TSTC Lectures: Theoretical & Computational Chemistry

Rigoberto Hernandez
Major Concepts, Part IV

• Review:
  – Fluid Structure
    • Gas, liquid, solid, …
    • Radial distribution function, $g(r)$
  – Potential of Mean Force
  – Classical Determination of $g(r)$:
    • Integral Equation Theories
    • Molecular Dynamics
    • Monte Carlo
    • Scattering experiments (e.g., x-ray, or SANS)

• Renormalization Group Theory
• Coarse Graining
Renormalization Group (RG) Theory, I

- Ken G. Wilson, 1982 Nobel Prize
- Ising Model as example...

• Each transformation consists of two steps:
  - Decimate (remove particles)
  - Renormalize (rescale distances)

• Group structure:
  - When transformations are exact (e.g., in 1D Ising), obtain an exact group, and an exact theory
  - When transformations are approximate (e.g., in 2D Ising), obtain a semigroup, and the predicted $T_c$ is only as good as the approximation.

• RG also gives critical exponents, and some observables
Renormalization Group Theory, II

• The transformation involves two steps:
  – Decimate $e^{-\beta \mathcal{H}/Q}$ (integrate/sum over chosen variables)
    ① In Ising Model, this means remove alternating spins
    ② Rescale $N/2$ to $N$ (i.e., $L/2$ to $L$)
  – So $\mathcal{H}(\mathbf{R}, \beta; \{p\}) \rightarrow F^{(2)}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\})$
• At each iteration, you do the same transformation
  – $F^{(n)}(\mathbf{R}, \beta^{(n)}; \{p^{(n)}\}) \rightarrow F^{(n+1)}(\mathbf{R}, \beta^{(n+1)}; \{p^{(n+1)}\})$
  – If $F^{(n)}$ and $F^{(n+1)}$ have the same structure,
    • RG is then exact, and you have a group (with invertability)
    • The system is the same (at all length scales) at fixed points of the map, i.e. when $\beta^{(n)} = \beta^{(n+1)}$ and $\{p^{(n)}\} = \{p^{(n+1)}\}$
  – If not, then you must approximate
    • $F^{(n+1)}(\mathbf{R}, \beta^{(n+1)}; \{p^{(n+1)}\}) \approx F^{(n)}(\mathbf{R}, \beta^{(n+1)}; \{p^{(n+1)}\})$
  – And hope for the best ?!
Renormalization Group Theory, III

• In 1D Spin Ising System:
  – \( F^{(2)}(R, \beta^{(2)}; \{p^{(2)}\}) = \mathcal{H}(R, \beta^{(2)}; \{p^{(2)}\}) \)
  – So you get an exact group
  – The only fixed point is at \( \beta = \infty \) (\( T=0 \))
  – Hence RG correctly predicts no Critical point!

• In 2D Spin Ising System, Zeroth Order Semigroup:
  – \( F^{(2)}(R, \beta^{(2)}; \{p^{(2)}\}) \neq \mathcal{H}(R, \beta^{(2)}; \{p^{(2)}\}) \)
  – What if you just leave out the terms that are not nearest neighbor?
    • The structure of \( F^{(n)}(R, \beta^{(n)}; \{p^{(n)}\}) \) is exactly that of a separable product of two 1D Spin Ising systems
    • Incorrectly predicts no \( T_c \)!
Renormalization Group Theory, IV

• In 2D Spin Ising System, Next Order Semigroup:
  – $F^{(2)}(R, \beta^{(2)}; \{p^{(2)}\}) \neq \mathcal{H}(R, \beta^{(2)}; \{p^{(2)}\})$
  – Now recognize that $F^{(2)}(R, \beta^{(2)}; \{p^{(2)}\})$ has terms involving: (Migdal-Kadanoff Transformation)
    • Nearest neighbor, next-nearest neighbor and a 4-point term
    • Let $F^{(2)}(R, \beta^{(2)}; \{p^{(2)}\}) \approx F'(2)(R, \beta^{(2)}; \{p^{(2)}\})$, where the latter includes only NN and next-NN terms
  – Repeat the renormalization, i.e.,
    1. Decimate
    2. Rescale
    3. Migdal-Kadanoff (removing everything but NN and next NN)
  – Critical point(s) at the fixed points of:
    • $F^{(n)}(R, \beta^{(n)}; \{p^{(n)}\}) \rightarrow F^{(n+1)}(R, \beta^{(n+1)}; \{p^{(n+1)}\})$ for $n>2$
  • There now exists a nontrivial fixed point, $T_c$, but it’s not exact… WHY?

