Orbits of the Lennard-Jones Potential

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July 28, 2012

1 Introduction

The Lennard-Jones potential describes weak interactions between neutral atoms and molecules. Unlike the potentials proportional to $\frac{1}{r}$, the Lennard-Jones potential contains a point of static equilibrium. It is

$$U_{\mathrm{L-J}} = \varepsilon \left(\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^{6} \right) \tag{1}$$

where ε is the magnitude of the maximum depth of the potential well and r_m is the distance from the origin at which static equilibrium occurs. Static equilibrium can occur in the Lennard-Jones potential because close to the origin of the potential, overlapping electron orbitals cause the neutral particles to repel each other, while farther away, Van der Waals forces cause the neutral particles to attract each other. [1]

Because the Lennard-Jones potential is meant to describe the interactions between individual atoms and molecules, any in-depth analysis of its consequences frequently invokes quantum mechanics. Hence, it has not thus far been analyzed as a classical central force problem. Here, the points of dynamical equilibrium of the Lennard-Jones potential as well as the conditions for closed orbits will be analyzed by considering a one-body problem of a point mass particle in said effective potential.

2 Dynamics

As has been shown before with gravity, the dynamics of a point mass in a central potential change markedly when angular momentum is considered. The advantage of considering a central potential is that after applying the Euler-Lagrange equation for the angle φ, the angular momentum vector $\mathbf{M}$ of the body can be found to be constant.

[1] https: //en.wikipedia.org/wiki/Lennard-Jones_potential

Because neither the Lennard-Jones potential nor the kinetic energies depend explicitly on time, the system Lagrangian does not explicitly depend on time. Performing a Legendre transformation of the time-independent Lagrangian with respect to the momenta and velocities yields the energy, which is conserved:

$$E = K + U = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2(\theta)\dot{\varphi}^2) + \varepsilon\left(\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right). \quad (2)$$

However, from the conservation of $\mathbf{M}$, $\dot{\varphi}$ is proportional to M, where M is the magnitude of $\mathbf{M}$. After substituting M into the equation for the energy, the term now involving M rather than $\dot{\varphi}$ (called the kinetic potential) can be grouped with the Lennard-Jones potential to yield the effective potential:

$$U_{\text{eff}} = U_K + U_{\text{L−J}} = \frac{M^2}{2mr^2} + \varepsilon\left(\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right). \quad (3)$$

3 Dynamical Equilibria

The Lennard-Jones potential is constructed such that r_m is the value of r that minimizes the potential. However, adding the kinetic potential to the Lennard-Jones potential complicates the situation. Finding the new dynamical equilibria means setting the partial derivative of U_{eff} with respect to r equal to 0; performing this yields the quintic equation

$$\frac{M^2}{m}r^{10} - 12\varepsilon r_m^6 r^6 + 12\varepsilon r_m^{12} = 0. \quad (4)$$

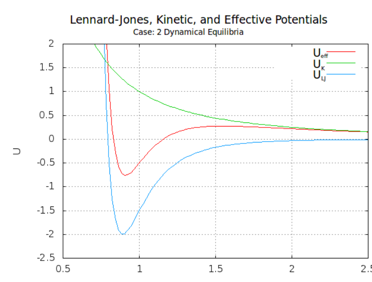

Figure 1: U_{eff}: case of 2 equilibria

Because this is a quintic equation with arbitrary coefficients, by the *Abel-Ruffini theorem* this cannot be analytically factored into a solution involving complex radicals. However, by definition quintic equations have 5 complex roots. Furthermore, because m and ε are by definition positive, the number of real roots becomes restricted between 0 and 2.

If there are 0 real roots, the effective potential has no points of equilibrium, so it monotonically decreases to zero with increasing r. This means that there are no closed orbits; all trajectories lead away from the origin.

If there is 1 real root, the effective potential decreases monotonically except for one saddle point. At this point, a circular orbit is possible, but if any perturbation occurs, the particle will move away from the origin unbounded.

If there are 2 real roots, as in figure (1), the effective potential decreases, increases, and then decreases again. There is thus one stable and one unstable equilibrium, with the latter occurring at a larger value of r than the former. Closed orbits are possible if the energy is at most equal to the effective potential at the unstable equilibrium and if the particle starts at a value of r less than that of the unstable equilibrium.

