ENGG 201 - Chapter 3 – Lennard Jones Potential

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Intermolecular Forces

- Several type of forces act between atoms and molecules (see text for details).
  - Some of these tend to pull these particles closer together, i.e. they are attractive forces.
  - Other forces prevent them from coming too close to each other, i.e. they are repulsive forces.

Balance of intermolecular forces

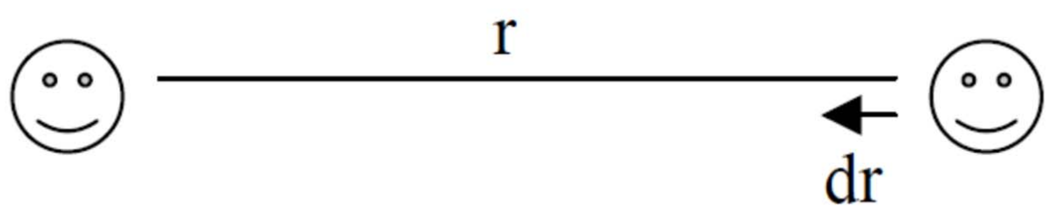
- The sum of these attractive and repulsive forces changes with the distance of separation between the particles.
- If the <u>net sum is attractive</u> the particles will move to come closer and if the <u>net sum of forces happened to be repulsive</u>, the particles will move further apart.
- At some distance the sum will be zero, and at that distance there would be no tendency to move (<u>equilibrium</u>).

Potential Energy

- Potential energy of two molecules separated by a distance 'r' is equal to the work done in bringing these molecules to this distance of separation starting from a very large distance. By large distance, we mean so large that the force between the two molecules is zero. Mathematically, it means infinity.

Potential Energy Calculation (1)

- Two molecules are sitting a distance 'r‘ apart
- There is a repulsive force 'F' acting between them. Now you push these molecules closer together a short distance 'dr‘



- The work done on the system in moving them a small distance Δr would be force multiplied by the distance, i.e.
- Work = (Force) x (Distance travelled) = F . Δr

Potential Energy Calculation (2)

- Force is not constant, it varies with the distance 'r' so:
  $W = F(r)\Delta r$ and for multiple steps $W = \sum F(r)\Delta r$
- Steps are small – work done in bringing the molecules to their current separation distance r from an infinite distance

$$W = \int_{\infty}^{r} F(r)\, dr$$

- This work done is equal to the potential energy that becomes stored in the pair of molecules

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$$\boxed{\phi(r) = \int_{\infty}^{r} F(r)\, dr}$$

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Relationship between Potential and Force

- Potential is the integral of force over the distance travelled starting from a reference position.
- - Force is the derivative of the potential function, i.e.

$$\boxed{F = \frac{d\phi}{dr}}$$

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- Now we will look at a model for F=f(r)

Lennard Jones Potential Function

- Potential Function:

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

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- Force (take the derivative)

$$F = \frac{d\phi(r)}{dr} = \frac{d}{dr}\left\{4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right\} = -\frac{48\varepsilon\sigma^{12}}{r^{13}} + \frac{24\varepsilon\sigma^{6}}{r^{7}}$$

Net Force

Repulsive (-)

Attractive (+)

- If Net Force is + then attractive (if – then repulsive)

Equilibrium Separation Distance (1)

- Equilibrium = Net Force = zero

$$F = -\frac{48\varepsilon\sigma^{12}}{r^{13}} + \frac{24\varepsilon\sigma^{6}}{r^{7}} = 0$$

$$-\frac{2\sigma^6}{r^6} + 1 = 0$$

$$r^6 = 2\sigma^6, \text{ or } r = 2^{(1/6)}\sigma$$

The equilibrium distance is given by:

$$\boxed{r_o = 1.122\ \sigma}$$

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Equilibrium Separation Distance (2)

- Equilibrium **F = 0**

$$r_o = 1.122\ \sigma$$

- Plug r_o into Energy (Φ)

$$\boxed{\phi(r_o) = -\varepsilon}$$ **********

This represents the minimum potential energy between 2 molecules (negative epsilon)

