

# Chemical Kinetics: Simulation of Rare Events

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## Learning Goals

- ◆ Reaction path on the potential surface
- ◆ Transition state theory
- ◆ Simulating rare events
- ◆ Sampling transition pathways

## References

- ◆ D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press, San Diego (1996)



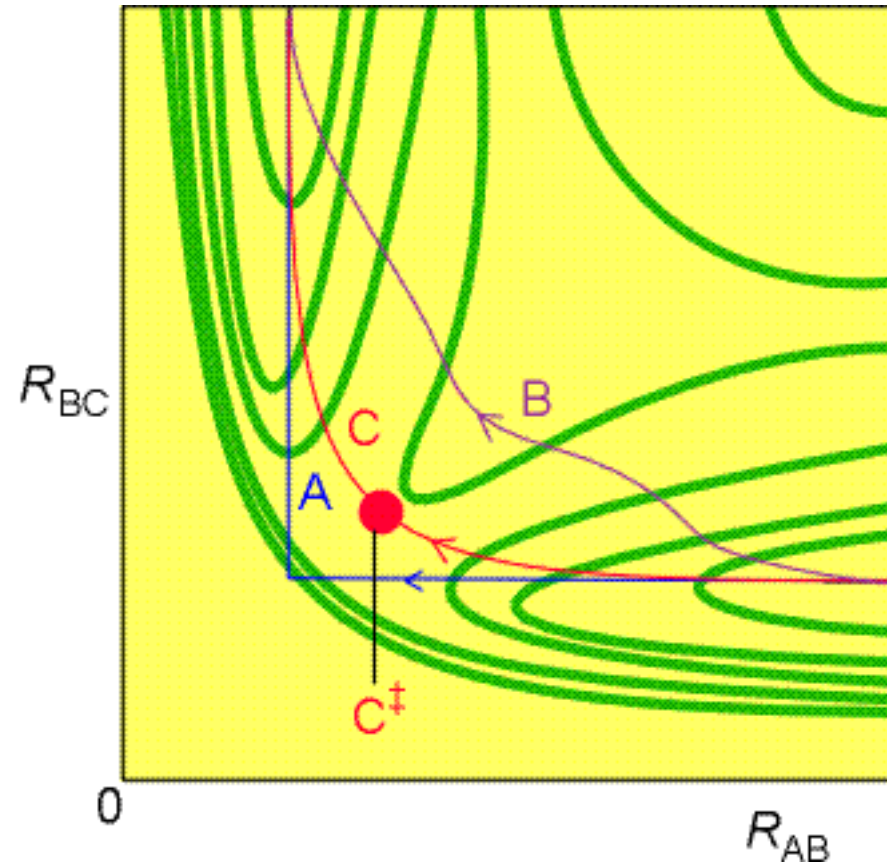
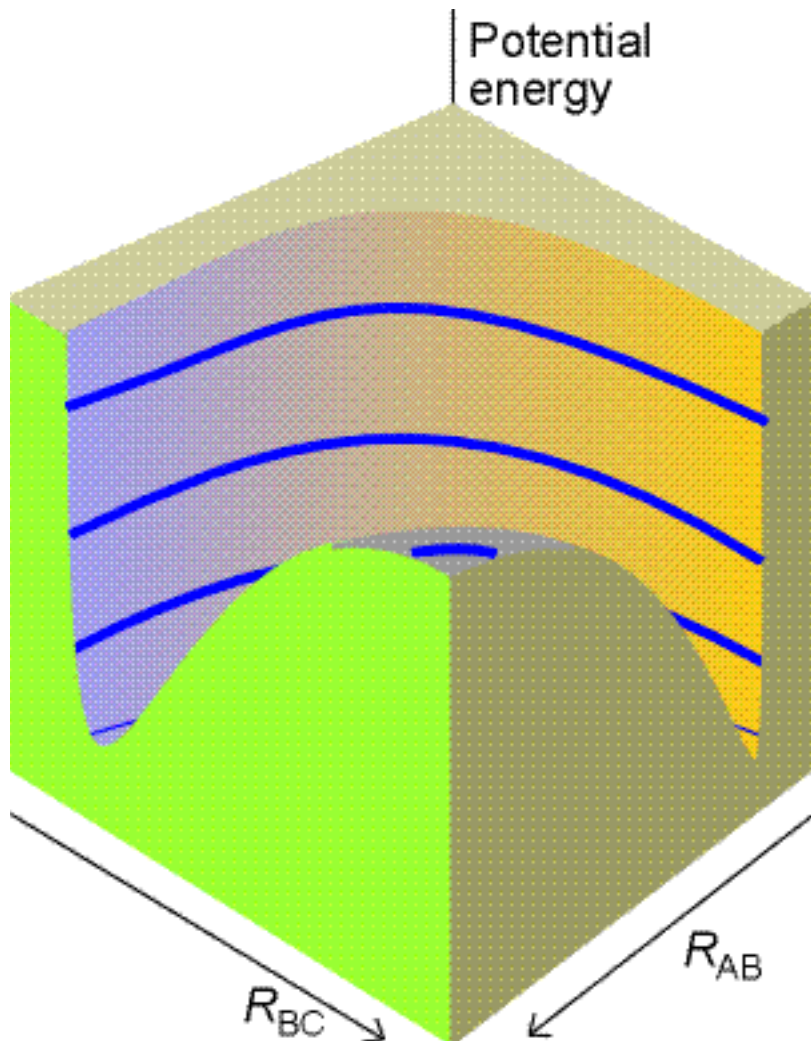
- ◆ Chandler, D., <http://gold.cchem.berkeley.edu:8080/pubs.html>
  - ◆ "Barrier Crossing: Classical Theory of Rare But Important Events"
  - ◆ "Electron Transfer in Water and Other Polar Environments, How It Happens"
  - ◆ "Finding Transition Pathways: Throwing Ropes Over Rough Mountain Passes, in the Dark"
- ◆ B. J. Berne  
<http://www.chem.columbia.edu/~bernegrp/publications.html>
- ◆ TheRate 1.1 Manual (transition state theory)  
<http://therate.hec.utah.edu/manual/index.html>
- ◆ Mark Tuckerman,  
[http://homepages.nyu.edu/~mt33/jpc\\_feat/jpc\\_feat\\_part.html](http://homepages.nyu.edu/~mt33/jpc_feat/jpc_feat_part.html)



- ◆ Saddle point and reaction path
- ◆ Reaction path
- ◆ Searching saddle points
- ◆ Intrinsic reaction path
- ◆ Non-adiabatic reactions