4 An Example Lennard-Jones Potential: $\varepsilon = 2$ and $r_m = 1$

These three cases for the effective potential can be achieved by changing either the Lennard-Jones parameters, being the well position or the well depth, or the angular momentum. The Lennard-Jones parameters are set by the properties of the interaction between the two particles, so the only true modifiable parameter is the angular momentum. Let us consider a case where, in some unit system, $\varepsilon = 2$ and $r_m = 1$. This implies that the Lennard-Jones potential is

$$U_{\mathrm{L-J}} = 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right) \tag{5}$$

in this case. Furthermore, let us use units where $m = 1$. This implies that

$$U_{\mathrm{eff}} = \frac{M^2}{2r^2} + 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right) \tag{6}$$

for this system. In general, rewriting the energy to make use of the conservation of angular momentum yields

$$E = \frac{1}{2}m\dot{r}^2 + \frac{M^2}{2mr^2} + \varepsilon\left(\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^6\right) \tag{7}$$

and in this case the energy would be

$$E = \frac{1}{2}\dot{r}^2 + \frac{M^2}{2r^2} + 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right). \tag{8}$$

Energy is conserved in a central potential, and this is no exception, so applying a total time derivative to the energy equation and bearing in mind that the angular momentum M is conserved yields the equations of motion

$$m\ddot{r} = \frac{M^2}{mr^3} + 12\varepsilon\left(\frac{r_m^{12}}{r^{13}} - \frac{r_m^6}{r^7}\right) \tag{9}$$

$$\dot{\theta} = \frac{M}{mr^2} \tag{10}$$

the latter equation coming from our definition of angular momentum. In our particular case, these become

$$\ddot{r} = \frac{M^2}{r^3} + 24\left(\frac{1}{r^{13}} - \frac{1}{r^7}\right) \tag{11}$$

$$\dot{\theta} = \frac{M}{r^2}. \tag{12}$$

Do note that in the last two sets of equations, θ has been redefined from being the vertical angle to being the azimuthal angle, as is conventional when all polar motion takes place on a plane.

The angular momentum M can be changed to yield zero, one, or two dynamical equilibria. A low value of M will yield two, a high value will yield zero, and a precise value somewhere in between will yield exactly one. As with any central potential, the orbit is fully specified by the values of E and M. However, this orbit cannot be computed analytically, so numerical simulations must be done, and those require the specification of the initial values of r, $\dot{r}$, and θ due to the number and orders of the differential equations of motion.

5 $M = 2$: Two Equilibria

For the case of low M, let us take $M = 2$. This implies an effective potential given by

$$U_{\text{eff}} = \frac{2}{r^2} + 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right) \tag{13}$$

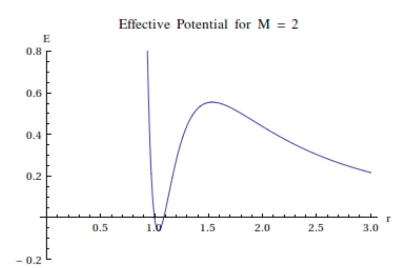

Figure 2: U_{eff}: $M = 2$

and equations of motion given by

$$\ddot{r} = \frac{4}{r^3} + 24\left(\frac{1}{r^{13}} - \frac{1}{r^7}\right) \tag{14}$$

$$\dot{\theta} = \frac{2}{r^2}. \tag{15}$$

This effective potential has a global minimum at $r \approx 1.0362$ with $U_{\text{eff}} \approx -0.063468$ at that point. This is very close to the minimum of the standard Lennard-Jones potential which occurs by definition at $r_m = 1$, so this shows how the centrifugal/kinetic potential does not affect the form of the Lennard-Jones potential that much. At that minimizing r, orbits are perfectly circular.

For $-0.063468 \leq E \leq 0$, all orbits are bounded. In this neighborhood, the effective potential has an approximately parabolic shape, so r visibly behaves almost like a trigonometric function as θ increases. That said, r is not a conic function of θ as it would be in a standard gravitational potential. In fact, r is multivalued with respect to θ, and this is generally true for stable noncircular orbits in a Lennard-Jones potential, implying that said orbits never fully close upon themselves in a finite amount of time.

