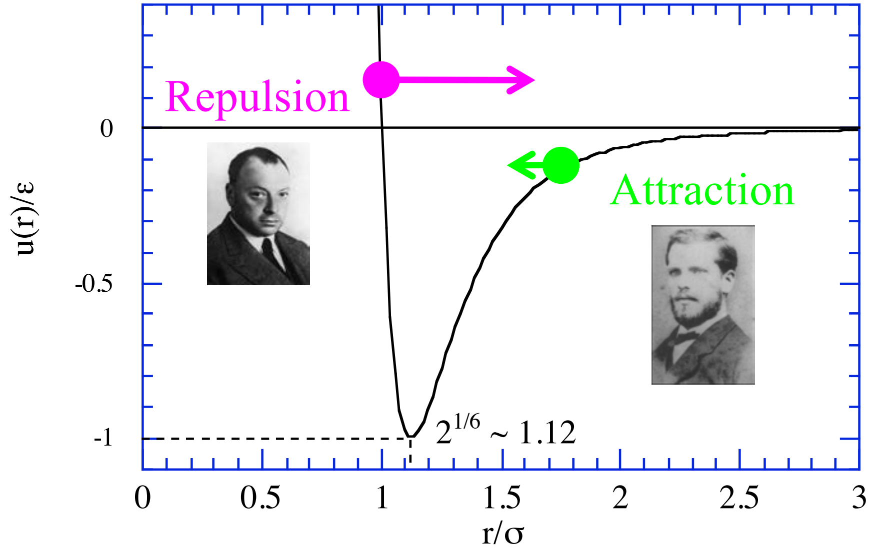
Recap: Lennard-Jones Potential

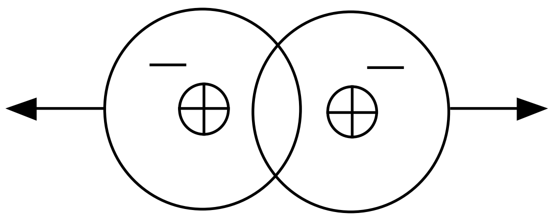
$$V\left(\vec{r}^{\,N}\right) = \sum_{i<j} u(r_{ij}) = \sum_{i=0}^{N-2} \sum_{j=i+1}^{N-1} u(|\vec{r}_{ij}|)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ **and**

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



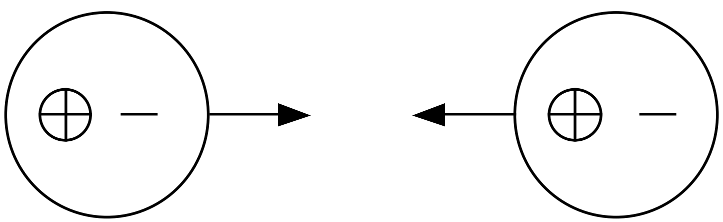
Short-range repulsion by Pauli exclusion between electrons



Wolfgang Pauli
Nobel Physics
Prize (1945)

John E. Lennard-Jones
PPS **43**, 461 (1931)

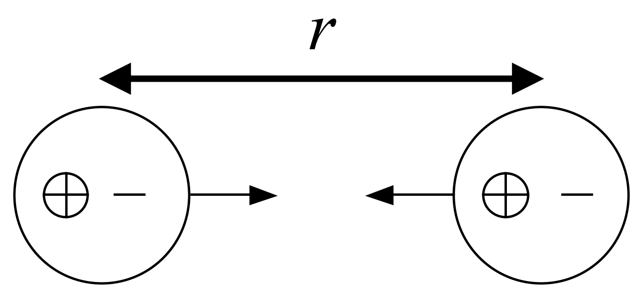
Long-range attraction by polarization



Johanes D. van der Waals
Nobel Physics Prize (1910)

Q: Where Are the 12-6 Powers from?

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Long-range attraction by polarization: electrostatics

Multipole expansion of electrostatic potential (*cf.* fast multipole method lecture)

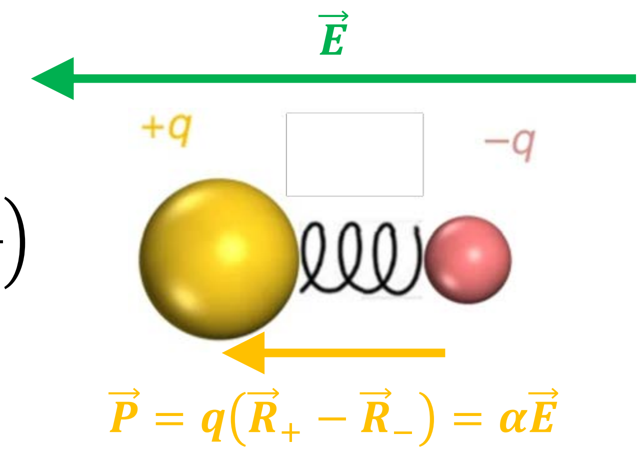
https://aiichironakano.github.io/phys516/FMM.pdf

Electrostatic potential: $\phi(r) \sim \overbrace{O\left(\frac{1}{r}\right)}^{\substack{\oplus + \ominus = 0 \\ \propto \text{charge}}} + \overbrace{O\left(\frac{1}{r^2}\right)}^{\substack{\oplus \leftarrow \ominus = \vec{P} \\ \propto \text{dipole}}} + \cdots = O\left(\frac{1}{r^2}\right)$ for neutral atom

Electric field: $\vec{E}(\vec{r}) = -\frac{\partial \phi}{\partial \vec{r}} = O\left(\frac{1}{r^3}\right)$

Induced dipole: $\vec{P}(\vec{r}) = \overbrace{\tilde{\alpha}}^{\text{polarizability}} \vec{E}(\vec{r}) = O\left(\frac{1}{r^3}\right)$

Dipole energy: $-P(\vec{r}) \bullet E(\vec{r}) \sim \frac{1}{r^3} \bullet \frac{1}{r^3} = O\left(\frac{1}{r^6}\right)$



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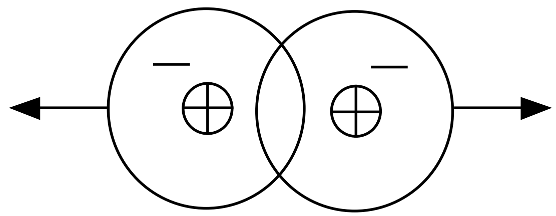
Short-range repulsion by Pauli exclusion between electrons



To these, London's dispersive (attractive) forces are added: these are instantaneous dipole-induced dipole interactions between non-polar molecules. They act at relatively short distances, distinctly longer, however, than the repulsive forces.

There is no theoretical equation describing the repulsive forces. That is why one must use empirical potentials. The potential derived by the English physicist John Lennard-Jones is the one most widely used.

https://aiichironakano.github.io/phys516/Battimelli-ComputerMeetsPhysics-Springer20.pdf, p. 58

cf. Buckingham potential

$$u(r) = A\exp(-Br) - \frac{C}{r^6}$$