Values for ε and σ

- ε
  - List ε/k (units of K) where k is Boltzman constant
  - $k=R/N_A$ = 1.3805 x10^{-23} J/K

Values for ε and σ in Table 3-6

- σ
  - Define b_o (units m3/kmol)

$$b_o = \frac{2\pi}{3}\sigma^3 N_a$$

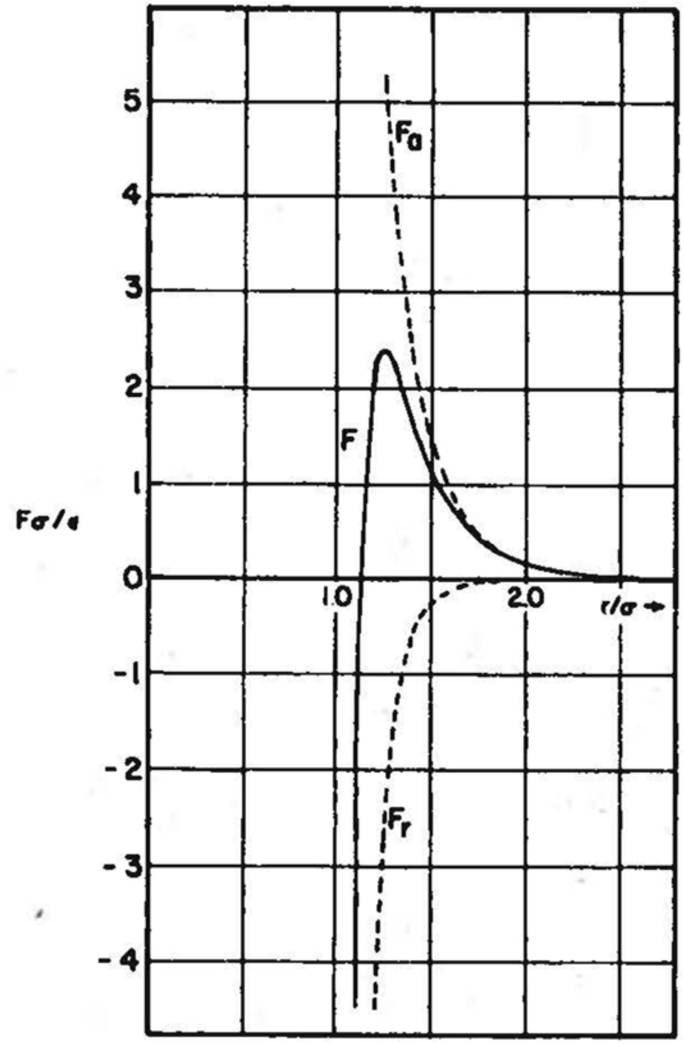


Figure 3-7 Intermolecular Force from Lennard-Jones Potential. F_a, Attractive Force; F_r, Repulsive Force.