For $0 < E \leq 0.55472$, the upper bound being the value of the effective potential at its single local maximum, orbits are bounded for $0.94561 \leq r \leq 1.5342$. The shape of the potential in this region diverges further from being a parabolic function of r, so while r still varies periodically over time, it is no longer as close to varying like a trigonometric function. At $r \approx 1.5342$, the effective potential achieves its local maximum, so a circular orbit is achieved. This orbit, while closed, is unstable, because for $r > 1.5342$, the effective potential monotonically decreases to zero, and for those values of r, the orbit curves slightly in the beginning but quickly approaches rectilinear inertial motion with r steadily and ceaselessly increasing (though true rectilinear motion is never fully achieved in finite time).

For $E > 0.55472$, the orbit has enough energy to overcome the local maximum in the effective potential, so any $r \in (0, \infty)$ is a valid initial condition. If the orbit starts at $r < 1.5342$, the orbit will curve quite a bit as it climbs up the effective potential energy barrier, but after crossing that barrier it will once again approach a rectilinear inertial path.

6 $M = 10$: No Equilibria

Now let us consider the case of high M; for this, let us take $M = 10$. This implies an effective potential given by

$$U_{\text{eff}} = \frac{50}{r^2} + 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right) \tag{16}$$

and equations of motion given by

$$\ddot{r} = \frac{100}{r^3} + 24\left(\frac{1}{r^{13}} - \frac{1}{r^7}\right) \tag{17}$$

$$\dot{\theta} = \frac{10}{r^2}. \tag{18}$$

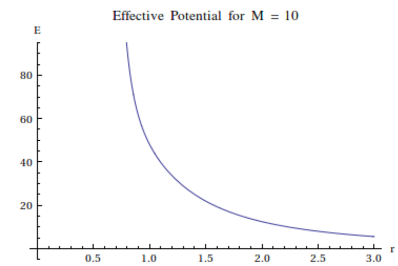

Figure 3: U_{eff}: $M = 10$

In this case, any $E \geq 0$ is allowed, and because the effective potential here has no global minimum or local maximum at finite r, stable orbits are not allowed and neither are circular orbits (stable or unstable). All orbits are unstable and start with a little curvature followed by a quick approach to rectilinear inertial motion; only the details of the curvature vary depending on the initial value of r, which is allowed to be anything more than zero.

7 $M = 6\left(\frac{2}{5}\right)^{\frac{5}{6}}$: One Equilibrium

Finally, let us consider the case where M is such that the effective potential has a saddle point. This implies that our equation of dynamical equilibrium, which after plugging in our choices for parameters reads

$$M^2 r^{10} - 24r^6 + 24 = 0 \tag{19}$$

must not only be true in itself, but because there should only be one equilibrium r for the chosen M, the condition on the derivative of this equation with respect to r

$$10M^2 r^9 - 144r^5 = 0 \tag{20}$$

must also be true. This is a system of two equations with two unknowns (M and r) and can be solved analytically. The result is that $M = 6(\frac{2}{5})^{\frac{5}{6}}$ produces an effective potential that monotonically decreases with r save for one saddle point.

This implies an effective potential given by

$$U_{\text{eff}} = \frac{36\left(\frac{2}{5}\right)^{\frac{2}{3}}}{5r^2} + 2\left(\frac{1}{r^{12}} - \frac{2}{r^6}\right) \tag{21}$$

and equations of motion given by

$$\ddot{r} = \frac{72\left(\frac{2}{5}\right)^{\frac{2}{3}}}{5r^3} + 24\left(\frac{1}{r^{13}} - \frac{1}{r^7}\right) \tag{22}$$

$$\dot{\theta} = \frac{6(\frac{2}{5})^{\frac{5}{6}}}{r^2}. \tag{23}$$

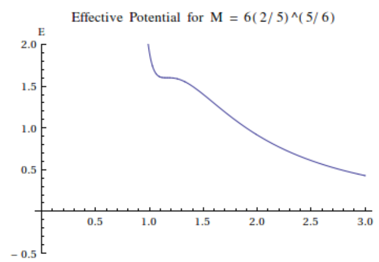

Figure 4: U_{eff}: $M = 6(\frac{2}{5})^{\frac{5}{6}}$

The saddle point occurs at $r = (\frac{5}{2})^{\frac{1}{6}}$. That point represents a circular orbit, but that orbit is unstable because of the shape of the effective potential. There are no stable orbits and there are no other closed orbits, and the energy is allowed to be any positive value. All other orbits are unstable and their qualitative properties are similar to those of the case of a higher M, and if the initial $r < (\frac{5}{2})^{\frac{1}{6}}$, there will again be some initial noticeable curvature in the orbit, though the amount curvature will qualitatively lie between the cases of high and low M.

