# Transition State Theory without Dividing Surfaces

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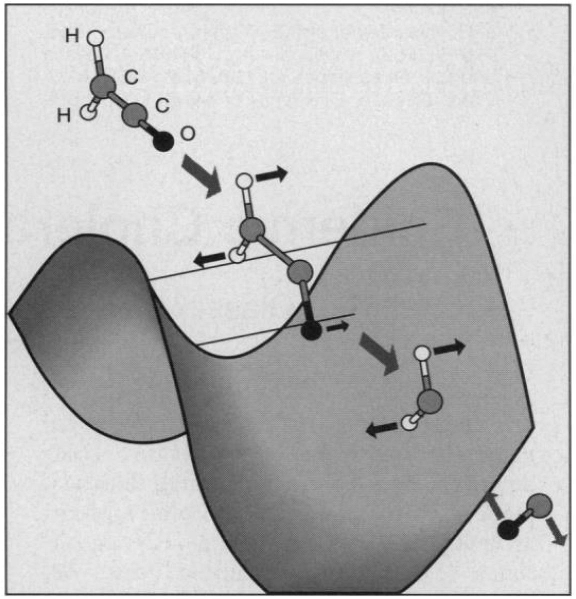
# Transition State Theory

Crossing of an energy barrier:

Crucial reaction dynamics in small Transition State region.

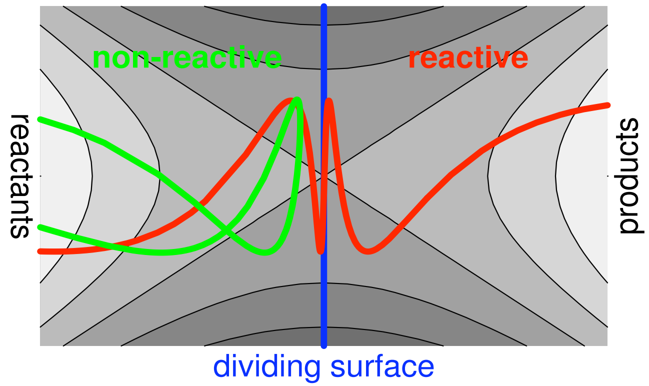



(Marcus: Science **256** (1992) 1523)

Provides

- simple zero time rate formula
- simple picture of the reaction mechanism

Reaction rate is counted in a dividing surface that should be free from recrossings.




Dual purpose:

- Define reactant and product regions
- Identify reactive trajectories

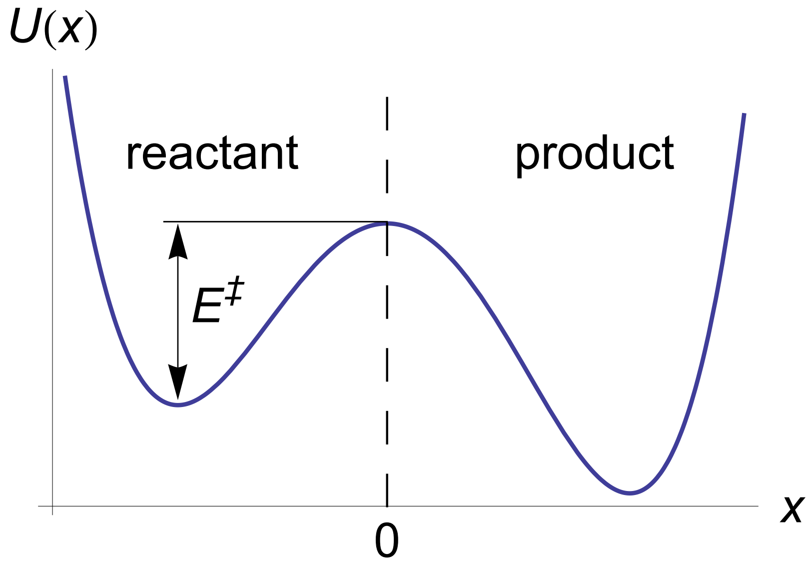
# Reaction rates

Reactive-flux rate formula:

$$k = \frac{\text{flux out of the reactant region}}{\text{population of reactant region}}$$

$$= \frac{e^{-E^{\ddagger}/kT}}{Q} \left\langle \int dv\, e^{-v^2/2kT}\, v\, \chi_\alpha(q=0,v) \right\rangle_\alpha$$

Crucial ingredient: characteristic function $\chi$ identifies reactive trajectories.




