May 2009, Lecture #3 Statistical Mechanics: Nonequilibrium Systems

#### 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

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### 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)
  - $\text{ So } \mathcal{H}(\boldsymbol{R},\boldsymbol{\beta};\,\{p\}) \to F^{(2)}(\boldsymbol{R},\,\boldsymbol{\beta}^{(2)};\,\{p^{(2)}\})$
- At each iteration, you do the same transformation
  - $\ F^{(n)}(\pmb{R}, \, \beta^{(n)}; \, \{p^{(n)}\}) \to F^{(n+1)}(\pmb{R}, \, \beta^{(n+1)}; \, \{p^{(n+1)}\})$
  - 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 ?!

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#### Renormalization Group Theory, III

- In 1D Spin Ising System:
  - $\ \mathcal{F}^{(2)}(\pmb{R}, \, \beta^{(2)}; \, \{p^{(2)}\}) = \mathcal{H}(\pmb{R}, \, \beta^{(2)}; \, \{p^{(2)}\})$
  - 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:  $E(2)(\mathbf{P}, P(2)) \neq q(\mathbf{P}, P(2))$ 
  - $F^{(2)}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\}) \neq \mathcal{H}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\})$
  - What if you just leave out the terms that are not nearest neighbor?
    - The structure of *F<sup>(n)</sup>*(*R*, β<sup>(n)</sup>; {*p<sup>(n)</sup>*}) is exactly that of a separable product of two 1D Spin Ising systems
    - Incorrectly predicts no  $T_{\rm c}!$

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#### Renormalization Group Theory, IV

• In 2D Spin Ising System, Next Order Semigroup:

 $- F^{(2)}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\}) \neq \mathcal{H}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\})$ 

- Now recognize that  $F^{(2)}(\mathbf{R}, \beta^{(2)}; \{p^{(2)}\})$  has terms involving: (Migdal-Kadanoff Transformation)
  - Nearest neighbor, next-nearest neighbor and a 4-point term
  - Let *F*<sup>(2)</sup>(*R*, β<sup>(2)</sup>; {*p*<sup>(2)</sup>}) ≈ *F*<sup>'(2)</sup>(*R*, β<sup>(2)</sup>; {*p*<sup>(2)</sup>}), 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:
  - $F^{(n)}(\mathbf{R}, \beta^{(n)}; \{p^{(n)}\}) \rightarrow F^{(n+1)}(\mathbf{R}, \beta^{(n+1)}; \{p^{(n+1)}\})$  for  $n \ge 2$
- There now exists a nontrivial fixed point, T<sub>c</sub>, but it's not exact... WHY?

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## **Ising Spin: Summary**

T <sub>c</sub> /(J/k <sub>B</sub> )	Numerical (Exact)	Onsager	MFT	RG
1D	0	0	2	0
2D	2.3	2.269	4	1.97
3D	~4		6	~4
4D	~8		8	

#### • MFT is not always accurate.

Accuracy increases with increasing dimensionality because higher dimension means more neighbors, and hence mean field appoximation 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

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#### E.g., Random Walk Model

• What is P(R,N)?

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

$$But \qquad \frac{1}{z} \sum_{i=1}^{z} (b_{i\alpha}) = 0 \quad \text{and} \qquad \frac{1}{z} \sum_{i=1}^{z} (b_{i\alpha} b_{i\beta}) = \frac{\delta_{\alpha\beta} b^2}{D}$$
  

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

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

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

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#### **Gaussian Chains**

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

$$P(\mathbf{R},N) = \left(\frac{D}{2\pi Nb^{2}}\right)^{D/2} e^{\left(-DR^{2}/2Nb^{2}\right)} \longrightarrow P(\mathbf{r},N) = \left(\frac{D}{2\pi b^{2}}\right)^{D/2} e^{\left(-Dr^{2}/2b^{2}\right)}$$
$$P(\{R_{n}\}) = \prod_{n=1}^{N} P(R_{n} - R_{n-1}) = \left(\frac{D}{2\pi b^{2}}\right)^{ND/2} \exp\left(-\frac{D}{2b^{2}}\sum_{n=1}^{N} (r_{n})^{2}\right)$$

Bead-Spring model potential:

$$P(\lbrace R_n \rbrace) \propto \exp\left(-\frac{\beta k}{2} \sum_{n=1}^{N} (R_n - R_{n-1})^2\right) \qquad k = \frac{D}{\beta b^2}$$