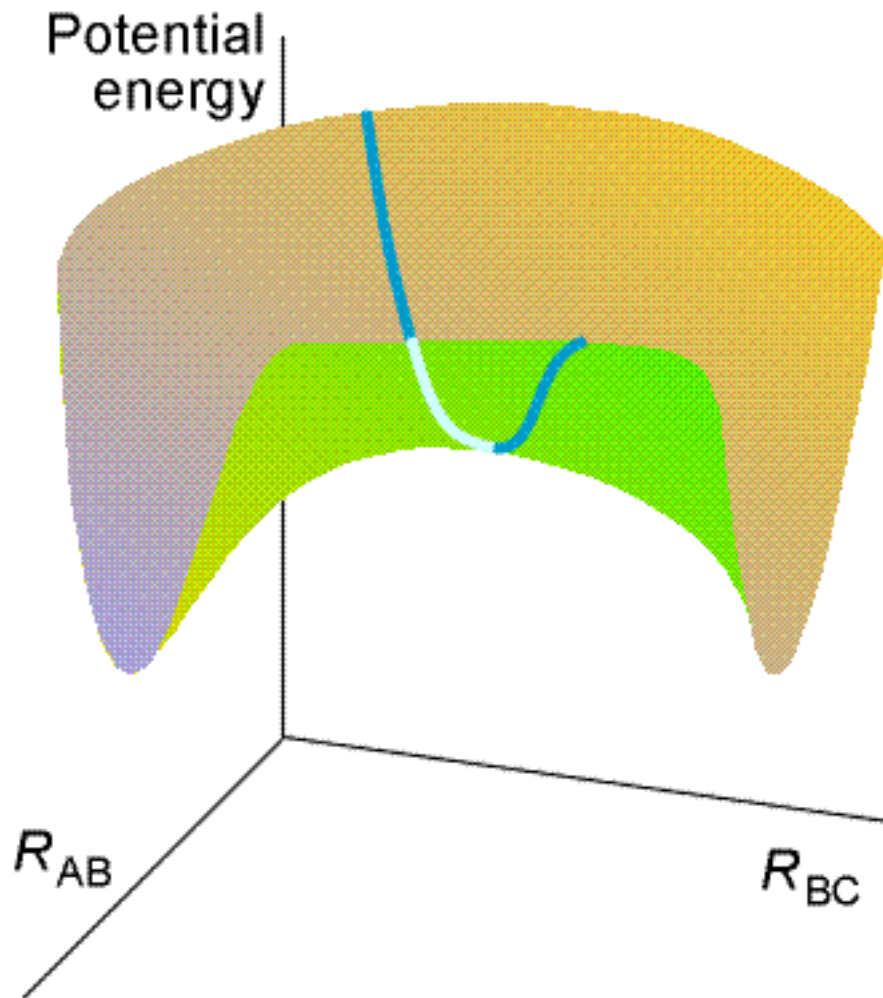
# Saddle point and reaction path

- ◆ A model reaction  $AB + C = A + BC$  {two coordinates,  $r(AB)$  and  $r(BC)$ }

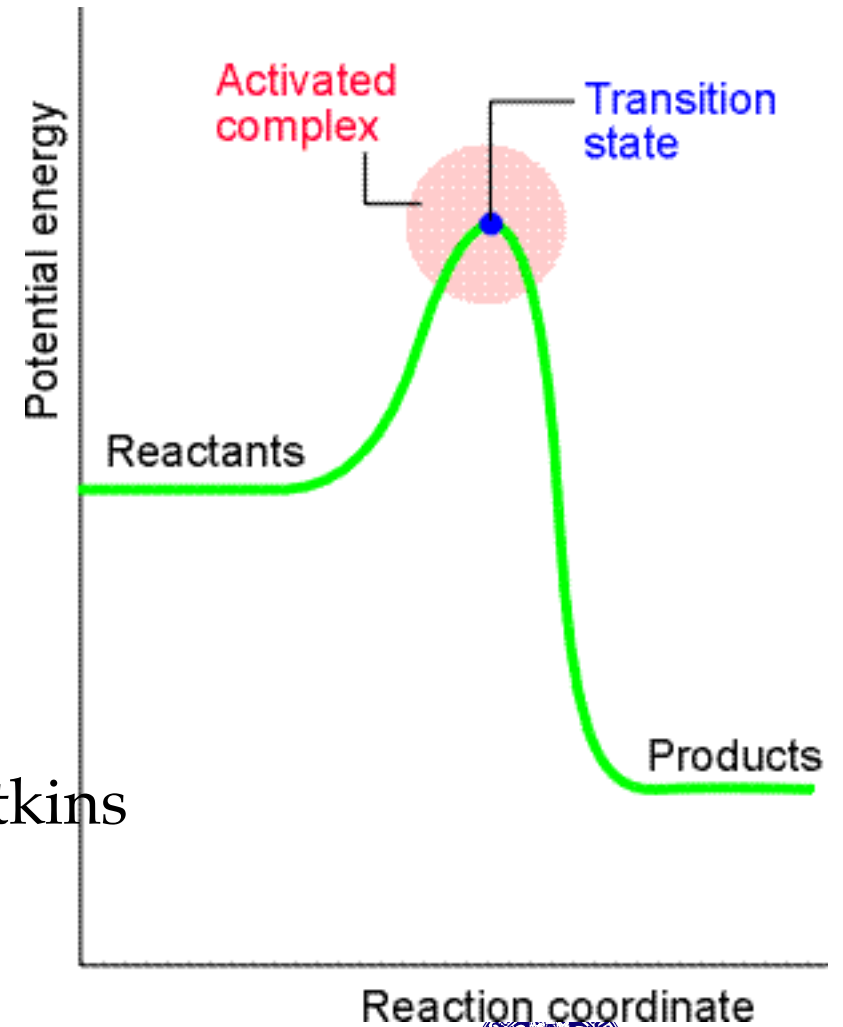


from Atkins

- ◆ Chemical kinetics:  $E_a \gg k_B T$



from Atkins



- ◆ Stationary point of  $U(\vec{x})$ :  $\nabla U = 0$  or  $\partial U / \partial x_i = 0$
- ◆  $\lambda_i$  is a eigenvalue of the U Hessian at the stationary point
  - ◆ if all  $\lambda_i$  are positive we have minimum
  - ◆ if only one  $\lambda_i$  is negative - a first order saddle point
- ◆ A common strategy: to start from the minimum
  - ◆ In simple cases - chemical intuition and then “try and error”
  - ◆ Modification of Newton-Raphson algorithm: eigenmode-following methods
- ◆ Systematic search: a modification of Branch and Bound algorithm (K.M. Westerberg, J. Chem. Phys. 1999, v. 110, N 18, p.9259)
  - ◆ Alanine: 17 minima, 62 1st order saddles, 83 2nd order saddles, 46 3rd order saddles, 7 max.

