Rare Event Simulations

Theory 16.1

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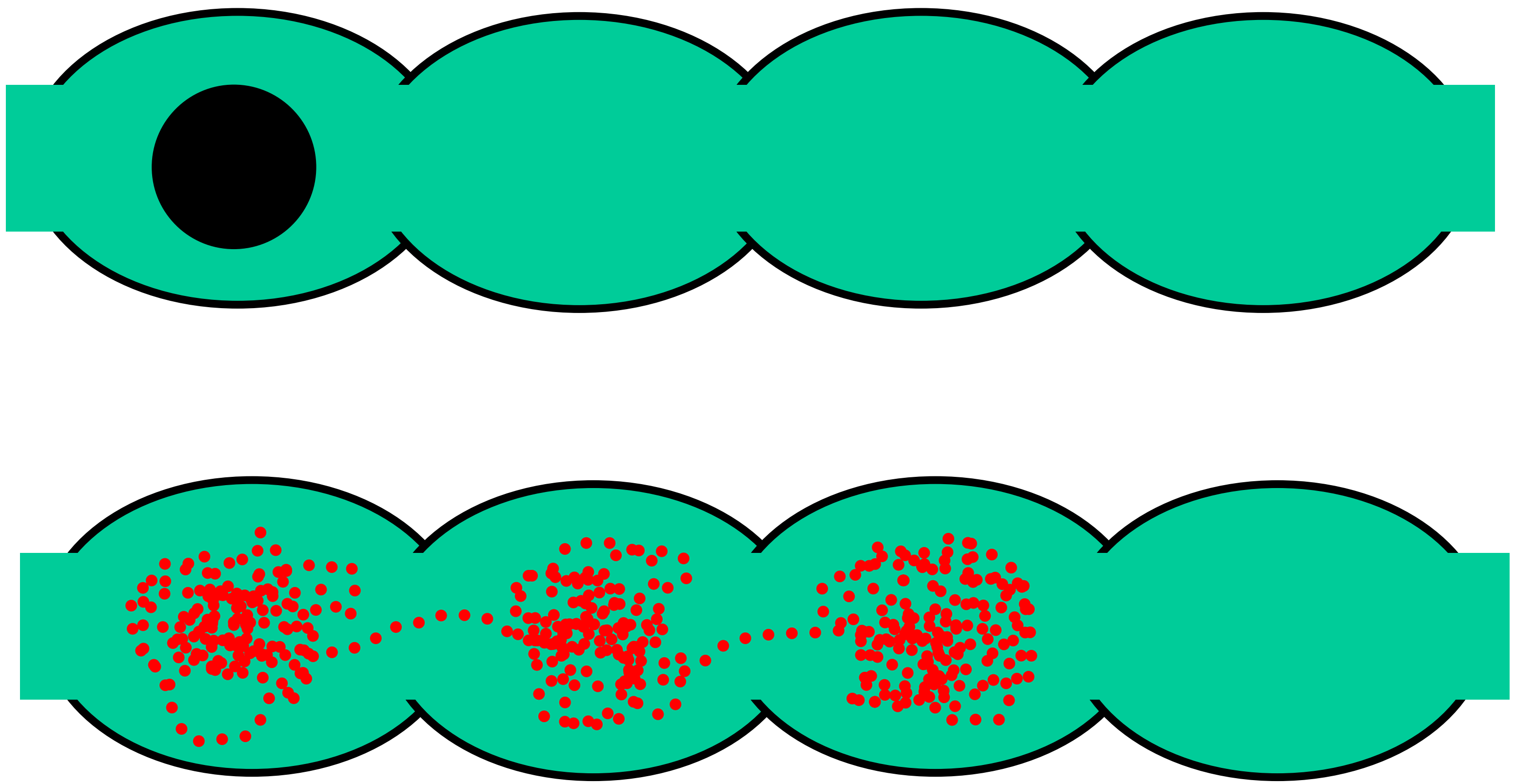
Transition path ensemble 16.4

Diffusion in porous material



Theory: macroscopic phenomenological

Chemical reaction $A \leftrightarrow B$

$$\frac{\mathrm{d}c_A(t)}{\mathrm{dt}} = -k_{A\to B}c_A(t) + k_{B\to A}c_B(t)$$

$$\frac{\mathrm{d}c_B(t)}{\mathrm{dt}} = +k_{A\to B}c_A(t) - k_{B\to A}c_B(t)$$

Total number of molecules

$$\frac{\mathrm{d}\left[c_A(t)+c_B(t)\right]}{\mathrm{dt}} = 0$$

Equilibrium:

$$\dot{c}_A(t) = \dot{c}_B(t) = 0$$

$$\frac{\langle c_A\rangle}{\langle c_B\rangle} = \frac{k_{B\to A}}{k_{A\to B}}$$

Make a small perturbation

$$c_A(t) = \langle c_A\rangle + \Delta c_A(t) \qquad c_B(t) = \langle c_B\rangle - \Delta c_A(t)$$

$$\frac{\mathrm{d}\Delta c_A(t)}{\mathrm{dt}} = -k_{A\to B}\Delta c_A(t) - k_{B\to A}\Delta c_A(t)$$

$$\Delta c_A(t) = \Delta c_A(0)\exp\left[-\left(k_{A\to B} + k_{B\to A}\right)t\right]$$