TST: $\chi(q=0,v) = \begin{cases} 1 & \text{if } v > 0 \\ 0 & \text{if } v < 0 \end{cases}$

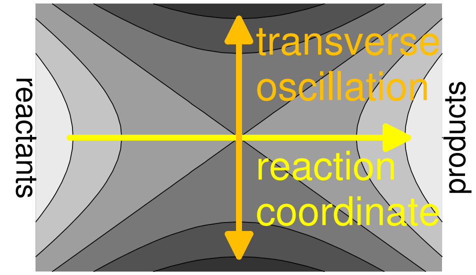
$$\Rightarrow k^{\text{TST}} = \nu_0 e^{-E^{\ddagger}/kT}$$

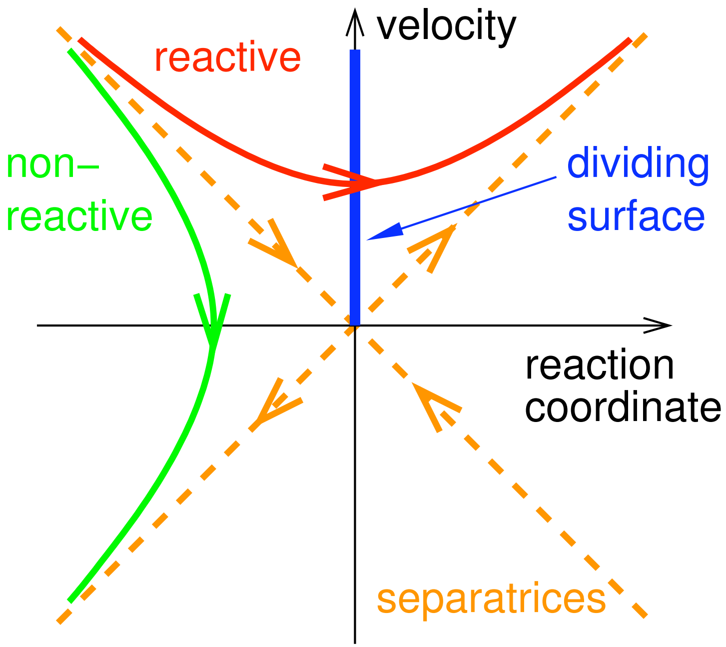
general: $k = \kappa k^{\text{TST}}$

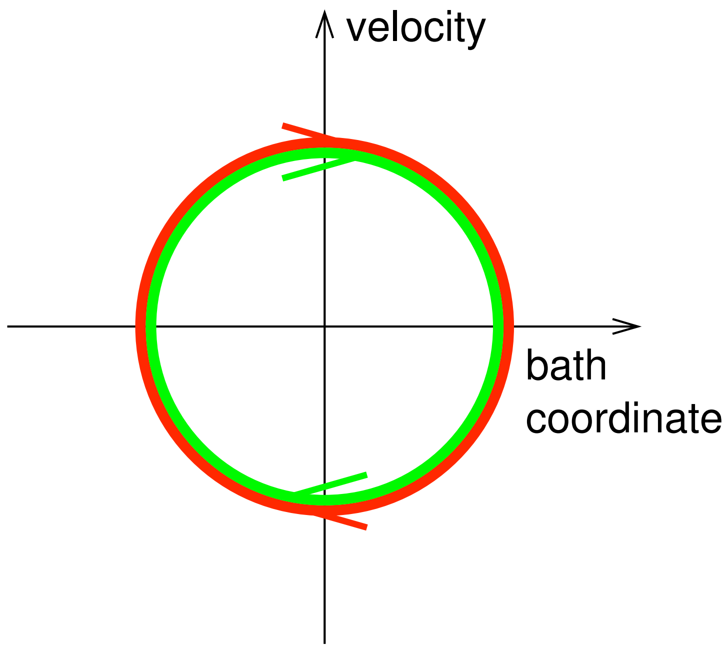
“transmission factor”

# A reaction seen in phase space

In the harmonic approximation the reaction coordinate and transverse degrees of freedom decouple.