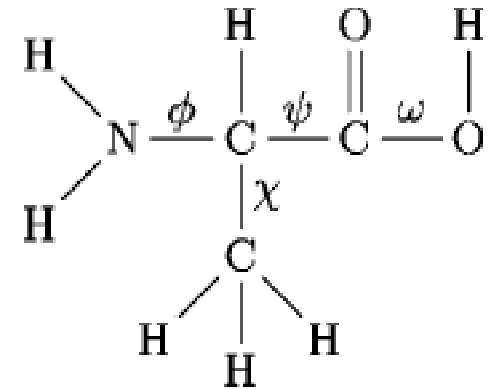


FIG. 19. Alanine.



- ◆ Use mass-weighted coordinate: corresponds to the complete dumping of energy
- ◆ Start from the saddle point
- ◆ Make a small move along the eigenvector with the negative eigenvalue
- ◆ Then follow steepest descent path (negative gradient) by small steps

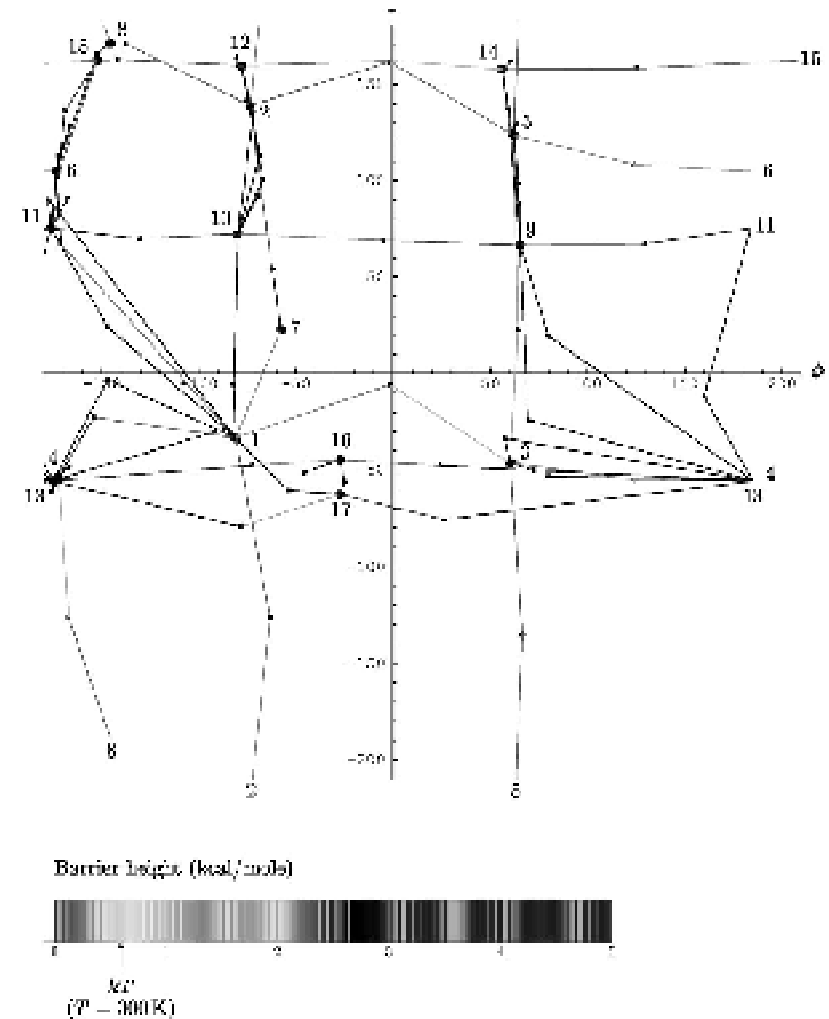
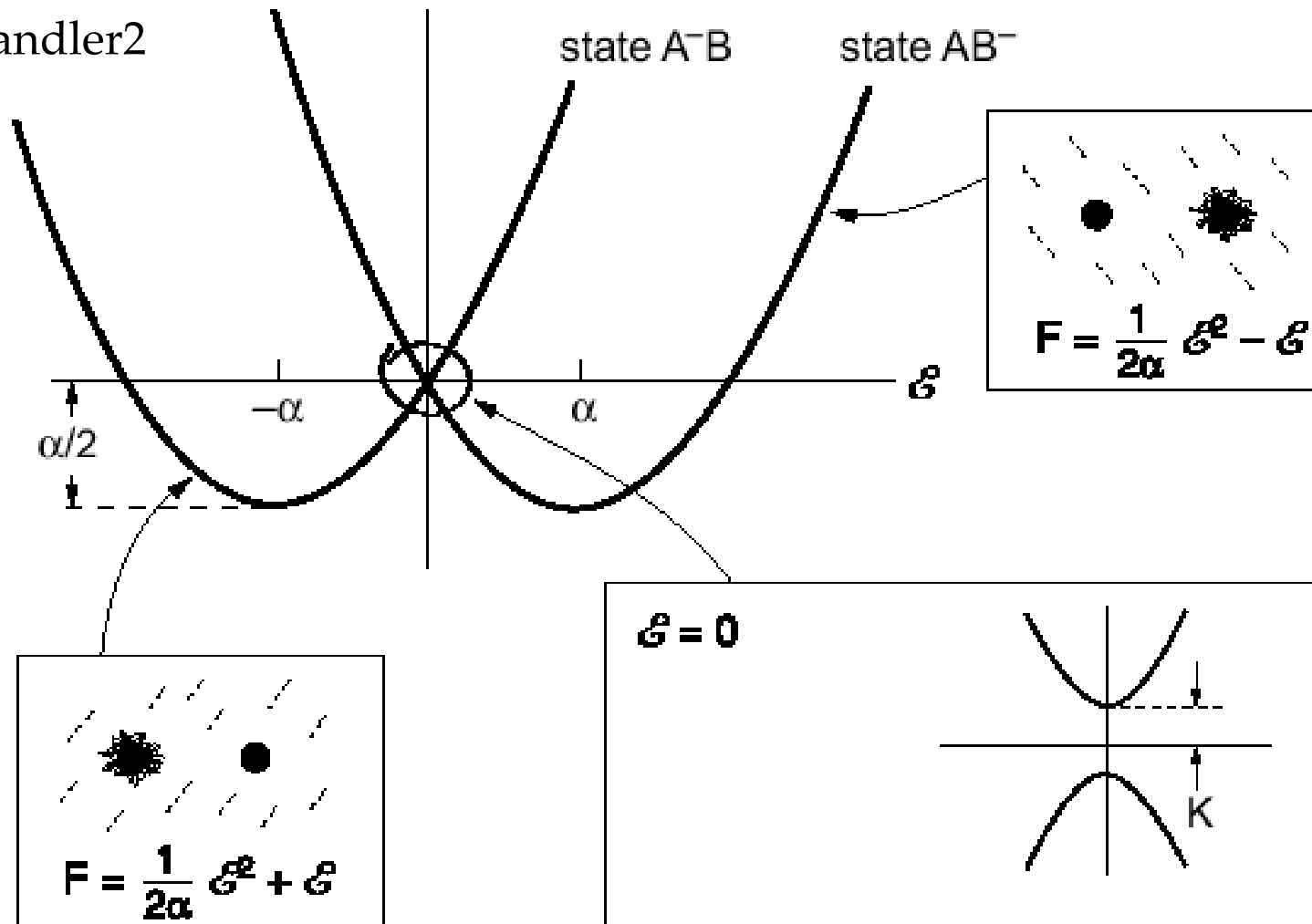


