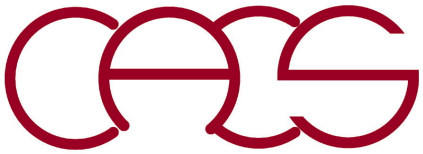
Kinetic Monte Carlo Simulation

Aiichiro Nakano

Collaboratory for Advanced Computing & Simulations
Department of Computer Science
Department of Physics & Astronomy
Department of Quantitative & Computational Biology
University of Southern California

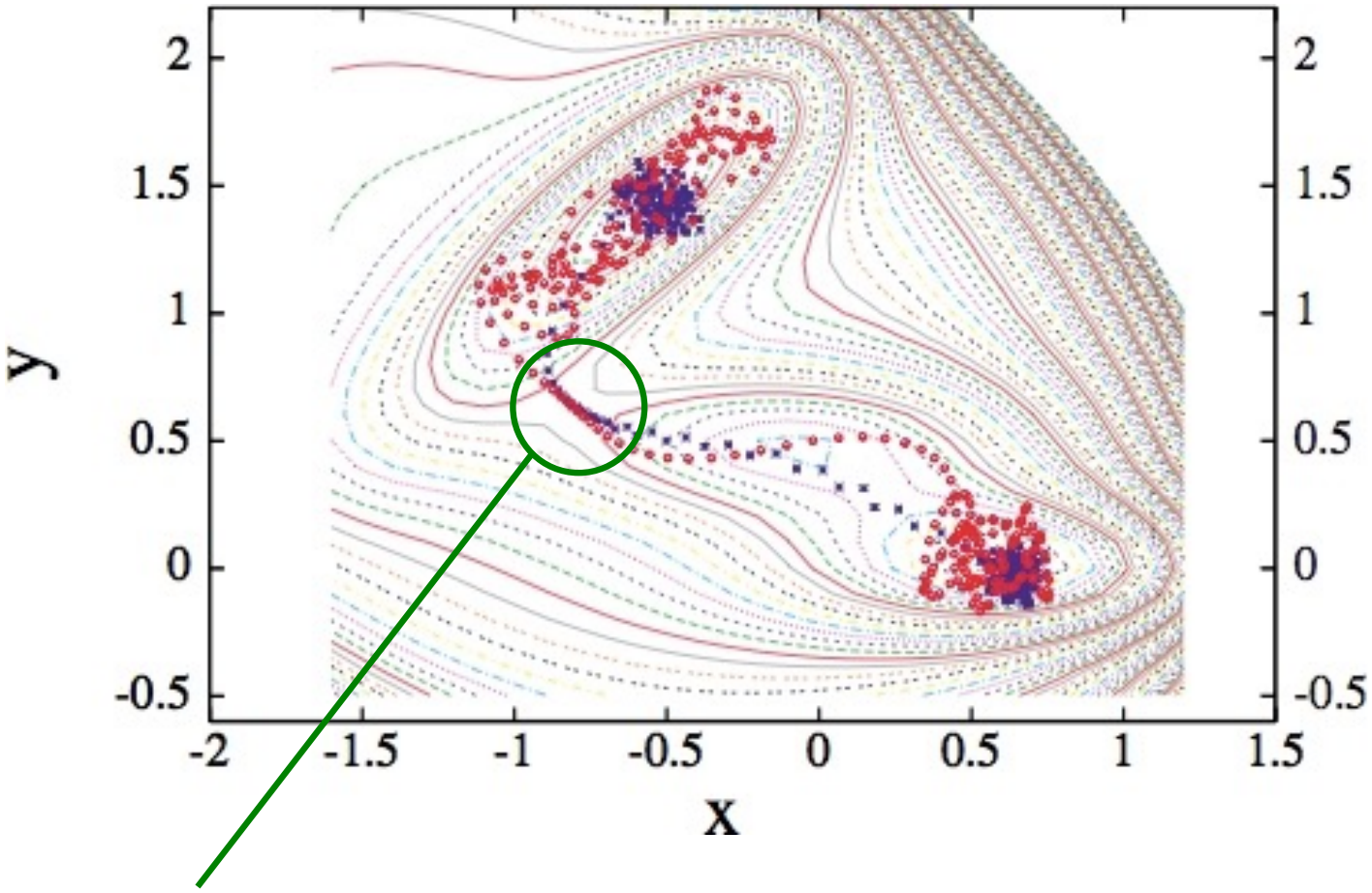
Email: anakano@usc.edu

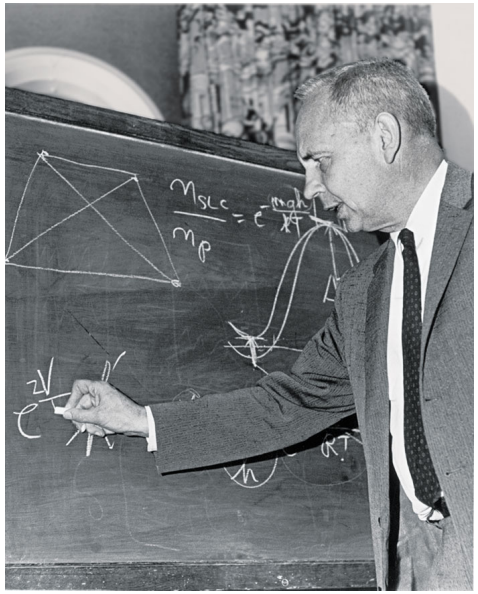
Goal: Predicting long-time dynamics



Rare Events

- **Infrequent transitions from a local minimum to another local minimum**





- **Transition state theory to understand chemical reaction rates: Michael Polanyi & Henry Eyring in 1920's & 1930's**
- **Renewed interests in understanding self-organization (protein folding, life, *etc*.)**

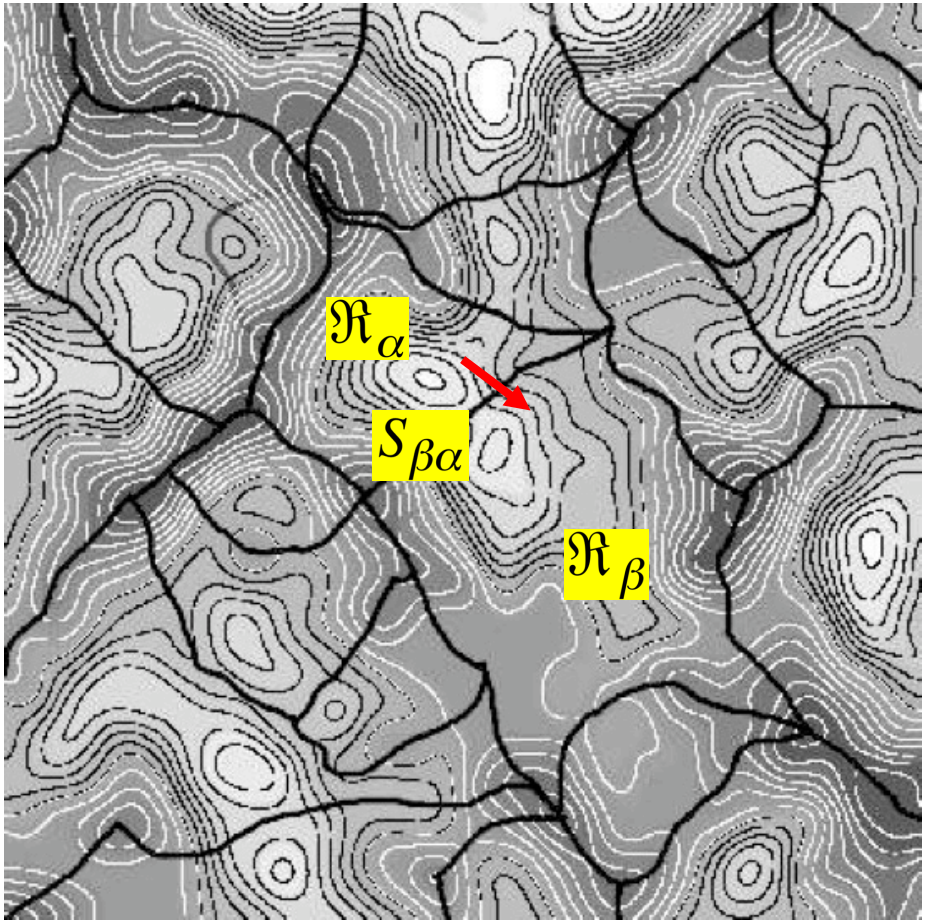
cf. H. Ostrom *et al*., *Science* **347**, 978 ('15)

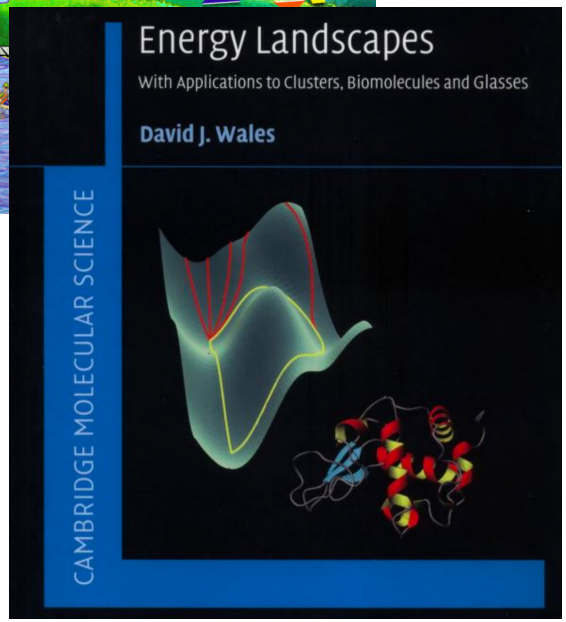
Energy Landscape

- **Discrete abstraction: Partitioned configuration space**

$$\Re^{3N} = \bigcup_{\alpha} \Re_{\alpha} \; ; \Re_{\alpha} \cap \Re_{\alpha} = \emptyset$$

where a 3*N*-dimensional configuration q ∈ $\Re_\alpha$ converges to the α-th local minimum upon local minimization (*N* is the number of atoms)