TSTC Lecture #3
July '09

Statistical Mechanics
R. Hernandez
@ Georgia Tech
**Ising Spin: Summary**

<table>
<thead>
<tr>
<th>$T_c/(J/k_B)$</th>
<th>Numerical (Exact)</th>
<th>Onsager</th>
<th>MFT</th>
<th>RG</th>
</tr>
</thead>
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<tr>
<td>1D</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
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<tr>
<td>2D</td>
<td>2.3</td>
<td>2.269</td>
<td>4</td>
<td>1.97</td>
</tr>
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</tr>
<tr>
<td>4D</td>
<td>~8</td>
<td></td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

- **MFT** is not always accurate.

  Accuracy increases with increasing dimensionality because higher dimension means more neighbors, and hence mean field approximation is better.

- **RG: Renormalization Group Theory**

  Exact in 1D, but gets worse with increasing dimensionality because of the increasing error in ignoring higher order terms in the construction of the semigroup.
E.g., Random Walk Model

- What is $P(R,N)$?

$$P(R,N) = \frac{1}{z} \sum_{i=1}^{z} P(R-b_i,N-1) = \frac{1}{z} \sum_{i=1}^{z} \left( P(R,N) - \frac{\partial P}{\partial N} \cdot 1 - \frac{\partial P}{\partial R_\alpha} b_i \alpha - \frac{\partial^2 P}{\partial R_\alpha \partial R_\beta} b_i \alpha b_i \beta \right)$$

But \( \frac{1}{z} \sum_{i=1}^{z} (b_i \alpha) = 0 \) and \( \frac{1}{z} \sum_{i=1}^{z} (b_i \alpha b_i \beta) = \frac{\delta_{\alpha \beta} b^2}{D} \)

$$\Rightarrow \frac{\partial P}{\partial N} = \frac{b^2}{2D} \frac{\partial^2 P}{\partial R^2} = \frac{b^2}{2D} \nabla^2 R^2 P$$

$$\Rightarrow P(R,N) = \left( \frac{D}{2\pi Nb^2} \right)^{D/2} e^{-\frac{DR^2}{2Nb^2}}$$

So end-to-end distribution is a Gaussian!
Gaussian Chains

• Take \( P(R,N) \) from RW model to describe a segment...

\[
P(R,N) = \left( \frac{D}{2\pi Nb^2} \right)^{D/2} e^{-\frac{DR^2}{2Nb^2}}
\]

\[
P(r,N) = \left( \frac{D}{2\pi b^2} \right)^{D/2} e^{-\frac{Dr^2}{2b^2}}
\]

\[
P(\{R_n\}) = \prod_{n=1}^{N} \left( \frac{D}{2\pi b^2} \right)^{ND/2} \exp \left( -\frac{D}{2b^2} \sum_{n=1}^{N} (r_n)^2 \right)
\]

Bead-Spring model potential:

\[
U(\{R_n\}) = \frac{k}{2} \sum_{n=1}^{N} (R_n - R_{n-1})^2
\]

\[
P(\{R_n\}) \propto \exp \left( -\frac{\beta k}{2} \sum_{n=1}^{N} (R_n - R_{n-1})^2 \right)
\]

\[k = \frac{D}{\beta b^2}\]
Radius of Gyration

- A measure of “size” or “volume”

\[ R_G = \left( \frac{\sum_{n=1}^{N} m_n R_n}{\sum_{n=1}^{N} m_n} \right) = \frac{1}{N} \sum_{n=1}^{N} R_n \quad \text{assuming equal masses} \]

\[ R_g^2 = \frac{1}{N} \sum_{n=1}^{N} \left\langle (R_n - R_G)^2 \right\rangle = \frac{1}{2N^2} \sum_{m,n} \left\langle (R_n - R_m)^2 \right\rangle \]

For Gaussian chains…

\[ \left\langle (R_n - R_m)^2 \right\rangle = |n - m| b^2 \]

\[ R_g^2 = \frac{b^2}{2N^2} \sum_{m,n} |n - m| \approx \frac{b^2}{N^2} \int_0^n \int_0^N (n - m) = \frac{1}{6} N b^2 = \frac{1}{6} \left\langle R^2 \right\rangle \]
Rg Using Renormalization

- Suppose that \( N = 2^n \) segments
- **Decimate** half the monomers, so now \( N' = 2^{n-1} \)