$$= \Delta c_A(0)\exp\left[-t/\tau\right]$$

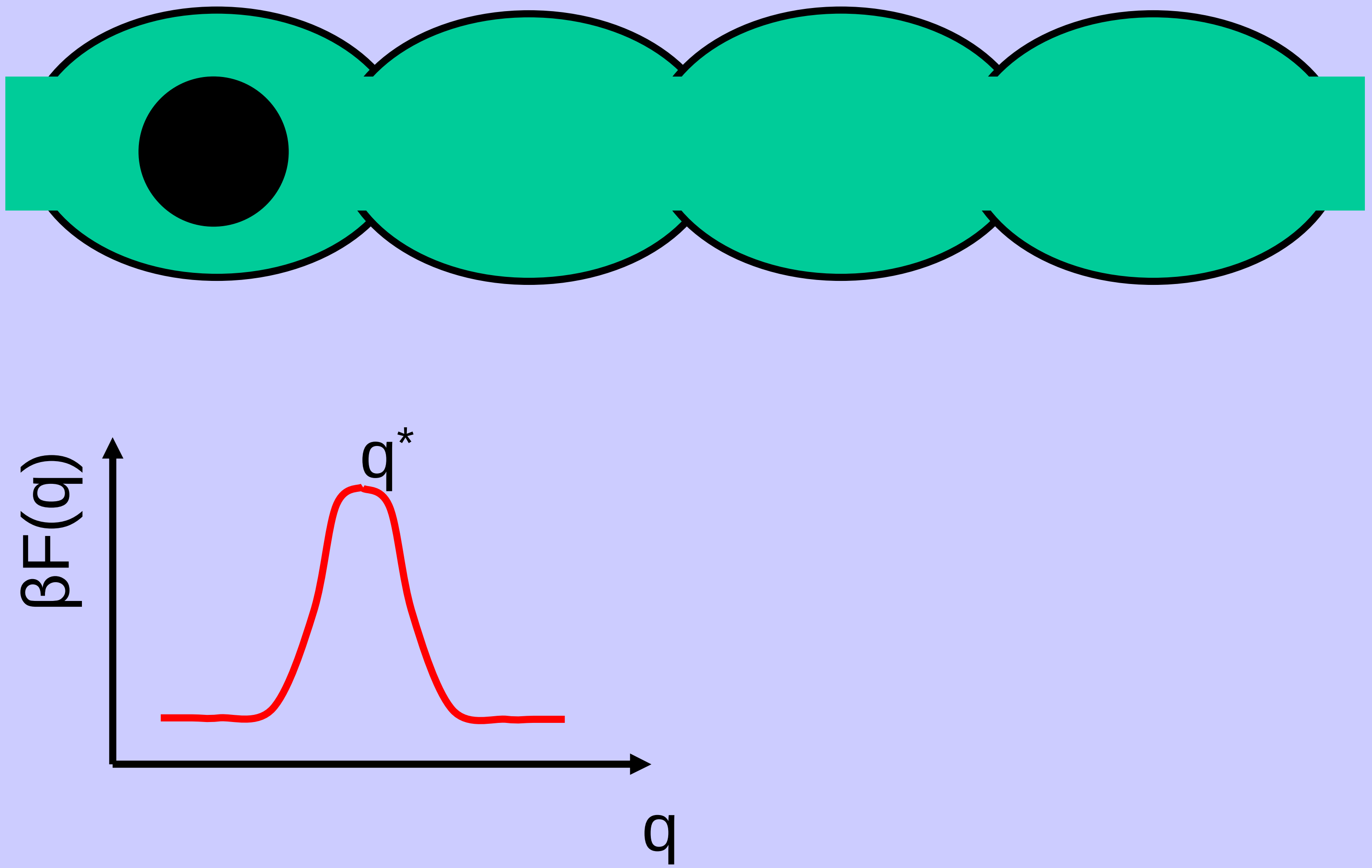
$$\tau = \left(k_{A\to B} + k_{B\to A}\right)^{-1}$$

$$= k_{A\to B}^{-1}\left(1+\langle c_A\rangle/\langle c_B\rangle\right)^{-1} = \frac{\langle c_B\rangle}{k_{A\to B}}$$

Microscopic description of the reaction

Theory: microscopic linear response theory

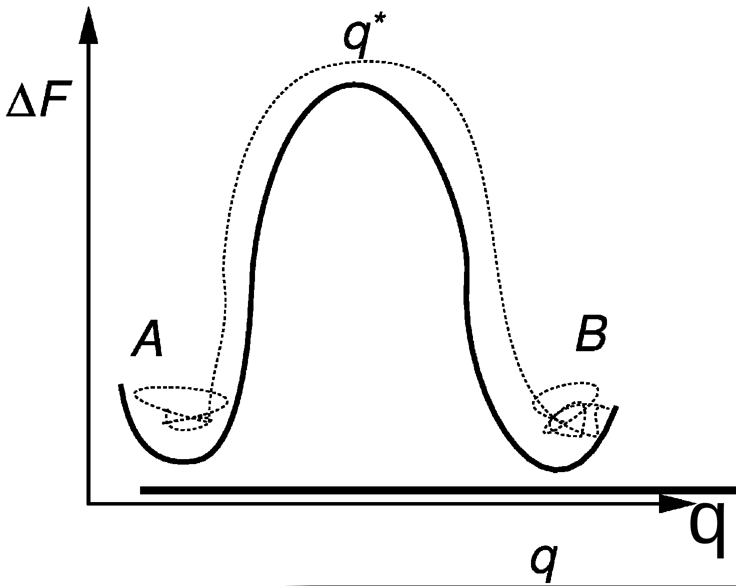
Reaction coordinate



Theory: microscopic linear response theory

Microscopic description of the reaction

Reaction coordinate



Reactant A: $q < q^*$

Product B: $q > q^*$

Lowers the potential energy in A

Increases the concentration of A

Perturbation: $H = H_0 - \varepsilon g_A(q - q^*)$

Heaviside θ-function

$$\theta(q-q^*) = \begin{cases} 0 & q-q^* < 0 \\ 1 & q-q^* > 0 \end{cases}$$

$$g_A(q-q^*) = 1 - \theta(q-q^*) = \theta(q^*-q)$$

$$\Delta c_A = \langle c_A \rangle_\varepsilon - \langle c_A \rangle_0$$

$$\Delta c_A = \langle g_A \rangle_\varepsilon - \langle g_A \rangle_0$$

Probability to be in state A

Very small perturbation: linear response theory

$$\Delta c_A = \langle g_A \rangle_\varepsilon - \langle g_A \rangle_0$$

$$H = H_0 - \varepsilon g_A (q - q^*)$$

$$\frac{\partial \Delta c_A}{\partial \varepsilon} = \beta \left(\left\langle (g_A)^2 \right\rangle_0 - \langle g_A \rangle_0^2 \right)$$

$$= \beta \left(\langle g_A \rangle_0 \left(1 - \langle g_A \rangle_0 \right) \right)$$

$$= \beta \left(\langle c_A \rangle_0 \left(1 - \langle c_A \rangle_0 \right) \right) = \beta \langle c_A \rangle_0 \langle c_B \rangle_0$$

Outside the barrier $g_A = 0$ or 1:
$g_A(x)\, g_A(x) = g_A(x)$

Switch of the perturbation: dynamic linear response

$$\Delta c_A(t) = \Delta c_A(0) \frac{\langle \Delta g_A(0) \Delta g_A(t) \rangle}{\langle c_A \rangle \langle c_B \rangle}$$

$$= \Delta c_A(0) \exp[-t/\tau]$$

Holds for sufficiently long times!

