Statistical Molecular Thermodynamics

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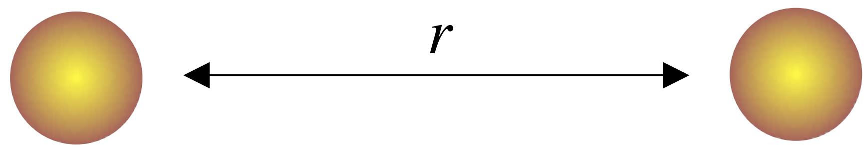
Video 2.6

Molecular Interactions

Molecular Interaction

The virial expansion derives from *exact relationships between virial coefficients and intermolecular interactions*



If 2 molecules interaction 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

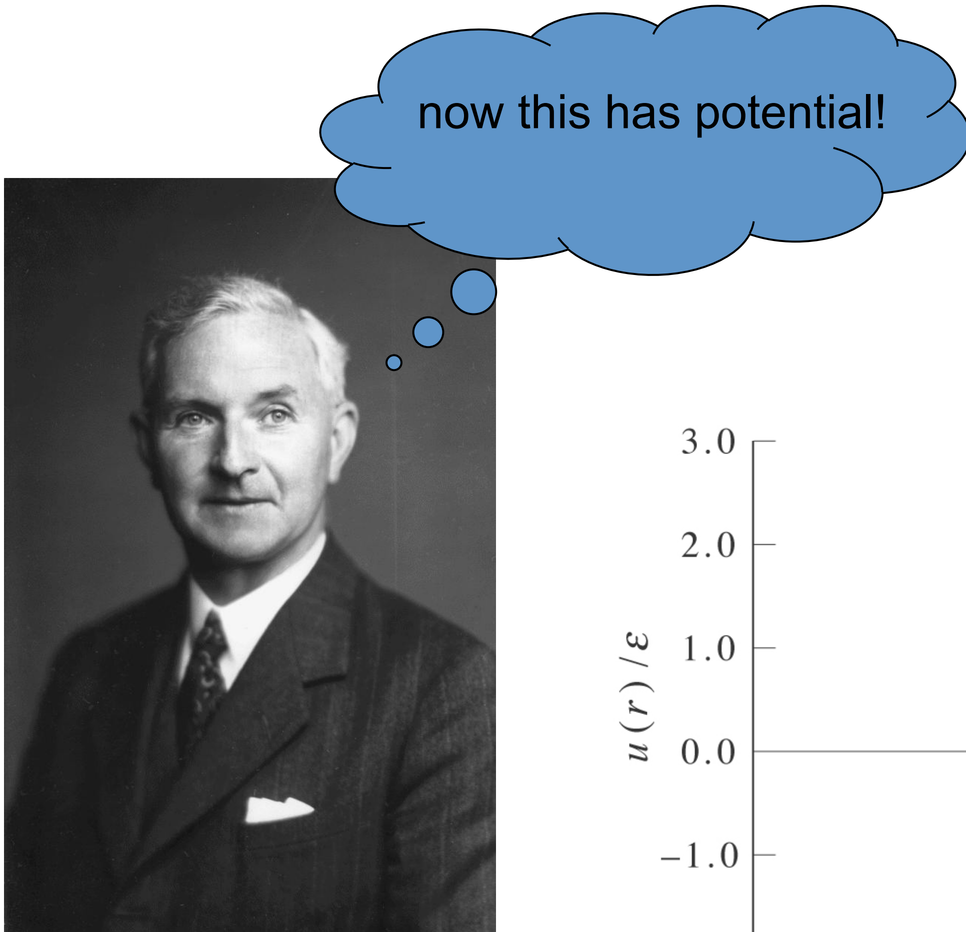
Observation indicates:

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

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

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

The Lennard-Jones Potential

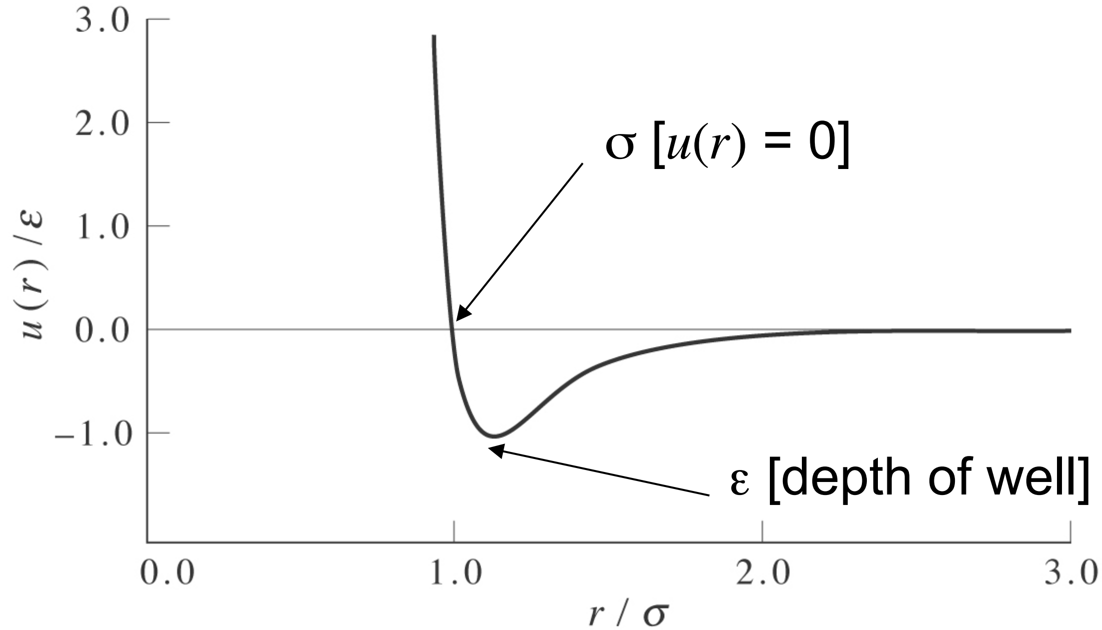


John Lennard-Jones

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

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

$$c_{6} = 4\varepsilon\sigma^{6}$$



Some Lennard-Jones Parameters

Gas	(ε / k_B), K	σ, pm
He	10.22	256
Ne	35.6	275
Ar	120	341
Kr	164	383
Xe	229	406
H_2	37.0	293
N_2	95.1	370
O_2	118	358

ε has units of energy, σ has units of length

A Closer Look at B_{2V}

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[e^{-u(r)/k_B T} - 1 \right] r^2 dr \qquad u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

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

$T^* = k_B T/\varepsilon$ 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}

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

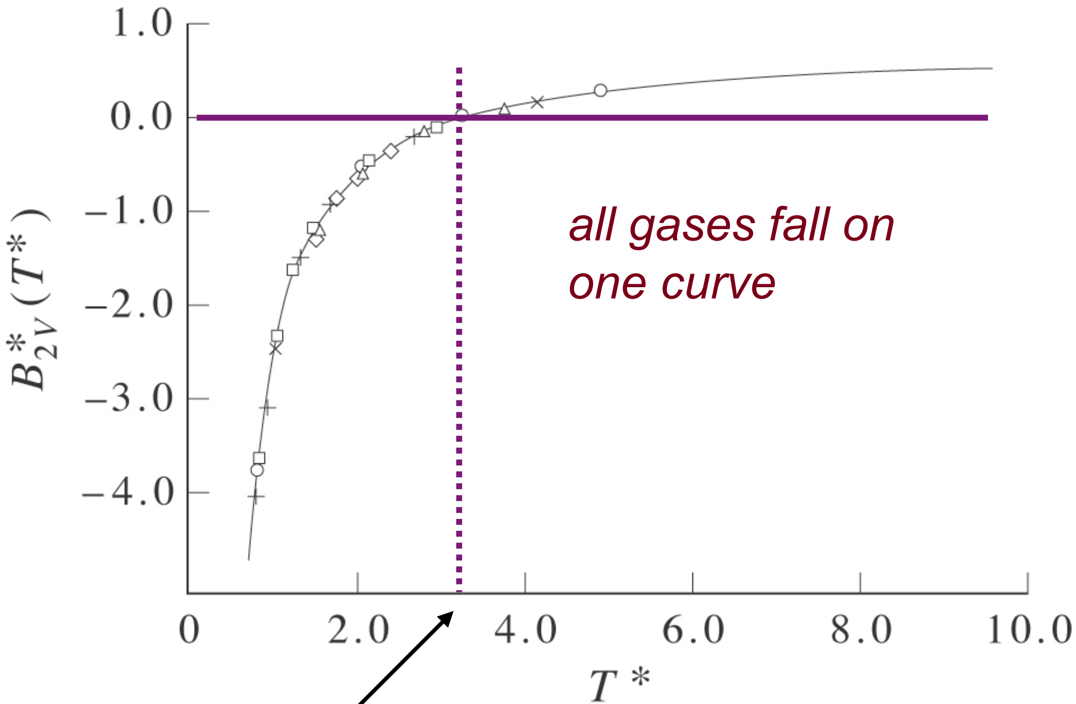
$$B_{2V}^*(T^*) = {B_{2V}(T^*)}\Big/{\tfrac{2}{3}\pi\sigma^3 N_A}$$ ← a characteristic volume•mol^{-1}

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

Another Law of Corresponding States

If one measures $B_{2v}(T^*)$, divides by $2/3\pi N_A\sigma^3$

and plots this vs $T^* = k_BT/\varepsilon$ then…



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

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