# A Winter Short Course on Statistical Mechanics for Molecular Simulations

## Lecture 7: MD Simulations & Chemical Kinetics

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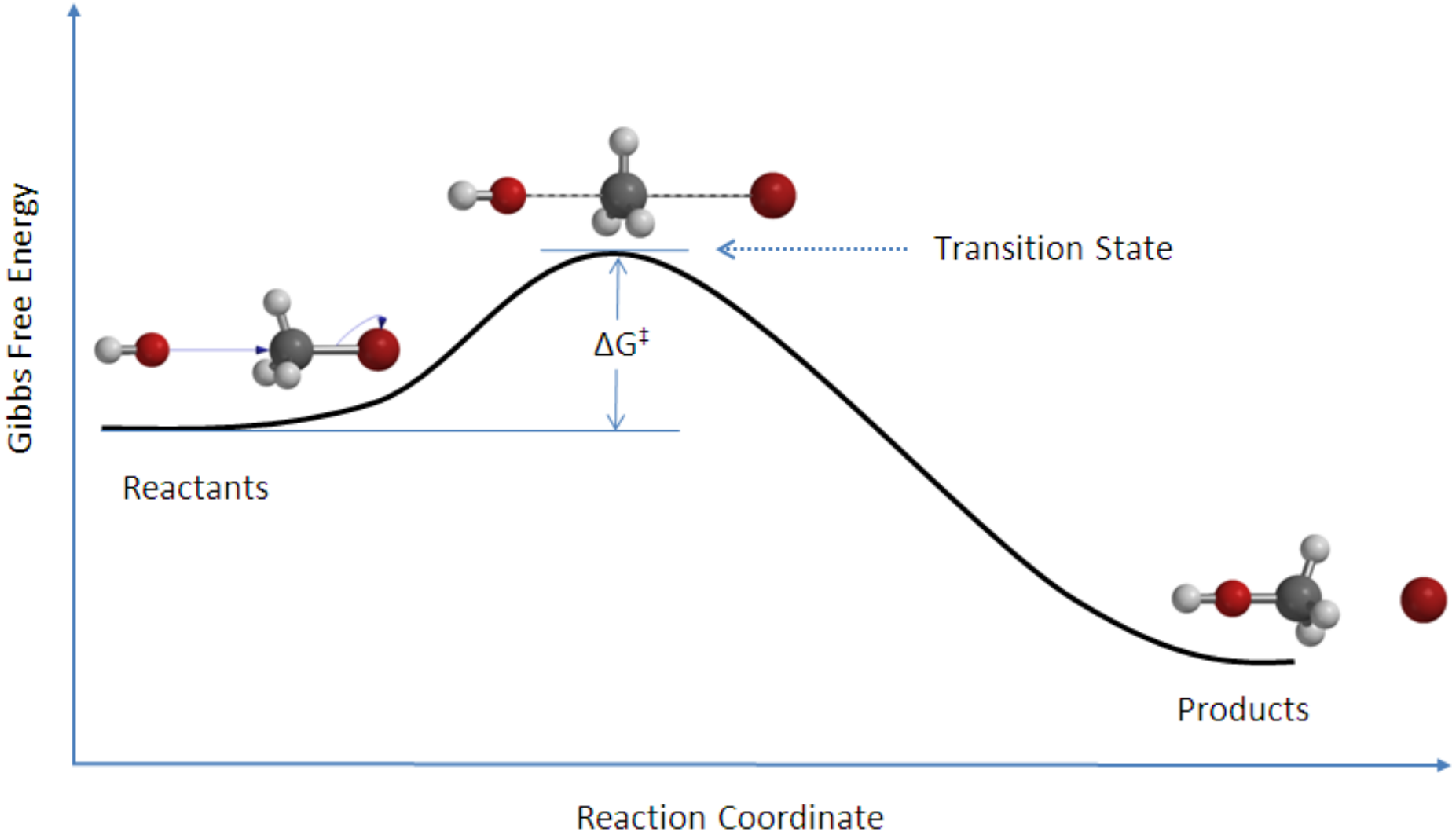



