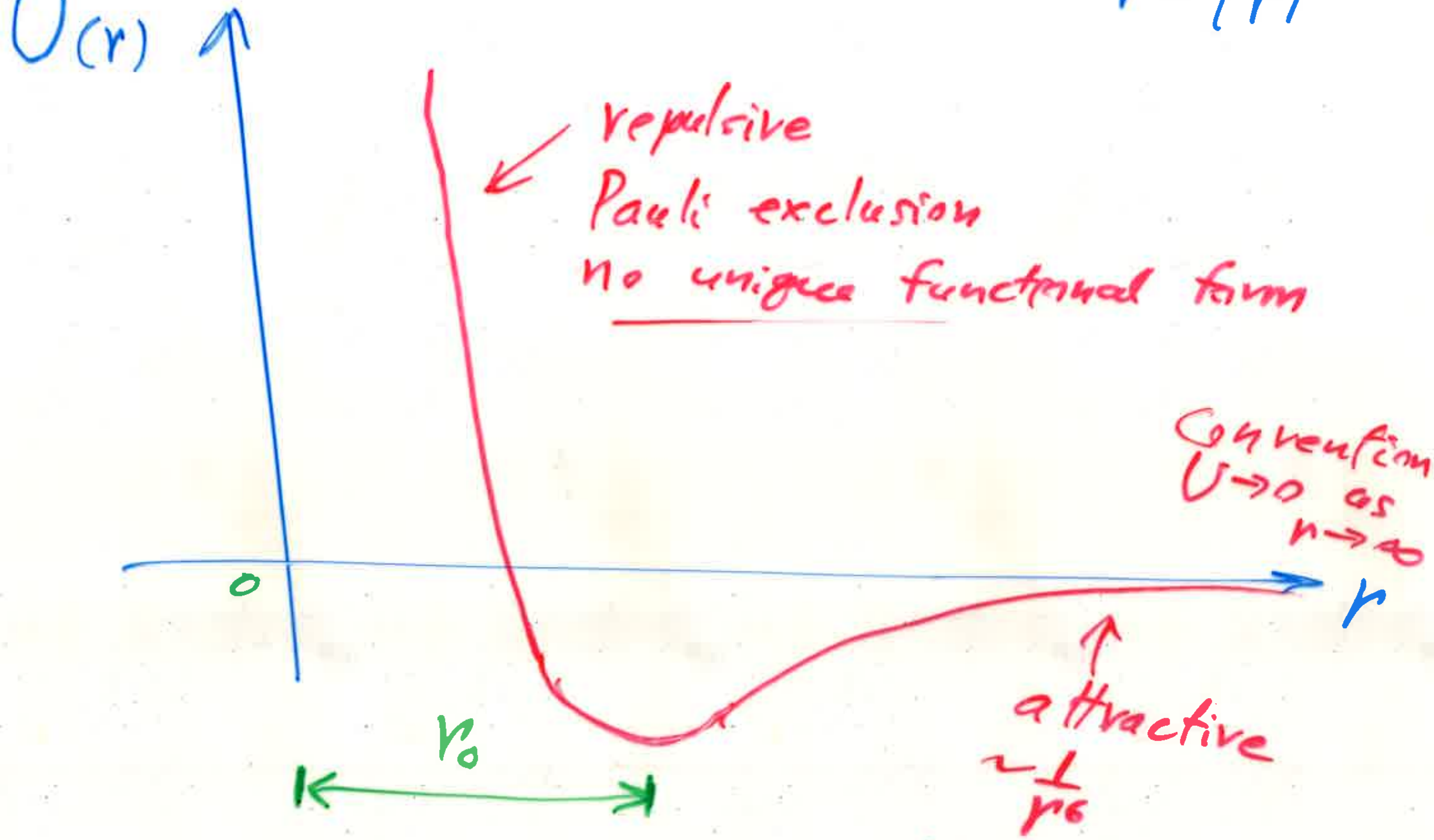
van der Waals – London

$r = |\vec{r}|$



van der Waals (vdW)

induced dipoles

purely Quantum Mechanical effect. $\propto \hbar$

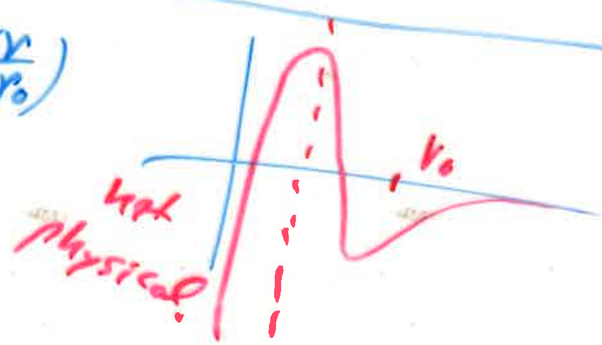
Lennard-Jones (6-12)

$$U(r) = \frac{-A}{r^6} + \frac{B}{r^{12}} = 4\epsilon\left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12}\right]$$

$-A/r^6$ ← attraction; B/r^{12} ← repulsion; ϵ ← energy; σ ← distance; $-(\sigma/r)^6$ ← att.; $(\sigma/r)^{12}$ ← repuls.

