24-623 Molecular Simulation of Materials

Junrong Huang Assignment 7

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 trhis approximation should be good for

$$\sqrt{\frac{\beta S}{2}}(q - x_0) > 1.8$$

   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.

   Answer:

   (a)

   Harmonic transition theory:

$$\begin{aligned} U(x - x_0) &\approx U(x_0) + (x - x_0)\left.\frac{\partial U}{\partial x}\right|_{x=x_0} + \frac{1}{2}(x - x_0)^2\left.\frac{\partial^2 U}{\partial x^2}\right|_{x=x_0} \\ &= u_0 + \frac{1}{2}S(x - x_0)^2 \end{aligned}$$

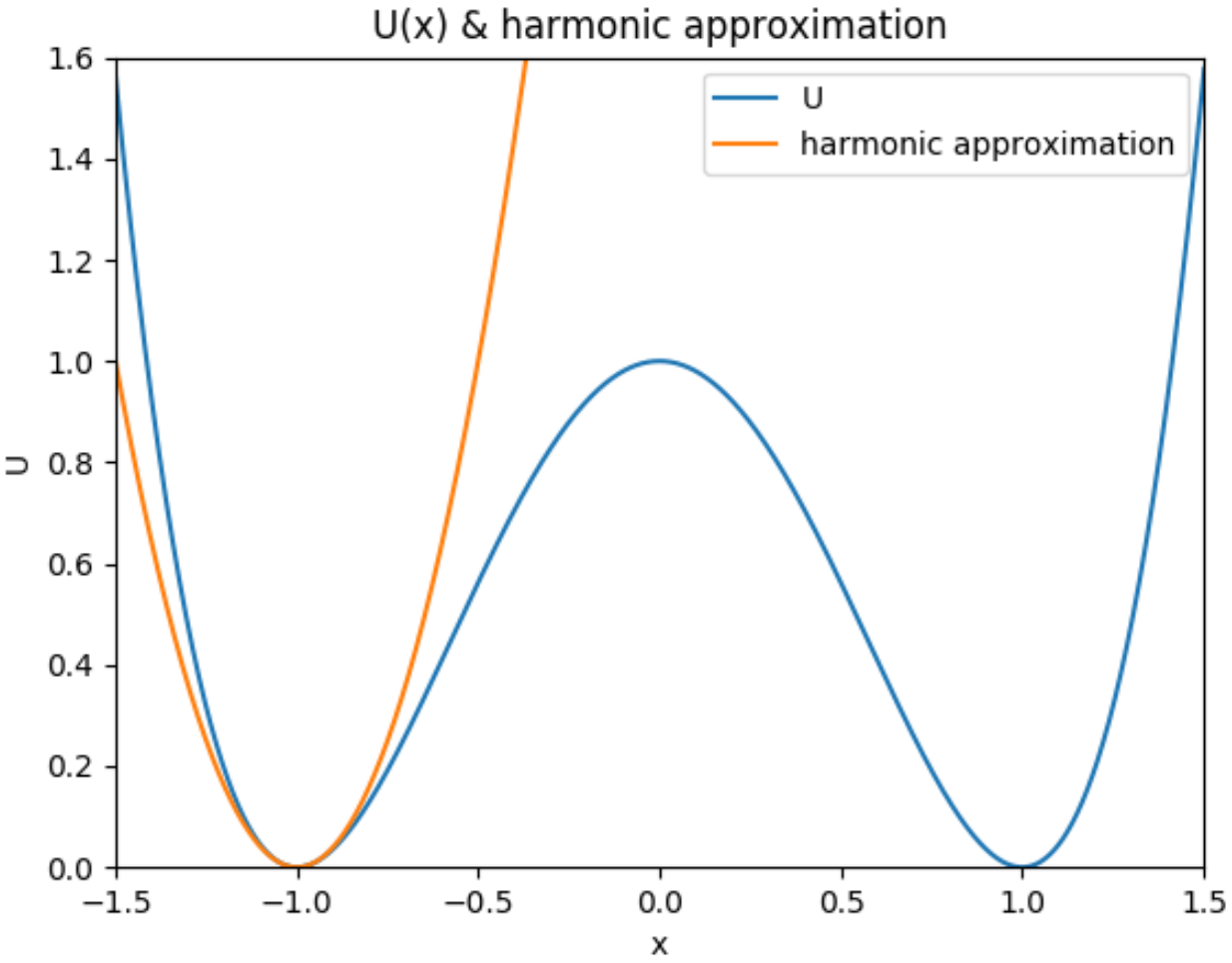
   Where:

$$x_0 = -1, u_0 = 0, S = \left.\frac{\partial^2 U}{\partial x^2}\right|_{x=x_0} = 12x^2 - 4 = 8$$

Therefore,

$$U(x - x_0) = 4(x + 1)^2$$

Plot the U(x) and the harmonic approximation in the A well on the same graph:

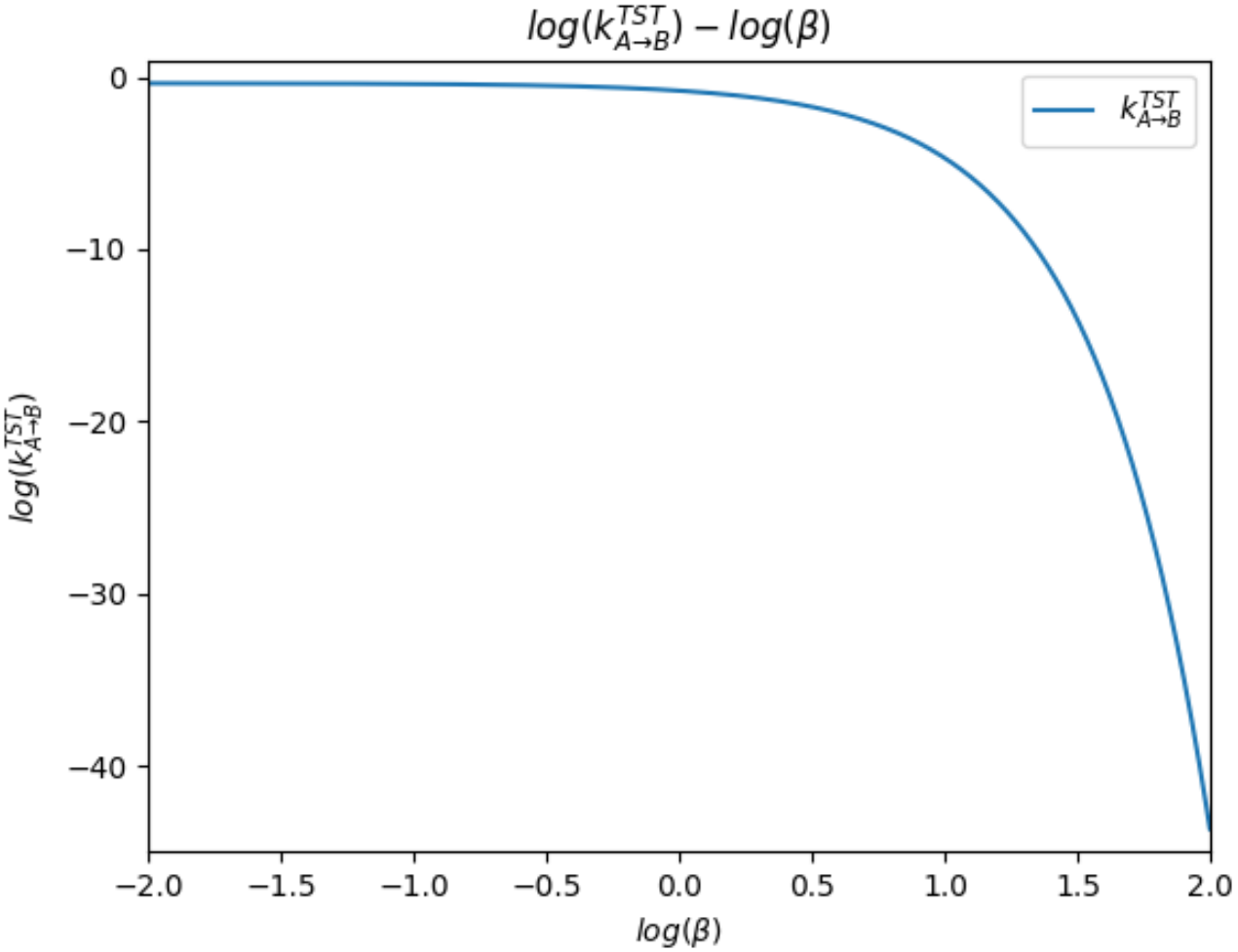


(b)