- What is the value of the ratio,
  \[
  \frac{R_g(N)}{R_g(N/2)} = \frac{R_g(n)}{R_g(n-1)}?
  \]
- Let \( r \) denote the value of this ratio
- Then \( \frac{R_g(n)}{R_g(1)} = r^n \)

- But \( R_g^2(1) = \frac{b^2}{6} \)
  \[
  \Rightarrow \quad R_g^2(n) = r^{2n} \frac{b^2}{6}
  \]
- If, \( r = 2^{1/2} \),
  \[
  \Rightarrow \quad R_g^2(N) = 2^n \frac{b^2}{6} = N \frac{b^2}{6}
  \]
E.g., Coarse-Graining

• **Strategy:**
  - Remove (decimate) some number of degrees of freedom (the fine-grained variables) by integrating out the others
  - This leads to a reversible work function
  - Use this PMF as the potential in the e.o.m. for the coarse-grained variables

• **Implications?**
  - Timescales are too fast!
    - Add dissipation
    - Rescale times
  - Lose information about fine-grained variables
  - Is the PMF reducible to a sum of two-body terms?
  - Can one construct transferable coarse-grained potentials?

Major Concepts, Part V

• Nonequilibrium Dynamics
  – Correlation Functions
  – Langevin & Fokker-Planck Equations

• Chemical Kinetics & Rates
  – Kramers Turnover
  – Transition Path Ensemble (Chandler & others)
  – Moving TST (Uzer, Hernandez & others)
Nonequilibrium Dynamics

• Far-from-equilibrium, systems are different!
  – Doesn’t the solvent average it all out???

• Zwanzig’s Topics:
  – Brownian Motion & Langevin Equations
  – Fokker-Planck Equations
  – Master Equations
  – Reaction Rates & Kinetics
  – Classical vs. Quantum Dynamics
  – Linear Response Theory
    • Use thermodynamic quantities to predict Non-Eq
  – Nonlinearity

Time Dependent Correlation Functions

- Time-correlation function of a dynamical variables A and B is given by

\[ C_{AB}(t', t'') = \langle A(t')B^*(t'') \rangle \]

- We can also exclude the average values of the dynamical variables and define the correlation function as:

\[ C_{AB}(t) = \langle [A(t) - \langle A \rangle][B^* - \langle B^* \rangle] \rangle \]

  \[= \text{Written in this way, } C_{AB}(t) \to 0 \text{ as } t \to \infty \]

- The Fourier transform of the time correlation function is the power spectrum

\[ C_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C_{AB} \exp(i\omega t) dt \]

- And the Laplace transform is defined as:

\[ \tilde{C}_{AB}(z) = \int_{0}^{\infty} C_{AB} \exp(-zt) dt \]

- Autocorrelation functions are real even functions of t and \( \omega \)
Louisville Operator and Dynamical Variables

- A is some dynamical variable dependent upon coordinates and momenta
- Following equation propagates A in time:

\[ A(t) = \exp(iLt)A(0) \]

- where L is the Louisville operator [note \( \{A,B\} \) is the Poisson Bracket]

\[ L = -i\{H,\} \]

\[ \{A, B\} = \sum_{i=1}^{N} \left( \frac{\delta A}{\delta r_i} \cdot \frac{\delta B}{\delta p_i} - \frac{\delta A}{\delta p_i} \cdot \frac{\delta B}{\delta r_i} \right) \]

- For two dynamical variables A and B, inner product give correlation function.

\[ \langle A(t')B^*(t'') \rangle = C_{AB}(t', t'') \]

\[ \langle A(t)B^* \rangle = (B, A(t)) \]
Time Dependent Correlation Functions

Why are time dependent correlations functions important?

• Provide a quantitative description of the dynamics in liquids
• Power spectrum is what is measured by many spectroscopic techniques.
• Linear transport coefficients of hydrodynamics are related to time integrals of time dependent correlation functions.
Linear Response Theory

• Suppose:
  \[ A(t,x,\lambda \xi) = \lambda A(t,x,\xi) \] for small \( \xi \)
  \[ A(t,x+\delta x,\xi) = A(t,x,\xi) + \Delta A(t,x,\xi) \cdot \delta x \] for small \( \delta x \)

• Then:
  \[ \Delta A(t,\xi) \approx \xi \beta \langle \delta A(t) \delta A(0) \rangle \]

• Why does linear response work?
• When does linear response not work?
• What does \( \langle A(t) \rangle \) mean?
Correlation Functions

