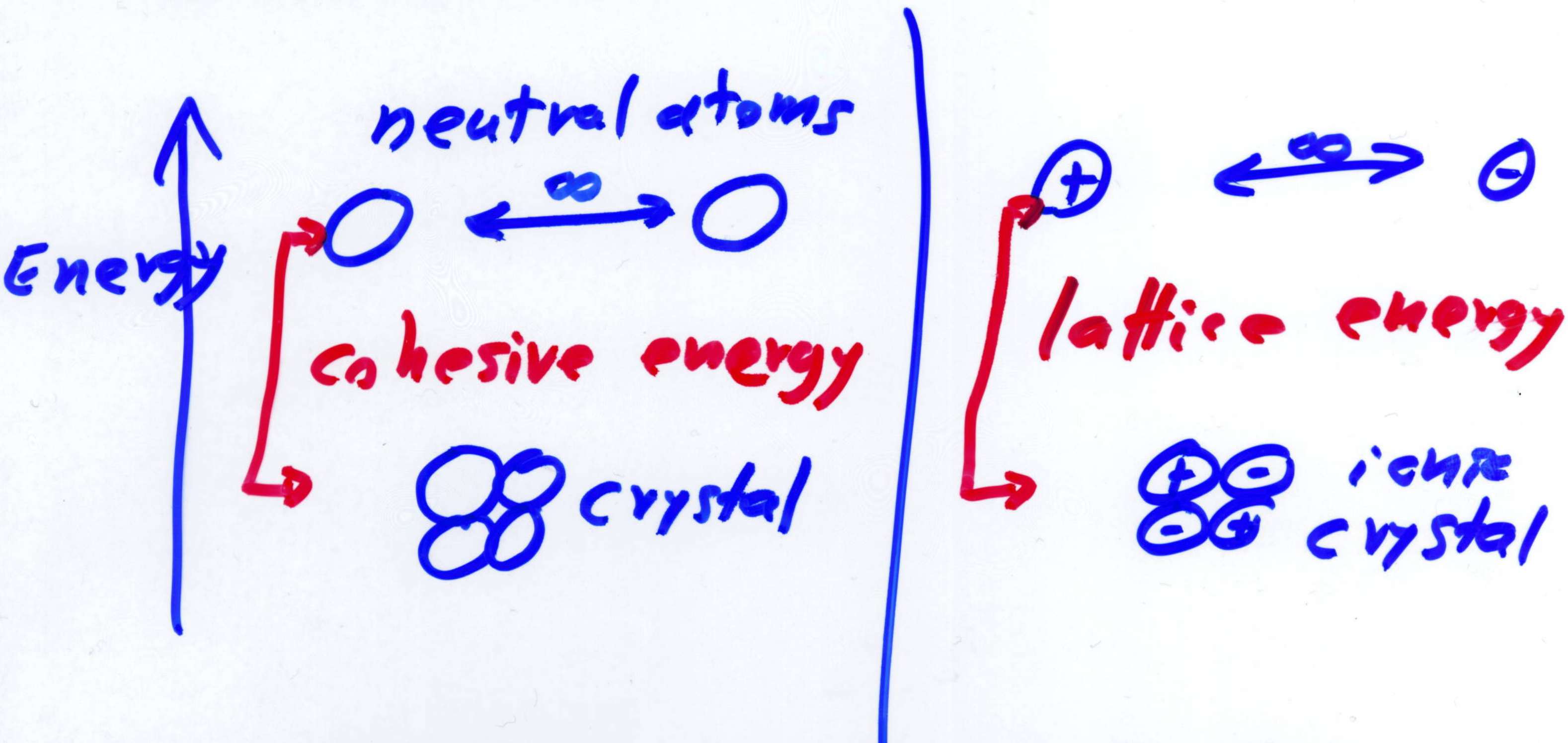
Crystal Binding

1. Van der Waals
2. Ionic
3. Covalent
4. Metal
5. Hydrogen

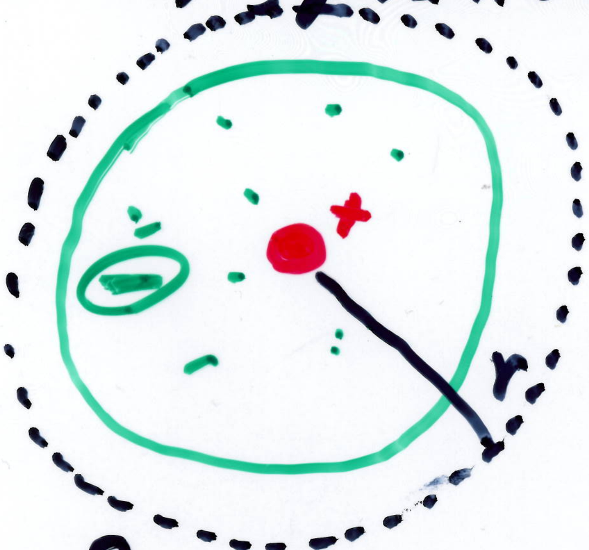


Ionic binding easy to understand

Coulomb attraction ⊕ →F   F← ⊖

Inert gases : eg. Ne, Kr, Ar...

Closed electron shells
→ spherically symmetric