$S = 8, m = 1, u^* = U(x = 0) = 1, u_0 = 0$

$$k_{A\to B}^{TST} = \frac{1}{2\pi}\sqrt{\frac{S}{m}}exp[-\beta(u^* - u_0)]$$
$$= \frac{\sqrt{2}}{\pi}exp(-\beta)$$

Plot the $k_{A\to B}^{TST} - \beta$ function with log-log scale:



(c)

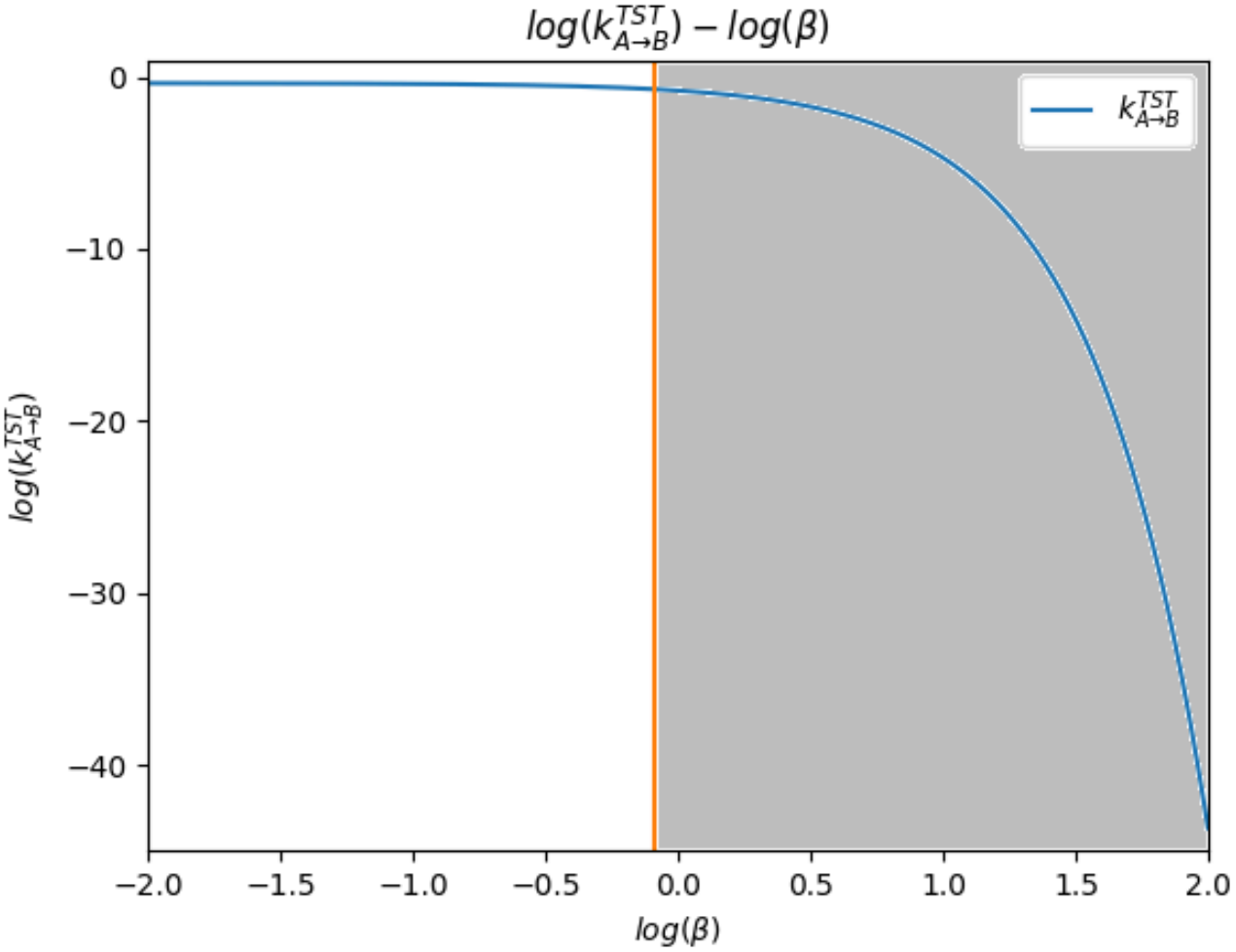
With $S = 8, q = 0, x_0 = -1$

$$\sqrt{\frac{\beta S}{2}}(q - x_0) > 1.8$$

Therefore,

$$\beta > 0.81$$

The line in grey zone is the good approximation part.



Explain from a physical standpoint why increasing each of β, S, and q will improve the validity of this approximation:

$\beta = 1/(k_B T)$, increasing β means a decrease in temperature, which will lead to the less kinetic energy. The particle's vibration will be decreased, i.e., fewer atoms will be allowed to across the energy well barrier from A to B. Therefore, the approximation will be more accurate.