• Recall: \( \langle A \rangle = \frac{1}{\tau} \int_0^\tau dt' A(t') \)
  
  Let: \( \delta A(t) \equiv A(t) - \langle A \rangle \)

• The time correlation function is:
  \[
  C_{AA}(t) = \frac{1}{\tau} \int_0^\tau dt' \delta A(t' + t) \delta A(t')
  = \langle A(t)A(0) \rangle
  \]

• The diffusion equation:
  \[
  \frac{\partial}{\partial t} n(x, t) = D \frac{\partial^2}{\partial x^2} n(x, t)
  \]
  where \( n(x, t) \) is the concentration

• The diffusion constant is:
  \[
  D = \int_0^\infty dt \langle v(t)v(0) \rangle = \int_0^\infty dt C_{vv}(t)
  \]
Brownian Motion & the Langevin Equation

System, $x$, and bath, $y$, with all coordinates explicit, leads to a EoM for $x$, updated at each $y(t)$:

**LE:**

$$m\ddot{x}(t) = - \frac{\partial U(x(t))}{\partial x} + f_b(t) - γ\dot{x}$$

**GLE:**

$$m\ddot{x}(t) = - \frac{\partial V(x(t))}{\partial x} + δf(t) - β\int_0^t dt'\langle δf(t)δf(t')\rangle_b \dot{x}(t')$$

$$C_{vv}(t) = \frac{1}{mβ}e^{-\left(\frac{γ}{m}\right)t} \implies D = \frac{1}{mβ} \int_0^∞ dt e^{-\left(\frac{γ}{m}\right)t} = \frac{1}{βγ}$$

Fokker–Planck Equation:

$$\frac{∂ψ}{∂t} = \frac{∂}{∂v} \left[ γνψ + D\frac{∂ψ}{∂v} \right]$$

at steady state:

$$ψ(x) ∝ e^{-\frac{1}{2}βmv^2} ∝ e^{-β(K.E.)}$$

･Brown, Robert, “A brief account of microscopical observations made in the months of June, July and August, 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies.” Phil. Mag. 4, 161-173, 1828.

Chemical Kinetics

• Simple Kinetics—Phenomenology
  – Master Equation
  – Detailed Balance
  – E.g.: apparent rate for isomerization: \( \tau_{\text{rxn}}^{-1} = k_{AB} + k_{BA} \)

• Microscopic Rate Formula
  – Relaxation time
  – Plateau or saddle time (Chandler)
Rates

\[ C_{\theta\theta}(t) = \langle \theta(x(t))\theta(x(0)) \rangle \]
where \( \theta(\cdot) \) is the heaviside function and 0 is a DS

• **The rate is:** E.g., in the apparent rate for isomerization: \( \tau_{\text{rxn}}^{-1} = k_{AB} + k_{BA} \)

\[ k(t) = -\frac{d}{dt} \ln C_{\theta\theta}(t) \]

– \( k(0) \) is the transition state theory rate

– After an initial relaxation, \( k(t) \) plateaus (Chandler):
  • the plateau or saddle time: \( t_s \)
  • \( k(t_s) \) is the rate (and it satisfies the TST Variational Principle)

– After a further relaxation, \( k(t) \) relaxes to 0

• **Other rate formulas:**
  – Miller’s flux-flux correlation function
  – Langer’s Im \( F \)
Transition State Theory

• Objective:
  • Calculate reaction rates
  • Obtain insight on reaction mechanism

• Eyring, Wigner, Others..
  1. Existence of Born-Oppenheimer $V(x)$
  2. Classical nuclear motions
  3. No dynamical recrossings of TST

• Keck, Marcus, Miller, Truhlar, Others...
  • Extend to phase space
  • Variational Transition State Theory
  • Formal reaction rate formulas

• Pechukas, Pollak...
  • PODS—2-Dimensional non-recrossing DS

• Full-Dimensional Non-Recrossing Surfaces
  • Miller, Hernandez developed good action-angle variables at the TS using CVPT/Lie PT to construct semiclassical rates
  • Jaffé, Uzer, Wiggins, Berry, Others... extended to NHIM’s, etc
Langevin Dynamics (open systems)

- Langevin Equation:
  \[ \ddot{x} = -\gamma \dot{x} - \frac{\partial U(x)}{\partial x} + \xi(t) \]
  \[ \langle \xi(t) \xi(t') \rangle = 2k_B T \gamma \delta(t-t') \]

- Identify a Reaction/Dynamic Variable (Order Parameter?)