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 $U(\lbrace R_n \rbrace) = \frac{k}{2} \sum (R_n - R_{n-1})^2$ 

n=1



#### **Radius of Gyration**

• A measure of "size" or "volume"

$$\boldsymbol{R}_{\rm G} = \left(\sum_{n=1}^{N} m_n \boldsymbol{R}_n \middle/ \sum_{n=1}^{N} m_n \right) = \frac{1}{N} \sum_{n=1}^{N} \boldsymbol{R}_n \quad \text{assuming equal masses}$$
$$\boldsymbol{R}_{\rm g}^{2} = \frac{1}{N} \sum_{n=1}^{N} \left\langle \left(\boldsymbol{R}_n - \boldsymbol{R}_{\rm G}\right)^2 \right\rangle = \frac{1}{2N^2} \sum_{m,n} \left\langle \left(\boldsymbol{R}_n - \boldsymbol{R}_{m}\right)^2 \right\rangle$$

For Gaussian chains... 
$$\left\langle \left( \mathbf{R}_n - \mathbf{R}_m \right)^2 \right\rangle = |n - m|b^2$$

$$\mathbf{R}_{g}^{2} = \frac{b^{2}}{2N^{2}} \sum_{m,n} |n-m| \approx \frac{b^{2}}{N^{2}} \int_{0}^{N} dn \int_{0}^{n} dm (n-m) = \frac{1}{6} N b^{2} = \frac{1}{6} \left\langle R^{2} \right\rangle$$

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# R<sub>g</sub> Using Renormalization

- Suppose that *N*=2<sup>*n*</sup> segments
- **Decimate** half the monomers, so now  $N'=2^{n-1}$
- What is the value of the ratio,  $R_{g}(N)/R_{g}(N/2)=R_{g}(n)/R_{g}(n-1)?$
- Let r denote the value of this ratio
- Then  $R_g(n)/R_g(1)=r^n$
- But  $R_g^2(1)=b^2/6$
- If, *r*=2<sup>1/2</sup>,

→ 
$$R_g^2(n) = r^{2n}b^2/6$$
  
→  $R_g^2(N) = 2^n b^2/6 = N b^2/6$ 

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## 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?

"Coarse-Graining of Condensed Phase and Biomolecular Systems," G. A. Voth, Editor (CRC Press/Taylor and Francis Group, Boca Raton, FL, 2009).

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## 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

See, e.g., R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, 2001) TSTC Lecture #3 Statistical Mechanics *R. Hernandez* 14 July '09 *Georgia Tech* 

#### **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:

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

- Written in this way,  $C_{AB}(t) \rightarrow 0$  as  $t \rightarrow \infty$ 

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:

$$ilde{C}_{AB}(z) = \int_0^\infty C_{AB} \exp(-zt) dt$$

- Autocorrelation functions are real even functions of t and  $\boldsymbol{\omega}$ 

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#### Louisville Operator and Dynamical Variables

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

 $A(t) = \exp(i\mathcal{L}t)A(0)$ 

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

$$\mathcal{L} = -i\{H,\}$$
$$\{A,B\} = \sum_{i=1}^{N} \left(\frac{\delta A}{\delta r_{i}} \cdot \frac{\delta B}{\delta p_{i}} - \frac{\delta A}{\delta p_{i}} \cdot \frac{\delta B}{\delta r_{i}}\right)$$

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

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

 $\langle A(t)B^*\rangle = (B,A(t))$ 

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#### **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  $\xi$ 

 $A(t,x,\xi)$ :: observable,

x :: internal variable  $\xi$  :: external variable

 $A(t, x + \delta x, \xi) = A(t, x, \xi) + \Delta A(t, x, \xi) \cdot \delta x \text{ for small } \delta x$ 

• Then:

 $\Delta A(t,\xi) \approx \xi \beta \left\langle \delta A(t) \delta A(0) \right\rangle$ 

- Why does linear response work?
- When does linear response not work?
- What does <*A*(*t*)> mean?

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#### **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:

$$D = \int_0^\infty dt \langle v(t)v(0) \rangle = \int_0^\infty dt \, C_{vv}(t)$$

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#### **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):

$$m\ddot{x} = -\frac{\partial U(x)}{\partial x} + \delta f(x, \vec{y})$$

Fokker – Planck Equation : 
$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial v} \left[ \gamma v \psi + D \frac{\partial \psi}{\partial v} \right]$$
  
at steady state :  $\psi(x) \propto e^{-\frac{1}{2}\beta m v^2} \propto e^{-\beta (\text{K.E.})}$ 

•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.