for isolated atom



S

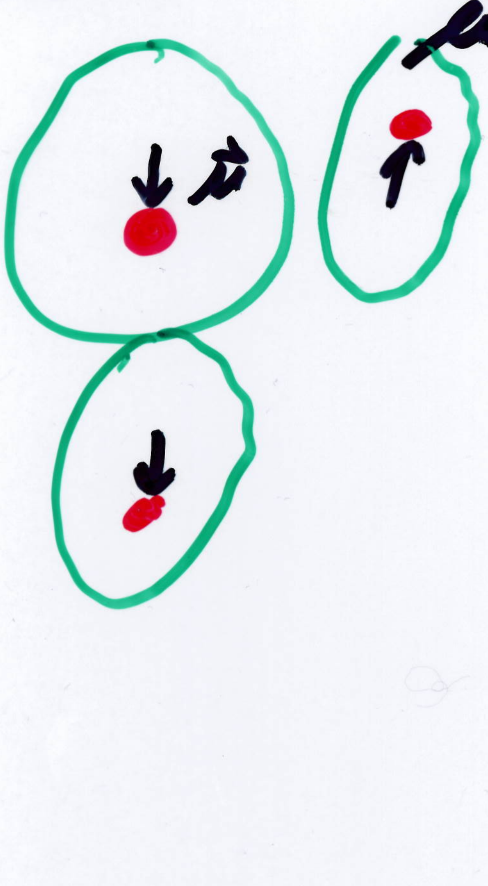
Gaussian Surface

Gauss' Law

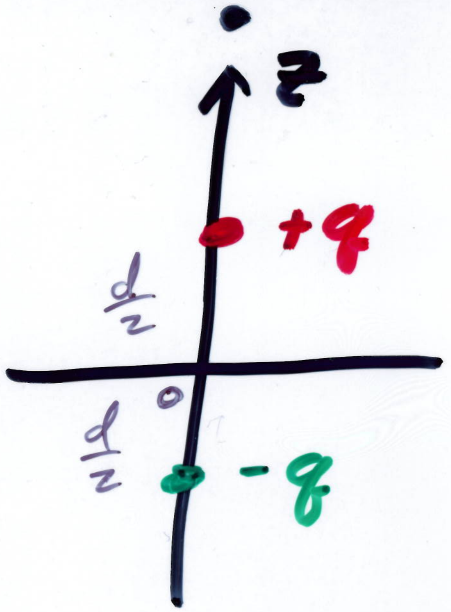
$$\oiint_S \vec{E}\cdot d\vec{a} = \frac{Q_{enc}}{\epsilon_0}$$

$$E\,4\pi r^2 = 0$$

⊞



$\vec{\mu}$ electric dipole moment vector



Find electric field on the z axis.

