If 2 molecules interact according to a potential energy function that depends only on their separation $r$, then $B_{2V}$ can be expressed as:

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[ e^{-u(r)/k_B T} - 1 \right] r^2 dr$$
Limiting Interactions

In principle, $u(r)$ can be calculated from quantum mechanics, but this can be a challenging computational undertaking.

Observation indicates:

at long range: $u(r) \rightarrow -\frac{c_6}{r^6}$ (attractive)

at short range: $u(r) \rightarrow \frac{c_{12}}{r^{12}}$ (repulsive)

add them up: $u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}$
The Lennard-Jones Potential

now this has potential!

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

$$c_{12} = 4\varepsilon \sigma^{12}$$

$$c_6 = 4\varepsilon \sigma^6$$

John Lennard-Jones
### Some Lennard-Jones Parameters

<table>
<thead>
<tr>
<th>Gas</th>
<th>$(\varepsilon / k_B)$, K</th>
<th>$\sigma$, pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>10.22</td>
<td>256</td>
</tr>
<tr>
<td>Ne</td>
<td>35.6</td>
<td>275</td>
</tr>
<tr>
<td>Ar</td>
<td>120</td>
<td>341</td>
</tr>
<tr>
<td>Kr</td>
<td>164</td>
<td>383</td>
</tr>
<tr>
<td>Xe</td>
<td>229</td>
<td>406</td>
</tr>
<tr>
<td>$H_2$</td>
<td>37.0</td>
<td>293</td>
</tr>
<tr>
<td>$N_2$</td>
<td>95.1</td>
<td>370</td>
</tr>
<tr>
<td>$O_2$</td>
<td>118</td>
<td>358</td>
</tr>
</tbody>
</table>

$\varepsilon$ has units of energy, $\sigma$ has units of length
A Closer Look at $B_{2V}$

\[ B_{2V}(T) = -2\pi N_A \int_0^\infty \left[ e^{-u(r)/k_BT} - 1 \right] r^2 dr \]

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

\[ B_{2V}(T) = -2\pi N_A \int_0^\infty \left[ \exp \left\{ -\frac{4\varepsilon}{k_BT} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \right\} - 1 \right] r^2 dr \]

\[ T^* = k_B T / \varepsilon \text{ and } x = r / \sigma \]

\[ B_{2V}(T^*) = -2\pi \sigma^3 N_A \int_0^\infty \left[ \exp \left\{ -\frac{4}{T^*} \left[ x^{-12} - x^{-6} \right] \right\} - 1 \right] x^2 dx \]
A Closer Look at $B_{2v}$

$T^* = \frac{k_B T}{\varepsilon}$ and $x = \frac{r}{\sigma}$

$$B_{2v}(T^*) = -2\pi\sigma^3 N_A \int_0^\infty \left[ \exp\left\{ -\frac{4}{T^*} \left[ x^{-12} - x^{-6} \right] \right\} - 1 \right] x^2 \, dx$$

$$B_{2v}^*(T^*) = \frac{B_{2v}(T^*)}{\frac{2}{3} \pi \sigma^3 N_A}$$

$$B_{2v}^*(T^*) = -3 \int_0^\infty \left[ \exp\left\{ -\frac{4}{T^*} \left[ x^{-12} - x^{-6} \right] \right\} - 1 \right] x^2 \, dx$$

a characteristic volume•mol$^{-1}$
Another Law of Corresponding States

If one measures $B_{2v}(T^*)$, divides by $2/3\pi N_A \sigma^3$ and plots this vs $T^* = k_B T/\varepsilon$ then…

Recall, LJ parameters are determined from experimental $B_{2v}$ values

At $T^* \sim 3.2$, which defines the “Boyle temperature”, $B^*_{2v}(T^*)=0$, which means every gas behaves as though ideal at its characteristic Boyle temperature!