·Einstein, A. (1905), "Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüsigkeiten suspendierten Teilchen", Annalen der Physik **17**: 549-560

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#### **Chemical Kinetics**

- Simple Kinetics—Phenomenology
  - Master Equation
  - Detailed Balance
  - E.g.: apparent rate for isomerization:  $\tau_{rxn}^{-1} = k_{AB} + k_{BA}$
- 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:  $\tau_{_{TXN}}^{_{-1}} = k_{_{AB}} + k_{_{BA}}$   $k(t) = -\frac{d}{dt} \ln C_{\theta\theta}(t)$ 
  - 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

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## 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

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(Marcus: Science **256** (1 1523)



R Hernandez

@ Georgia Tech

#### Langevin Dynamics (open systems)

9230 J. Chem. Phys., Vol. 117, No. 20, 22 November 2002 T. D. Shepherd and R. Hernandez



FIG. 2. The activated escape rate,  $\Gamma_0$ , across a bistable potential  $U_0$  ( $\lambda = 4$  and  $V^{\ddagger} = 4k_BT$ ) is displayed as a function of the friction constant  $\gamma$ . Inverse MFPTs were obtained numerically using the following prescriptions: FP<sub> $\tau$ </sub> (circles),  $\partial \Omega_x^{\ddagger}$  (dashed line),  $\partial \Omega_x^0$  (dotted line),  $\partial \Omega_{x,p}$  (solid line). Also shown are Mel'nikov Meshkov theory (Ref. 29) (MMT) rates (crosses) and the rates reported by Cartling (Ref. 46) (CFPB) for a bistable potential (squares).

Langevin Equation:

$$\ddot{x} = -\gamma_{\rm th} \dot{x} - \frac{\partial U(x)}{\partial x} + \xi_{\rm th}(t)$$
$$\left\langle \xi_{\rm th}(t) \xi_{\rm th}(t') \right\rangle = 2k_{\rm B}T\gamma_{\rm th}\delta(t - t)$$



- 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

Shepherd and Hernandez; J. Chem. Phys. 117, 9227-9233 (2002). (variational MFPT)

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#### 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

García-Müller, Borondo, Hernandez and Benito; Phys. Rev. Let. 101, 178302 (2008)

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#### 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 energydiffusion regime (rates increasing with increasing friction)

García-Müller, Borondo, Hernandez and Benito; Phys. Rev. Let. 101, 178302 (2008)

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We will find a time-dependent non-recrossing dividing surface.

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Decoupling from the noise  $\ddot{\vec{q}}_{\alpha}(t) = \Omega \, \vec{q}_{\alpha}(t) - \Gamma \, \dot{\vec{q}}_{\alpha}(t) + \vec{\xi}_{\alpha}(t)$ 

Choose trajectory  $\vec{q}_{\alpha}^{\ddagger}(t)$ that never leaves the transition region as the "moving saddle point"

→ unique stochastic Transition State Trajectory

→ w.r.t, Relative coordinate:  $\Delta \vec{q}(t) = \vec{q}_{\alpha}(t) - \vec{q}_{\alpha}^{\ddagger}(t)$  the E.o.M are noiseless



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## Construction of the TS trajectory

Rewrite Langevin equation in phase space,  $\vec{x} = \begin{pmatrix} \vec{q} \\ \vec{v} \\ \vec{j} \end{pmatrix}$ 

$$\dot{\vec{x}}_{\alpha}(t) = \mathbf{A} \vec{x}_{\alpha}(t) + \begin{pmatrix} 0 \\ \vec{\xi}_{\alpha}(t) \end{pmatrix} \quad \text{with} \quad \mathbf{A} = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ \Omega & -\Gamma \end{pmatrix}$$

Scalar equations decouple when **A** is diagonalized (eigenvalues  $\varepsilon_j$ ):  $\dot{x}_{\alpha j}(t) = \varepsilon_j x_{\alpha j}(t) + \xi_{\alpha j}(t)$ 

Δ



General solution:

$$x_{\alpha j}(t) = c_{\alpha j} e^{\varepsilon_{j} t} + \int_{-\infty}^{0} d\tau \ e^{-\varepsilon_{j} \tau} \xi_{\alpha j}(t+\tau) \text{ for } \operatorname{Re} \varepsilon_{j} < 0$$
$$x_{\alpha j}(t) = c_{\alpha j} e^{\varepsilon_{j} t} - \int_{0}^{\infty} d\tau \ e^{-\varepsilon_{j} \tau} \xi_{\alpha j}(t+\tau) \text{ for } \operatorname{Re} \varepsilon_{j} > 0$$

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

→ TS trajectory  $x_{\alpha j}^{\ddagger}(t)$  is given as an explicit function of the noise.