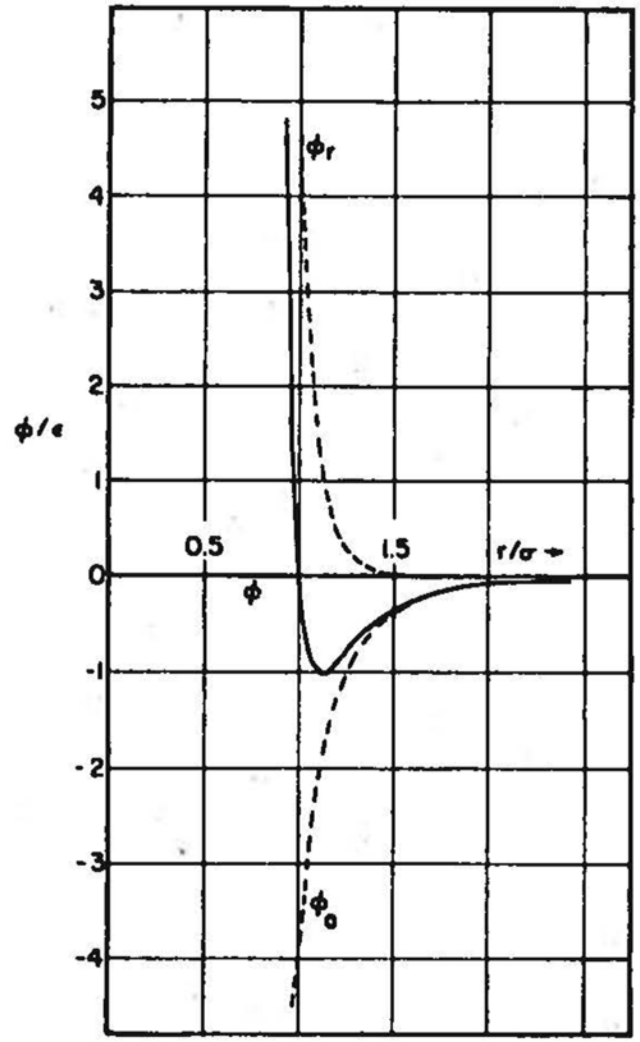
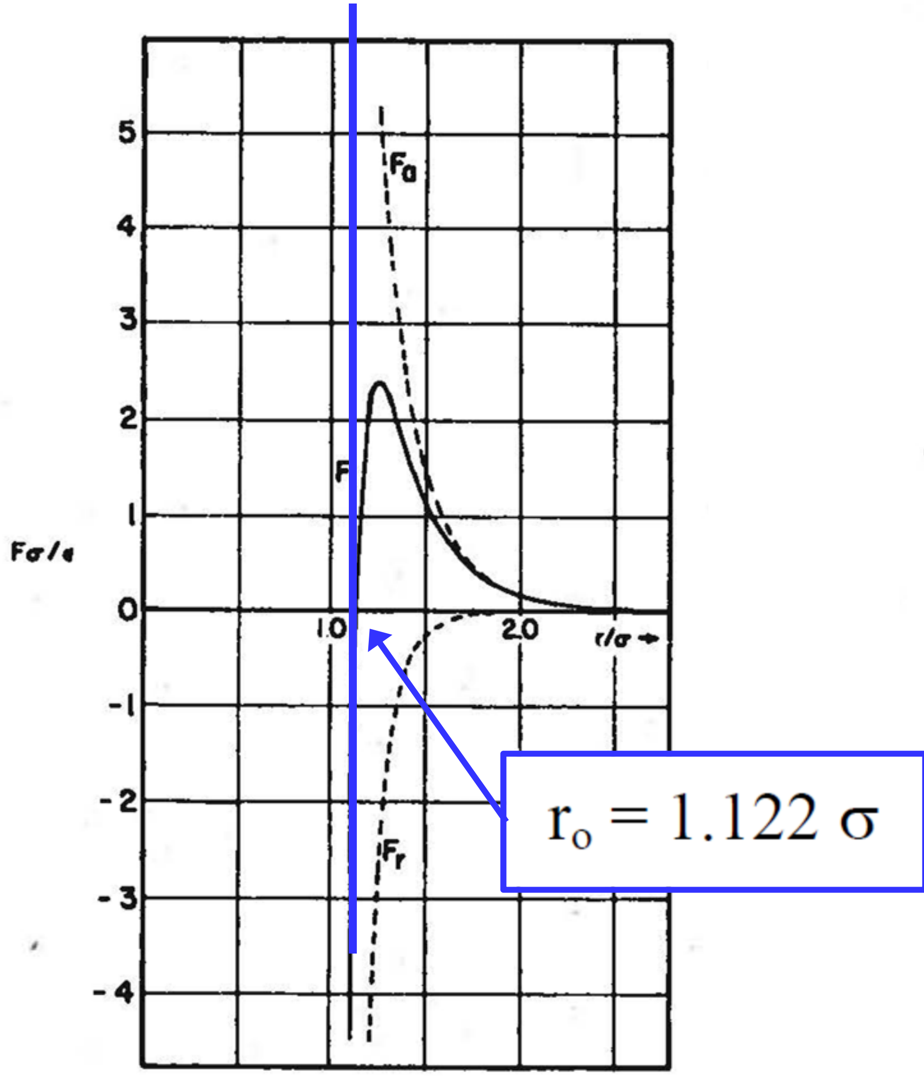


Figure 3-8 Lennard-Jones Potential, ϕ_a, Attractive; ϕ_r, Repulsive.