Linear response theory: static

$$H = H_0 - \varepsilon B$$

$$\langle \Delta A \rangle = \langle A \rangle - \langle A \rangle_0$$

$$\langle A \rangle = \frac{\int \mathrm{d}\Gamma A \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]}{\int \mathrm{d}\Gamma \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]} \qquad \langle A \rangle_0 = \frac{\int \mathrm{d}\Gamma A \exp\left[-\beta H_0\right]}{\int \mathrm{d}\Gamma \exp\left[-\beta H_0\right]}$$

$$\left\langle \frac{\partial(\Delta A)}{\partial \varepsilon} \right\rangle = \frac{\int \mathrm{d}\Gamma \beta A B \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right] \int \mathrm{d}\Gamma \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]}{\left\{\int \mathrm{d}\Gamma \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]\right\}^2}$$

$$- \frac{\int \mathrm{d}\Gamma A \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right] \int \mathrm{d}\Gamma \beta B \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]}{\left\{\int \mathrm{d}\Gamma \exp\left[-\beta\left(H_0 - \varepsilon B\right)\right]\right\}^2}$$

$$\left\langle \frac{\partial(\Delta A)}{\partial \varepsilon} \right\rangle = \beta \left\{ \langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \right\}$$

$$\exp[-t/\tau] = \frac{\langle \Delta g_A(0)\,\Delta g_A(t)\rangle}{\langle c_A\rangle\langle c_B\rangle}$$

Δ has disappeared because of derivative

Derivative

$$-\frac{1}{\tau}\exp[-t/\tau] = \frac{\langle g_A(0)\,\dot g_A(t)\rangle}{\langle c_A\rangle\langle c_B\rangle} = -\frac{\langle \dot g_A(0)\,g_A(t)\rangle}{\langle c_A\rangle\langle c_B\rangle}$$

For sufficiently short t

$$k_{A\to B}(t) = \frac{\langle \dot g_A(0)\,g_A(t)\rangle}{\langle c_A\rangle}$$

$$\dot g_A(q-q^*) = \dot q\,\frac{\partial g_A(q-q^*)}{\partial q} = -\dot q\,\frac{\partial g_B(q-q^*)}{\partial q}$$

$$k_{A\to B}(t) = \frac{\left\langle \dot q(0)\,\frac{\partial g_B(q(0)-q^*)}{\partial q}\,g_B(t)\right\rangle}{\langle c_A\rangle}$$

Stationary

$$\frac{d}{dt}\left\langle A(t)\,B(t+t')\right\rangle = 0$$

$$\left\langle A(t)\,\dot{B}(t+t')\right\rangle + \left\langle \dot{A}(t)\,B(t+t')\right\rangle = 0$$

$$\left\langle A(0)\,\dot{B}(t')\right\rangle = -\left\langle \dot{A}(0)\,B(t')\right\rangle$$

Eyring's transition state theory

$$k_{A\to B}(t) = \frac{\left\langle \dot{q}(0)\frac{\partial g_B\left(q(0)-q^*\right)}{\partial q} g_B(t)\right\rangle}{\langle c_A\rangle}$$

Only products contribute to the average

At t=0 particles are at the top of the barrier

$$= \frac{\left\langle \dot{q}(0)\,\delta\left(q(0)-q^*\right)\theta\left(q(t)-q^*\right)\right\rangle}{\left\langle \theta\left(q^*-q\right)\right\rangle}$$

Let us consider the limit: $t \to 0^+$

$$\lim_{t\to 0^+} = \theta\left(q(t)-q^*\right) = \theta\left(\dot{q}(t)\right)$$

$$k^{TST}_{A\to B}(t) = \frac{\left\langle \dot{q}(0)\,\delta\left(q(0)-q^*\right)\theta\left(\dot{q}\right)\right\rangle}{\left\langle \theta\left(q^*-q\right)\right\rangle}$$

$$g_B(q-q^*) = 1 - g_A(q-q^*) = \theta(q-q^*)$$

$$g_A(q-q^*) = 1 - \theta(q-q^*) = \theta(q^*-q)$$

$$\frac{\partial g_B(q-q^*)}{\partial q} = \delta(q-q^*)$$

Bennett-Chandler approach

Conditional average: $\dot{q}(0)\theta(q(t)-q^*)$
given that we start on top of the barrier

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

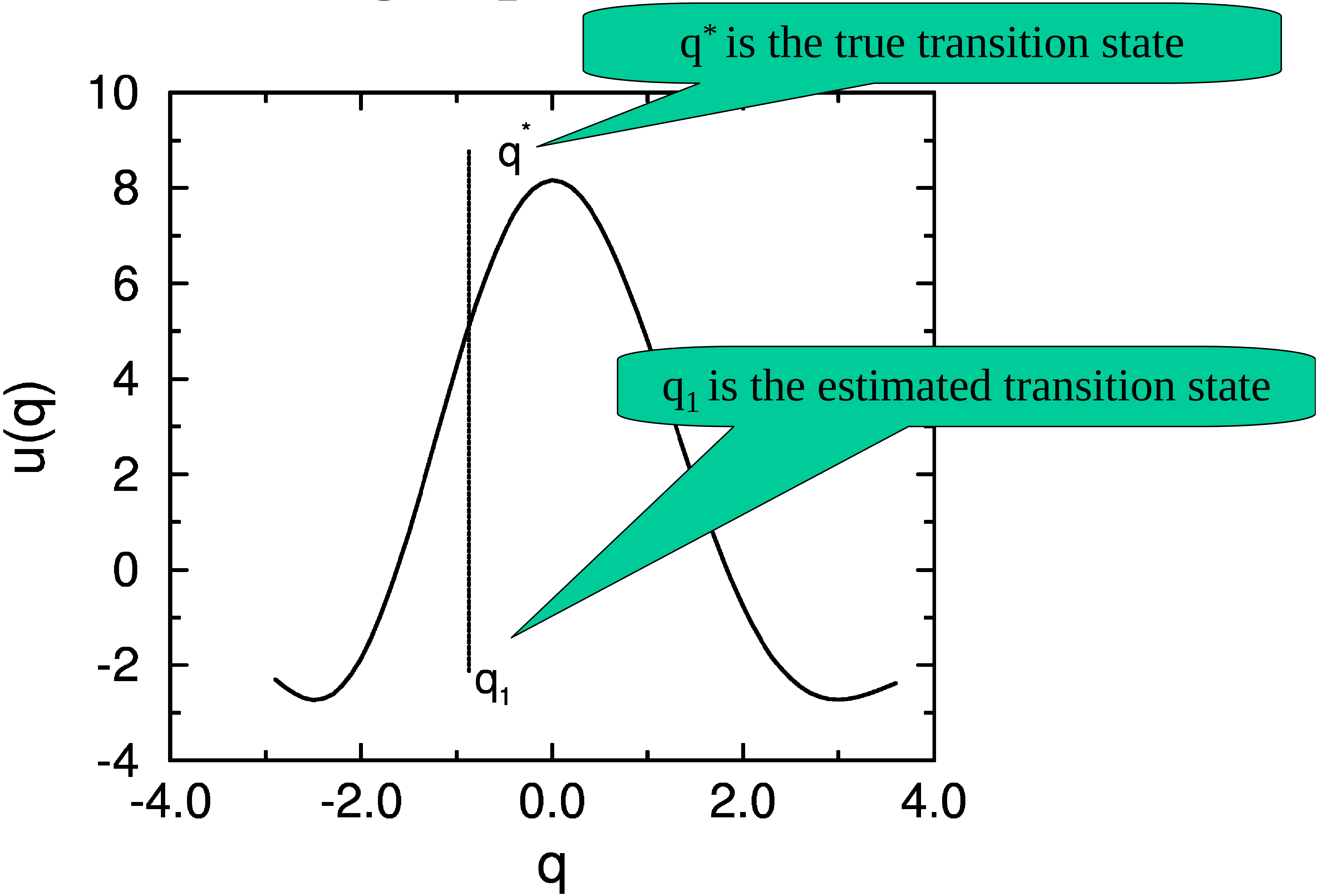
$$k_{A\to B}(t) = \frac{\left\langle \dot{q}(0)\delta(q(0)-q^*)\theta(q(t)-q^*)\right\rangle}{\left\langle \delta(q(0)-q^*)\right\rangle} \times \frac{\left\langle \delta(q(0)-q^*)\right\rangle}{\left\langle \theta(q^*-q)\right\rangle}$$