$$E(z) = \frac{q}{4\pi\epsilon_0}\frac{1}{\left(z-\frac{d}{2}\right)^2} + \frac{(-q)}{4\pi\epsilon_0}\frac{1}{\left(z+\frac{d}{2}\right)^2}$$

Expand with binomial series: $z \gg d$

$$E(z) = \frac{q}{4\pi\epsilon_0}\left[\frac{1}{z^2}\right]\left[\frac{1}{\left(1-\frac{d}{2z}\right)^2} - \frac{1}{\left(1+\frac{d}{2z}\right)^2}\right]$$

$$= \frac{q}{4\pi\epsilon_0 z^2}\left[\left(1+\frac{d}{z}+\cdots\right) - \left(1-\frac{d}{z}+\cdots\right)\right]$$

$$= \frac{q}{4\pi\epsilon_0 z^2}\frac{2d}{z} + \mathcal{O}\left(\frac{d^3}{z^5}\right)$$

Define $\mu = qd$

Dipole Electric field

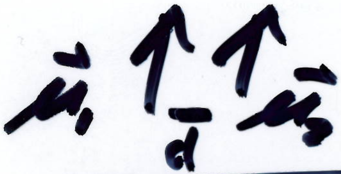
$$\vec{E}(\vec{r}) = \frac{1}{4\pi\epsilon_0}\frac{1}{r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right]$$

U = Energy of interaction between an electric dipole $\vec{\mu}$ and an electric field $\vec{E}$.

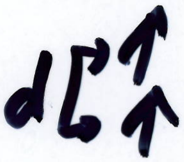
$$U = -\vec{\mu}\cdot\vec{E} \propto \frac{1}{r^6}$$

van der Waals - London binding

Two dipoles near each other



$$U = \frac{1}{4\pi\epsilon_0}\frac{\mu_1 \mu_2}{d^3} > 0$$



$$U = \frac{-1}{4\pi\epsilon_0}\frac{2\mu_1 \mu_2}{d^3} < 0 \text{ bound}$$

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If attraction $\sim \frac{1}{r^6}$

Only outside the closed electron shells

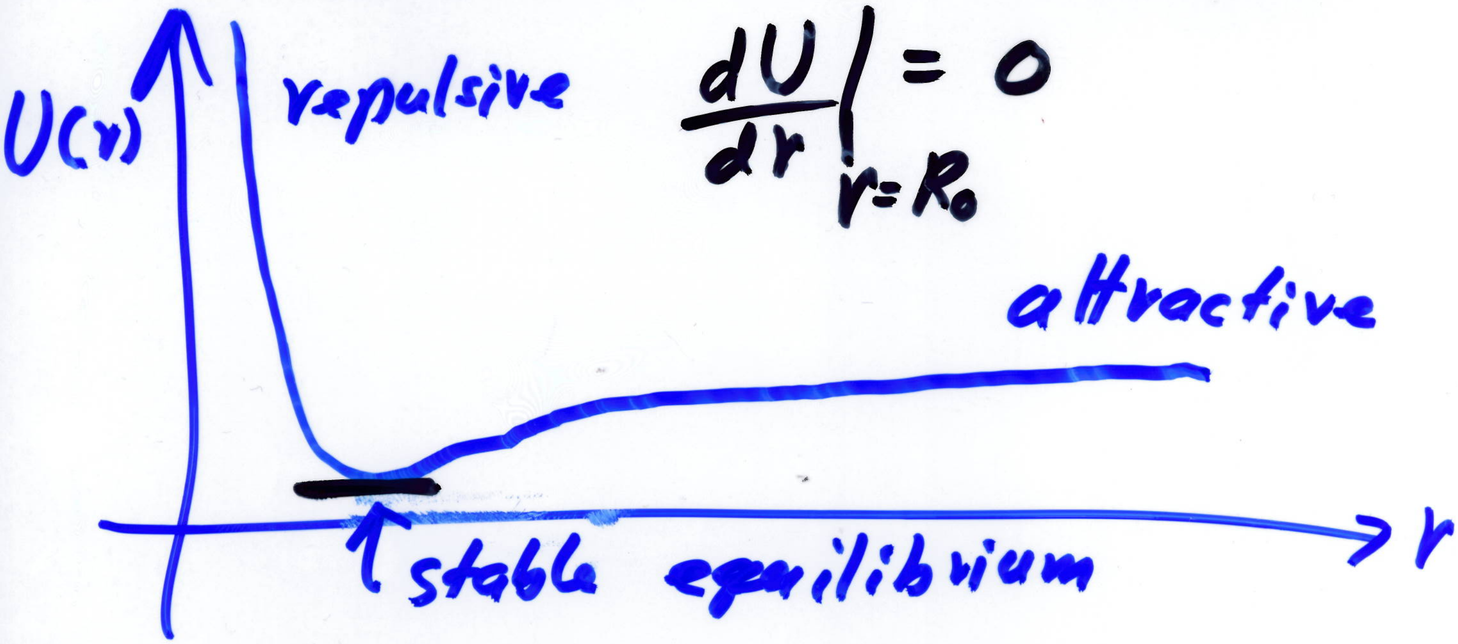
If you try to shrink r, Pauli exclusion keeps the atoms apart.

