POTENTIAL ENERGY $V(r)$ of a **pair** of molecules is defined by:

$$F(r) = -\frac{\mathrm{d}V(r)}{\mathrm{d}r}$$

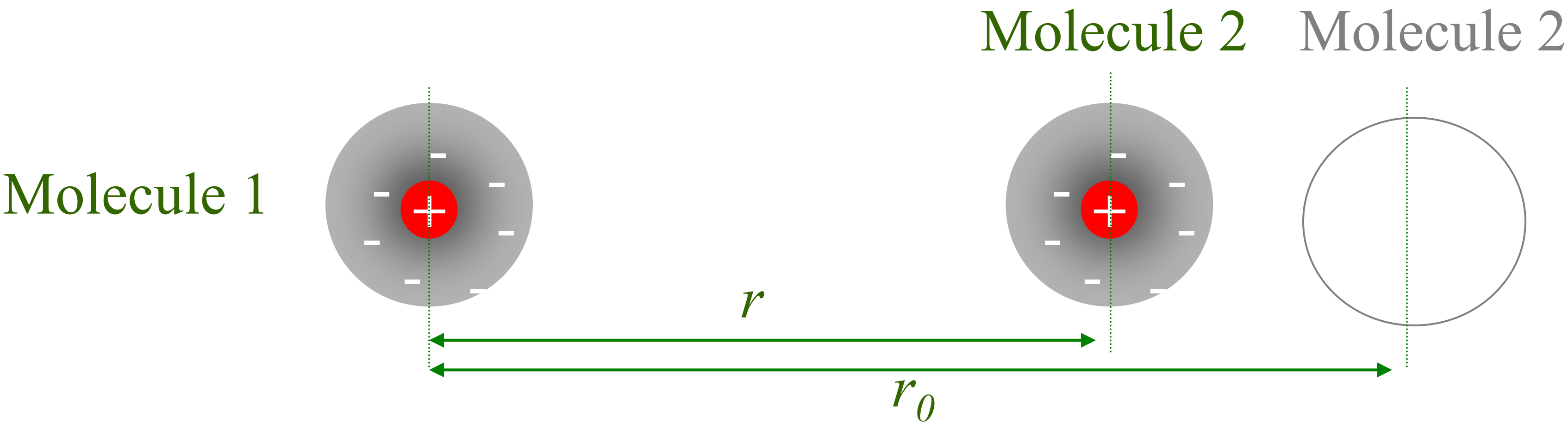
To find an explicit expression for $V(r)$ integrate between two different values of r

$$\int_{r_0}^{r} \frac{\mathrm{d}V(r')}{\mathrm{d}r'}\mathrm{d}r' = -\int_{r_0}^{r} F(r')\mathrm{d}r'$$

$$V(r) - V(r_0) = -\int_{r_0}^{r} F(r')\mathrm{d}r'$$

$$\boxed{V(r) = V(r_0) - \int_{r_0}^{r} F(r')\mathrm{d}r'}$$

What does this mean?



Fix molecule 1 and move molecule 2 from r_0 (at rest) to r. To do this we have to apply an equal and opposite force to balance $F(r)$, i.e. -$F(r)$ and

$-\int_{r_0}^{r} F(r')\mathrm{d}r' =$ WORK done **on** the pair of molecules to change separation r_0 to r

$V(r) = V(r_0) +$ EXTERNAL WORK done on the molecules to move from separation r_0 to r

constant

$V(r)$=POTENTIAL ENERGY OF PAIR=STORED WORK

Regard r_0 as a reference separation to choose as we like d$V(r_0)$/dr=0 and hence V(r_0) can be chosen to be what we like without altering the force r_0

Convention: if $F(r)$=0 at infinite separation choose $r_0 = \infty$ and hence V(r_0) =0

$$\boxed{V(r) = -\int_{\infty}^{r} F(r')\mathrm{d}r'}$$

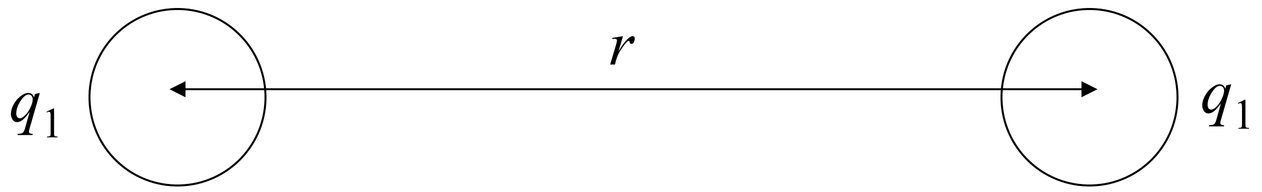
Example 1:

$$F(r) = \mathrm{A}\left(\frac{1}{r}\right)^{n} - \mathrm{B}\left(\frac{1}{r}\right)^{7}$$

$$V(r) = -\int_{\infty}^{r}\left[\mathrm{A}\left(\frac{1}{r'}\right)^{n} - \mathrm{B}\left(\frac{1}{r'}\right)^{7}\right]\mathrm{d}r' = \left[\frac{A}{n-1}\frac{1}{r'^{n}} - \frac{B}{6}\frac{1}{r'^{6}}\right]_{\infty}^{r}$$

$$= \frac{A}{n-1}\left(\frac{1}{r}\right)^{n-1} - \frac{B}{6}\left(\frac{1}{r}\right)^{6}$$

Example 2: Molecules that are *not* neutral but have electrical charge q_1 and q_2



Example 2 contd.

$$F(r) = \mathrm{A}\left(\frac{1}{r}\right)^{n} - \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$

Coulomb force

$$V(r) = -\int_{\infty}^{r}\left[\mathrm{A}\left(\frac{1}{r'}\right)^{n} - \frac{q_1 q_2}{4\pi\varepsilon_0 r'^2}\right]\mathrm{d}r' \quad = \left[\frac{A}{n-1}\frac{1}{r'^{n}} - \frac{q_1 q_2}{4\pi\varepsilon_0 r'}\right]_{\infty}^{r}$$

$$= \frac{A}{n-1}\left(\frac{1}{r}\right)^{n-1} - \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

Coulomb potential

General way to write *V*(*r*):

$$V(r) = \left(\frac{pq}{p-q}\right)\varepsilon\left[\left(\frac{\sigma}{r}\right)^{p} - \left(\frac{\sigma}{r}\right)^{q}\right]$$

4 constants, p,q, ε, a_0

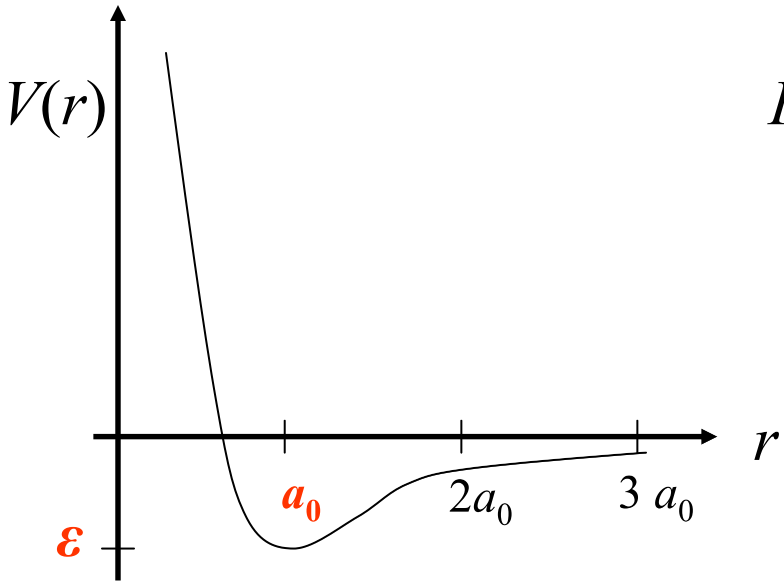
$$F(r) = -\frac{\mathrm{d}V(r)}{\mathrm{d}r} = \left(\frac{pq}{p-q}\right)\varepsilon\left[\frac{p\sigma^{p}}{r^{p+1}} - \frac{q\sigma^{q}}{r^{q+1}}\right]$$