Computational scheme:

Probability to find q on top of the barrier

1. Determine the probability from the free energy
2. Compute the conditional average from a MD simulation

Ideal gas particle and a hill



Transition state theory

The motion of the particle is ballistic

In the product or reactant state in can exchange energy

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

Assumed transition state

$$\frac{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}{\left\langle \theta\left(q_1-q\right)\right\rangle}=\frac{\int \mathrm{d}q\delta\left(q(0)-q_1\right)\exp\left[-\beta U(q)\right]}{\int \mathrm{d}q\delta\left(q(0)-q_1\right)\exp\left[-\beta U(q)\right]}$$

$$=\frac{\exp\left[-\beta U(q_1)\right]}{\int_{-\infty}^{q_1}\mathrm{d}q\exp\left[-\beta U(q)\right]}$$

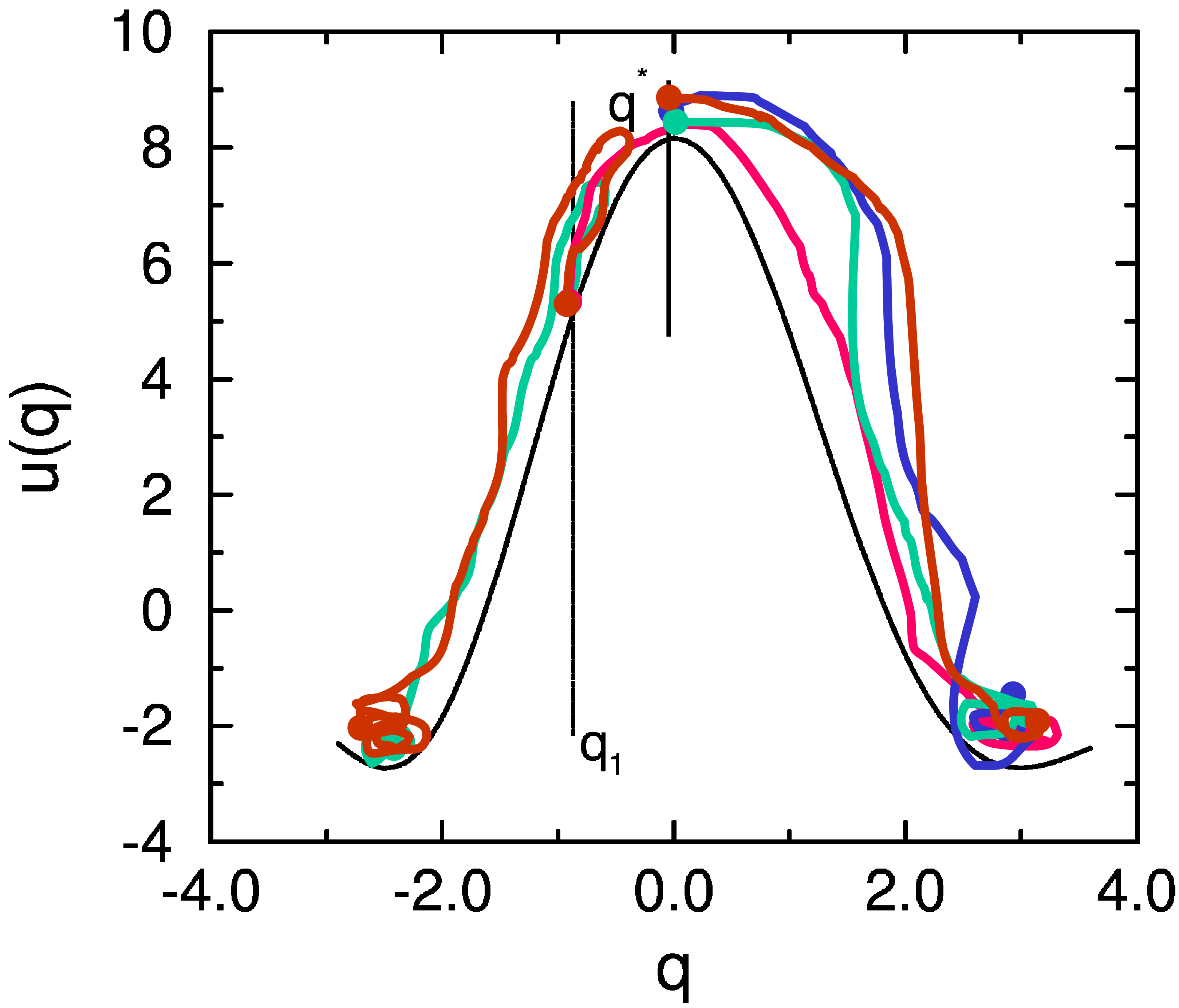
$$\frac{\left\langle \dot{q}(0)\delta\left(q(0)-q_1\right)\theta\left(\dot{q}\right)\right\rangle}{\left\langle \delta\left(q(0)-q_1\right)\right\rangle}=\frac{\int \mathrm{d}q\dot{q}(0)\delta\left(q(0)-q_1\right)\theta\left(\dot{q}\right)\exp\left[-\beta U(q)\right]}{\int \mathrm{d}q\delta\left(q(0)-q_1\right)\exp\left[-\beta U(q)\right]}$$

$$=0.5\left|\dot{q}(0)\right|\frac{\int \mathrm{d}q\delta\left(q(0)-q_1\right)\exp\left[-\beta U(q)\right]}{\int \mathrm{d}q\delta\left(q(0)-q_1\right)\exp\left[-\beta U(q)\right]}$$