These geometric structures persist in strongly coupled systems: Invariant manifolds

Centre of the construction: dynamical fixed point.

# Decoupling from the noise

Choose trajectory $\vec{q}_\alpha^\ddagger(t)$

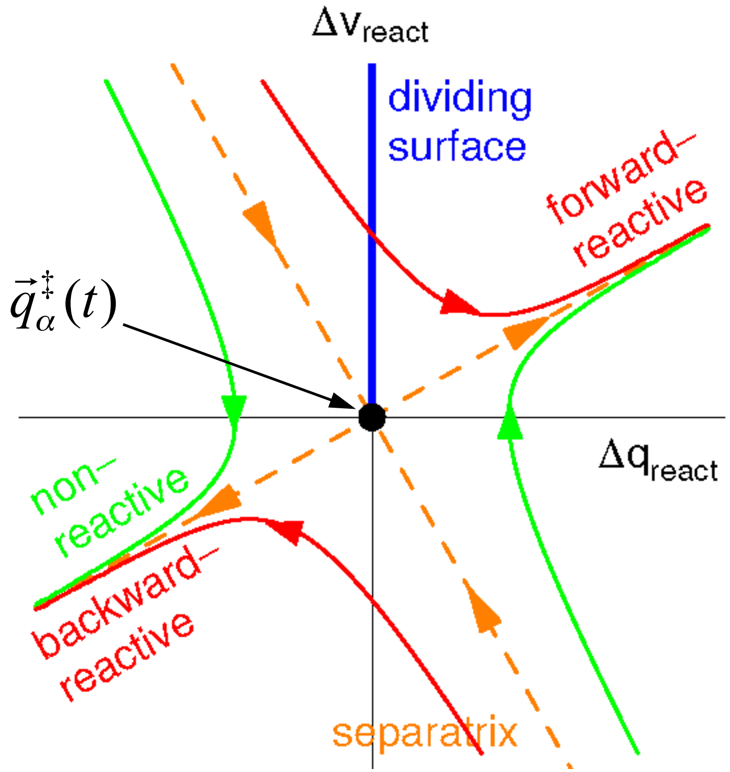
that never leaves the transition region

as ``moving saddle point´´

➔ unique stochastic Transition State Trajectory

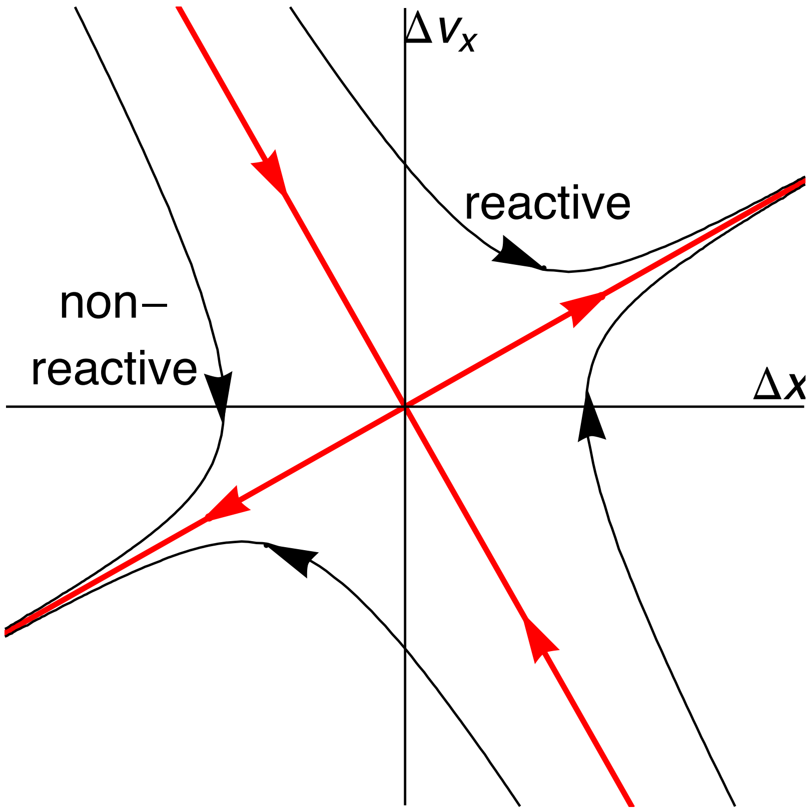
➔ Relative coordinate $\Delta\vec{q}(t) = \vec{q}_\alpha(t) - \vec{q}_\alpha^\ddagger(t)$