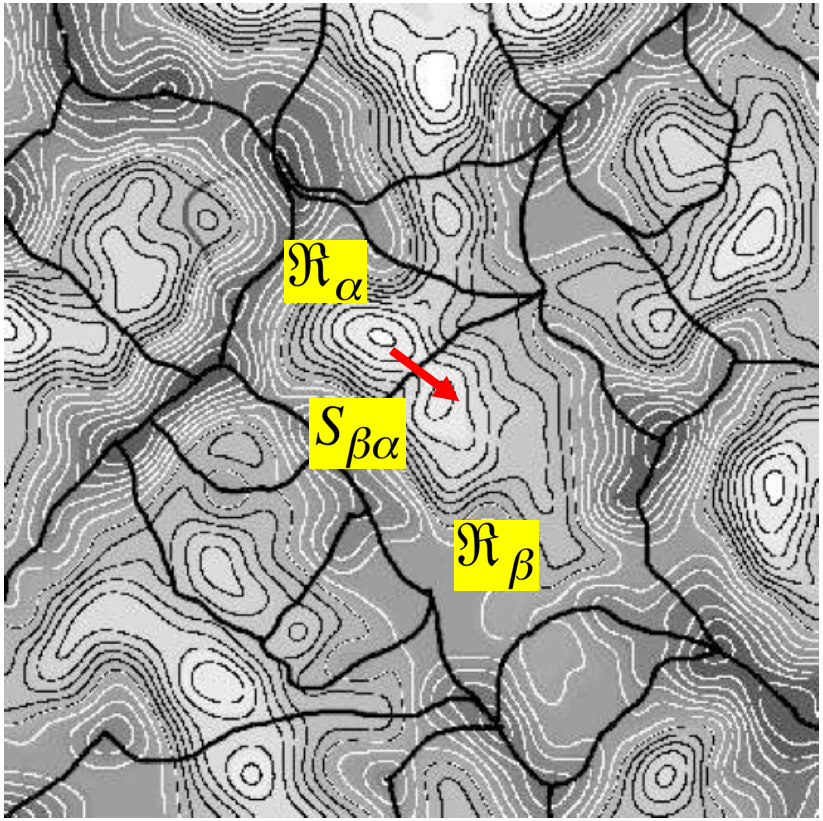
Phase Space Distribution

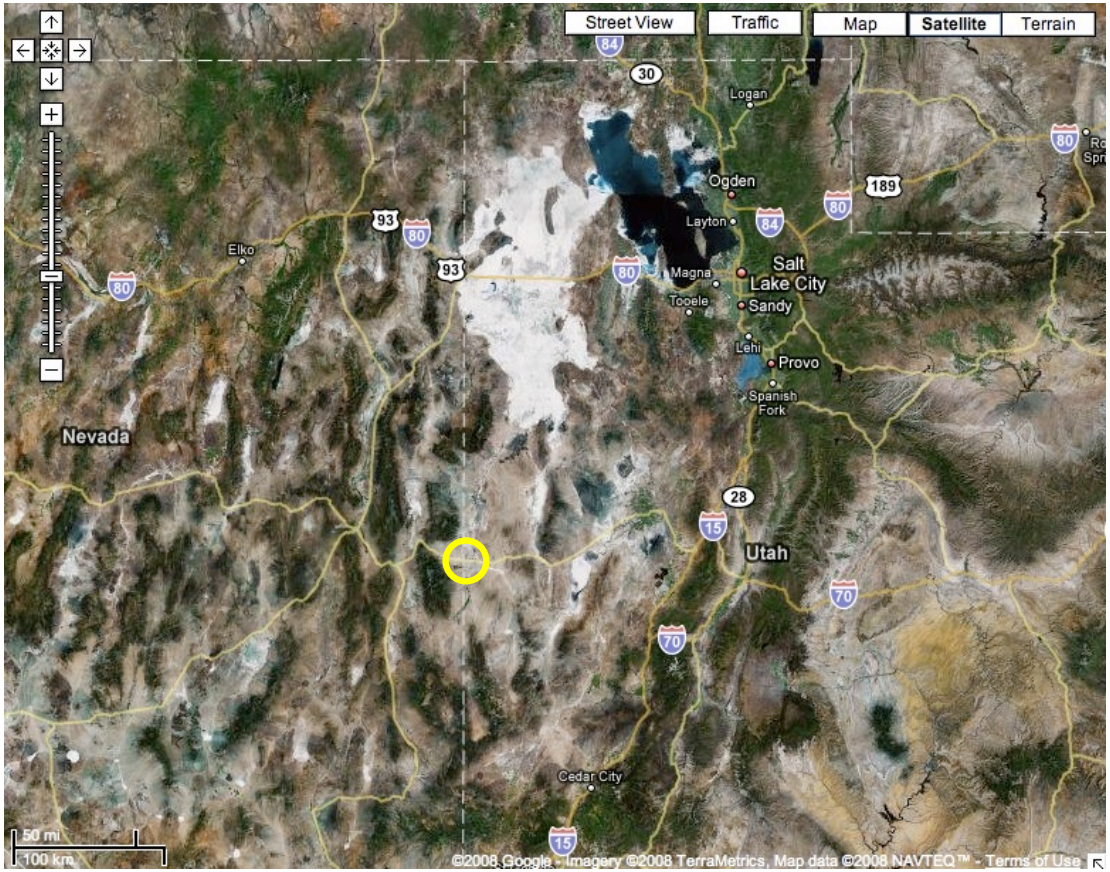
- **Phase-space distribution $f(\mathrm{q}, \mathrm{p}, t)$: probability to find the system at $3N$-dim. position $\mathrm{q} = (q_1, ..., q_N)$ & $3N$-dim. momentum $\mathrm{p} = (p_1, ..., p_N)$ at time t**
- **Probability to find the system in $\Re_\alpha$ at time t (h is the Planck constant)**

$$P_\alpha(t) = \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} f(q,p,t)$$

cf. Plane-wave basis

$$\sum_k = \frac{L}{2\pi} \int dk = \frac{L}{2\pi\hbar} \int \hbar dk = \frac{L}{h} \int dp \to \frac{1}{h} \int dq \int dp$$





Outline

- **Master equation**

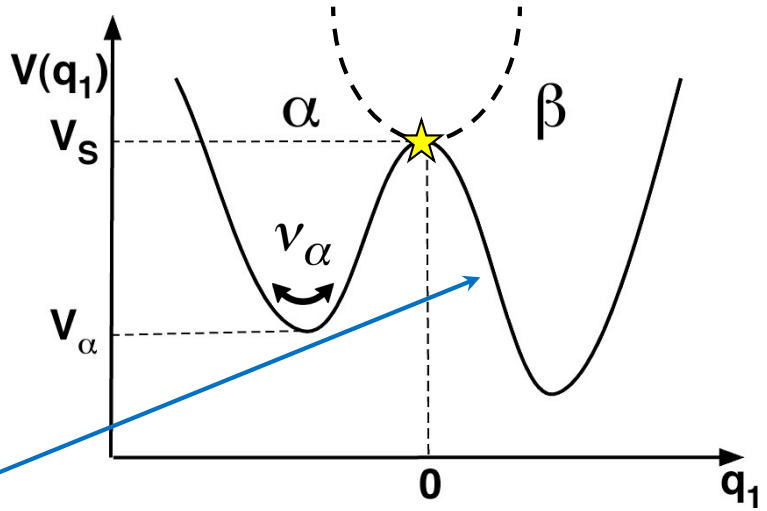
$$\frac{dP_\alpha}{dt} = -\sum_\beta W_{\beta\alpha} P_\alpha(t) + \sum_\beta W_{\alpha\beta} P_\beta(t)$$

$W_{\beta\alpha}$: Transition rate from state α to state β

- **How to compute $W_{\alpha\beta}$? Transition state theory**

$$W_{\beta\alpha} \cong \nu_\alpha \exp\left(-\frac{V_s - V_\alpha}{k_B T}\right)$$

Vibration frequency at the α-th local minimum

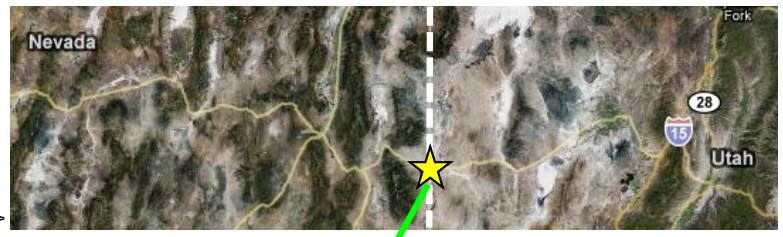


Minimum energy path along a saddle point (transition state)

- **How to simulate the master equation: Kinetic Monte Carlo simulation**

Let $\{r_1, r_2, ...\}$ be a set of possible escape events, $r = \Sigma_i r_i$, and u_1 & u_2 are uniform random numbers in [0,1]:

1. **Pick the next event *i* as** $i = \min_j \left\{ \sum_{k=1}^{j} \frac{r_k}{r} > u_1 \right\}$
2. **Advance the time by** $t = -\ln(u_2)/r$



Dynamics of Phase Space Distribution

- **Phase-space distribution $f(\mathbf{q}, \mathbf{p}, t)$: probability to find the system at $3N$-dim. position $\mathbf{q} = (q_1, ..., q_N)$ & $3N$-dim. momentum $\mathbf{p} = (p_1, ..., p_N)$ at time t**
- **Probability to find the system in $\Re_\alpha$ at time t (h is the Planck constant)**

$$P_\alpha(t) = \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} f(q,p,t)$$

- **Time derivative (L = Liouville operator; $H(\mathbf{q},\mathbf{p})$ = Hamiltonian)**

$$\frac{dP_\alpha}{dt} = \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} \frac{\partial}{\partial t} f(q,p,t)$$

$$= \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} [-Lf(q,p,t)]$$

$$= \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} \left[-\left(\frac{\partial H}{\partial \mathbf{p}} \bullet \frac{\partial}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}} \bullet \frac{\partial}{\partial \mathbf{p}} \right) f(q,p,t) \right]$$

See supplementary note 1: Liouville equation

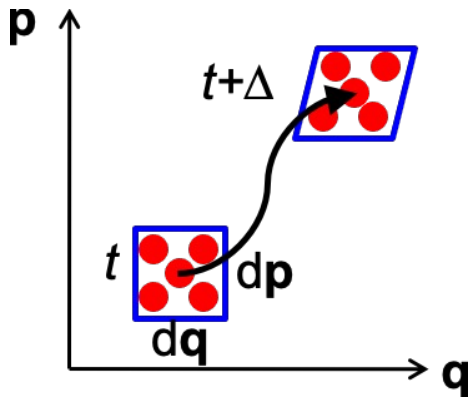
Sketch of Proof: Liouville Operator

$$\frac{d}{dt}\overbrace{\mathbf{X}}^{(\mathbf{q},\mathbf{p})} = \overbrace{\dot{\mathbf{X}}\bullet\frac{\partial}{\partial\mathbf{X}} = \dot{\mathbf{q}}\bullet\frac{\partial}{\partial\mathbf{q}}+\dot{\mathbf{p}}\bullet\frac{\partial}{\partial\mathbf{p}} = \frac{\partial H}{\partial\mathbf{p}}\bullet\frac{\partial}{\partial\mathbf{q}} - \frac{\partial H}{\partial\mathbf{q}}\bullet\frac{\partial}{\partial\mathbf{p}}}^{\hat{L}}\mathbf{X}$$