Reaction: $HO^- + CH_3Br \rightarrow [HO{-}{-}{-}CH_3{-}{-}{-}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

# Problems of TST

- Must know the reaction coordinate and the free energy surface (i.e. transition state)
- Assumes no re-crossings
- Only yields an upper bound to the rate

It turns out that in many cases, MD simulations can be used to compute the rate of such activated processes. Such calculations were first performed by Bennett in the context of diffusion in solids [457]. Subsequently, Chandler extended and generalized the approach to the calculation of reaction rates [187, 458]. The basic idea behind these MD calculations is that the rate at which a barrier crossing proceeds is determined by the product of a static term, namely the probability of finding the system at the top of the barrier, and a dynamic term that describes the rate at which systems at the top of the barrier move to the other valley.

[457] C.H. Bennett. Exact defect calculations in model substances. In A.S. Nowick and J.J. Burton, editors, *Diffusion in Solids: Recent Developments*, pages 73–113. Academic Press, New York, 1975.

[458] D. Chandler. Statistical mechanics of isomerization dynamics in liquids and the transition state approximation. *J. Chem. Phys.*, 68:2959–2970, 1978.

# Bennett-Chandler method

$$k_{A\to B}^{TST}(t)=\frac{\left\langle \dot{q}(0)\delta\left(q(0)-q_1\right)\theta(\dot{q})\right\rangle}{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}\times\frac{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}{\left\langle \theta\left(q_1-q\right)\right\rangle}$$

$$k_{A\to B}(t)=\frac{\left\langle \dot{q}(0)\delta\left(q(0)-q_1\right)\theta\left(q(t)-q_1\right)\right\rangle}{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}\times\frac{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}{\left\langle \theta\left(q_1-q\right)\right\rangle}$$

Transmission coefficient: $\kappa(t)\equiv\frac{k_{A\to B}(t)}{k_{A\to B}^{TST}}$

$q_1$: estimated transition state

$$=\frac{\left\langle \dot{q}(0)\delta\left(q(0)-q_1\right)\theta\left(q(t)-q_1\right)\right\rangle}{0.5\left\langle \left|\dot{q}(0)\right|\right\rangle}$$

# Bennett-Chandler method

First calculate the TST rate:

$$k_{A\to B}^{TST}(t) = 0.5\left\langle \left|\dot{q}(0)\right| \right\rangle \frac{\exp\left[-\beta U(q_1)\right]}{\int_{-\infty}^{q_1} \mathrm{d}q \exp\left[-\beta U(q)\right]}$$

$$= \sqrt{\frac{k_B T}{2\pi m}} \frac{\exp\left[-\beta U(q_1)\right]}{\int_{-\infty}^{q_1} \mathrm{d}q \exp\left[-\beta U(q)\right]}$$