- The “bath coordinates” are subsumed by the Friction and Random Force

- Kramers Turnover Rates

- Mel’nikov-Pollak-Grabert-Hänggi (PGH) Theory & Rates

Kramer’s Turnover in LiCN

LiCN in Ar bath (low $P$ and high $T$)

- Calculate exact Rates:
  - Reactive Flux as a function of pressure
  - Convert abscissa to microscopic friction

- PGH (TST-like) Rates
  - Construct Langevin Eq.
  - Need PMF
  - Need Friction Kernel

- Compare Rates

Kramer’s Turnover in LiCN

LiCN in Ar bath (low $P$ and high $T$)

- Comparing forward and backward isomerization rates
- Agreement is nearly quantitative (despite ohmic friction assumption)
- Observation of energy-diffusion regime (rates increasing with increasing friction)

Reactions with noise

Langevin equation:

\[ \ddot{q}_\alpha(t) = \Omega \dot{q}_\alpha(t) - \Gamma \dot{q}_\alpha(t) + \xi_\alpha(t) \]

-deterministic potential mean force (PMF)
-damping
-white noise

We will find a time-dependent non-recrossing dividing surface.
Decoupling from the noise

\[ \ddot{\bar{q}}_\alpha (t) = \Omega \bar{q}_\alpha (t) - \Gamma \dot{\bar{q}}_\alpha (t) + \xi_\alpha (t) \]

Choose trajectory \( \bar{q}_\alpha^+ (t) \)
that never leaves the transition region
as the “moving saddle point”

\( \Rightarrow \) unique stochastic Transition State Trajectory

\( \Rightarrow \) w.r.t, Relative coordinate: \( \Delta \bar{q}(t) = \bar{q}_\alpha (t) - \bar{q}_\alpha^+ (t) \)
the E.o.M are noiseless
Construction of the TS trajectory

Rewrite Langevin equation in phase space, \( \ddot{\mathbf{x}} = \left( \begin{array}{c} \ddot{q} \\ \ddot{\mathbf{v}} \end{array} \right) \)

\[
\dot{x}_\alpha(t) = A \dot{x}_\alpha(t) + \begin{pmatrix} 0 \\ \xi_\alpha(t) \end{pmatrix} \quad \text{with} \quad A = \begin{pmatrix} 0 & 1 \\ \Omega & -\Gamma \end{pmatrix}
\]

Scalar equations decouple when \( A \) is diagonalized (eigenvalues \( \varepsilon_j \)):

\[
\dot{x}_{\alpha,j}(t) = \varepsilon_j x_{\alpha,j}(t) + \xi_{\alpha,j}(t)
\]

General solution:

\[
x_{\alpha,j}(t) = c_{\alpha,j} e^{\varepsilon_j t} + \int_{-\infty}^{0} d\tau \; e^{-\varepsilon_j \tau} \xi_{\alpha,j}(t + \tau) \quad \text{for Re} \; \varepsilon_j < 0
\]

\[
x_{\alpha,j}(t) = c_{\alpha,j} e^{\varepsilon_j t} - \int_{0}^{\infty} d\tau \; e^{-\varepsilon_j \tau} \xi_{\alpha,j}(t + \tau) \quad \text{for Re} \; \varepsilon_j > 0
\]

Set \( c_{\alpha,j}=0 \) so as to keep \( x_{\alpha,j}(t) \) finite for \( t \rightarrow \pm \infty \)

\( \Rightarrow \) TS trajectory \( x^\pm_{\alpha,j}(t) \) is given as an explicit function of the noise.
The TS Trajectory
in unstable phase space

- Remains near col for all time
- It gives rise to an associated moving dividing surface
- Fixed dividing surface is crossed many times, but moving dividing surface is not
- TS trajectory is defined for each manifestation of the noise....
  ** But can still average over IC’s of the particle/subsystem

An arbitrary trajectory in configuration space

Statistics of the TS Trajectory

- The distribution of the TS trajectory is stationary.
- Components are Gaussian distributed with zero mean.
- Time-correlation functions are known explicitly, e.g.

\[
\left\langle x_{\alpha j}^\perp(t)x_{\alpha k}^\perp(0) \right\rangle_\alpha = \frac{K_{jk}}{-(\varepsilon_j + \varepsilon_k)} e^{\varepsilon_j t} \text{ if } \Re \varepsilon_{j,k} < 0
\]

Variance of TS position, one-dimensional example

\[
\frac{\langle x_{\alpha j}^2 \rangle_\alpha}{(k_B T_{\omega_b}^2)}
\]
Great, you have a non-recrossing (moving TS) dividing surface,
So WHAT?