$S = \partial^2 U/\partial x^2$, increasing S will lead to the result that the energy well be more precipitous, which makes the particle more difficult to jump from A to B since the energy barrier is increased.

q means the position that the energy peak exist. Increasing q makes $(q - x_0)$ greater, i.e., the average trial distance from starting point to across the energy barrier is increased. Therefore, the increasing q will makes the particle more difficult to jump from A to B

In conclusion, the increasing each of β, S, q will improve the validity of this approximation. It can also be seen from the equation that given:

$$\sqrt{\frac{\beta S}{2}}(q - x_0)$$

The good approximation accptance is proportional to β, S and q

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.

Answer:

(a)

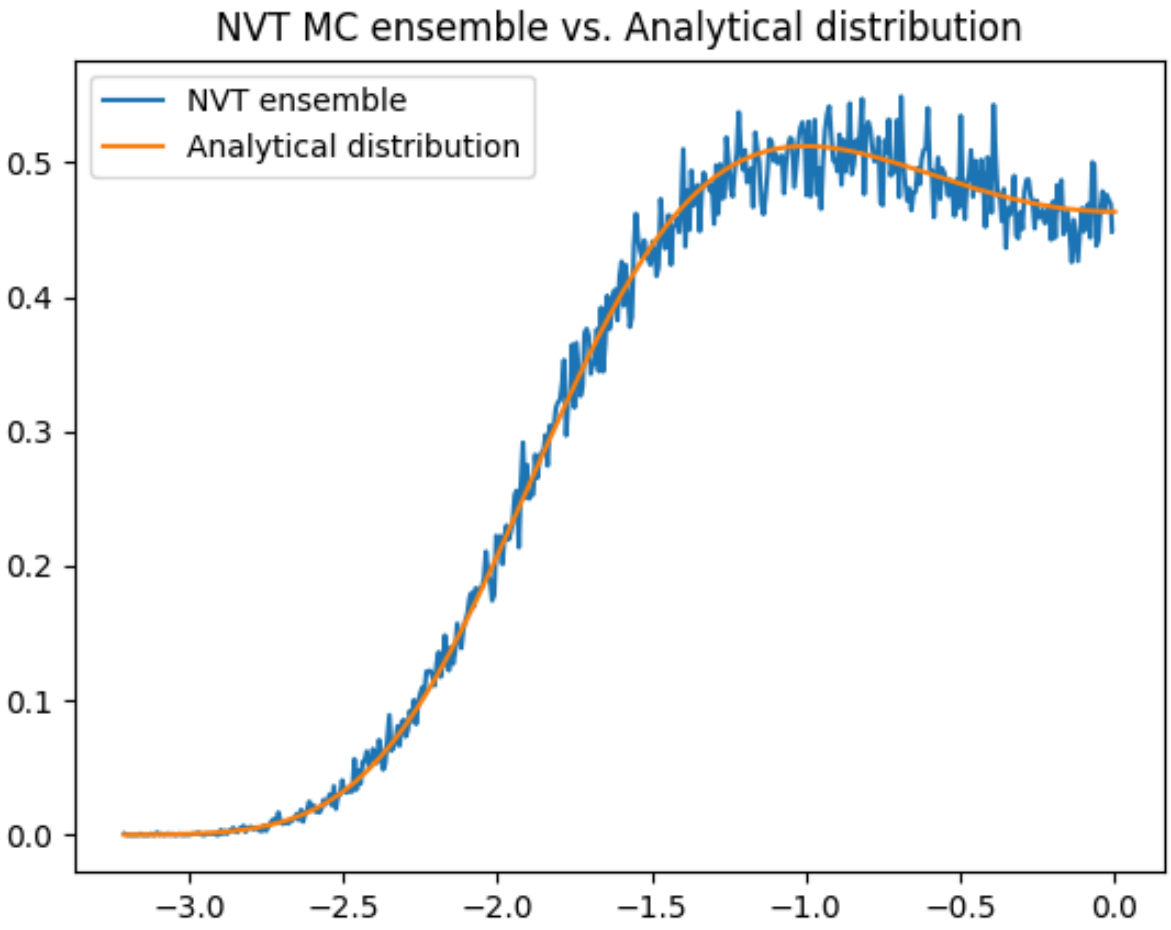
In this simulation, the basic algorithm is:

- Generate initial position of particle x_{start} w.r.t. Boltzmann distribution in range $(-\infty, q + \epsilon/2)$.
- Make trial moves from x_{start} to x_{new}
- Determine x_{new} according to metropoli accept/reject algorithm
- If x_{new} is in $[q - \epsilon/2, q + \epsilon/2]$, add to accountance M

Loop the four steps above for N times and get:

$$< \delta(x - q) >_A = \frac{M}{N} \cdot \frac{1}{\epsilon}$$

In step 1, to get x_{start}, I use the NVT Monte Carlo ensemble in A well with parameters: β varies with the given conditions, $STEP = 10000$, $trial_{max} = 2.5$(the result of HW5) to generate every x_{start} in the loop. When $x_{trial} > q + \epsilon/2$, reject this trial move. I generate $100,000$ points of x_{start} and make a probability distribution(***./2/x_generator/x_generator.cpp***). Plot the MC ensemble distribution and the Boltzmann distribution on the same graph(when $\beta = 0.1$, $\epsilon = 0.05$):

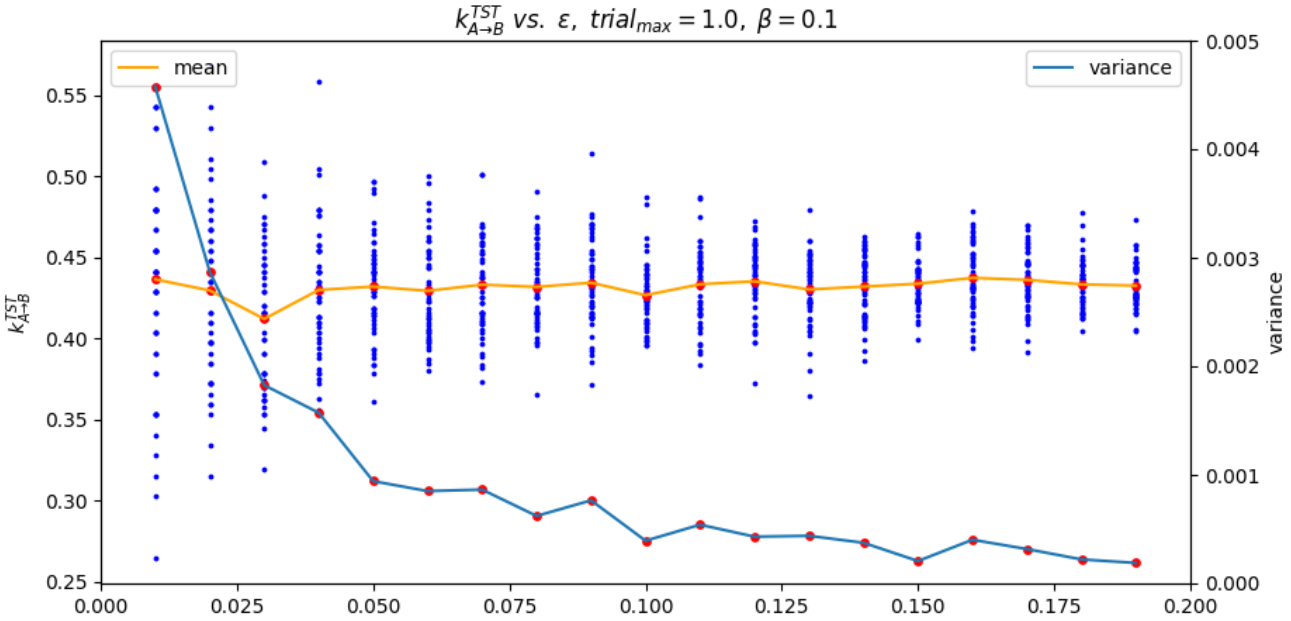


As shown in the graph, this algorithm can assure that the distribution of x_{start} obeys the Boltzmann distribution.

To determine $\#N$, δ_{max}, ϵ, I developed series of codes in ***./2*** floder.

- ϵ:

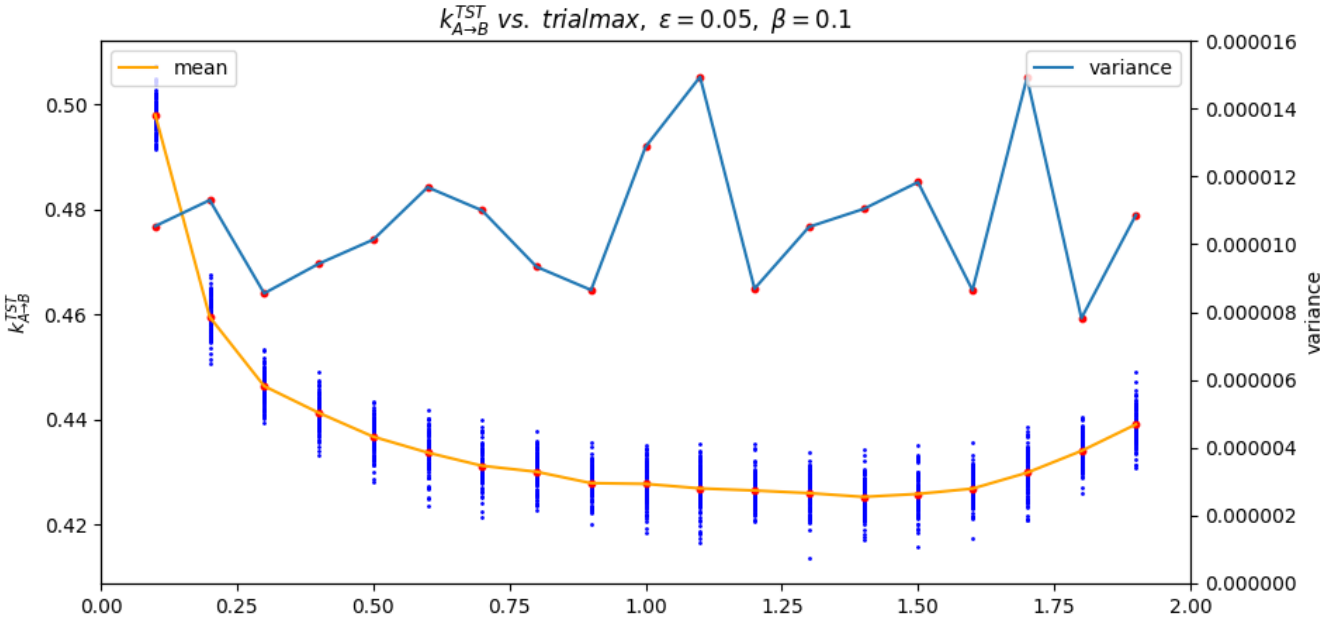
  To determine ϵ, I use the other parameter as $\#N = 1,000,000$, $trial_{max} = 1$. ϵ varies from 0.01 to 0.2 with step 0.01. I generate 50 $k_{A\to B}^{TST}$ values in each choice of ϵ to see whether the Monte Carlo results converge or not. Codes saved in ***./2/epsilon/2_epsilon.cpp***. Here is the $k_{A\to B}^{TST}$ $vs.$ ϵ scatter graph.