FIG. 20.  $\phi$ - $\phi$  plot for alanine.



◆ Example: electron transfer  $\text{Fe}^{2+} + \text{Fe}^{3+} = \text{Fe}^{3+} + \text{Fe}^{2+}$

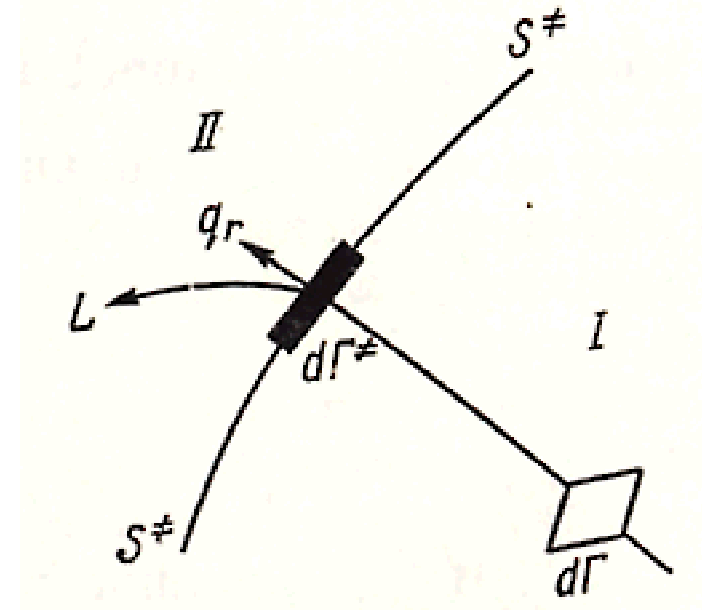
from 98Chandler2



- ◆ Terms in chemical kinetics
- ◆ Transition state theory, I
- ◆ Transition state theory, II
- ◆ Corrections

- ◆ Elementary reaction: a single step in a possible multi-step reaction mechanism
- ◆  $A \rightarrow B$  : unimolecular reaction,  $A + B \rightarrow$  : bimolecular reaction
- ◆ Reaction rate and the rate law:  $-\frac{1}{V} \frac{dn_A}{dt} = w = kc_A c_B$ 
  - ◆  $k$  - a macroscopic rate constant
- ◆ Microscopic rate constant is a rate for interaction of molecules in given quantum states that produces the product also in given quantum states
  - ◆  $A(i) + B(j) \rightarrow C(k) + D(l)$

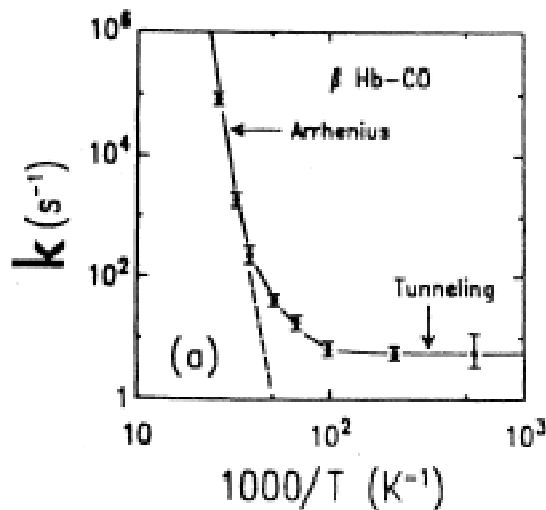
- ◆  $X + Y \rightarrow X' + Y'$
- ◆ Phase space  $\Gamma(\vec{q}, \vec{p})$
- ◆ Critical surface  $S^\ddagger$  divides the phase space to reagents (I) and products (II)
- ◆ Chemical reaction is a crossing of  $S^\ddagger$  by a phase point
- ◆ The distribution function  $f(\vec{q}, \vec{p})$  is Maxwell-Boltzmann: equilibrium kinetics
- ◆ The rate is equal to the flux over the dividing surface and there is no recrossing



Семиохин, Страхов, Осипов

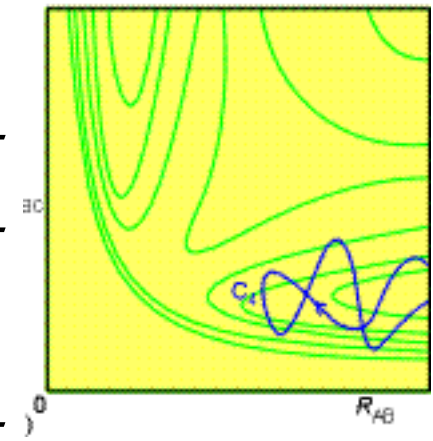
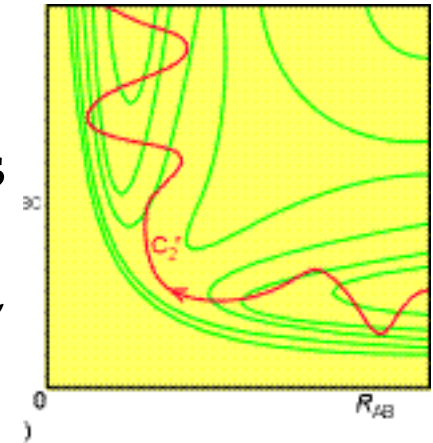
- ◆ Element of the phase space  $d\Gamma = \prod_i dp_i dq_i / h^s$
  - ◆ Reaction coordinate, normal to the dividing surface,  $q_r, p_r$ .
  - ◆ Dividing surface  $d\Gamma^\ddagger = \prod_{i \neq r} dp_i dq_i / h^s, \implies d\Gamma = d\Gamma^\ddagger dp_r dq_r / h$
  - ◆ The flux is  $\frac{dN}{dt} = f(\vec{q}, \vec{p}) \frac{d\Gamma}{dt} = \frac{f(\vec{q}, \vec{p})}{h} d\Gamma^\ddagger dp_r dq_r$
  - ◆ Rate constant  $k_{TST} = \frac{1}{h} \frac{\int f(\vec{q}, \vec{p}) d\Gamma^\ddagger dp_r dq_r}{\int f(\vec{q}, \vec{p}) d\Gamma}, H = H^\ddagger + H_r$
- $$k_{TST} = \frac{k_B T}{h} \frac{\int e^{-H^\ddagger / (k_B T)} d\Gamma^\ddagger}{\int e^{-H / (k_B T)} d\Gamma} = \frac{k_B T}{h} e^{(-\Delta F^\ddagger) / (k_B T)}$$
- ◆ After integration