8 Orbit Plots

The following plots have given values of M and $r(t = 0) = r_0$. They all have $\dot{r}(t = 0) = 0$ and $\theta(t = 0) = 0$, implying that $x(t = 0) = r_0$ and $y(t = 0) = 0$.

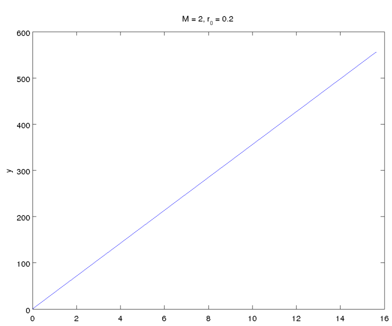

Figure 5: $M = 2$, $r_0 = 0.20$

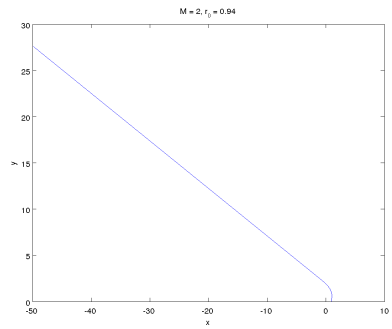

Figure 6: $M = 2$, $r_0 = 0.94$

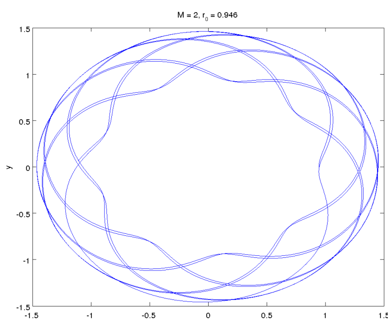

Figure 7: $M = 2$, $r_0 = 0.946$

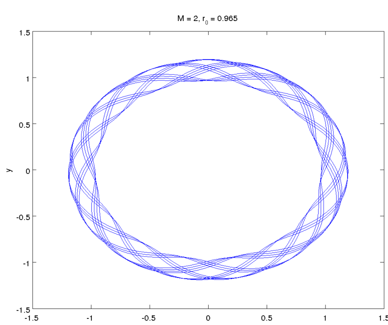

Figure 8: $M = 2$, $r_0 = 0.965$

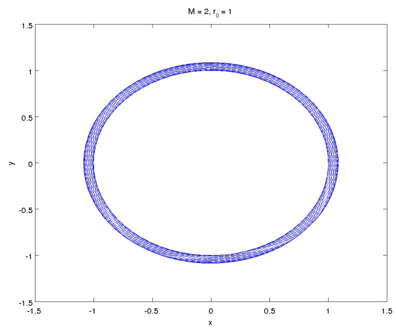

Figure 9: $M = 2$, $r_0 = 1.00$

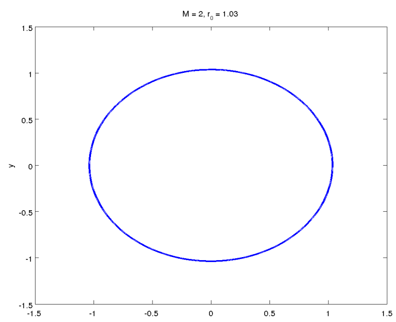

Figure 10: $M = 2$, $r_0 = 1.03$

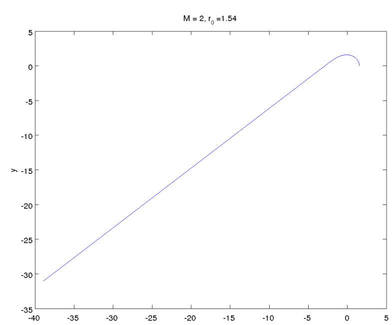

Figure 11: $M = 2$, $r_0 = 1.54$

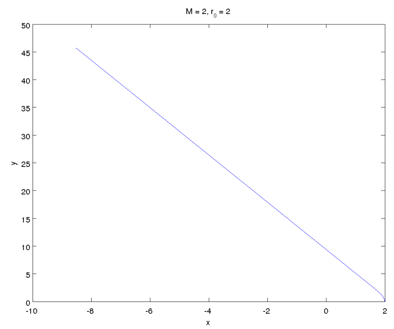