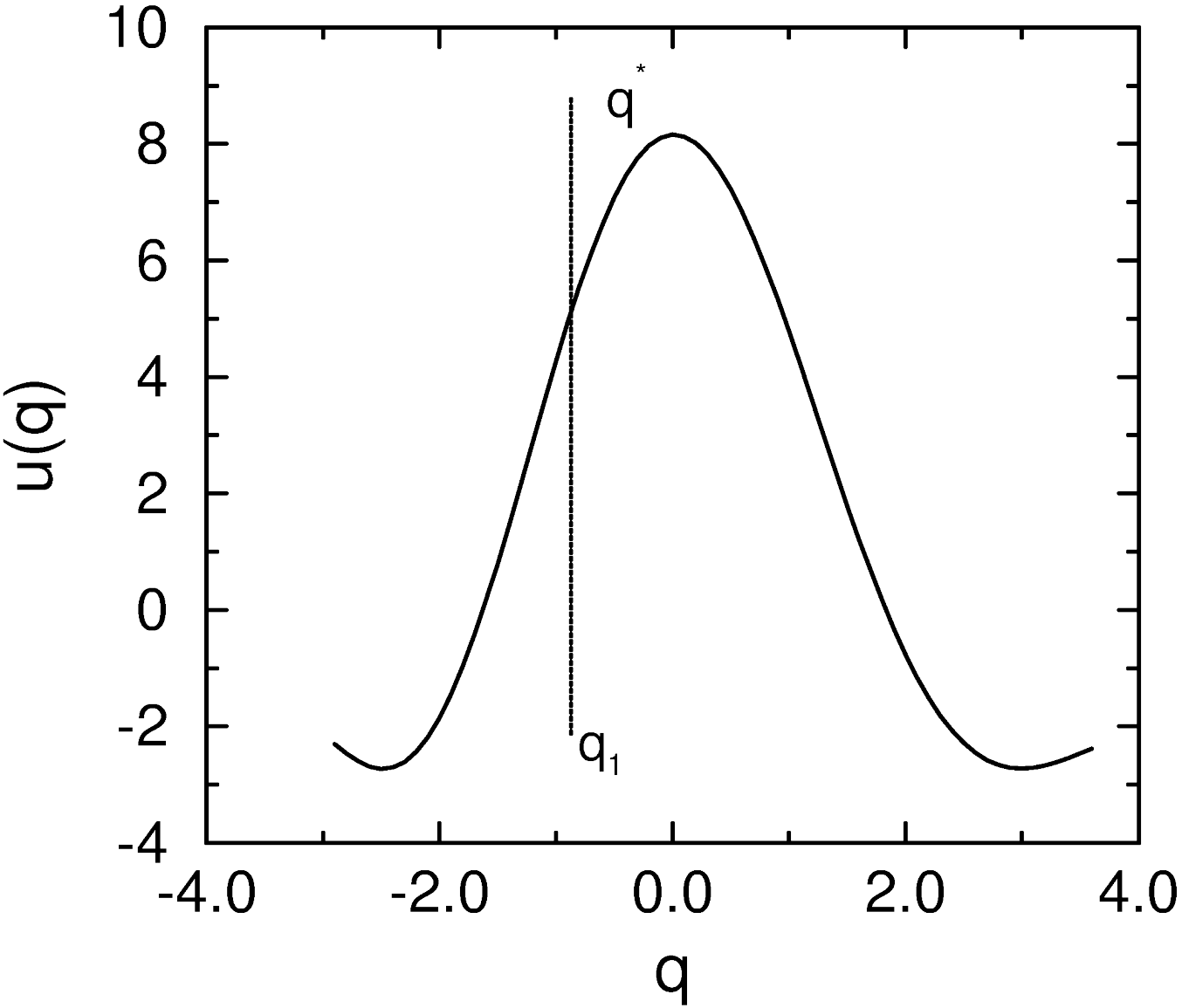
# Bennett-Chandler method

Use MD simulation to evaluate the transmission coefficient and correct the transition state result:

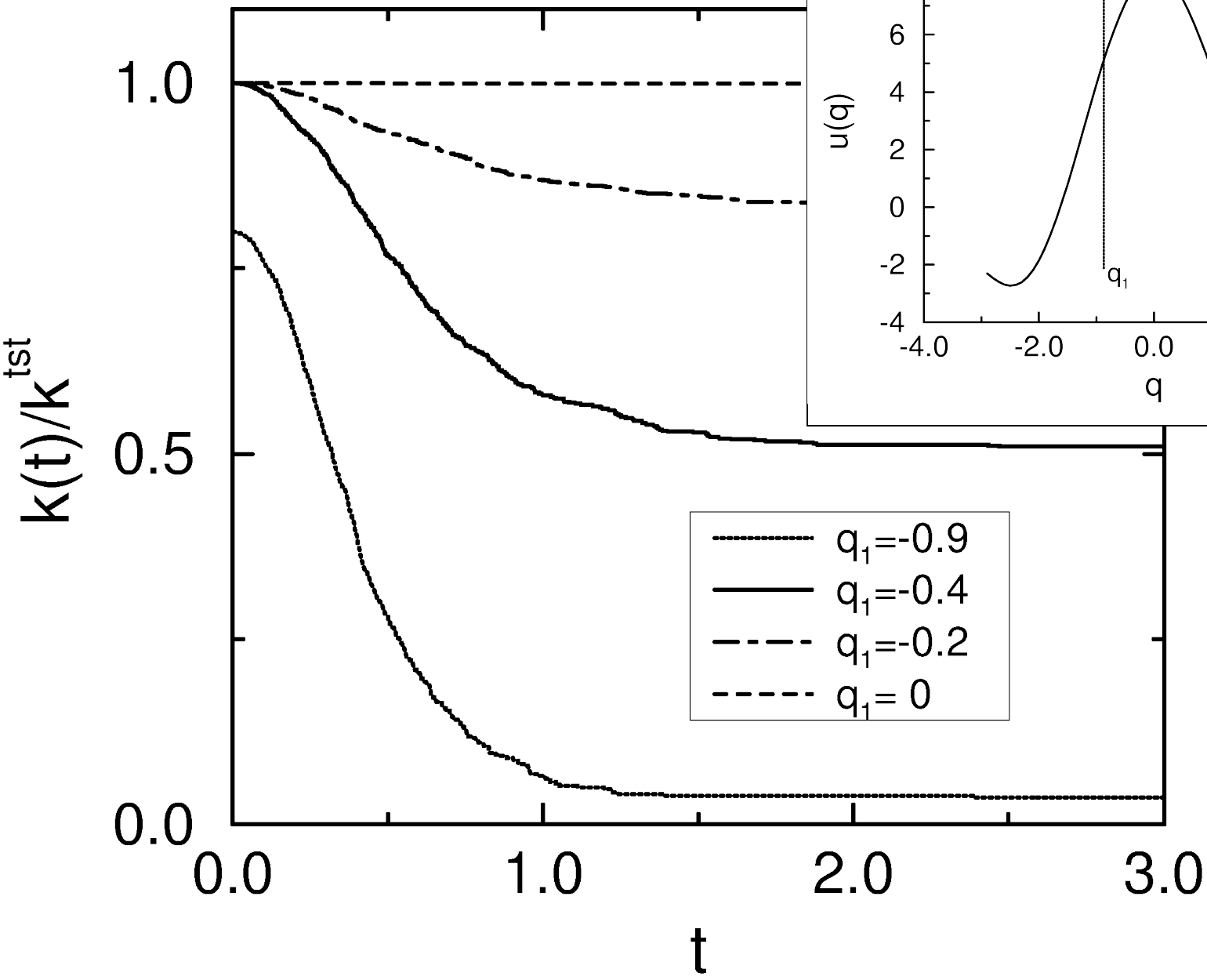
1. Set up the system at $q=q_1$ at $t=0$
2. Run many trajectories with different initial velocities (from canonical distribution)
3. Determine the ratio at the product state weighted with the initial velocity