Jacobian: Volume magnification factor $\left|\frac{\partial\mathbf{X}_t}{\partial\mathbf{X}_0}\right| d\mathbf{X}_0 = d\mathbf{X}_0$

Probability density as point crowd

$$N_{\text{sample}} f_0(\mathbf{X}_0) d\mathbf{X}_0 = N_{\text{sample}} f(\mathbf{X}_t, t) \overbrace{d\mathbf{X}_t}$$



Liouville's theorem

$$\left|\frac{\partial\mathbf{X}_t}{\partial\mathbf{X}_0}\right| = 1$$

Liouville lecture, p. 4

$$(1+\delta t)^{\frac{1}{\delta t}} \xrightarrow[\delta t\to 0]{} e$$

$$(1+\delta t^2)^{\frac{1}{\delta t}} \xrightarrow[\delta t\to 0]{} 1$$

$f(x) = \ln(1+x) = 0\ (x=0);\ \frac{df}{dx} = \frac{1}{1+x} = 1\ (x=0)$

$\therefore \ln(1+x) = f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \cdots = x + \cdots$

$\ln(1+\delta t)^{\frac{1}{\delta t}} = \frac{1}{\delta t}\ln(1+\delta t) \xrightarrow[\delta t\to 0]{} \frac{1}{\delta t}\delta t = 1$

$\therefore (1+\delta t)^{\frac{1}{\delta t}} \xrightarrow[\delta t\to 0]{} e$

$\ln(1+\delta t^2)^{\frac{1}{\delta t}} = \frac{1}{\delta t}\ln(1+\delta t^2) \xrightarrow[\delta t\to 0]{} \frac{1}{\delta t}\delta t^2 = 0$

$\therefore (1+\delta t^2)^{\frac{1}{\delta t}} \xrightarrow[\delta t\to 0]{} 1$

$$\overbrace{f(\mathbf{X}+\dot{\mathbf{X}}dt, dt)}^{f(\mathbf{X},dt)+\dot{\mathbf{X}}dt\bullet\frac{\partial f}{\partial\mathbf{X}}} = f(\mathbf{X}, 0)$$

$$\therefore \frac{f(\mathbf{X},dt)-f(\mathbf{X},0)}{dt} = -\dot{\mathbf{X}}\bullet\frac{\partial f}{\partial\mathbf{X}} = -Lf$$

or $\left(\frac{\partial}{\partial t} + L\right) f = 0$

population flux

Liouville lecture, p. 6

$$\frac{\partial}{\partial t} f(\mathbf{X}, t) + \frac{\partial}{\partial\mathbf{X}} \bullet \left(\dot{\mathbf{X}} f\right) = 0 \quad (\mathbf{X} = (\mathbf{q}, \mathbf{p}) \in \Re^{6N})$$

cf. $\frac{\partial}{\partial t}\rho + \nabla\bullet\vec{j} = 0$ (mass conservation)

Population Dynamics

- **Let**

$$H(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + V(\mathbf{q})$$

then

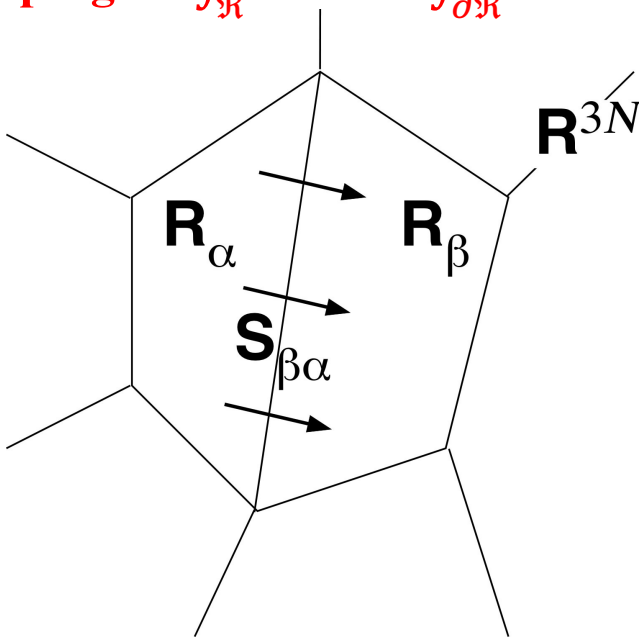
Note $\int_{-\infty}^{\infty} dp_i \frac{\partial}{\partial p_i} f(p_i) = [f(p_i)]_{-\infty}^{\infty} = 0$ (telescoping)

$$\frac{dP_\alpha}{dt} = -\frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \frac{\partial}{\partial q_i} f(\mathbf{q},\mathbf{p},t) + \frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} \sum_{i=1}^{3N} \frac{\partial V}{\partial q_i} \frac{\partial}{\partial p_i} f(\mathbf{q},\mathbf{p},t)$$

$$= -\frac{1}{h^{3N}} \int_{\Re_\alpha} d\mathbf{q} \int d\mathbf{p} \sum_{i=1}^{3N} \frac{\partial}{\partial q_i} \left(\frac{p_i}{m_i} f(\mathbf{q},\mathbf{p},t) \right)$$

$$= -\frac{1}{h^{3N}} \int_{\partial\Re_\alpha} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} f(\mathbf{q},\mathbf{p},t)$$

Gauss' theorem ~ telescoping $\int_{\Re} d\mathbf{q} \nabla = \int_{\partial\Re} d\mathbf{S}$



where *d*S is the surface element pointing outward normal to the surface $\partial\Re_\alpha$ that outlines $\Re_\alpha$

- ***dP*$_\alpha$/*dt* is negative of the outward flux through $\partial\Re_\alpha$**

$\int dq \frac{\partial}{\partial q} f = [f]_{\text{lower}}^{\text{upper}} = f dS_+ + f dS_-$

Population Flux

- **Partition the surface $\partial\Re_\alpha$ into**

$$\partial\Re_\alpha = \sum_\beta S_{\beta\alpha}$$

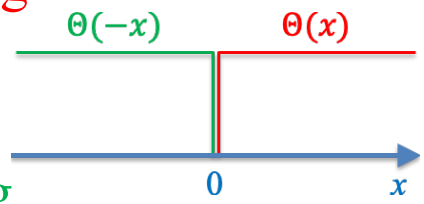
where $S_{\beta\alpha}$ is the surface splitting $\Re_\alpha$ & $\Re_\beta$ (β to α)

$$\frac{dP_\alpha}{dt} = -\sum_\beta \frac{1}{h^{3N}} \int_{S_{\beta\alpha}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f(\mathbf{q},\mathbf{p},t) \quad \text{outgoing}$$

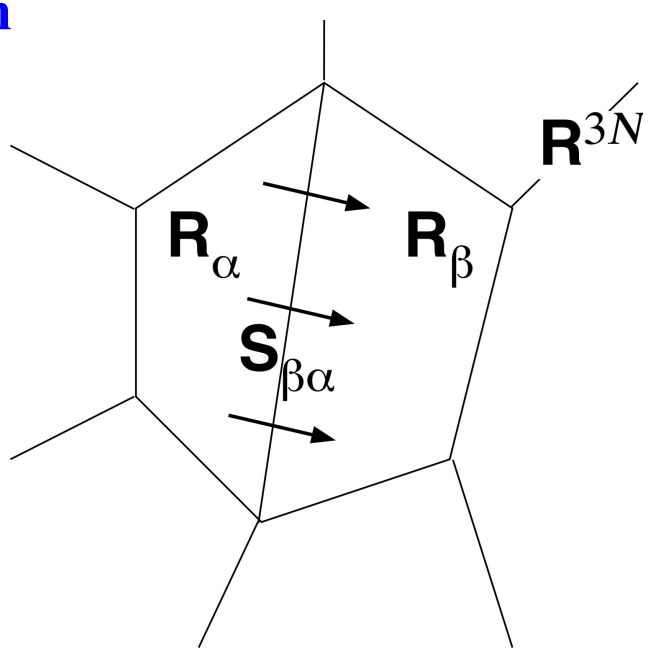
$$+\sum_\beta \frac{1}{h^{3N}} \int_{S_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f(\mathbf{q},\mathbf{p},t) \quad \text{incoming}$$

Partition of unity

$\Theta(x) + \Theta(-x) = 1$



where $\Theta(x) = 1$ ($x \geq 0$) & 0 ($x < 0$) is the step function



Local Equilibration Approximation

- **Assume that within each $\Re_\alpha$, the phase space distribution is locally in thermal equilibrium, weighted to reproduce the current population (time scale of inter-state population transfer >> intra-state thermal equilibration time)**

$$f(\mathbf{q},\mathbf{p},t) \cong \frac{P_\alpha(t)}{P_\alpha(\mathrm{eq})} f_{\mathrm{eq}}(\mathbf{q},\mathbf{p})$$

where

$$f_{\mathrm{eq}}(\mathbf{q},\mathbf{p}) = \frac{1}{Q}\exp\left(-H(\mathbf{q},\mathbf{p})/k_{\mathrm{B}}T\right)$$

and the partition function is split into

$$Q = \iint \frac{d\mathbf{q}d\mathbf{p}}{h^{3N}}\exp\left(-H(\mathbf{q},\mathbf{p})/k_{\mathrm{B}}T\right) = \sum_\alpha \iint_{\Re_\alpha} \frac{d\mathbf{q}d\mathbf{p}}{h^{3N}}\exp\left(-H(\mathbf{q},\mathbf{p})/k_{\mathrm{B}}T\right) = \sum_\alpha Q_\alpha$$