is noiseless.

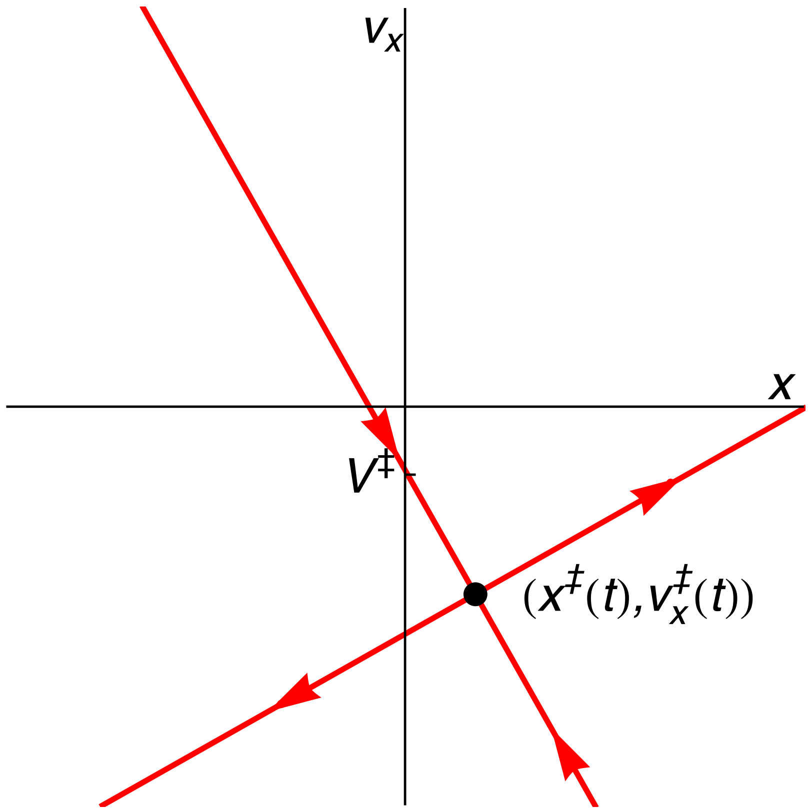



Invariant manifolds are moving through phase space.

