Properties of the Lennard-Jones Potential

8.223 Final Project

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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.

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.

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:

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

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

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:

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

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

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

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.

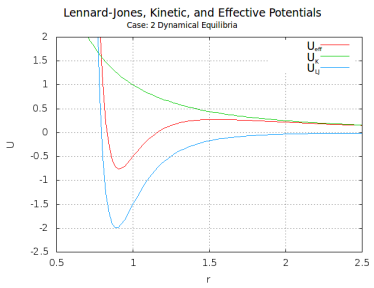

Figure 1: U_{eff}: case of 2 equilibria

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.