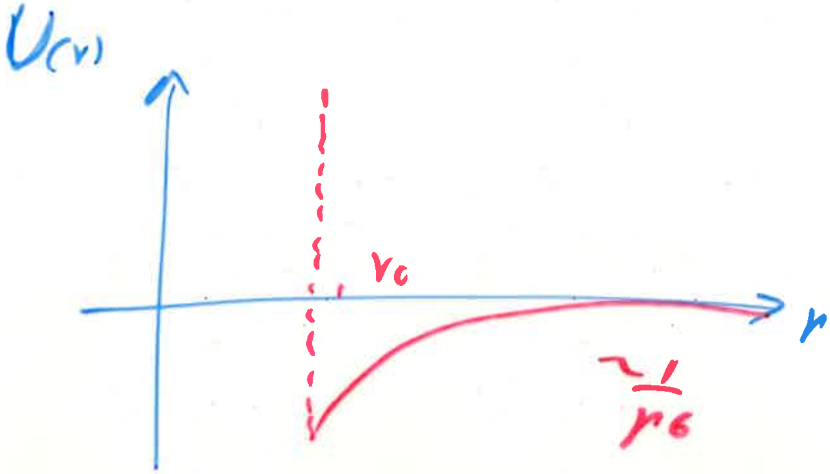
Exponential (6-exp)

$$U(r) = \frac{-A}{r^6} + C\,e^{-\left(\frac{r}{r_0}\right)}$$



Hard wall

$$U(r) = \begin{cases} -\frac{A}{r^6}, & r > r_0 \\ \infty, & r < r_0 \end{cases}$$



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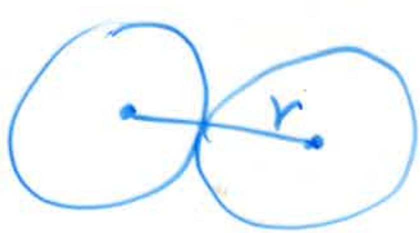
noble gases (not Nobel gases)
↑
inert

L-J: $\frac{d}{dr}\left[-\frac{A}{r^6} + \frac{B}{r^{12}}\right]\Bigg|_{r=r_0} = 0$

$$\Rightarrow \quad \frac{6A}{r_0^7} - \frac{12B}{r_0^{13}} = 0 \quad \Longrightarrow \quad \frac{6(Ar_0^6 - 2B)}{r_0^{13}} = 0$$

$$r_0 = \left(\frac{2B}{A}\right)^{1/6}$$

determine A, B or equivalently ϵ, σ from gas phase.



Cohesive energy of Xtal (neglect KE), N atoms

$$U(R) = \frac{1}{2} N 4\epsilon \left[-{\sum_j}' \left(\frac{\sigma}{p_{ij} R}\right)^6 + {\sum_j}' \left(\frac{\sigma}{p_{ij} R}\right)^{12} \right]$$

prime → $j \neq i$

R_{ij} distance between atom i and atom j

$R_{ij} = p_{ij} R$

↑ length, ↑ number, ↑ length

$$\sum_{j=1}^{N}{}' p_{ij}^{-6} = P_6$$

$$\sum_{j=1}^{N}{}' p_{ij}^{-12} = P_{12}$$

Once the lattice is specified, the two sums can be evaluated.

fcc: $P_6 = 14.4539210435$ $P_{12} = 12.1318801965$

coordination number = 12

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hcp: $P_6 = 14.4548972779$ coordination # = 12

$P_{12} = 12.1322937691$

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bcc: $P_6 = 12.2533$ $P_{12} = 9.11418$

coordination number = 8

$$\left.\frac{dU(R)}{dR}\right|_{R=R_0} = 0 = 2N\epsilon\left[6(P_6)\frac{\sigma^6}{R_0^7} - 12(P_{12})\frac{\sigma^{12}}{R_0^{13}}\right]$$

$$\Longrightarrow \frac{R_0}{\sigma} = \left(\frac{2P_{12}}{P_6}\right)^{1/6}$$

$$U(R_0) = ? < 0$$

$-U(R_0)$ energy required to disassemble the crystal into neutral atoms at infinite separation. $\Longrightarrow$ Cohesive energy.