

Potential Energy Functions

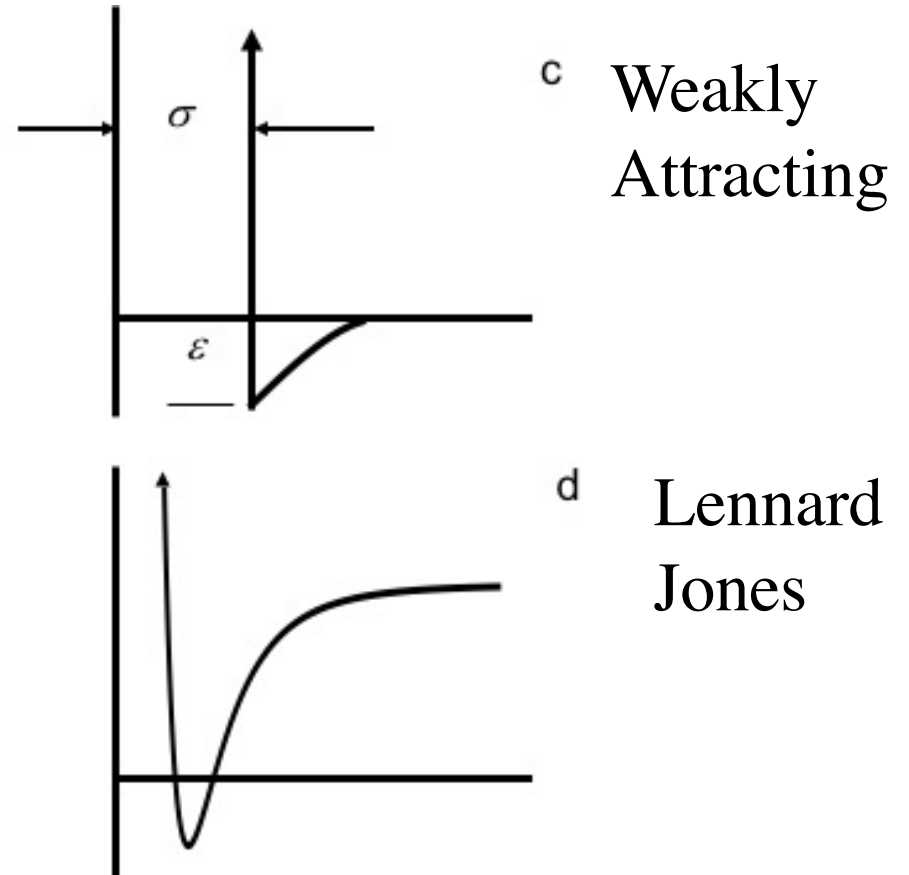
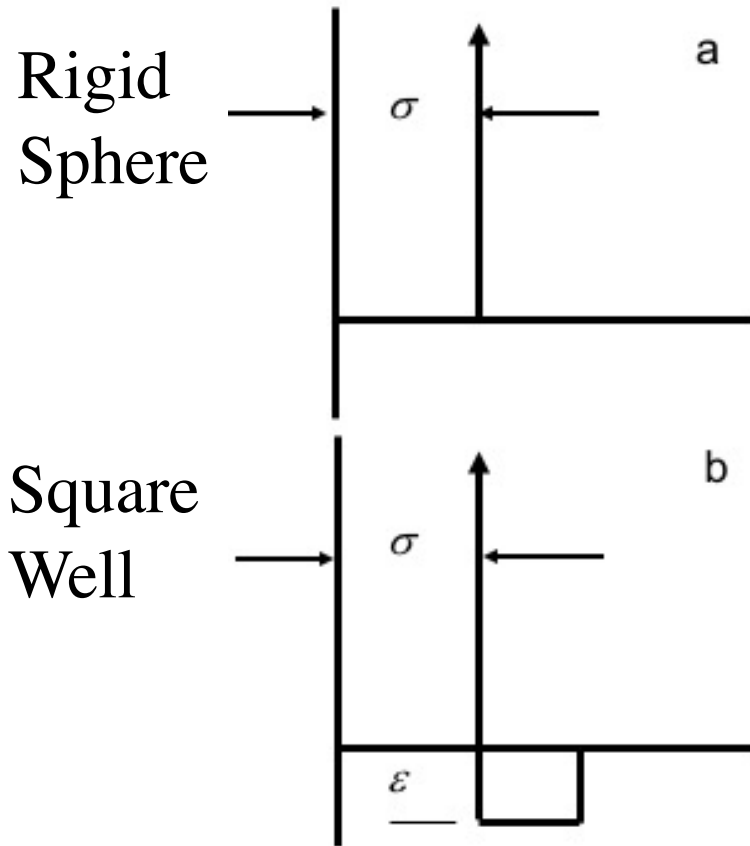
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Potential Energy Functions

- To evaluate $B(T)$ requires knowing the potential energy function.
- Here we will explore some simple algebraic forms.
- Then look at more realist forms

Potential Energy Functions



Evaluating $B(T)$ for Rigid Sphere

- Recall

$$B(T) = -2\pi \int_0^{\infty} f(r) dr$$

- Rigid Sphere

$$B(T) = -2\pi \left\{ \int_0^{\sigma} (0 - 1)r^2 dr + \int_{\sigma}^{\infty} (1 - 1)r^2 dr \right\}$$

$$B(T) = 2\pi \frac{\sigma^3}{3}$$

Rigid Sphere

- Note that the volume occupied by a spherical molecule is

$$\frac{4\pi}{3}r^3 = \frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3$$

- This is called the co-volume. It is the volume excluded to other molecules.
- $B(T) = 4$ volume of spherical molecule

Rigid Sphere

- Now
$$p = \frac{RT}{v} + \frac{RTB(T)}{v^2}$$
- If $B \ll v$ (and substituting $b = B$) then

$$P = \frac{RT}{(v - b)}$$

- This is the first term in van der Waal's equation and represents the addition of a repulsion term to the ideal gas relation.

Weakly Attracting Spheres

- Evaluate $B(T)$

$$B(T) = 2\pi \left\{ \int_0^{\sigma} r^2 dr + \int_{\sigma}^{\infty} (1 - e^{-\frac{cr^{-\gamma}}{kT}}) r^2 dr \right\} = 2\pi \left(\frac{\sigma^3}{3} - \frac{c}{kT} \frac{\sigma^{3-\gamma}}{3-\gamma} \right)$$

- This can be written as

$$B(T) = b - \frac{a}{RT}$$



Weakly Attracting Spheres

- If $b \ll a/RT$

$$P = \frac{RT}{(v - b)} - \frac{a}{v^2}$$

- This is van der Waals equation!
- It includes both repulsion and attraction.

van der Waal's Equation

- I love van der Waals equation because it very simply illustrates the physics of p v T behavior.
- As you try to increase the density of the gas, at first it becomes easier due to attractive forces. Thus less of a pressure increase is needed.
- But if the particles get too close, then repulsive force dominate and a much greater increase in pressure is needed.