24-623/12-623 2015 HW#7

Total points: 40
Assigned: November 23, 2015.
Due: December 10, 2015, midnight to Blackboard. Please use the Blackboard discussion board to ask questions of the instructor or the other students.

In this homework, you will use transition state theory and Monte Carlo simulation to further study the properties of the single oscillator with potential energy $U(x) = x^4 - 2x^2 + 1$ (seen previously in HW#2 and HW#5). Define state A as the left well and state B as the right well.

1. (15 points)

(a) On the same graph, plot $U(x)$ and its harmonic approximation in the A well.

(b) Estimate $k_{A\to B}^{TST}$ from the harmonic theory expression developed in class. Plot $k_{A\to B}^{TST}$ as a function of β on a log-log plot for $0.01 \leq \beta \leq 100$.

(c) We showed in class that the harmonic theory expression is derived by changing the upper limit of an integral from q to ∞ and that this approximation should be good for

$$\sqrt{\frac{\beta k}{2}}(q - x_o) > 1.8.$$

Show this limit on your plot from (b). Explain from a physical standpoint why increasing each of β, k, and q will improve the validity of this approximation.

2. (25 points)

(a) Using the method described in class, use Metropolis NVT Monte Carlo simulations to predict $k_{A\to B}^{TST}$ for $\beta = 0.01$, 0.1, 1, 10, and 100. Plot these points with the results of problem 1(b). Explain how you ran your simulations (i.e., how did you choose the number of steps, the maximum step size, and ϵ).

(b) Comment on how your two predictions for $k_{A\to B}^{TST}$ compare to each other and on their overall physical significance.