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# The TS Trajectory



- 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

Bartsch, Hernandez and Uzer: Phys. Rev. Lett. 95 058301 (2005)

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### An arbitrary trajectory

#### in configuration space



Bartsch, Hernandez and Uzer: *Phys. Rev. Lett.* **95** 058301 (2005) Bartsch, Uzer and Hernandez: *J. Chem. Phys.* **123** 204102 (2005)

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## 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.

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Great, you have a nonrecrossing (moving TS) dividing surface, So WHAT?

- Dynamics can be replaced by GEOMETRY
- Calculate Rates
- Obtain Mechanisms

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#### Phase Space View of Reaction



The geometric structures persist even in strongly coupled systems: Normally Hyperbolic Invariant manifolds (NHIM)

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#### The barrier ensemble

Averaging over many trajectories

Sample trajectories in the Transition State region

- located at fixed "TS" q<sub>react</sub>=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.



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#### Reaction probabilities (Committors)

# Reaction probabilities for each point in phase space:

 $P_{+} = \operatorname{Prob} ( \operatorname{product} \text{ for } t \rightarrow \infty)$  $= \operatorname{Prob} ( \Delta x_{u}(0) > 0)$ 

$$= \frac{1}{2} \operatorname{erfc} \left( -\frac{x_u(0)}{\sqrt{2}\sigma_u} \frac{1}{\dot{j}} \right)$$

$$P_{-} = \mathsf{Prob} (\mathsf{product for } t \rightarrow -\infty)$$

$$= \frac{1}{2} \operatorname{erfc} \left( -\frac{x_s(0)}{\sqrt{2}\sigma_s} \frac{1}{\dot{j}} \right)$$



In particular: The Stochastic Separatrices have been identified

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## **Identifying Reactive Trajectories**

0.6

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 probablilities obtained from moving surface converge

- monotonically
- faster than with fixed surface

*a priori* probabilities are reproduced asymptotically.



Bartsch, Uzer, Moix and Hernandez; J. Chem. Phys. 124, 244310 (2006).

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#### **Anharmonic barriers**

anharmonic potential energy surface

 $V(x, y) = -\frac{1}{2}\omega_x^2 x^2 + \frac{1}{2}\omega_y^2 y^2 + kx^2 y^2$ 

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

- → moving surface is *approximately* free of recrossings
- → advantages of moving surface persist for *k* not too large:
  - fast convergence
  - monotonic approach to limit

Bartsch, Uzer, Moix and Hernandez; J. Chem. Phys. 124, 244310 (2006).

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### **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



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#### Harmonic Rates

$$\kappa(t) = \frac{k(t)}{k^{\text{TST}}} = \frac{\left\langle \delta\left(x(0) - x^{\ddagger}\right) v_x(0) \Theta(x(t) - x^{\ddagger})\right\rangle}{\left\langle \delta(x(0) - x^{\ddagger}) v_x(0) \Theta(v_x(0))\right\rangle}$$

- Compute using fixed surface
- Compute using moving TST surface
- Average over the known critical velocity from the NHIM:

$$\kappa = \left\langle \exp\left\{-\frac{v_{\alpha}^{+2}}{2k_{\rm b}T}\right\} \right\rangle_{\alpha}$$

where  $v_{\alpha}^+ \equiv \text{critical velocity}$ 



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#### **Anharmonic Rates**

 $\kappa(t) = \frac{k(t)}{k^{\text{TST}}} = \frac{\left\langle \delta\left(x(0) - x^{\ddagger}\right) v_x(0) \Theta\left(x(t) - x^{\ddagger}\right) \right\rangle}{\left\langle \delta\left(x(0) - x^{\ddagger}\right) v_x(0) \Theta\left(v_x(0)\right) \right\rangle}$ 

- Compute using fixed surface
- Compute using moving TST surface



Bartsch, Uzer, Moix and Hernandez; J. Phys. Chem. B 112, 206-212 (2008)

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### **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!

Bolhuis, P. G., D. Chandler, C. Dellago, and P. Geissler, Ann. Rev. of Phys. Chem., 59, 291-318 (2002) C. Dellago, P. G. Bolhuis and P. L. Geissler, "Transition Path Sampling", Advances in Chemical Physics, 123, 1-78 (2002)

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From Chandler: http://gold.cchem.berkeley.edu/ research path.html

R. Hernandez



## 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

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