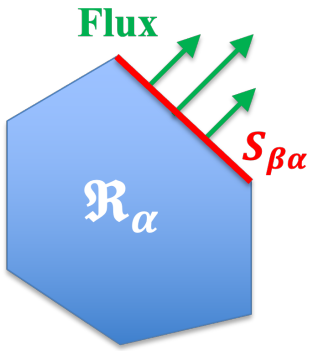
$$\therefore P_\alpha(\mathrm{eq}) = \frac{Q_\alpha}{Q} = \frac{1}{Q}\iint_{\Re_\alpha} \frac{d\mathbf{q}d\mathbf{p}}{h^{3N}}\exp\left(-H(\mathbf{q},\mathbf{p})/k_{\mathrm{B}}T\right)$$

Master Equation

- **Substituting the local-equilibration approximation into the population-flux equation, we obtain**

$$\frac{dP_\alpha}{dt} = -\sum_\beta \frac{1}{h^{3N}} \int_{S_{\beta\alpha}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f_{eq}(\mathbf{q},\mathbf{p}) \frac{P_\alpha(t)}{P_\alpha(\mathrm{eq})}$$

$$+\sum_\beta \frac{1}{h^{3N}} \int_{S_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f_{eq}(\mathbf{q},\mathbf{p}) \frac{P_\beta(t)}{P_\beta(\mathrm{eq})}$$



$$\therefore \frac{dP_\alpha}{dt} = -\sum_\beta W_{\beta\alpha} P_\alpha(t) + \sum_\beta W_{\alpha\beta} P_\beta(t)$$

$$W_{\alpha\beta} = \frac{1}{h^{3N}} \int_{S_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f_{eq}(\mathbf{q},\mathbf{p}) \Big/ P_\beta(\mathrm{eq})$$

Weighted average of flux on surface

$$= \frac{1}{h^{3N}} \int_{S_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int d\mathbf{p} \sum_{i=1}^{3N} \frac{p_i}{m_i} \Theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) e^{-H(\mathbf{q},\mathbf{p})/k_B T} \Big/ \frac{1}{h^{3N}} \iint_{\Re_\beta} d\mathbf{q} d\mathbf{p} e^{-H(\mathbf{q},\mathbf{p})/k_B T}$$

See supplementary note 2: Master equation

A. P. J. Jansen, *Introduction to KMC Simulations of Surface Reactions* (Springer, '12)

Transition State Theory

- **Reaction coordinate q_1 along a minimum-energy path separates the phase space into 2 regions — A ($q_1 < 0$) & B ($q_1 > 0$); all the other coordinates & momenta are collectively denoted as X = (q, p) = (q_2, ..., q_{3N}, p_2, ..., p_{3N})**
- **Probability to find the system being in B**

$$P_B(t) = \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \Theta(q_1) f(q_1, p_1, \mathbf{X}, t)$$

- **Time derivative (L = Liouville operator)**

$$\frac{dP_B}{dt} = \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \Theta(q_1) \frac{\partial}{\partial t} f(q_1, p_1, \mathbf{X}, t)$$

$$= \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \Theta(q_1)\left(-Lf(q_1, p_1, \mathbf{X}, t)\right)$$

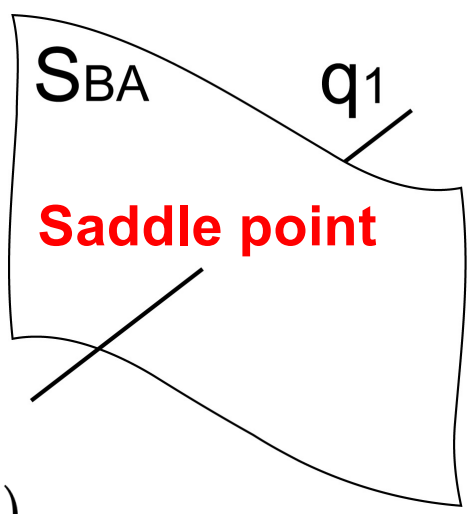
Integration by part

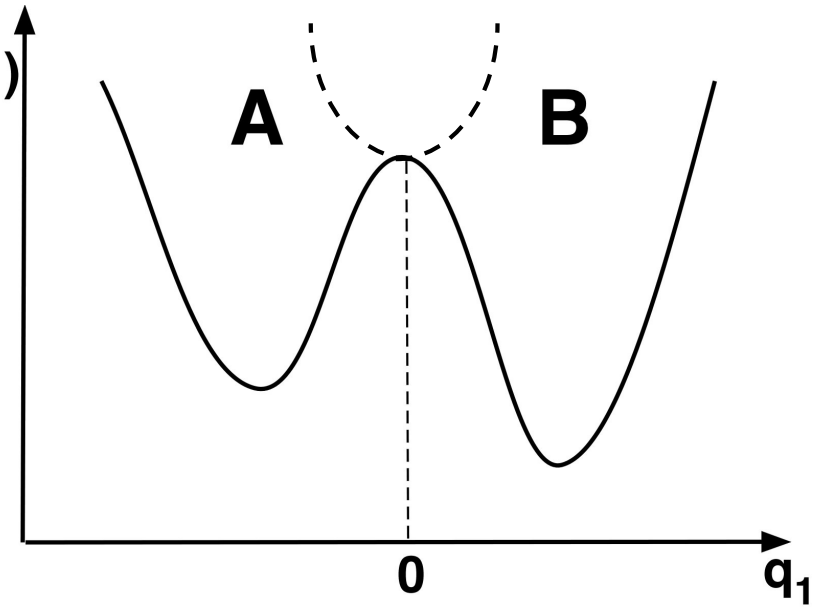
$$= \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \left(L\Theta(q_1)\right) f(q_1, p_1, \mathbf{X}, t)$$

$$= \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \left(\frac{p_1}{m_1}\delta(q_1)\right) f(q_1, p_1, \mathbf{X}, t)$$

Weighted average of flux on surface

$$= \iint \frac{dp_1 d\mathbf{X}}{h^{3N}} \frac{p_1}{m_1} f(0, p_1, \mathbf{X}, t)$$





Local Equilibration Approximation

- **Split the integral into the gain (A → B) & loss (B → A) terms**

$$\frac{dP_B}{dt} = \left(\frac{dP_B}{dt}\right)_{A\to B} + \left(\frac{dP_B}{dt}\right)_{B\to A} \qquad \Theta(p_1) + \Theta(-p_1) = 1$$

$$= \int_0^\infty \frac{dp_1}{h} \int \frac{d\mathbf{X}}{h^{3N-1}} \frac{p_1}{m_1} f(0,p_1,\mathbf{X},t) + \int_{-\infty}^0 \frac{dp_1}{h} \int \frac{d\mathbf{X}}{h^{3N-1}} \frac{p_1}{m_1} f(0,p_1,\mathbf{X},t)$$

- **Regions A & B locally (*i.e.*, within the region) maintain the equilibrium distribution weighted to reproduce the current population**

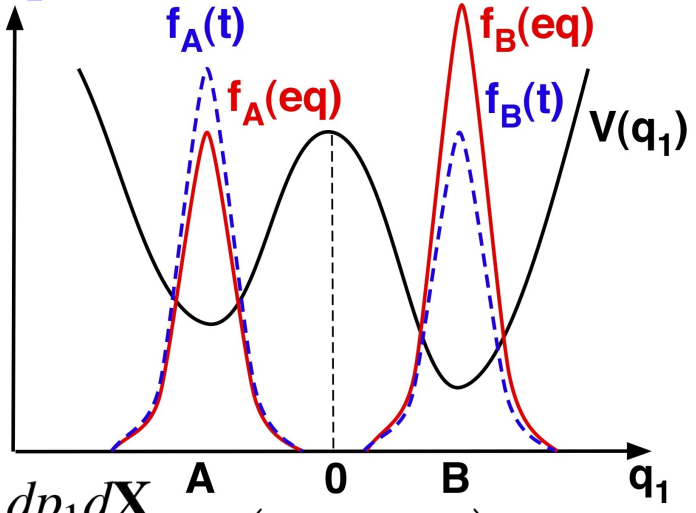
$$f_{\alpha,\text{local}} \cong \frac{P_\alpha(t)}{P_\alpha(\text{eq})} f_{\text{eq}} \quad (\alpha = A,B)$$

$$f_{\text{eq}} = \frac{1}{Q}\exp(-H/k_{\text{B}}T)$$

$$Q = \iiint \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \exp(-H/k_{\text{B}}T) = Q_A + Q_B$$

$$Q_A = \iiint_{q_1<0} \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \exp(-H/k_{\text{B}}T) \qquad Q_B = \iiint_{q_1>0} \frac{dq_1 dp_1 d\mathbf{X}}{h^{3N}} \exp(-H/k_{\text{B}}T)$$

$$P_\alpha(\text{eq}) = \frac{Q_\alpha}{Q} \quad (\alpha = A,B)$$



Transition State Theory

- **Substituting the local equilibration approximation to the flux equation**

$$\left(\frac{dP_B}{dt}\right)_{A\to B} = \int_0^\infty \frac{dp_1}{h}\int \frac{d\mathbf{X}}{h^{3N-1}}\frac{p_1}{m_1} f_{\mathrm{eq}}(0,p_1,\mathbf{X})\frac{P_A(t)}{P_A(\mathrm{eq})}$$

$$\left(\frac{dP_B}{dt}\right)_{B\to A} = -\int_0^\infty \frac{dp_1}{h}\int \frac{d\mathbf{X}}{h^{3N-1}}\frac{p_1}{m_1} f_{\mathrm{eq}}(0,p_1,\mathbf{X})\frac{P_B(t)}{P_B(\mathrm{eq})}$$

$$\therefore \frac{dP_B(t)}{dt} = k_{BA}P_A(t) - k_{AB}P_B(t)$$

$$k_{BA} = \int_0^\infty \frac{dp_1}{h}\int \frac{d\mathbf{X}}{h^{3N-1}}\frac{p_1}{m_1} f_{\mathrm{eq}}(0,p_1,\mathbf{X})\frac{1}{P_A(\mathrm{eq})}$$

$$k_{AB} = \int_0^\infty \frac{dp_1}{h}\int \frac{d\mathbf{X}}{h^{3N-1}}\frac{p_1}{m_1} f_{\mathrm{eq}}(0,p_1,\mathbf{X})\frac{1}{P_B(\mathrm{eq})}$$