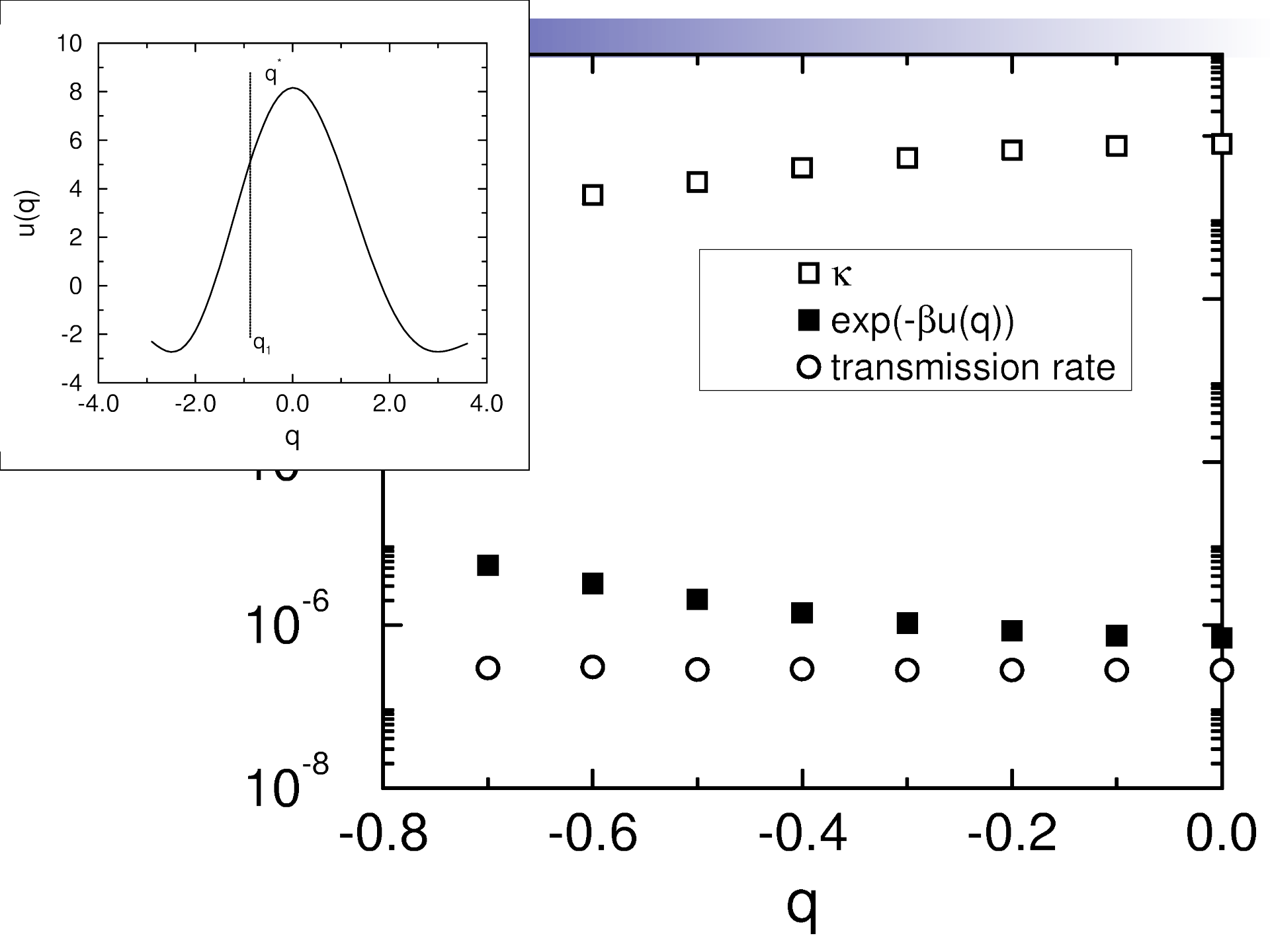
$$\kappa(t) = \frac{\left\langle \dot{q}(0)\delta\left(q(0)-q_1\right)\theta\left(q(t)-q_1\right)\right\rangle}{0.5\left\langle\left|\dot{q}(0)\right|\right\rangle}$$

# Ideal gas particle over a barrier




$q_1$: estimated transition state


1.0
0.5
0.0
k(t)/k^tst
0.0
1.0
2.0
3.0
t
q1=-0.9
q1=-0.4
q1=-0.2
q1= 0
10
8
6
4
2
0
-2
-4
u(q)
-4.0
-2.0
0.0
2.0
4.0
q
q*
q1


u(q)
q
q*
q1
κ
exp(-βu(q))
transmission rate
10^-6
10^-8
-0.8
-0.6
-0.4
-0.2
0.0
q

# Bennett-Chandler method

- Improvements upon TST: no need to determine the precise location of the transition state, re-crossing events included
- Problematic when the transmission coefficient is very small, could be due to
  - Bad reaction coordinate
  - Diffusive barrier crossing
- Even more? → transition path sampling