Figure 12: $M = 2$, $r_0 = 2.00$

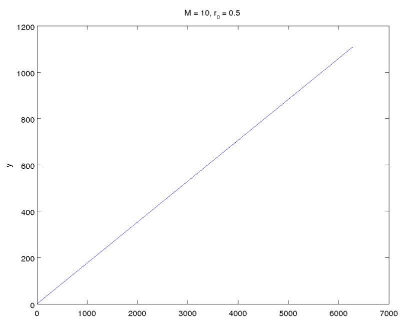

Figure 13: $M = 10$, $r_0 = 0.50$

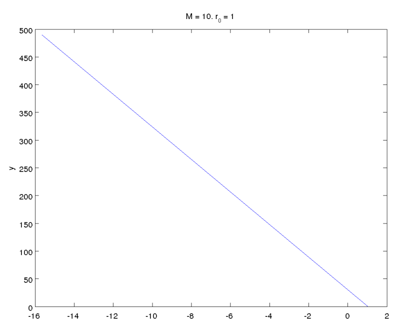

Figure 14: $M = 10$, $r_0 = 1.00$

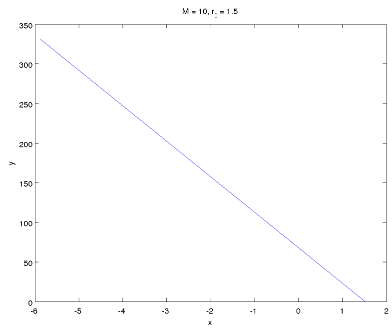

Figure 15: $M = 10$, $r_0 = 1.50$

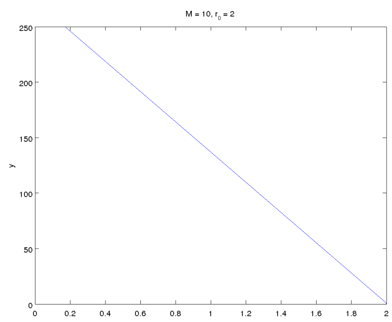

Figure 16: $M = 10$, $r_0 = 2.00$

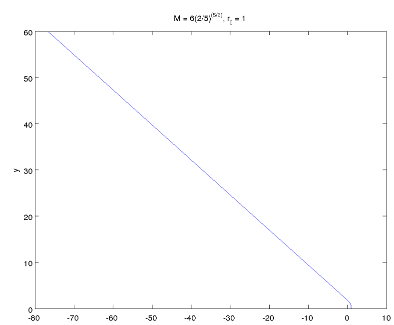

Figure 17: $M = 6(\frac{2}{5})^{\frac{5}{6}}$, $r_0 = 1.00$

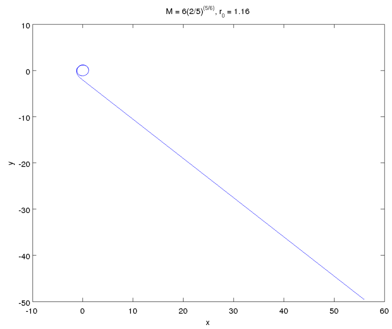

Figure 18: $M = 6(\frac{2}{5})^{\frac{5}{6}}$, $r_0 = 1.16$

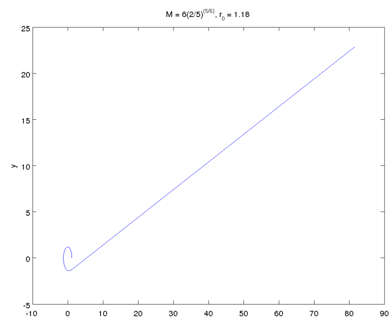

Figure 19: $M = 6(\frac{2}{5})^{\frac{5}{6}}$, $r_0 = 1.18$

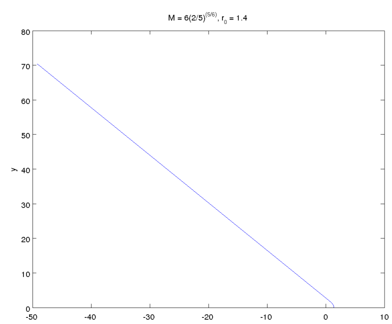

Figure 20: $M = 6(\frac{2}{5})^{\frac{5}{6}}$, $r_0 = 1.40$