24-623/12-623 2017 HW#7

Total points: 50
Assigned: November 15, 2017.
Due: December 7, 2017, midnight to Canvas. Please use the Canvas discussion board to ask questions of the instructor, the course assistant, 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. (20 points)

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

(b) Determine the expression for $k_{A\to B}^{TST,H}$ from the harmonic theory expression developed in class. Plot $k_{A\to B}^{TST,H}$ 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

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

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

2. (30 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. Present these results in a table along with the corresponding results from 1(b). Plot these points with the results of 1(b). Explain how you ran your simulations (i.e., how you chose the initial conditions, the number of steps, the maximum step size, and ϵ).

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