$$=0.5\left|\dot{q}(0)\right|$$

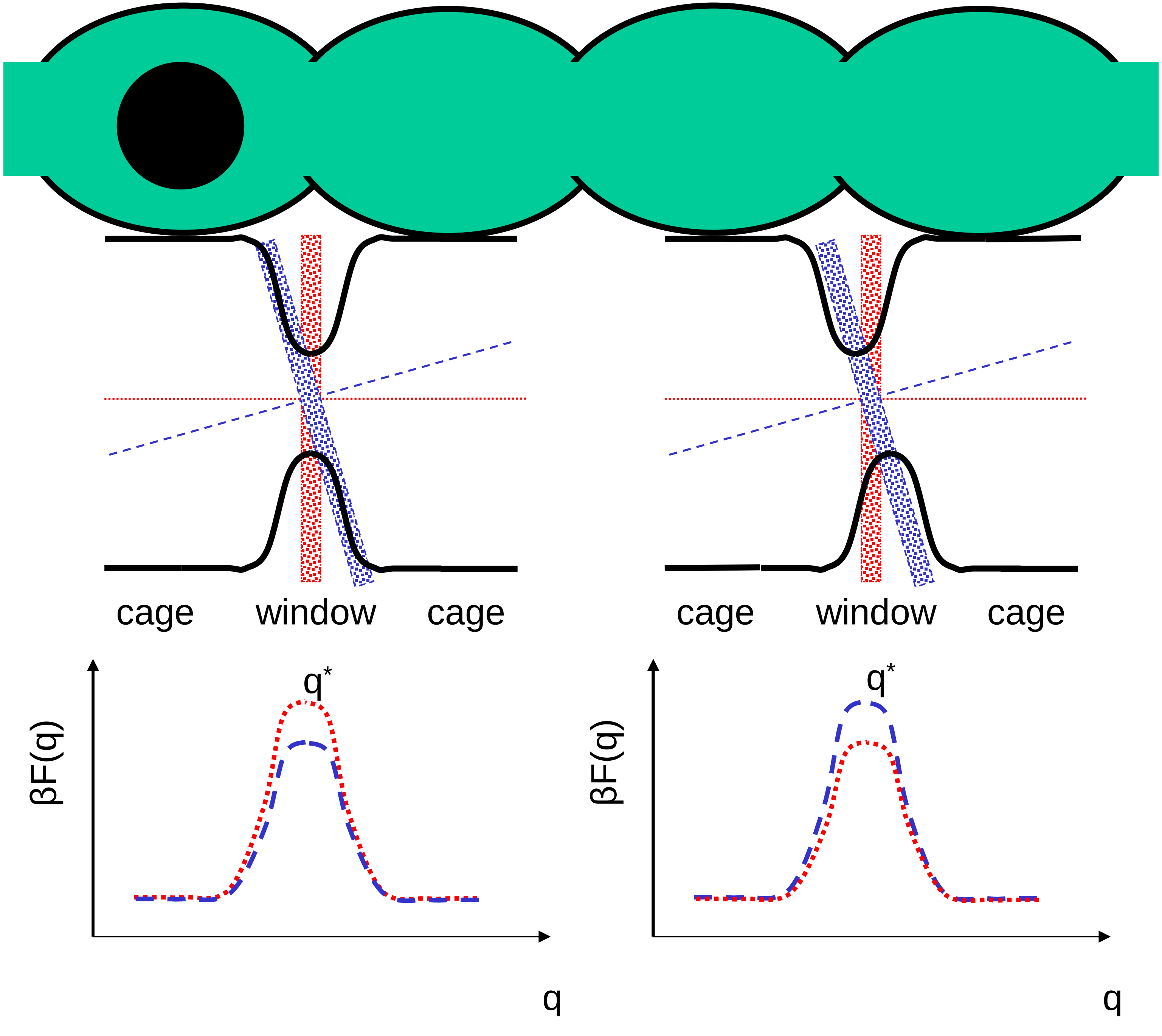
$$k_{A\rightarrow B}^{TST}(t) = 0.5\left|\dot{q}(0)\right| \frac{\exp\left[-\beta U(q_1)\right]}{\int_{-\infty}^{q_1} \mathrm{d}q \exp\left[-\beta U(q)\right]}$$

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



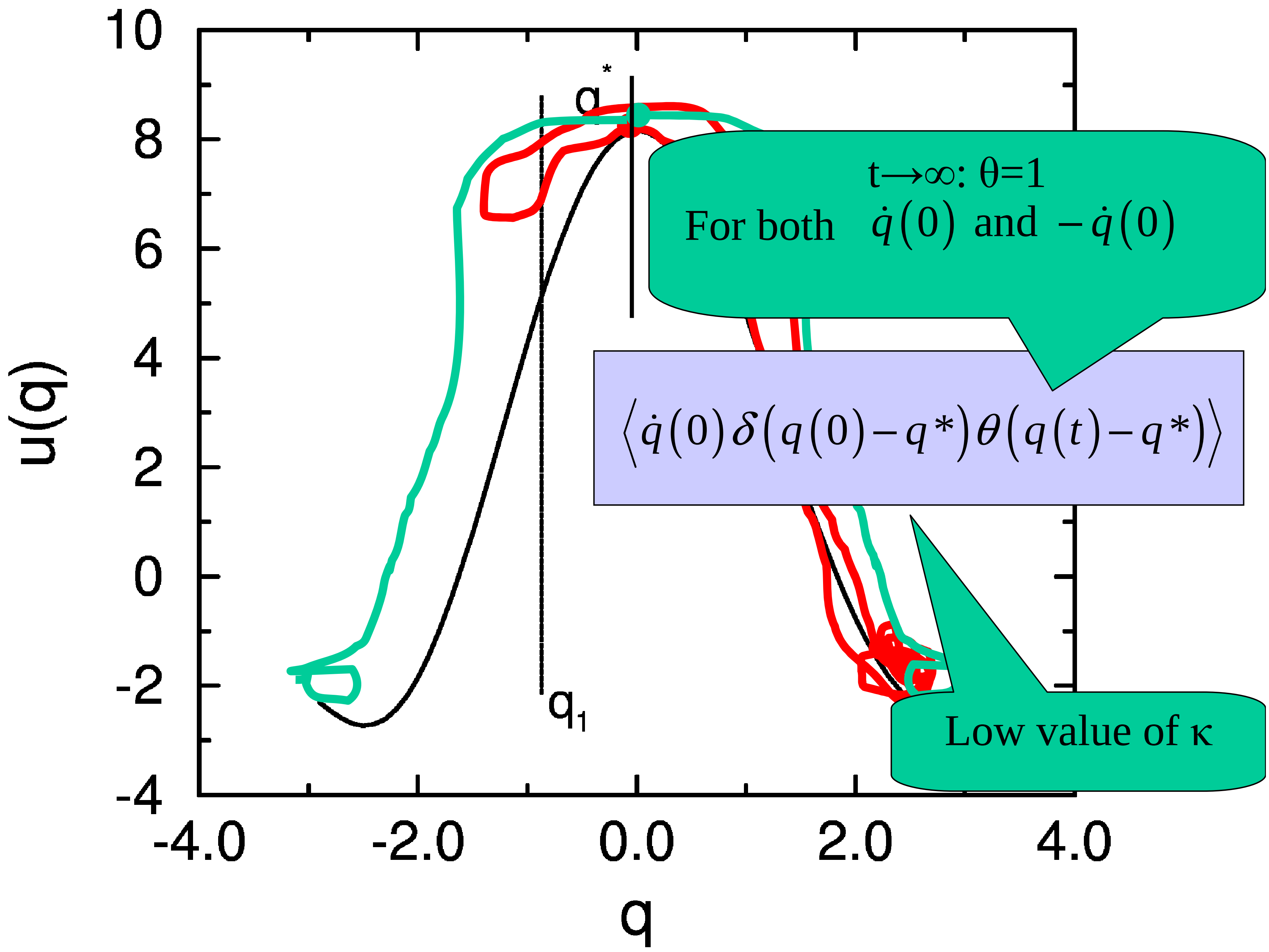
10
8
6
4
2
0
-2
-4
u(q)
q*
q1
-4.0
-2.0
0.0
2.0
4.0
q

