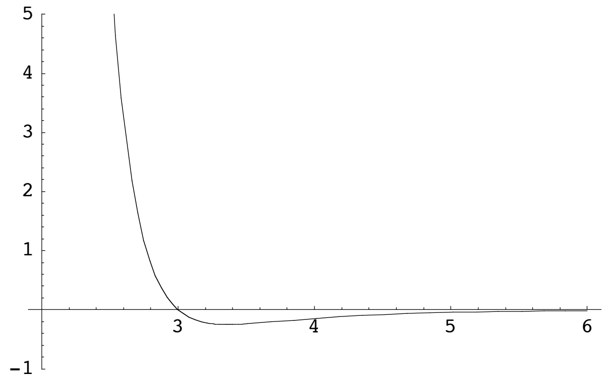
HW2, Problem 4

a. $$V(r) = \epsilon\, [\, (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\,]$$

V(r) has two parts. The $(\sigma/r)^{-12}$ part is larger than the -r^{-6} part for small r, so V(r) is positive for small r (heading towards positive infinity at r = 0). The r^{-12} term dies faster than the -r^{-6} part at large r, though, so V(r) is negative at large r, approaching zero from below as r goes to infinity. By continuity, there must be a minimum somewhere in the middle.



Ignore the number values on the graph above.

We see the r-axis is crossed when V(r) = 0....i.e. when r = σ. A bigger σ moves the graph farther right, so σ controls where the minimum occurs. A bigger ϵ stretches the graph vertically, so ϵ controls the well depth.

If V(r) represents the interaction potential of two atoms, σ is closely related to the equilibrium distance between them, while ϵ is closely related to the binding energy. Other parts of this question explore the specific details of these relations.

b. Let $V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$

This form only contains one occurance of each constant (and only to the first power), whereas there were two sigmas in the other form. This form is probably easier to manipulate algebraically, differentiate, integrate, etc. The form in part a, however, makes it easier to see how the constants control the shape of the graph.

c. Since the zero crossing is at r = σ, a glance at the graph says the minimum must occur at a larger r value. At the minimum, the first derivative of V(r) should be zero.

$\frac{dV}{dr} = 0$ gives, after some manipulations, $r_o = \sqrt[6]{2}\,\sigma$, which is $>\sigma$.

d. Force is given by the negative derivative (with respect to position) of potential:

$$F = -\frac{dV}{dr}$$

Certainly, the slope of V(r) is at a maximum as you approach the infinity at r = 0. That's the location of the maximum repulsive force between the atoms. A closer look at the graph shows that there is an inflection point a bit beyond r_o (the slopes must get bigger right after you pass the minimum, but they must flatten out again as you go to large r). We'd expect the location of this maximum attractive force to be at some $r > r_o$.

To find this maximum force, take the derivative of the force (which is the second derivative of V(r), and set it equal to zero. After some manipulation, $\frac{d^2 V}{dr^2} = 0$ gives:

$$r_{F0} = \sqrt[6]{\frac{26}{7}}\,\sigma, \text{ which is } > r_o$$

e. We want to replace $V(r) = \epsilon\, [\, (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\,]$ with $V(r) = Vo + \frac{k}{2}(r - r_o)^2$. Such a function is an upward opening parabola with its minimum sitting in the base of the well. Such an approximation not only makes for easier algebraic manipulation, but it also gives us an approximate solution to the equation of motion. It's not easy at all to solve Newton's Law:

$$\frac{d^2 r}{dt^2} = \frac{1}{m} F = -\frac{1}{m} \frac{dV}{dr}$$

if we use the full version of V(r), but we already know the solution if we use the harmonic oscillator approximate V(r)...just sines and cosines.

To figure out what Vo and k should be, we need to step back and ask what exactly we're trying to do here. We are trying to replace a complicated looking function with a simple second degree polynomial that is a good approximation to the complicated function around some value (r_o, to be specific). Sounds like what Taylor Series are for. Expanding V(r) to second order about the value r = $r_o = \sqrt[6]{2}\,\sigma$ gives, after some algebra:

$$V(r) = \frac{-\epsilon}{4} + \frac{9\in}{(\sigma^2)\sqrt[3]{2}}(r - r_o)^2$$

And comparison to the given form V(r) = Vo + $\frac{k}{2}(r - r_o)^2$ allows us to read off

$$Vo = \frac{-\epsilon}{4} \quad \text{and} \quad k = \frac{18\in}{(\sigma^2)\sqrt[3]{2}}$$