Equation of State (EOS)

- **The molecules have no extension in space (i.e.,they possess zero volume)**

- **The molecules do not interact with each other**

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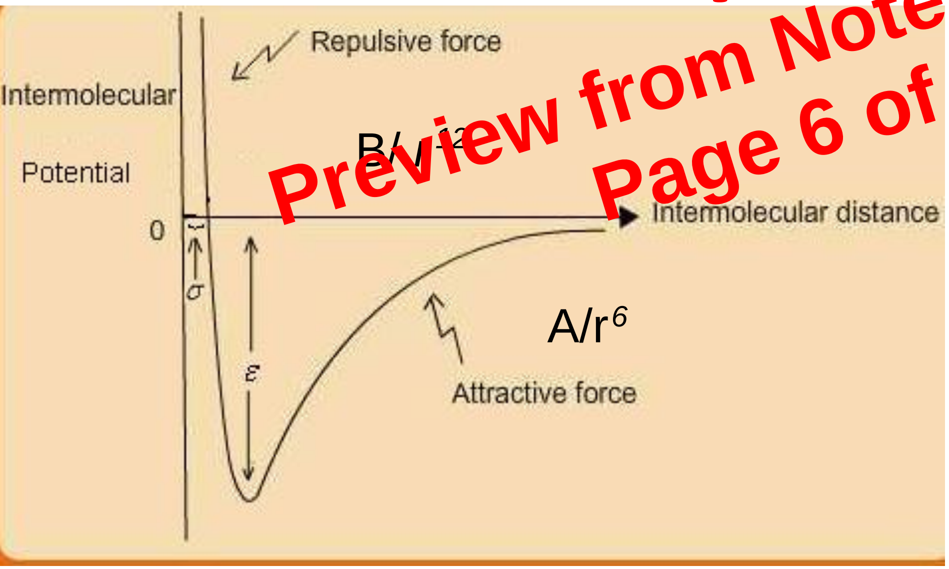
- For this, one needs to understand the interaction forces that exist between molecules of any substance, typically at very short intermolecular separation distances (~5–20Armstrong).

- Intermolecular interactions are not only attractive.

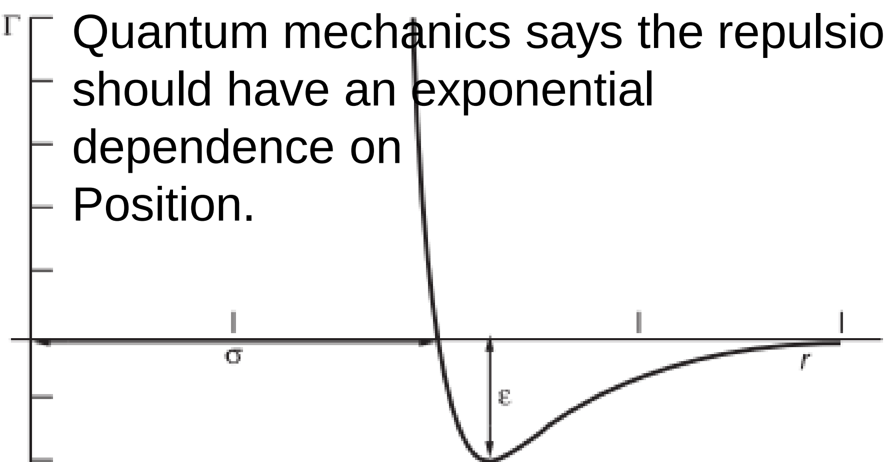
- When molecules approach to distances even less than ~ 5 or so, a repulsive interaction force comes into play due to overlap of the electron clouds of each molecule, which results in a repulsive force field between them.

Lennard-Jones (LJ) 12/6 pair-potential



A plot of the Lennard-Jones potential function. The parameters Eta and sigma can be physically interpreted as an energy parameter and a distance parameter,respectively. As illustrated in Figure, the energy parameter, eta, is given by the depth of the potential well, while the distance parameter, sigma, is given by the distance at which attractive and repulsive potentials are equal and is characteristic of the molecular size.

- Quantum mechanics says the repulsion should have an exponential dependence on Position.



When molecules approach to distances even less than ~ 5 A or so, a *repulsive interaction force comes into play due to overlap of the electron clouds of each molecule, which results in a repulsive force field between them.*

Van der Waals Equation of State

Volume correction:

$$P_{ideal} = \frac{RT}{V_{ideal}}$$

Now what Van der waal did to correct this ideal equation for real fluids.

$$V_{actual} = V_{ideal} + V_{molecules}$$
$$V_{ideal} = V_{actual} - V_{molecules}$$

$$V_{ideal} = V_{actual} - b$$

b?

We consider simple molecule as spherical shape,
So,

$$V_{molecule} = \frac{4}{3}\pi r^3$$

For total molecules:

$$V_{molecules} = \frac{4}{3}\pi r^3 \times N_A$$
$$V_{molecules} = b = \frac{4}{3}\pi r^3 \times N_A$$