Reaction coordinate



Transition state theory

- One has to know the free energy accurately
- Gives an upper bound to the reaction rate
- Assumptions underlying transition theory should hold: *no recrossings*



u(q)
q
q*
q1
t→∞: θ=1
For both $\dot{q}(0)$ and $-\dot{q}(0)$
$\left\langle \dot{q}(0)\,\delta\left(q(0)-q^*\right)\theta\left(q(t)-q^*\right)\right\rangle$
Low value of κ

Bennett Chandler Approach

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

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

Transmission coefficient

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

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

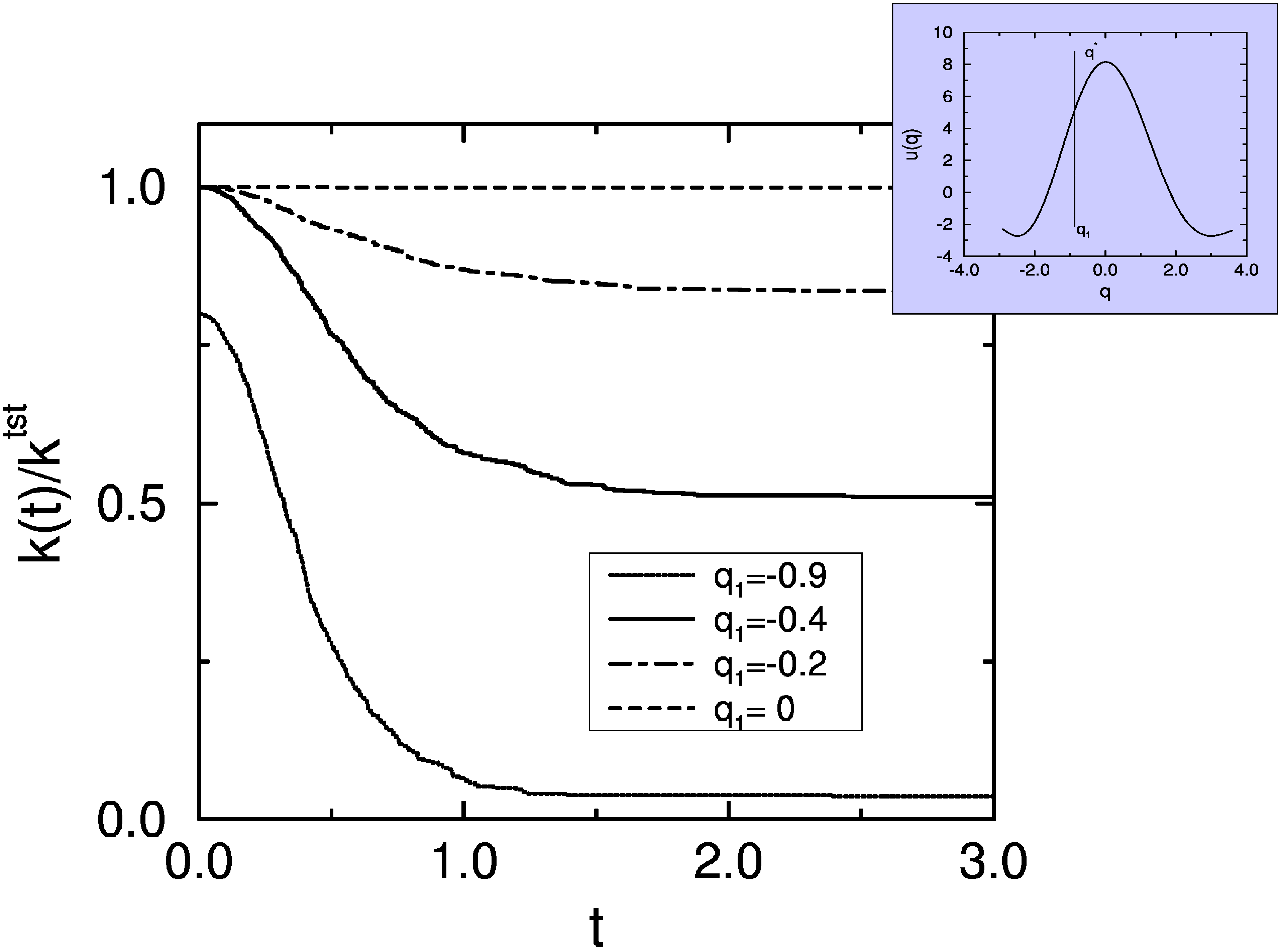
MD simulation:

1. At t=0 $q=q_1$
2. Determine the fraction at the product state weighted with the initial velocity

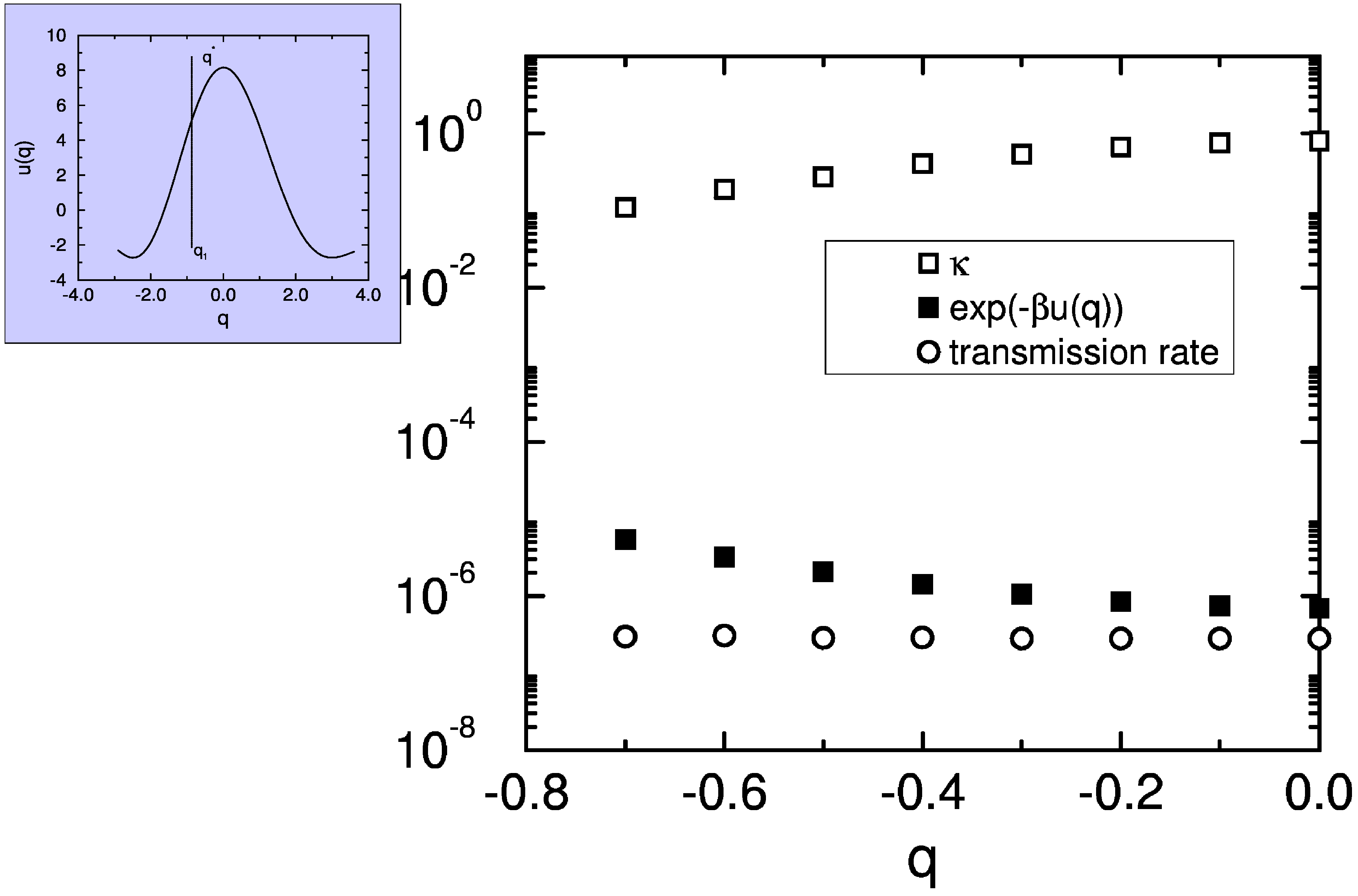
MD simulation to correct the transition state result!

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

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



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

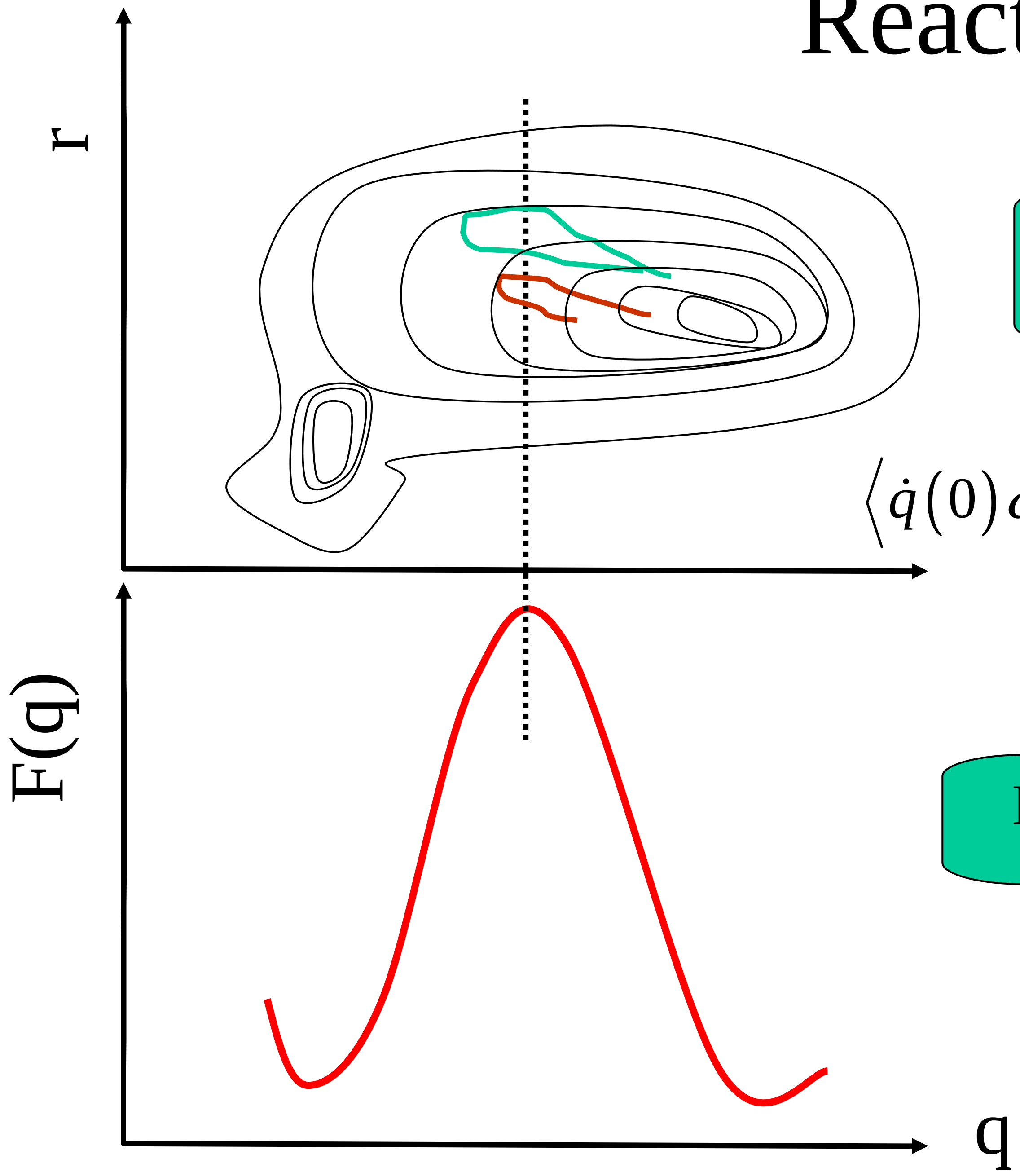


10
8
6
4
2
0
-2
-4
u(q)
-4.0
-2.0
0.0
2.0
4.0
q
q*
q1
10^0
10^-2
10^-4
10^-6
10^-8
κ
exp(-βu(q))
transmission rate
-0.8
-0.6
-0.4
-0.2
0.0
q