# Stochastic invariant manifolds

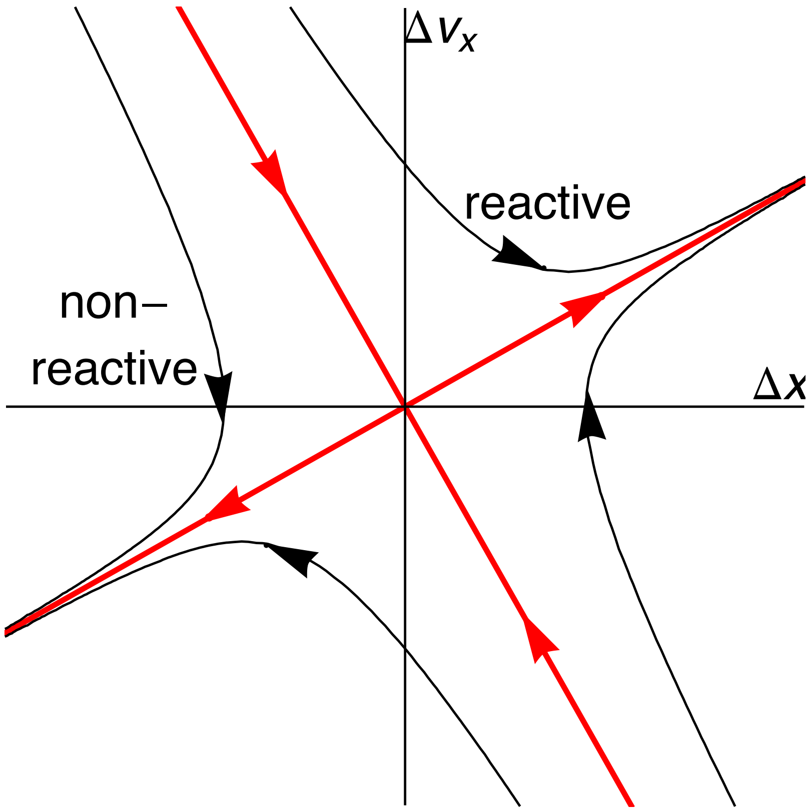



relative coordinates

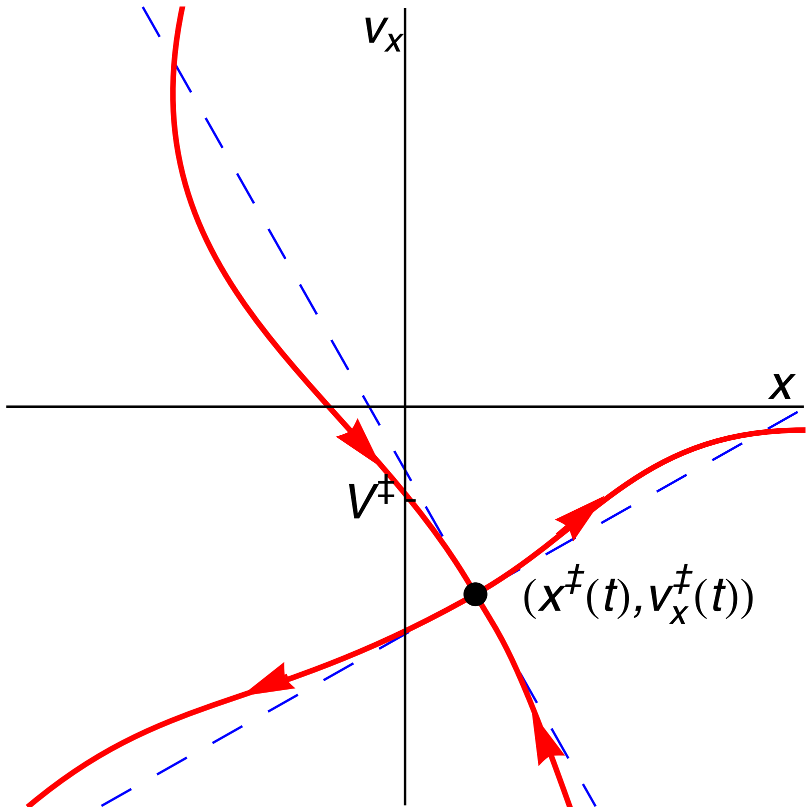



fixed coordinates:
moving manifolds

# Stochastic invariant manifolds




relative coordinates




anharmonic potential:
distorted manifolds

# The rate formula

$$k = \frac{e^{-E^{\ddagger}/kT}}{Q} \left\langle \int dv\, e^{-v^2/2kT}\, v\, \chi_\alpha(q=0,v) \right\rangle_\alpha$$

TST: $$\chi(q=0,v) = \begin{cases} 1 & \text{if } v > 0 \\ 0 & \text{if } v < 0 \end{cases}$$