- **Analytical integration over p_1**

$$k_{BA} = \int_0^\infty \frac{dp_1}{h}\frac{p_1}{m_1}\exp\left(-p_1^2/2m_1k_{\mathrm{B}}T\right)\int \frac{d\mathbf{X}}{h^{3N-1}}\frac{\exp(-H/k_{\mathrm{B}}T)_{q_1=p_1=0}}{Q}\frac{Q}{Q_A} = \frac{k_{\mathrm{B}}T}{h}\frac{Q^*}{Q_A}$$

$$Q^* = \int \frac{d\mathbf{X}}{h^{3N-1}}\exp(-H/k_{\mathrm{B}}T)_{q_1=p_1=0}$$

$k_{\mathrm{B}}T/h \sim 10^{13}\ \mathrm{s}^{-1}$ at room temperature

Harmonic Transition State Theory

- **In region A, we assume**

$$V(q_1,\ldots,q_{3N}) = V_A + \frac{1}{2}\sum_j m_j\left(\omega_j^A\right)^2\left(q_j - b_j\right)^2$$

$$\therefore Q_A = \left(\frac{2\pi k_B T}{h}\right)^{3N} \frac{\exp\left(-V_A / k_B T\right)}{\prod_{j=1}^{3N}\omega_j^A}$$

- **At the dividing surface, we assume**

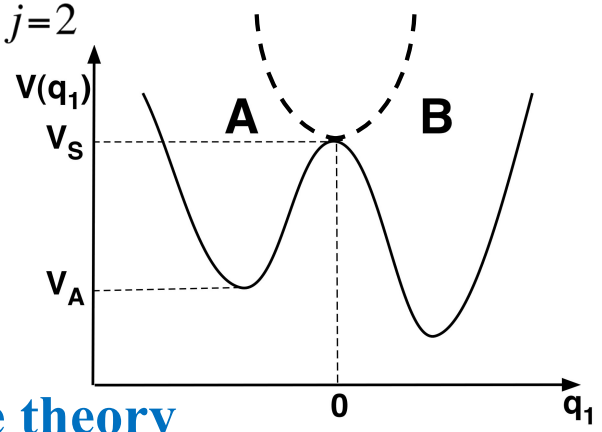
$$V(q_1,\ldots,q_{3N}) = V_S - \frac{1}{2}a_{11}q_1^2 + \frac{1}{2}\sum_{j=2}^{3N} m_j\left(\omega_j^*\right)^2 q_j^2$$

$$Q^* = \int \frac{d\mathbf{X}}{h^{3N-1}}\exp(-H/k_B T)_{q_1=p_1=0} = \left(\frac{2\pi k_B T}{h}\right)^{3N-1}\frac{\exp\left(-V_s / k_B T\right)}{\prod_{j=2}^{3N}\omega_j^*}$$

$$\therefore k_{BA} = \frac{1}{2\pi}\exp\left(-\frac{V_s - V_A}{k_B T}\right)\frac{\prod_{j=1}^{3N}\omega_j^A}{\prod_{j=2}^{3N}\omega_j^*} \cong \boxed{\frac{\omega_1^A}{2\pi}}\boxed{\exp\left(-\frac{V_s - V_A}{k_B T}\right)}$$

attempt frequency

acceptance probability



See supplementary note 3: Transition state theory

Digression: Save the World?

- **Solar land-area requirement (with 10% energy conversion efficiency) to supply the global energy** [Nathan Lewis, *Caltech*]

- **Need better catalyst for splitting water** [Lewis & Nocera, *PNAS* **103**, 15729 ('06)]

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2$$

COMPUTATIONAL METHODS

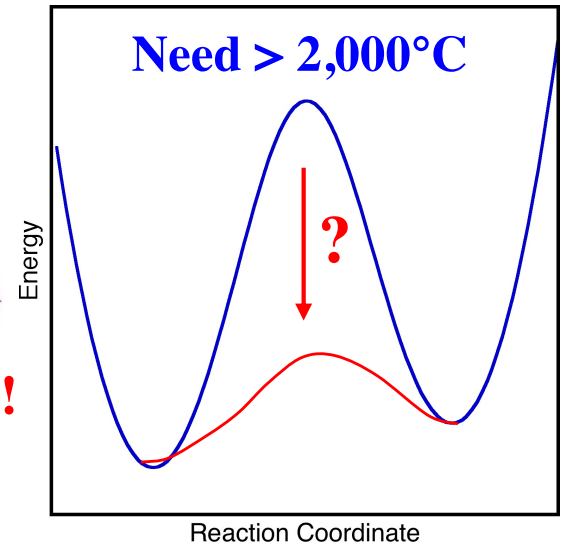
A search engine for catalysts

Trial and error has been the traditional method of finding the best catalyst for a reaction. A computational approach can reduce the lab work required.

MANOS MAVRIKAKIS
is in the Department of Chemical & Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA.

Just bring down the transition-state energy!

Nature Mater. **5**, 847 ('06)



Hydrogen Production@Home

A Job for Superatom

PRL 104, 126102 (2010) PHYSICAL REVIEW LETTERS week ending 26 MARCH 2010

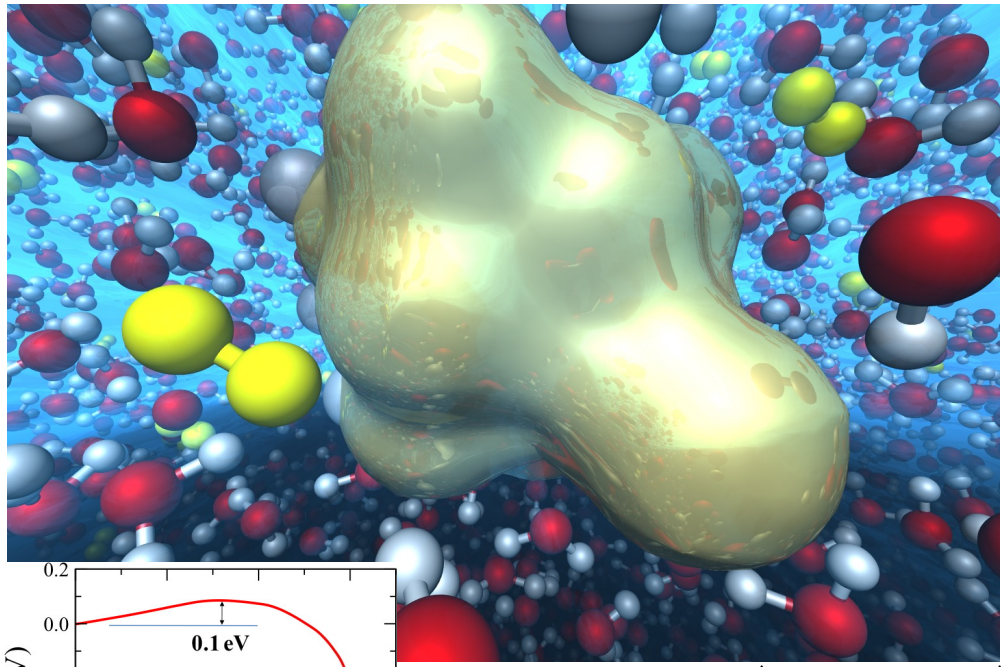
Molecular Dynamics Simulations of Rapid Hydrogen Production from Water Using Aluminum Clusters as Catalyzers

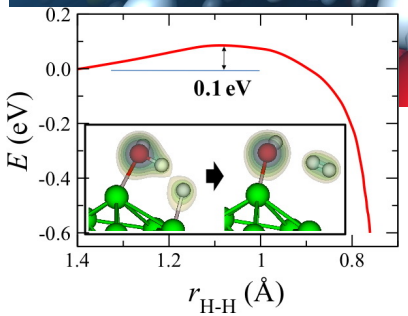
Fuyuki Shimojo,[1,2] Satoshi Ohmura,[1,2] Rajiv K. Kalia,[1] Aiichiro Nakano,[1] and Priya Vashishta[1]
[1]*Collaboratory for Advanced Computing and Simulations, Department of Computer Science, Department of Physics & Astronomy, Department of Chemical Engineering & Materials Science, University of Southern California, Los Angeles, California 90089-0242, USA*
[2]*Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan*
(Received 1 December 2009; published 26 March 2010)

$k_B T_{room}/h \sim 10^{13}\ (s^{-1})$

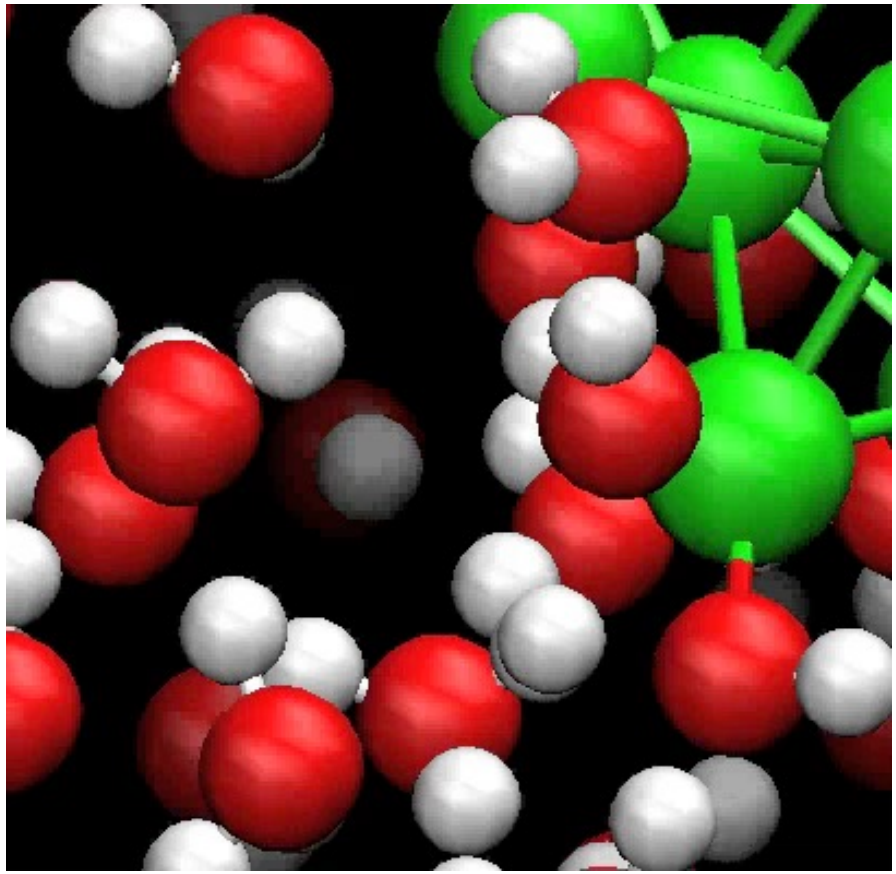
$1\ \text{eV}/k_B \sim 10{,}000\ \text{K}$