In these results, we can choose the $\epsilon = 0.05$ when $\beta = 0.1$, since the variance of $k^{TST}_{A\to B}$ is low enough after $\epsilon = 0.05$ and the mean of $k^{TST}_{A\to B}$ seems to be stable. We want the ϵ as small as possible in the case that the results are converged. Therefore, I choose $\epsilon = 0.05$

- δ_{max}:

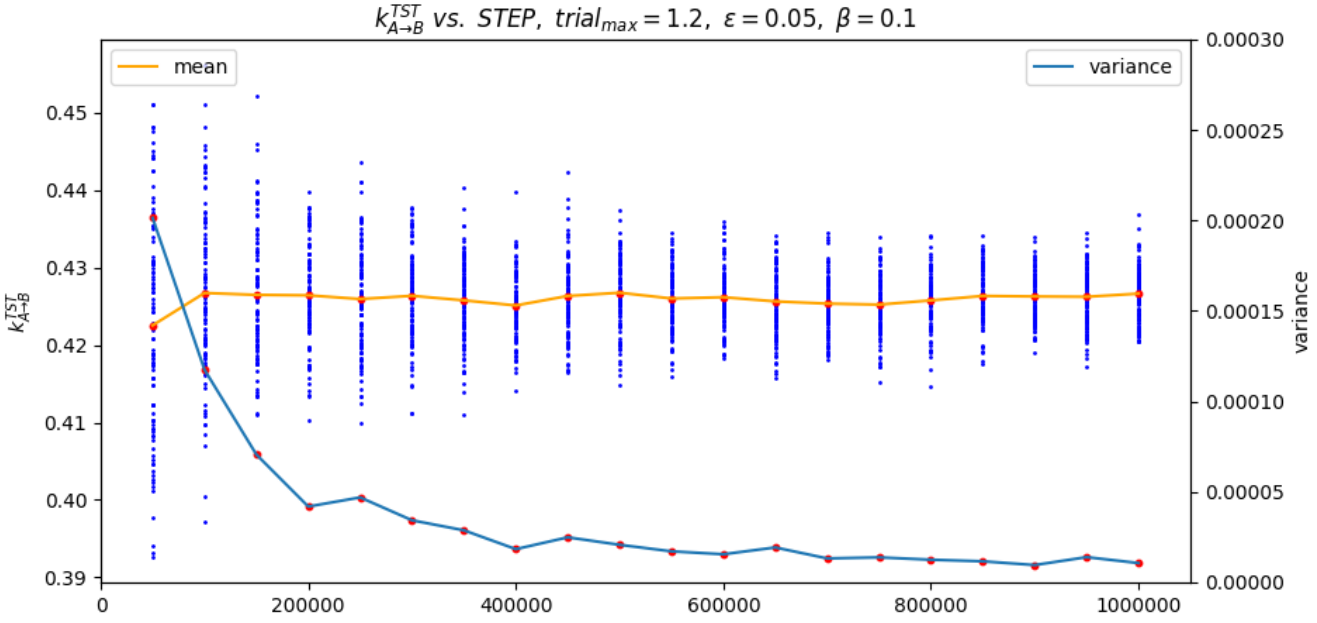
  To determine δ_{max}, same as ϵ, I use the other parameter as $\#N = 1,000,000$, $\epsilon = 0.05$. δ_{max} varies from 0.1 to 2 with step 0.1. Generate 100 $k^{TST}_{A\to B}$ values in each choice of δ_{max} to see whether the Monte Carlo results converge or not. Codes saved in ***./2/trialmax/2_trialmax.cpp***.