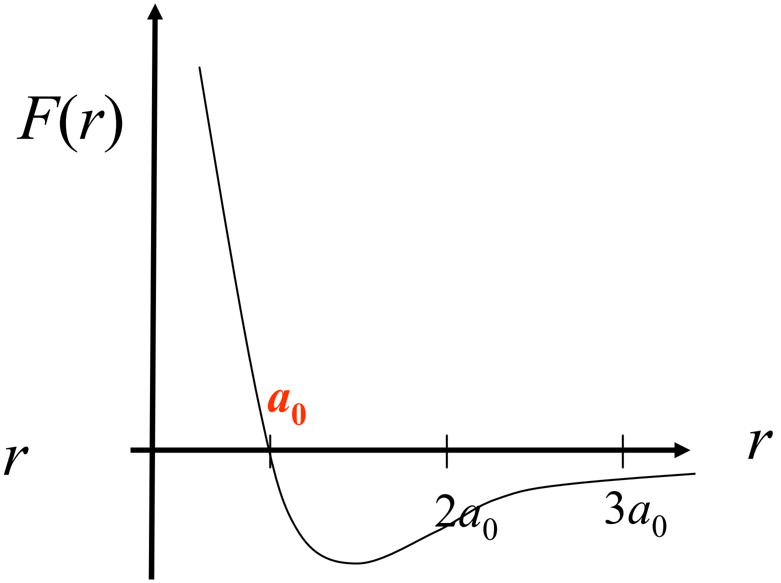
$$\boxed{F(r) = \left(\frac{pq}{p-q}\right)\frac{\varepsilon}{\sigma}\left[p\left(\frac{\sigma}{r}\right)^{p} - q\left(\frac{\sigma}{r}\right)^{q}\right]}$$

At $r = \sigma$, $V(r, \infty) = 0$

$$F(r) = \left.\frac{dV}{dr}\right|_{a_0} = 0 \qquad r \equiv a_0 = \left(\frac{p}{q}\right)^{\frac{1}{p-q}} \sigma, \qquad (a_0 = 2^{\frac{1}{6}} \sigma)$$

a_0 is the TURNING POINT of the potential





$$V(a_0) = \left(\frac{pq}{p-q}\right)\varepsilon\left[\frac{1}{p} - \frac{1}{q}\right] = \left(\frac{pq}{p-q}\right)\varepsilon\left[\frac{q-p}{pq}\right] = -\varepsilon$$

- This is an example of a POTENTIAL WELL
- If the molecules are separated by a_0 they are in EQUILIBRIUM
- Force between molecules is zero
- The system is at a MINIMUM of POTENTIAL ENERGY
- The system is said to be in MECHANICAL EQUILIBRIUM only if POTENTIAL ENERGY IS MINIMISED

a_0 = EQUILIBRIUM SEPARATION
ε = DEPTH OF POTENTIAL WELL

- To fully separate two molecules in equilibrium we must do an amount of work = ε =BINDING ENERGY

THESE CONCEPTS APPLY TO ANY POTENTIAL ENERGY FUNCTION

- The ‘*p*-*q*’potential is just one example of an infinate set of mathematical functions that might represent a molecular pair-potential
- For INERT GASES this is a good representation of potential between molecules because these gases comprise single atoms
- Often use the LENNARD-JONES potential (often called the ‘6-12’ potential) to describe inert gases:

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

The quantity *a* (sometimes called σ) is often taken as a rough measure of the DIAMETER of the molecule

The constants ε, a_0 or ε, σ are obtained by comparing theoretical predictions with experimental measurement. Typical Lennard-Jones parameters for simple substances are listed below:

	ε		σ	
He	$0.14(10^{-21})$ J	$0.088\ (10^{-2})$ eV	0.256 nm	2.56 Å
Ar	$1.70(10^{-21})$ J	$1.06(10^{-2})$ eV	0.340 nm	3.40 Å
Kr	$2.3(10^{-21})$ J	$1.44(10^{-2})$ eV	0.368 nm	3.68 Å
CCl_4	$4.5(10^{-21})$ J	$2.82(10^{-2})$ eV	0.588 nm	5.88 Å

i.e. typical L-J binding energy ~ 0.01 eV: this is very low compared to other energies within the atom

Exercise

(i) Show that the *L-J* potential can be written in the form:

$$V(X) = 4\varepsilon\left[\frac{1}{X^{12}} - \frac{1}{X^{6}}\right]$$

(ii) Show that the interatomic force for a pair of Argon atoms can be written:

$$F(X) = \frac{0.12}{X^{7}}\left[\frac{2}{X^{6}} - 1\right](10^{-9})\,\mathrm{Newtons}$$