$e^{-x} \sim 10^{-x/2}$



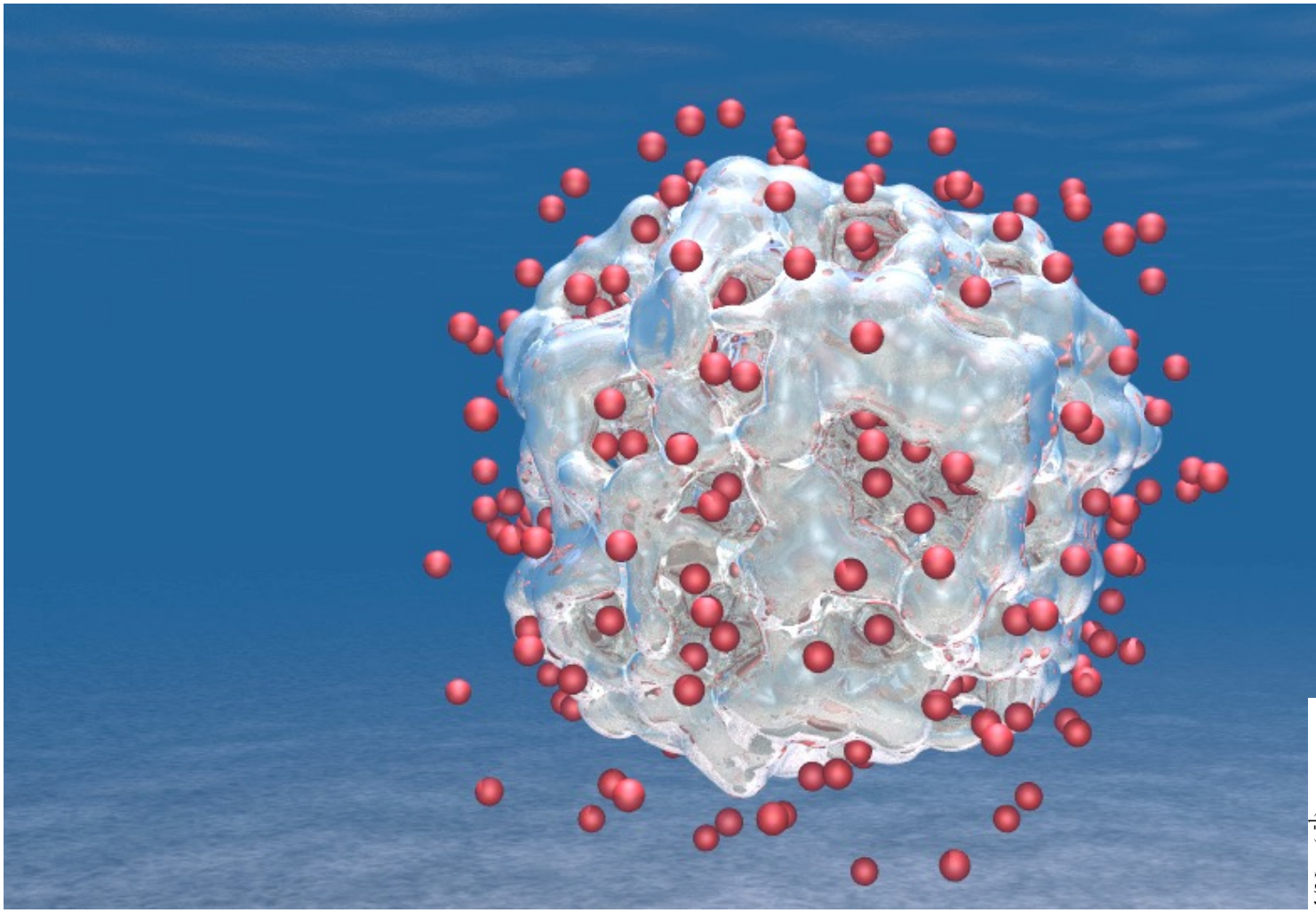


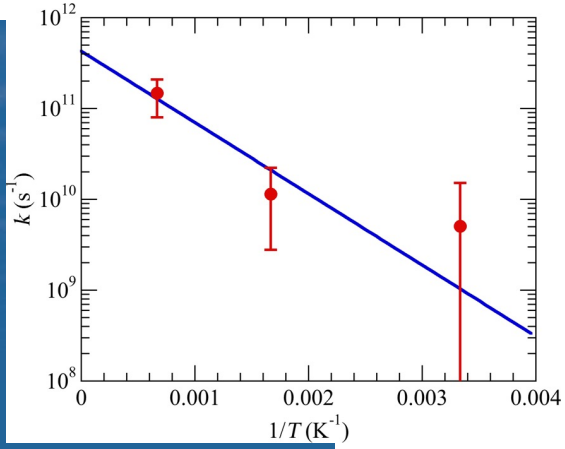
$$k_{H_2} = \frac{k_B T}{h} \exp\left(-\frac{\Delta}{k_B T_{room}}\right) = 10^{11}(s^{-1})$$

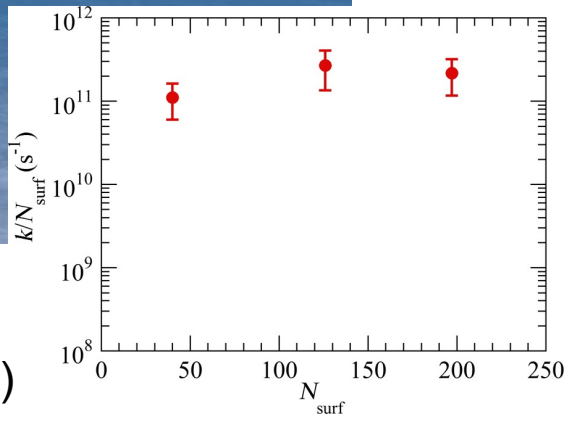


H_2 Production from Water Using LiAl Particles

16,661-atom QMD simulation of $Li_{441}Al_{441}$ in water on 786,432 IBM Blue Gene/Q cores





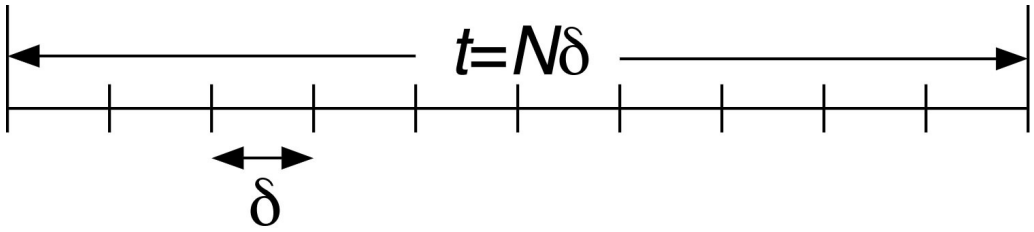


- **Scalable to industrially relevant particle sizes**

K. Shimamura *et al.*, *Nano Lett.* **14**, 4090 ('14)

Poisson Process

- **Poisson process = sequence of events, in which the probability of an event to occur in time $[t,t+\delta]$ is $r\delta$ (r is the rate) independent of history as $\delta \to 0$**
- **Probability $P(n,t)$ that n events occur in time interval $t=N\delta$**



$$P(n,t) = C(N,n)(r\delta)^n (1-r\delta)^{N-n} = \frac{N!}{n!(N-n)!}(r\delta)^n (1-r\delta)^{N-n}$$

$$\xrightarrow[N\to\infty]{} \frac{(rt)^n}{n!} e^{-rt}$$

$$\because \begin{cases} (1-rt/N)^{N/rt} \xrightarrow[N\to\infty]{} e^{-1} \\ N! \xrightarrow[N\to\infty]{} \sqrt{2\pi N} N^N e^{-N} \end{cases}$$

$$\lim_{N\to\infty}\left(1\pm\frac{1}{N}\right)^N = e^{\pm 1}$$

$$\because \ln\left(1\pm\frac{1}{N}\right)^N = N\ln\left(1\pm\frac{1}{N}\right) \xrightarrow[N\to\infty]{} N\left(\pm\frac{1}{N}\right) = \pm 1$$

- **Sum rule:**

$$\sum_{n=0}^{\infty} P(n,t) = \sum_{n=0}^{\infty} \frac{(rt)^n}{n!} e^{-rt} = 1$$

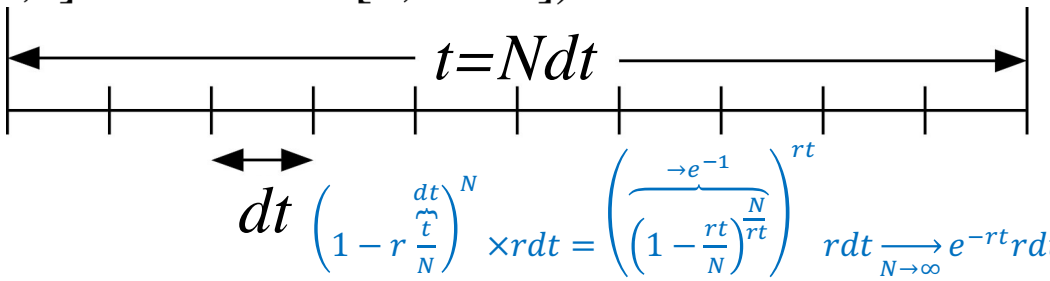
Kinetic Monte Carlo Simulation

- **Probability density $P(t)$ of time t between successive events**

$$P(t)dt = \text{probability}(\text{no event in } [0,t] \wedge 1 \text{ event in } [t, t+dt])$$

$$= P(0,t) \times rdt = e^{-rt} \times rdt$$

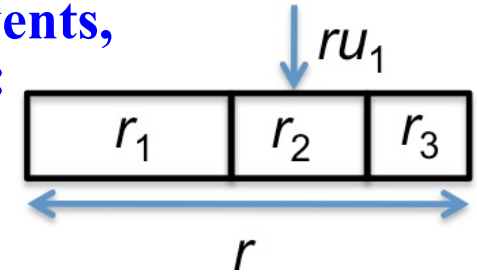
$$\therefore P(t) = re^{-rt}$$



- **Random time-interval generation: Let u be a uniform random number in [0,1] & generate $t = -\ln(u)/r \in [0,\infty]$**

$$\because P(t) = P(u)\left|\frac{du}{dt}\right| = 1 \times re^{-rt} = re^{-rt} \qquad u = e^{-rt}$$