Exact: $$\chi_\alpha(q=0,v) = \begin{cases} 1 & \text{if } v > V^{\ddagger} \\ 0 & \text{if } v < V^{\ddagger} \end{cases}$$

$$\kappa = \frac{k}{k^{\mathrm{TST}}} = \frac{\left\langle \int_{V^{\ddagger}}^{\infty} dv\, e^{-v^2/2kT}\, v \right\rangle_\alpha}{\int_0^{\infty} dv\, e^{-v^2/2kT}\, v}$$

$$\kappa = \frac{k}{k^{\mathrm{TST}}} = \left\langle e^{-V^{\ddagger 2}/2k_B T} \right\rangle_\alpha$$

a simple exact rate formula

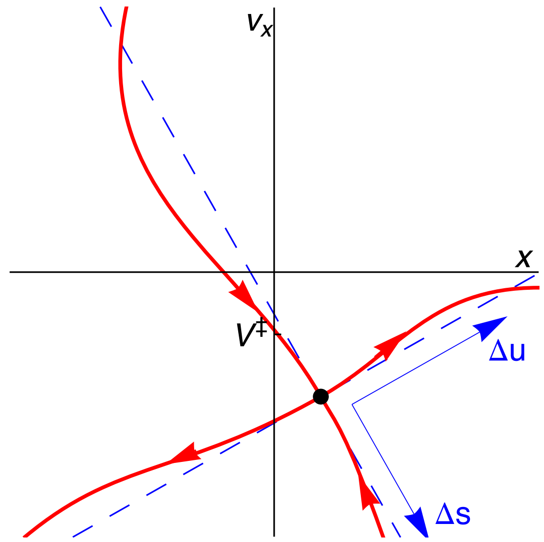
# Diagonal coordinates

Langevin equation $\ddot{x}(t) = -U'(x(t)) - \gamma\,\dot{x}(t) + \xi_\alpha(t)$

anharmonic force: $-U'(x) = \omega_b^2 x + f(x)$

Phase space coordinates $x$, $v_x$

New coordinates $\Delta u$, $\Delta s$




$$\Delta\dot{u} = \lambda_u \Delta u + \frac{f(x^{\ddagger} + \Delta u + \Delta s)}{\lambda_u - \lambda_s} \qquad \Delta\dot{s} = \lambda_s \Delta s - \frac{f(x^{\ddagger} + \Delta u + \Delta s)}{\lambda_u - \lambda_s}$$

Formal solution $\Delta u = C_u e^{\lambda_u t} - \frac{1}{\lambda_u - \lambda_s}\int_t^{\infty} e^{\lambda_u (t-\tau)} f(x^{\ddagger} + \Delta u + \Delta s)\,d\tau$

$$\Delta s = C_s e^{\lambda_s t} - \frac{1}{\lambda_u - \lambda_s}\int_0^{t} e^{\lambda_s (t-\tau)} f(x^{\ddagger} + \Delta u + \Delta s)\,d\tau$$

# The critical velocity

Boundary conditions:

$\Delta u(t)$ bounded as $t \to \infty$, i.e., $C_u = 0$

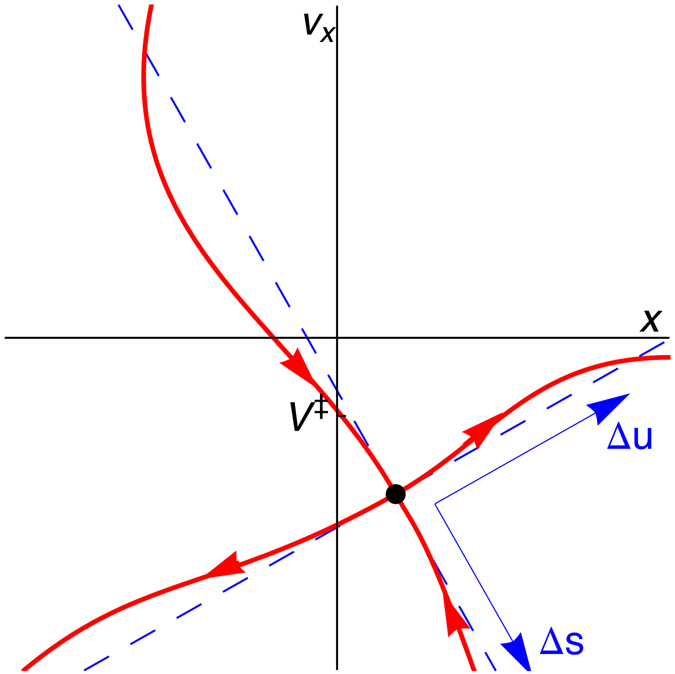
$x(0) = x^{\ddagger}(0) + \Delta u(0) + \Delta s(0) = 0$

$$V^{\ddagger} = v(0) = (\lambda_u - \lambda_s)\, u^{\ddagger}(0) + (\lambda_u - \lambda_s)\, \Delta u(0)$$