- Dynamics can be replaced by GEOMETRY
- Calculate Rates
- Obtain Mechanisms
Phase Space View of Reaction

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

The geometric structures persist even in strongly coupled systems: Normally Hyperbolic Invariant manifolds (NHIM)
The barrier ensemble
Averaging over many trajectories

Sample trajectories in the Transition State region

- located at fixed “TS” $q_{\text{react}}=0$
- Boltzmann-distributed in bath coordinates and in velocities

Reactive part of the ensemble is known a priori.

For each trajectory, a unique reaction time (or “First Passage time” to reach the moving TS) can be defined.
Reaction probabilities (Committors)

Reaction probabilities for each point in phase space:

\[ P_+ = \text{Prob ( product for } t \to \infty) \]
\[ = \text{Prob ( } \Delta x_u(0) > 0) \]
\[ = \frac{1}{2} \text{erfc} \left( - \frac{x_u(0)}{\sqrt{2\sigma_u}} \right) \]

\[ P_- = \text{Prob ( product for } t \to -\infty) \]
\[ = \frac{1}{2} \text{erfc} \left( - \frac{x_s(0)}{\sqrt{2\sigma_s}} \right) \]

In particular: The **Stochastic Separatrices** have been identified
Identifying Reactive Trajectories

For a fixed instance of the noise

- sample initial conditions from the Barrier Ensemble
- propagate forward and backward in time for a time $T_{int}$
- identify reactive trajectories

Reaction probabilities obtained from moving surface converge
- monotonically
- faster than with fixed surface

*a priori* probabilities are reproduced asymptotically.

Anharmonic barriers

anharmonic potential energy surface

\[ V(x, y) = -\frac{1}{2} \omega_x^2 x^2 + \frac{1}{2} \omega_y^2 y^2 + k x^2 y^2 \]

use moving TST dividing surface obtained at the harmonic limit, \( k=0 \)

\( \Rightarrow \) moving surface is approximately free of recrossings

\( \Rightarrow \) advantages of moving surface persist for \( k \) not too large:
  - fast convergence
  - monotonic approach to limit

Anharmonic Barriers

Is the approximate moving TS DS recrossing free?

- Identifying non-recrossing trajectories vs. time at increasing anharmonicity
- Fixed surface does poorly even for small anharmonicity
- Moving surface (obtained from harmonic reference!) does well up to very large anharmonicity
\[ \kappa(t) = \frac{k(t)}{k_{\text{TST}}} = \frac{\left\langle \delta(x(0)-x^+)v_x(0)\Theta(x(t)-x^+) \right\rangle}{\left\langle \delta(x(0)-x^+)v_x(0)\Theta(v_x(0)) \right\rangle} \]

- Compute using fixed surface
- Compute using moving TST surface
- Average over the known critical velocity from the NHIM:
  \[ \kappa = \left\langle \exp \left\{ -\frac{v_\alpha^+}{2k_bT} \right\} \right\rangle_\alpha \]
  where \( v_\alpha^+ \equiv \text{critical velocity} \)

Anharmonic Rates

\[ \kappa(t) = \frac{k(t)}{k_{\text{TST}}} = \frac{\langle \delta(x(0)-x^+)v_x(0) \Theta(x(t)-x^+) \rangle}{\langle \delta(x(0)-x^+)v_x(0) \Theta(v_x(0)) \rangle} \]

- Compute using fixed surface
- Compute using moving TST surface

Transition Path Ensemble

- "Finding Transition Pathways in Complex Systems: Throwing Ropes Over Rough Mountain Passes, In The Dark"

- Strategy:
  - Find a path between A & B
  - Each trial path is a perturbation of given path
  - Accept, if it connects A & B
  - Sample over the Path Ensemble!

From Chandler:
http://gold.cchem.berkeley.edu/research_path.html

Other Topics, Part VI

• Mode Coupling Theory
  – Wolfgang Götze
  – Matthias Fuchs
  – David Reichmann

• Fluctuation Theorems
  – Giovanni Gallavotti & E. G. D. Cohen
  – Denis Evans
  – Christopher Jarzynski
  – Jorge Kurchan

• Accelerated Dynamics
  – Art Voter: hyperdynamics, temperature acceleration, parallel replicas
  – Vijay Pande’s parallel replicas
  – Ron Elber’s Milestone Approach