- **Kinetic MC algorithm: Let $\{r_1, r_2, \ldots\}$ be a set of possible events, $r = \Sigma_i r_i$, and u_1 & u_2 are uniform random numbers in [0,1]:**



1. **Pick the next event i as** $i = \min_j \left\{ \sum_{k=1}^{j} \frac{r_k}{r} > u_1 \right\}$
   Pick i-th event with probability $p_i = r_i/r$
2. **Advance the time by** $t = -\ln(u_2)/r$

$$P(t)dt = \overbrace{e^{-rt}}^{\text{no evt in } [0,t]} \overbrace{(r_1 + r_2 + \cdots)dt}^{\text{evt 1 or 2 or ... in } [t,t+dt]}$$

K. A. Fichthorn & W. H. Weinberg, *J. Chem. Phys.* **95**, 1090 ('91)

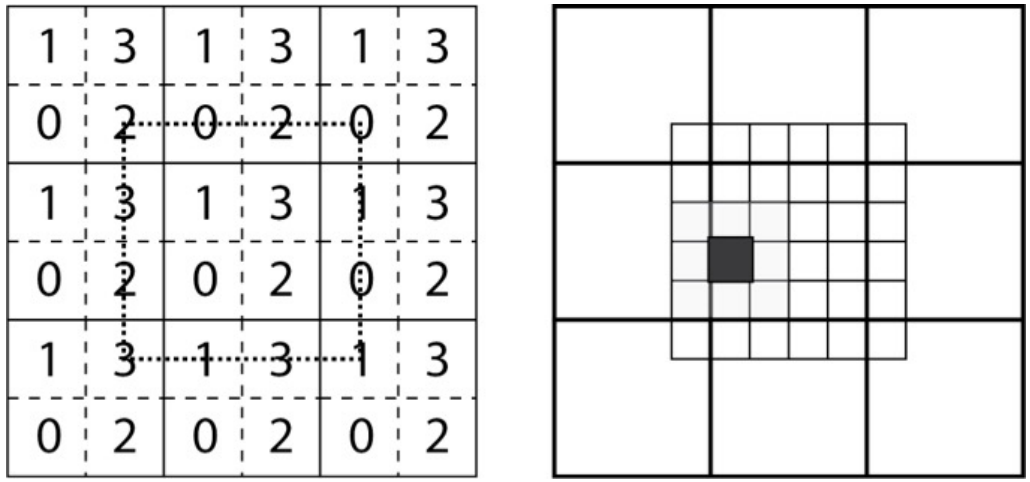
See supplementary note 4: Kinetic Monte Carlo simulation

Divide-&-Conquer KMC Algorithm

- **Domain decomposition: Concurrent events among multiple domains, *d***

$$\Delta t = -\ln(rnd) / \sum_d r_d = O(N^{-1}) \quad \Rightarrow \quad -\ln(rnd) / \max_d (r_d) = O(1)$$

- **Colored domain blocks: Avoids conflicting events by allowing concurrent events only with domains of the same color, which are well-separated**



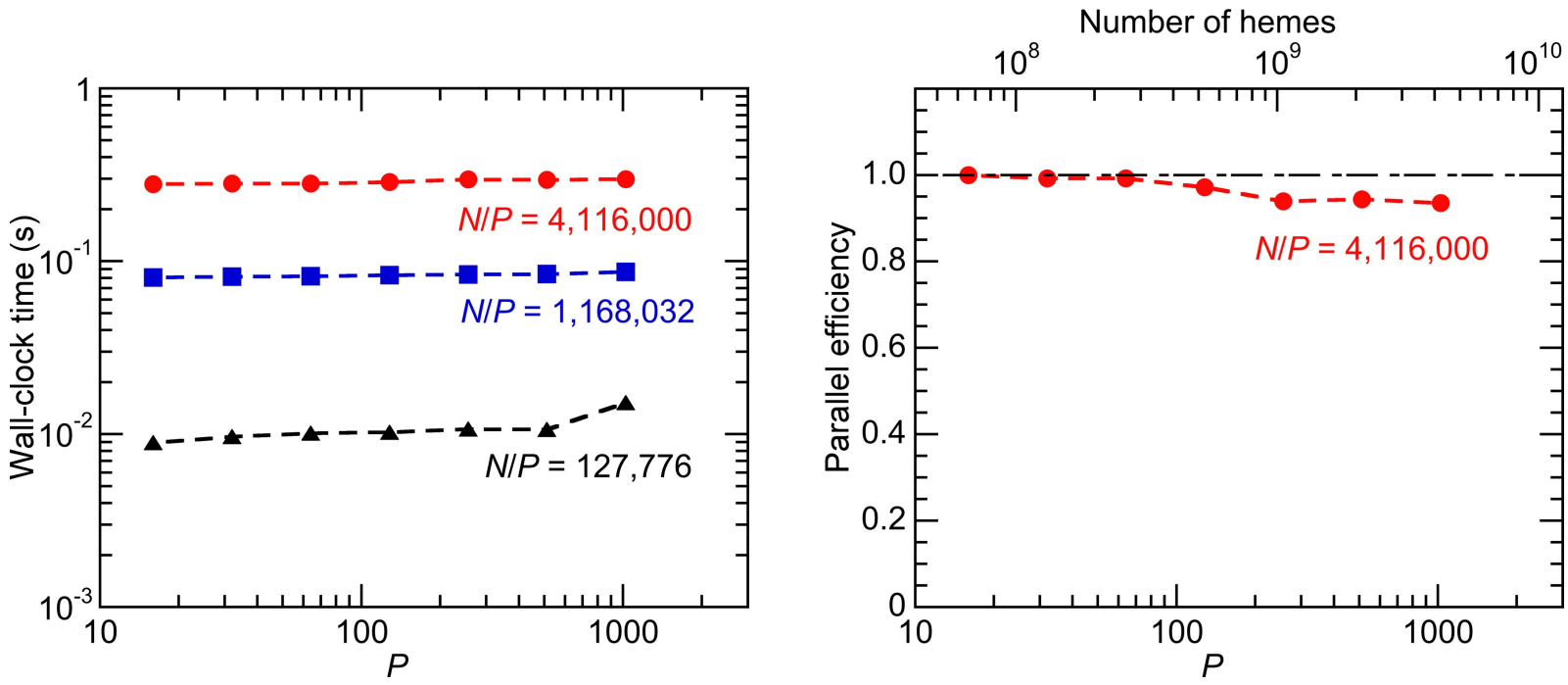
E. Martinez *et al.*, *J. Comp. Phys.* **230**, 1359 ('11)

- **Neighbor-domain caching for spatial decomposition via message-passing**
- **Dual linked-list cell method: (1) small cells for constructing neighbor lists for nearest-neighbor hopping events; (2) large cells for domain-block coloring**

H. Byun *et al.*, *Comput. Phys. Commun.* **219**, 246 ('17)

Scalable Parallel KMC

- **Benchmark tests on electron transfer in heme aggregates**
- **Better weak-scaling for coarser granularity (*N* hemes on *P* procesors)**



- **Weak-scaling parallel efficiency 0.935 for a 4.2 billion-heme system on 1,024 Intel Xeon processors**

H. Byun *et al.*, *Comput. Phys. Commun.* **219**, 246 ('17)

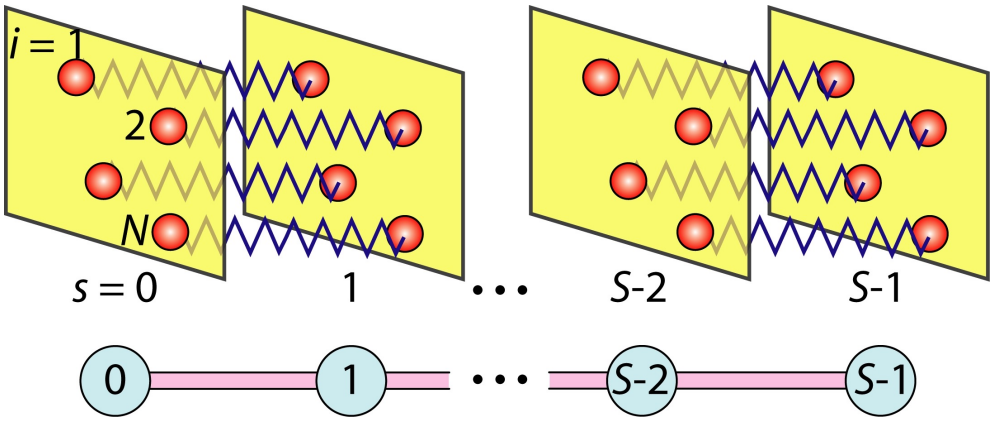
Temporal Locality in Long-Time Dynamics

- **Temporal locality:** Rare transitions between local minimum-energy states
- **Transition state theory:** Reformulate *sequential* long-time dynamics as *parallel* search for low activation-barrier transition events
- **Discrete graph abstraction:** Linear combinations of atomistic events (LCAE)

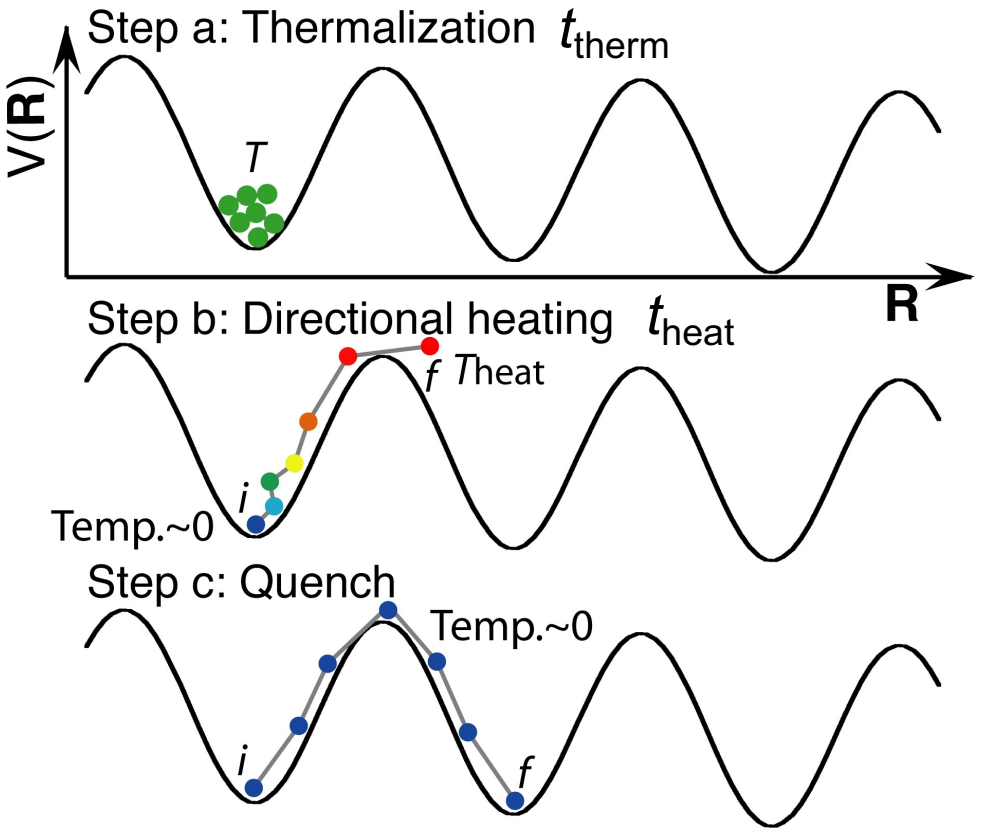
  A. Nakano, *Comput. Phys. Commun.* **176**, 292 ('07)