Bennett-Chandler approach

- Results are independent of the precise location of the estimate of the transition state, but the accuracy does.
- If the transmission coefficient is very low
  - Poor estimate of the reaction coordinate
  - Diffuse barrier crossing

Reaction coordinate



For both $t \to \infty$: $\theta = 1$ $\dot{q}(0)$ and $-\dot{q}(0)$

$$\left\langle \dot{q}(0)\,\delta\left(q(0)-q^*\right)\theta\left(q(t)-q^*\right)\right\rangle$$

Low value of κ

Transition path sampling

$$\exp\left[-t/\tau\right] = \frac{\langle \Delta g_A(0)\, \Delta g_A(t) \rangle}{\langle c_A \rangle \langle c_B \rangle}$$

x_t is fully determined by the initial condition

$$C(t) = \frac{\langle h_A(x_0)\, h_B(x_t) \rangle}{\langle h_A \rangle} \approx \langle h_B \rangle \left[1 - \exp(-t/\tau)\right]$$

$$h_A = \begin{cases} 1 & \text{in } A \\ 0 & \text{elsewhere} \end{cases}$$

$$C(t) = \frac{\int \mathrm{d}x_0 N(x_0) h_A(x_0)\, h_B(x_t)}{\int \mathrm{d}x_0 N(x_0) h_A(x_0)}$$

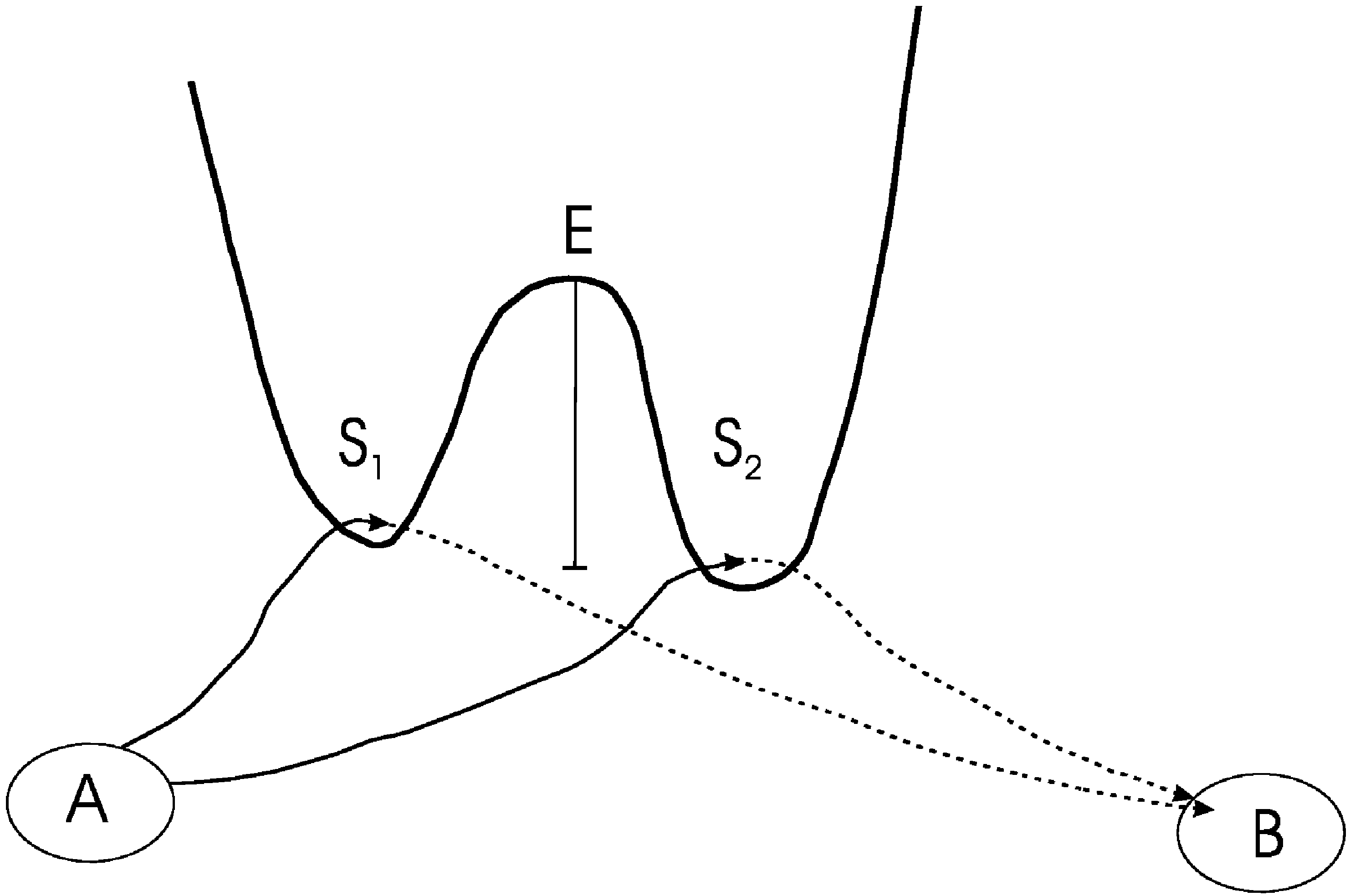
Path that starts at A and is in time t in B: importance sampling in these paths

$$C(t) = \langle h_B(x_t) \rangle_{A,t} \qquad P(\text{path}) = h_A(x_0)\, N(x_0)$$

$$C(t) = \frac{\langle h_A(x_0) h_B(x_t) \rangle}{\langle h_A(x_0) \rangle}$$

$$= \frac{\langle h_A(x_0) h_B(x_t) \rangle}{\langle h_A(x_0) h_B(x_t') \rangle} \frac{\langle h_A(x_0) h_B(x_t') \rangle}{\langle h_A(x_0) \rangle}$$

$$= \frac{\langle h_A(x_0) h_B(x_t) \rangle}{\langle h_A(x_0) h_B(x_t') \rangle} C(t')$$


E
S1
S2
A
B