From the graph shown above, when $\delta_{max} = 1.2$, the variance of these 100 $k^{TST}_{A\to B}$ values are small enough and the mean of $k^{TST}_{A\to B}$ values are acceptable. Therefore, I choose $\delta_{max} = 1.2$

- $\#N$:

  To determine the number of steps, I use the other parameter as $\epsilon = 0.05$, $\delta_{max} = 1.2$. $\#N$ varies from $50,000$ to $1,000,000$ with step $50,000$. Codes saved in ***./2/step/2_step.cpp***.



The results from $400,000$ to $1,000,000$ are similar with each other. Therefore, $\#N = 400,000$ is large enough for this MC simulation.

In conclusion, the parameters are determined as:

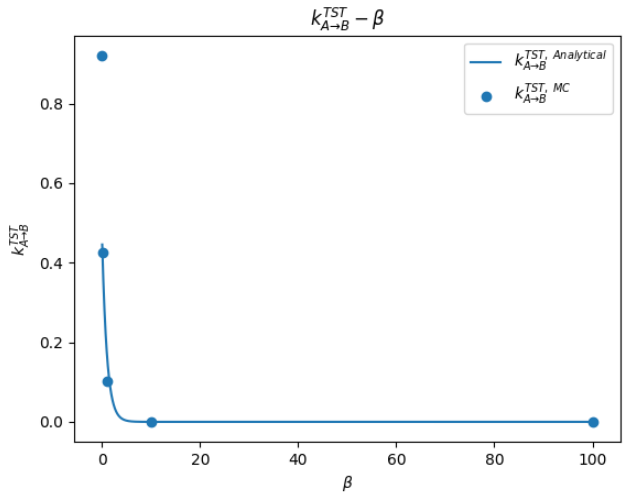
$\#N$	δ_{max}	ϵ
$400,000$	1.2	0.05

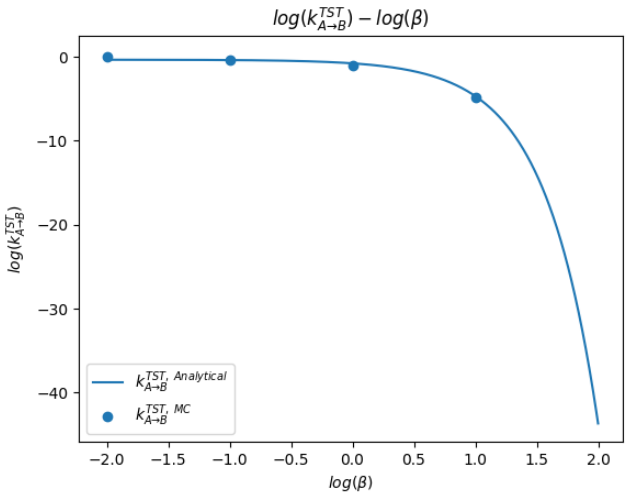
(b)

Use these values, calculate the $k^{TST}_{A\to B}$ with given $\beta = 0.01, 0.1, 1, 10, 100$, codes saved in ***./2/2_basic.cpp***:

β	$k^{TST,\,Analytical}_{A\to B}$	$k^{TST,\,MC}_{A\to B}$
0.01	0.44567009567	0.9210184
0.1	0.407319945	0.425028
1	0.16560392	0.1033059
10	2.0437148×10^{-5}	1.4508025×10^{-5}
100	$1.67462254928 \times 10^{-44}$	0.0

Plot the analytical result and the MC simulation result on the same graph with/without log scale:





There do exists difference between the results from MC simulation and the analytical deduction. However, both are in a same order of magnitude, which makes the points on the log-scaled graph show almost no differnece. In physical respect, when β is small, which means that the temperature is relatively high, the starting point distribution is more likely to be a unifrom distribution, and the trial moves are easier to be accepted since the $B = exp(-\beta\Delta U)$ is high. It will need more datapoints to be envolved to make the

simulation to be accurate. However, we choose the $\#N$ to be a constatn for each β, i.e. $400,000$, which causes the values difference is much more significant in comparing to large β.