- ◆  $k = \chi k_{TST}$ ,  $\chi$  is the transmission factor
- ◆ Tunneling: might be important at lower temperatures



Haenggi,  
Rev. Mod. Phys.  
1990, v. 62, N2,  
p.251

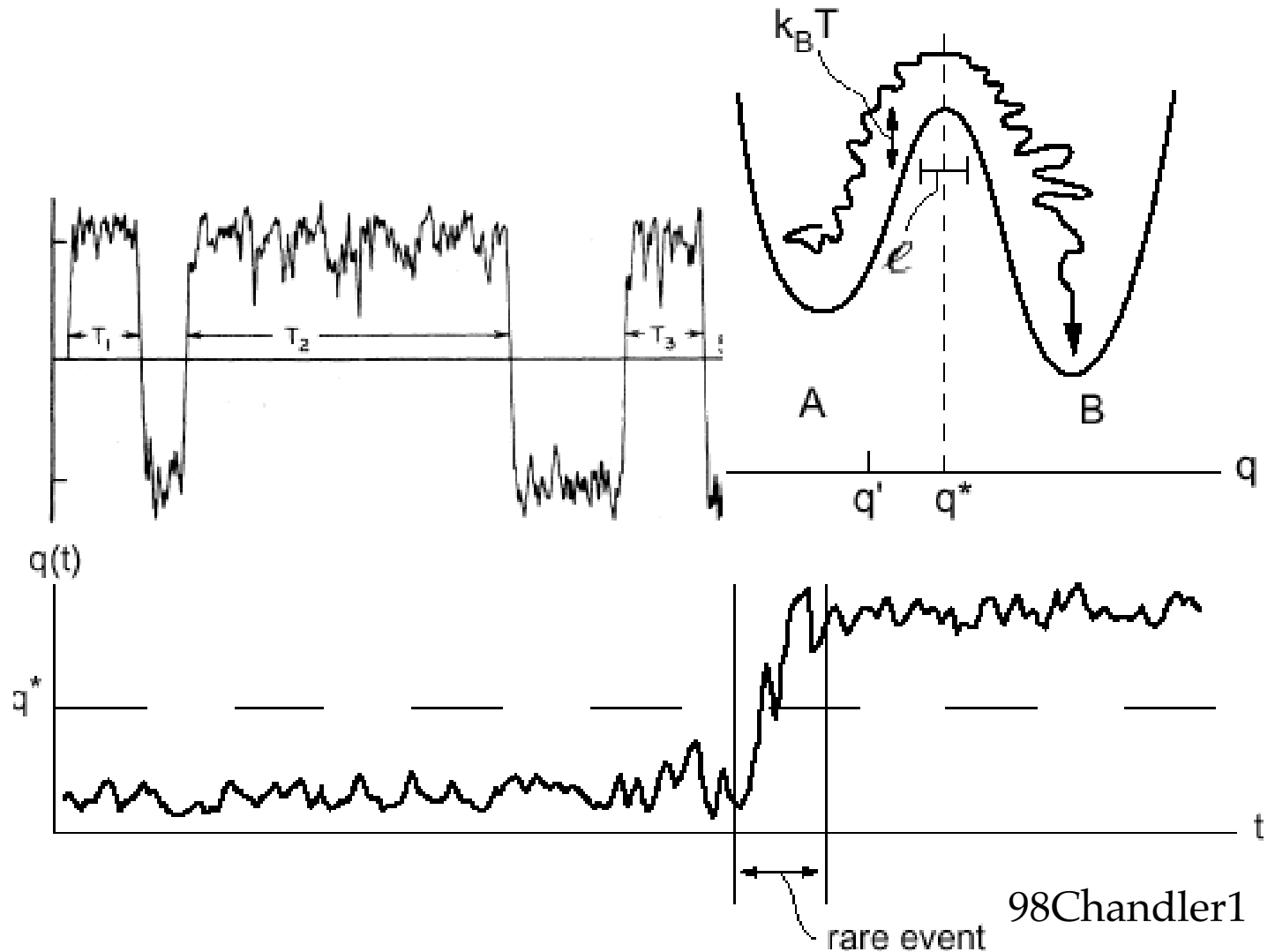
- ◆ Recrossing,  $\chi$  is less than one, demo from Atkins
- ◆  $k_{TST}$  is the upper limit
- ◆ The product  $\chi k_{TST}$  is independent on the position of the dividing surface
- ◆ Variational transition state theory



- ◆ Rare events
- ◆ Time correlation function
- ◆ Rate constant
- ◆ Simulation
- ◆ Coupling



- ◆ Example  $A = B$
- ◆  $\tau_{\text{reac}}$  is long time
- ◆  $\tau_{\text{mol}}$  is quick time,  $10^{-13}$  s
- ◆  $\tau_{\text{reac}} \sim \tau_{\text{mol}} e^{\beta F^{\ddagger}}$
- ◆ Direct simulation requires  $t \approx n\tau_{\text{reac}}$