Harmonic limit:

$\Delta u(t) = 0$

$\Delta s(t) = -x^{\ddagger}(0)\, e^{\lambda_s t}$




$$\text{First order: } \Delta u(t) = -\frac{1}{\lambda_u - \lambda_s} \int_t^{\infty} e^{\lambda_u (t-\tau)} f\left(x^{\ddagger}(\tau) - x^{\ddagger}(0)\, e^{\lambda_s \tau}\right) d\tau$$

# Rate corrections

$$\kappa = \left\langle e^{-(V_0^\ddagger + V_1^\ddagger + \ldots)^2/2k_BT} \right\rangle_\alpha$$

$$= \left\langle e^{-V_0^{\ddagger 2}/2k_BT} \right\rangle_\alpha - \frac{1}{k_BT} \left\langle e^{-V_0^{\ddagger 2}/2k_BT} V_0^\ddagger V_1^\ddagger \right\rangle_\alpha + \ldots$$

Leading term: $\kappa = \dfrac{\lambda_u}{\omega_b}$ (Kramers 1940)

Kramers prefactor derived

- from a zero time TST approach
- without using an explicit model for a heat bath

(cf. Pollak 1986)

# First order rate correction

for the quartic potential $U(x) = -\frac{1}{2}\omega_b^2 x^2 + \frac{c_4}{4} x^4$

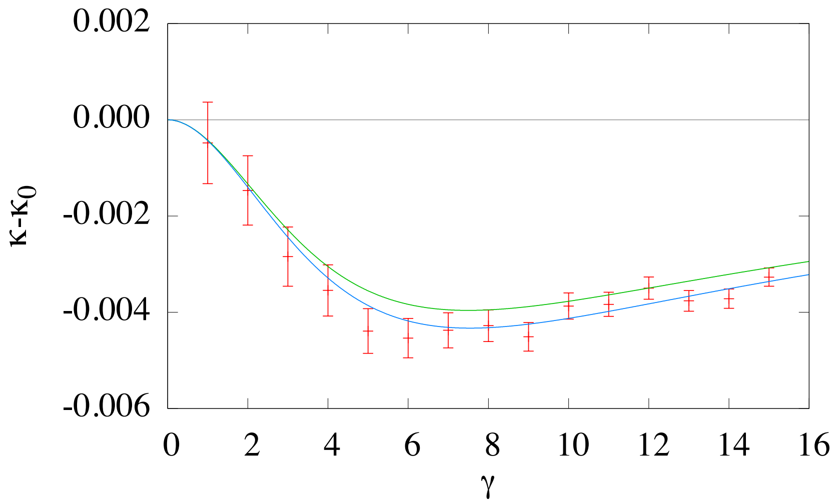
$$\kappa_1 = c_4 \frac{\lambda_u - \lambda_s}{k_B T} \int_0^\infty e^{-\lambda_u \tau} \left\langle e^{-V_0^{\ddagger 2}/2k_B T} u^\ddagger(0)\, X^3(\tau) \right\rangle_\alpha d\tau \qquad \text{with} \quad X(\tau) = x^\ddagger(\tau) - x^\ddagger(0) e^{\lambda_s \tau}$$

noise average:

multidimensional Gaussian moment

time integral:

over decaying exponentials




$$\frac{\kappa_1}{\kappa_0} = -\frac{3}{4} \frac{c_4 k_B T}{\omega_b^4} \left( \frac{1-\kappa_0^2}{1+\kappa_0^2} \right)^2$$

(Pollak and Talkner 1993)

# Conclusions

- The Transition State trajectory acts as a moving saddle point.
- Invariant manifolds indentify reactive trajectories.
- The precise choice of dividing surface is irrelevant.
- More to be done:
  - correlated noise
  - inclusion into a numerical scheme
  - atomistic models of the environment