Repulsive force for small r

2 models: $U(r) = \frac{-A}{r^6} + \frac{B}{r^{12}}$ Lennard-Jones

$$U'(r) = \frac{-A'}{r^6} + B' e^{-\frac{r}{s}}$$

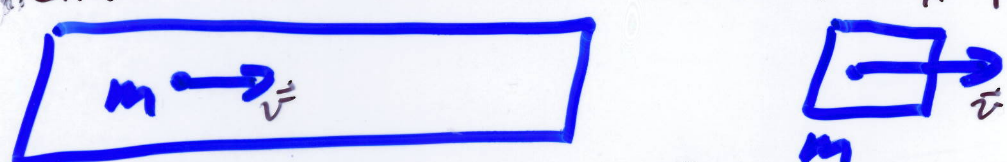
exponential



$$\left.\frac{dU}{dr}\right|_{r=R_0} = 0$$

Ne, Ar, Kr, Xe form fcc close-packed crystals [cubic close-packed ccc]

Helium is so light that Heisenberg uncertainty prevents it from crystalizing.



fcc - coordination number = 12

12 nearest neighbors at one atomic diameter

6 next to nearest neighbors at $\sqrt{2}$ one atomic diameter

⋮

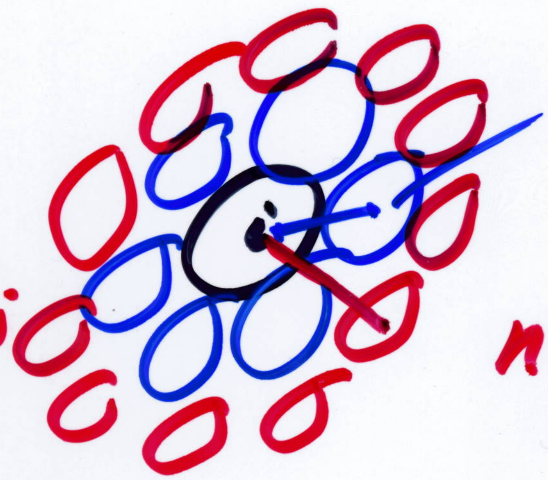
N items

$\frac{N(N-1)}{2}$ pairs

Binding energy for the whole crystal

$$U_{tot} = \frac{1}{2} N \left[\sum_j{}' \frac{A}{r_{ij}^6} + \sum_j{}' \frac{B}{r_{ij}^{12}} \right]$$

$j \neq i$



nearest neighbors r_{ij}

$p_{ij} \cdot R = r_{ij}$

next to nearest neighbors $-r_{ij}$

fcc

$$\sum_j{}' p_{ij}^{-6} = 14.45392$$

$$\sum_j{}' p_{12}^{-12} = 12.13188$$