◆  $\langle h\delta h(t) \rangle \sim \langle h\delta h(0) \rangle e^{-kt}$

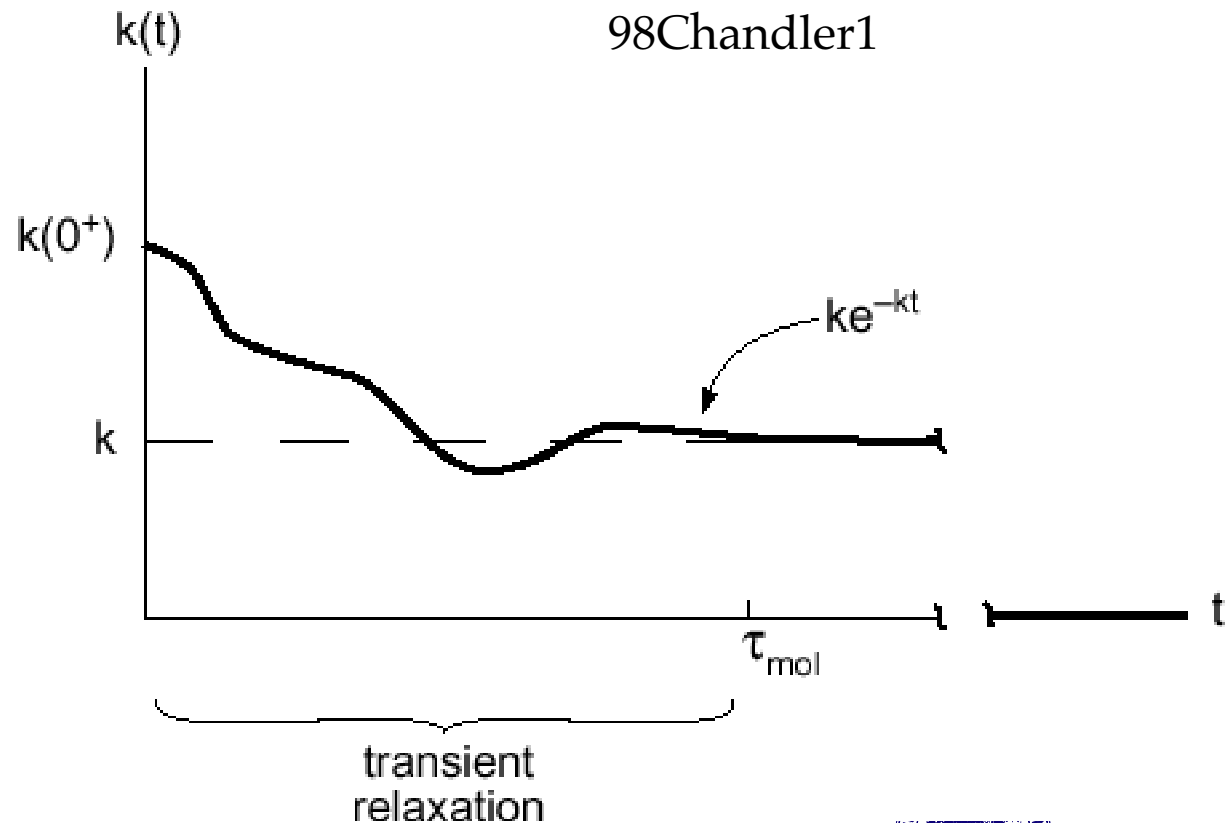
◆ Reactive flux correlation function  $k(t) \equiv -\frac{d}{dt} \frac{\langle h\delta h(t) \rangle}{\langle h\delta h(0) \rangle} \sim k e^{-kt}$

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◆  $k(0+) = k_{TST}$

◆  $\chi = k(\tau_{mol})/k(0+)$

◆ working equation  
 $k = \chi k_{TST}$

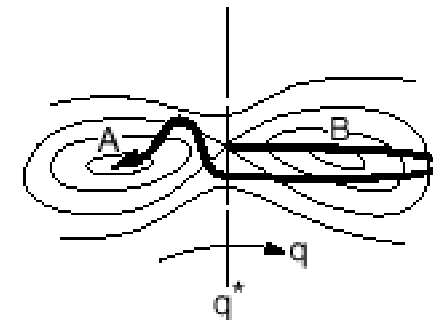
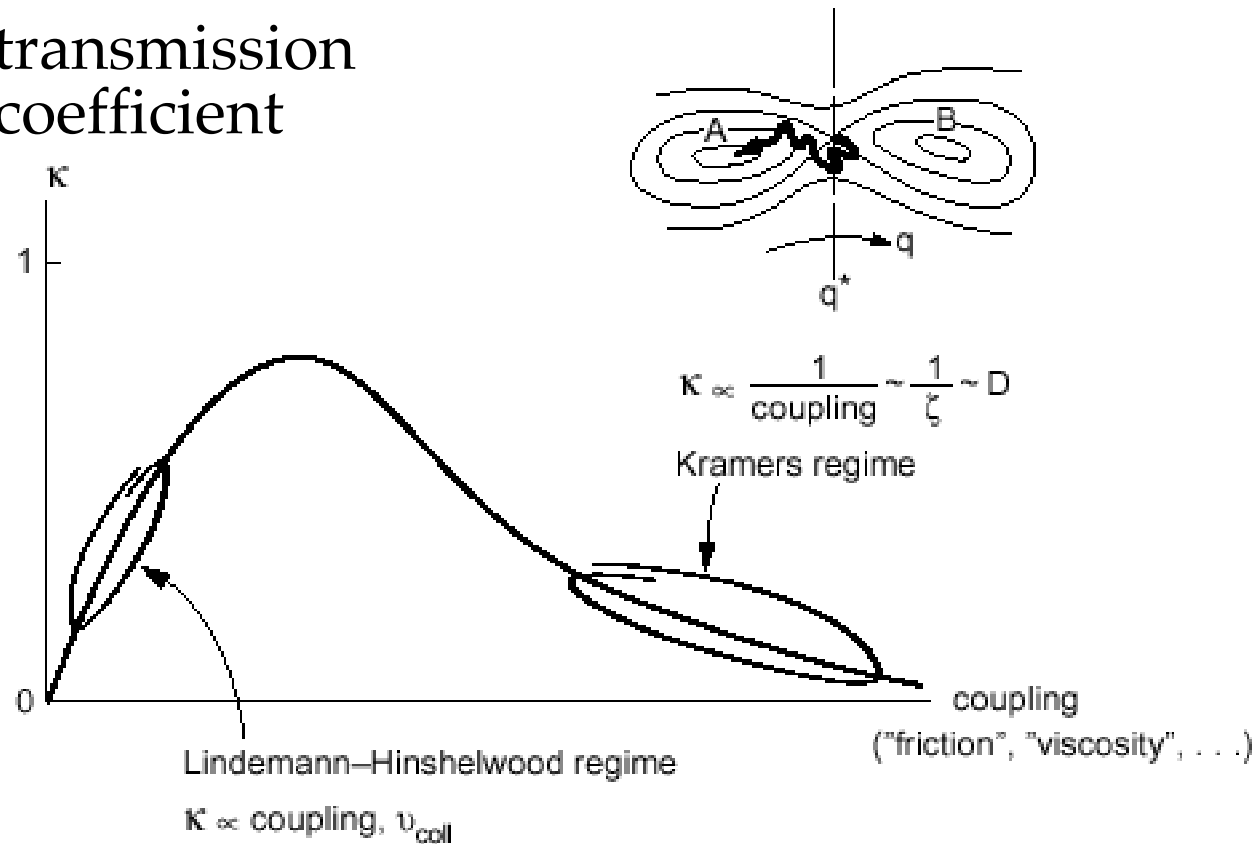