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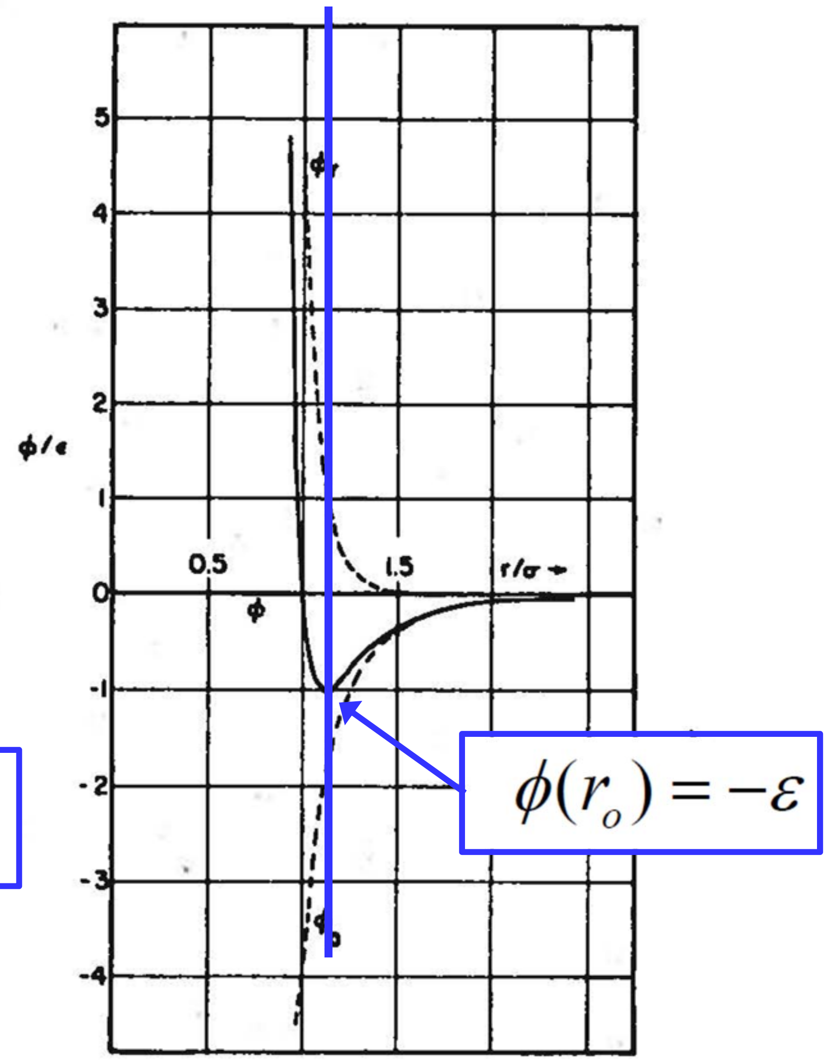

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Summary

- Potential energy is zero at $r = \sigma$.
- Potential energy is minimum at the equilibrium distance.
- Net force is zero at the equilibrium distance.
- The equilibrium distance is given by $r_o = 1.122\ \sigma$
- The value of potential at the equilibrium distance is $-\varepsilon$.
- Attractive Force = +, Repulsive Force = -
- Attractive Energy = -, Repulsive Energy = +

$$\phi(r) = \int_{\infty}^{r} F(r)\ dr \qquad \phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad F = \frac{d\phi}{dr}$$