- ◆ Choose a transition state,  $q^\ddagger$
- ◆ Perform free energy perturbation simulation to estimate  $\Delta F^\ddagger$ 
  - ◆ you have  $k_{TST} = \frac{k_B T}{h} \exp\left(-\frac{\Delta F^\ddagger}{k_B T}\right)$  and also a number of equilibrated point at the transition state
- ◆ Run trajectories from the transition state for  $\tau_{mol}$  to determine transmission factor
- ◆ Computational advantage
  - ◆ Direct simulation time is  $N\tau_{reac}$
  - ◆ Time of sampling trajectories from transition state  $\tau_{eq} + N\tau_{mol}$



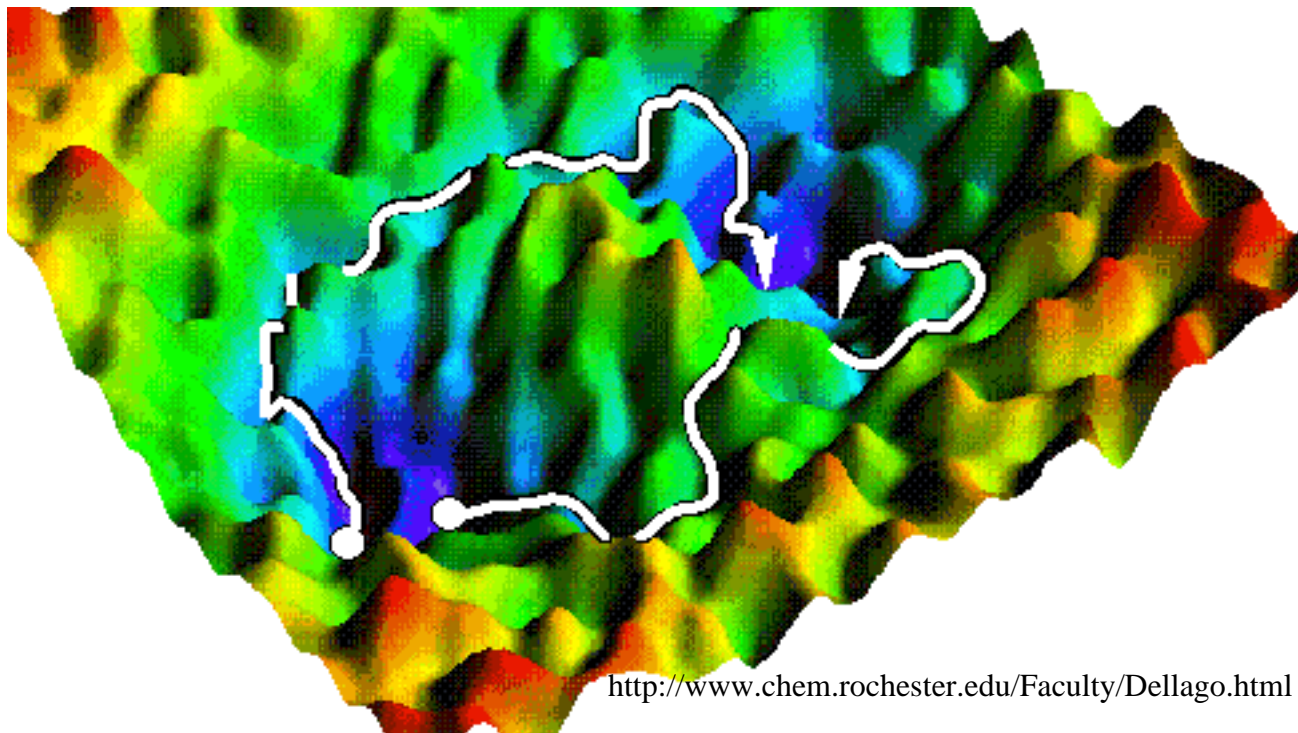
- ◆  $M\ddot{x} + C\dot{x} + \nabla V(x) = D\dot{W}(t)$ ,  $C = \gamma M$ , friction parameter

transmission coefficient



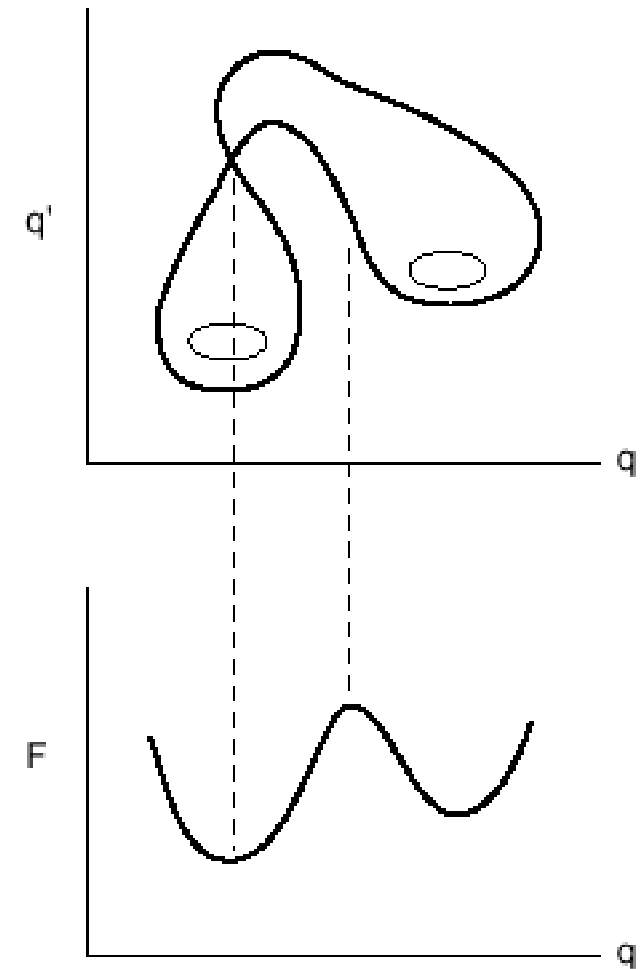
- ◆ Complex potential surface
- ◆ “Throwing ropes in the dark”
- ◆ Example: cluster reorganization kinetics

- ◆ Example: dissociation of NaCl in water
- ◆ Order parameter  $R(\text{Na}^+ - \text{Cl}^-)$ 
  - ◆ Does not take into account solvation shell



<http://www.chem.rochester.edu/Faculty/Dellago.html>

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◆ time slice  $t$ , separated by  $\Delta\tau$ ,  $P_A[r(t)] = h_A(r_0)\rho(r_0)\Pi_t P(r_t, r_{t+1})$

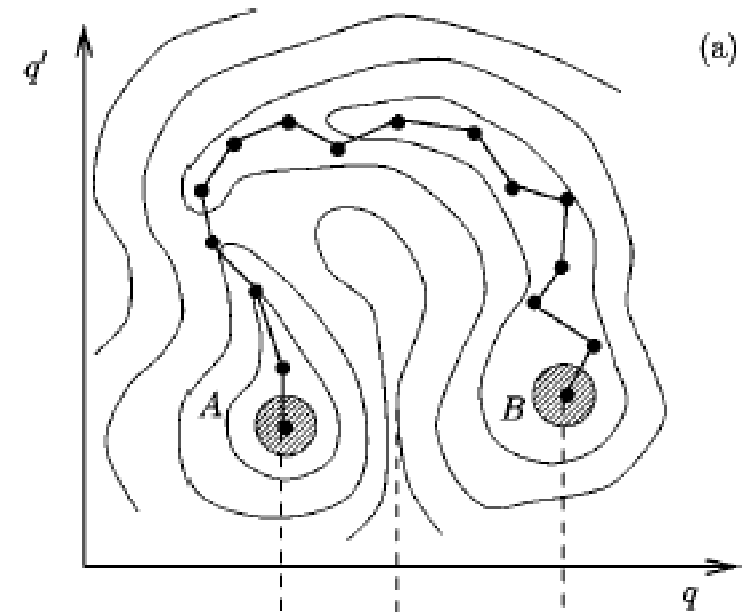
◆  $P_{AB}[r(t)] = h_A(r_0)\rho(r_0)\Pi_t P(r_t, r_{t+1})h_B(r_L)$

◆ time correlation function

$$\frac{\langle h_A h_B(\tau) \rangle}{\langle h_A \rangle} = \frac{\int Dr(t) (P_{AB}[r(t)])}{\int Dr(t) (P_A[r(t)])}$$

◆  $\tau$  is of the order of plateau time

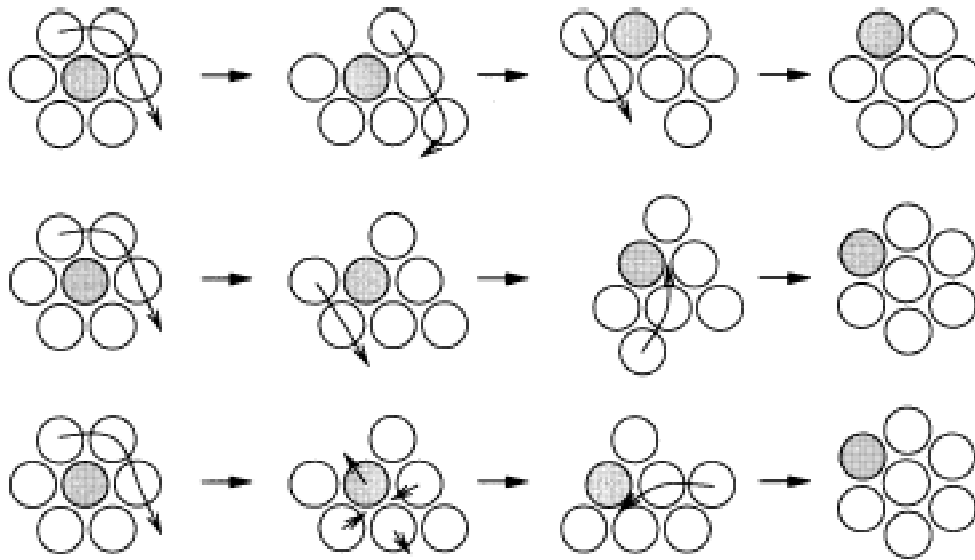
$$\frac{\langle h_A h_B(\tau) \rangle}{\langle h_A \rangle} \sim k_{AB}\tau$$



Dellago, J. Chem. Phys. 1998, v. 108, N 5, p. 1964

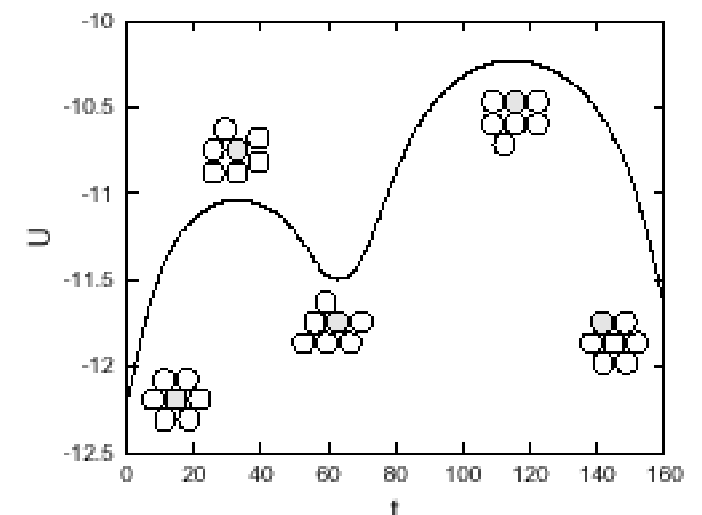
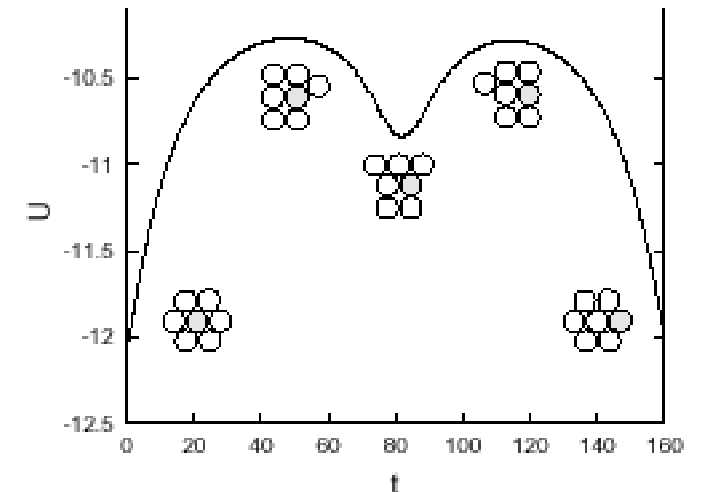


- ◆ Cold cluster of seven Lennard-Jones disks,  $k_B T = 0.05 \epsilon$



Predominant pathways

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- ◆ Reaction path on the potential surface
- ◆ Transition state theory
- ◆ Simulating rare events
- ◆ Sampling transition pathways