- **Directionally heated nudged elastic band (NEB) method:** Search for thermally activated events without the knowledge of final states

$$\mathbf{M}\ddot{\mathbf{R}}_s = \mathbf{F}_s - M\gamma_s\dot{\mathbf{R}}_s \ (s = 0, \ldots, S-1)$$



$$\mathbf{F}_s = \begin{cases} -\left.\dfrac{\partial V}{\partial \mathbf{R}_s}\right|_{\perp} + \left.\mathbf{F}_s^{\mathrm{spr}}\right|_{\parallel} & (1 \le s \le S-2) \\ -\dfrac{\partial V}{\partial \mathbf{R}_s} & (s = 0, S-1) \end{cases}$$



Space-Time-Ensemble Parallel (STEP) NEB

- **Path ensemble method (PEM): Long-time simulation in the framework of kinetic Monte Carlo—*molecular kinetics simulation***

$$r_b = \left\{ t_{\text{therm}} + t_{\text{heat}} \exp\left[\frac{\Delta_b}{k_B} \left(\frac{1}{T} - \frac{1}{T_{\text{heat}}} \right) \right] \right\}^{-1}$$

$$P_b = \frac{r_b}{r} = \frac{r_b}{\sum_{b=0}^{B-1} r_b}$$

- **Space-time-ensemble parallelism (STEP)**

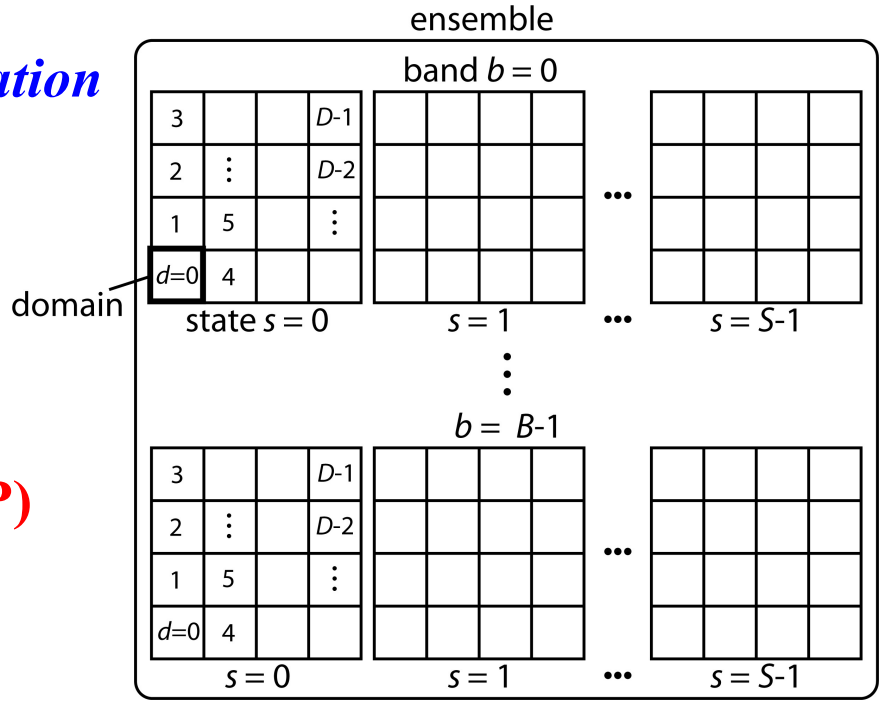
= **spatial decomposition within each state (*D* domains)**

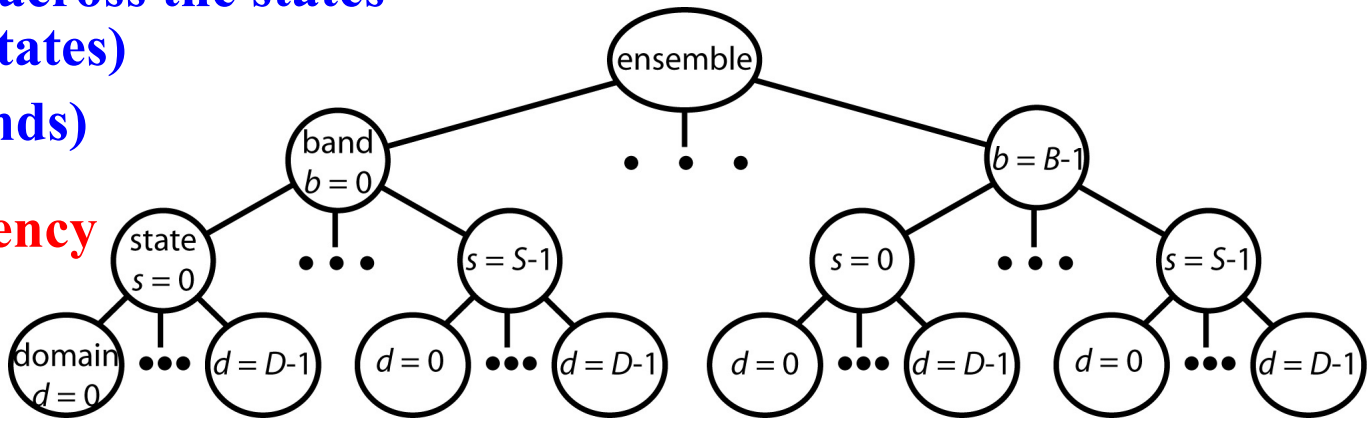
+ **temporal parallelism across the states within each band (*S* states)**

+ **band ensemble (*B* bands)**

- **Hierarchical concurrency**

$P = BSD$





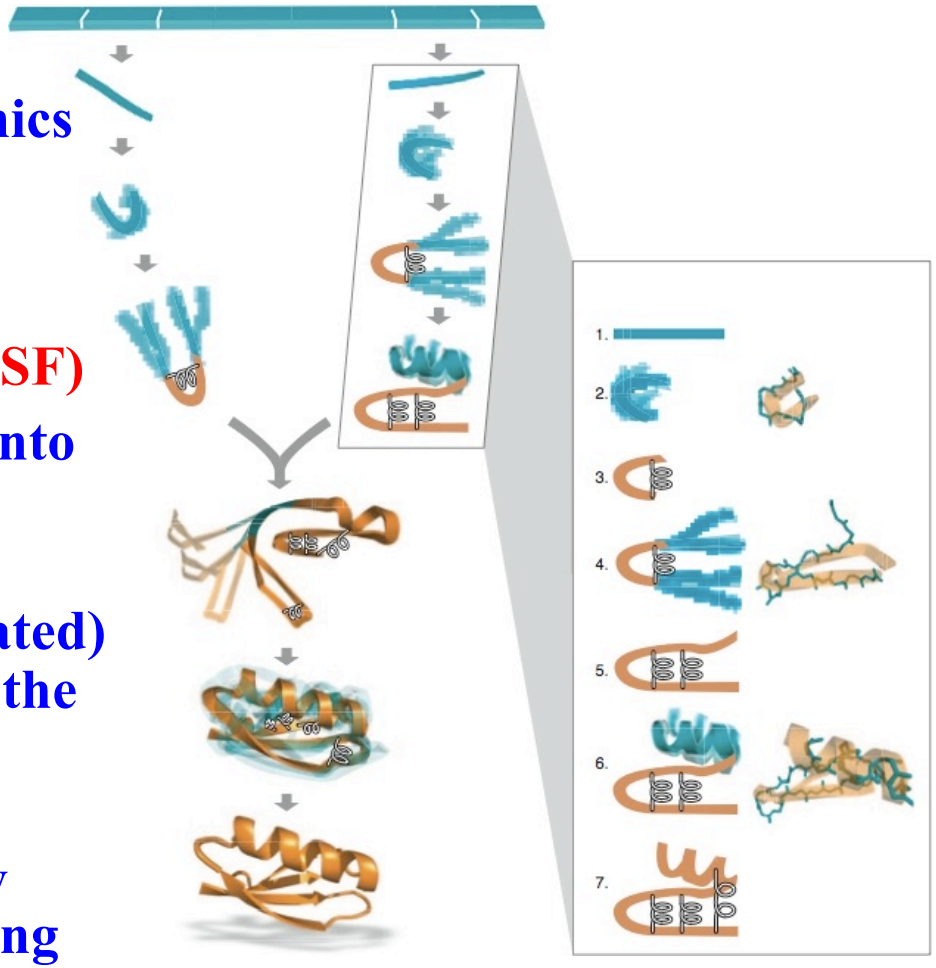
A. Nakano, *Comput. Phys. Commun.* **178**, 280 ('08)

Divide-&-Conquer Protein Folding

- **Levinthal paradox (1968): How the Nature folds an amino-acid sequence into a global energy minimum 3D structure (which is known to be NP complete) within microseconds (~ billion molecular-dynamics steps).**
- **Sequential KMC not good enough.**

Zip-&-assembly algorithm (Ken Dill at UCSF)

1. **(Divide) Chop the amino-acid sequence into ~10 residue fragments.**
2. **(Conquer) For each fragment, perform replica-exchange (~ temperature accelerated) molecular dynamics simulation & detect the formation of any stable hydrophobic contacts.**
3. **(Combine) Grow the stable fragments by adding surrounding residues while freezing (~ constraint) the found stable contacts.**



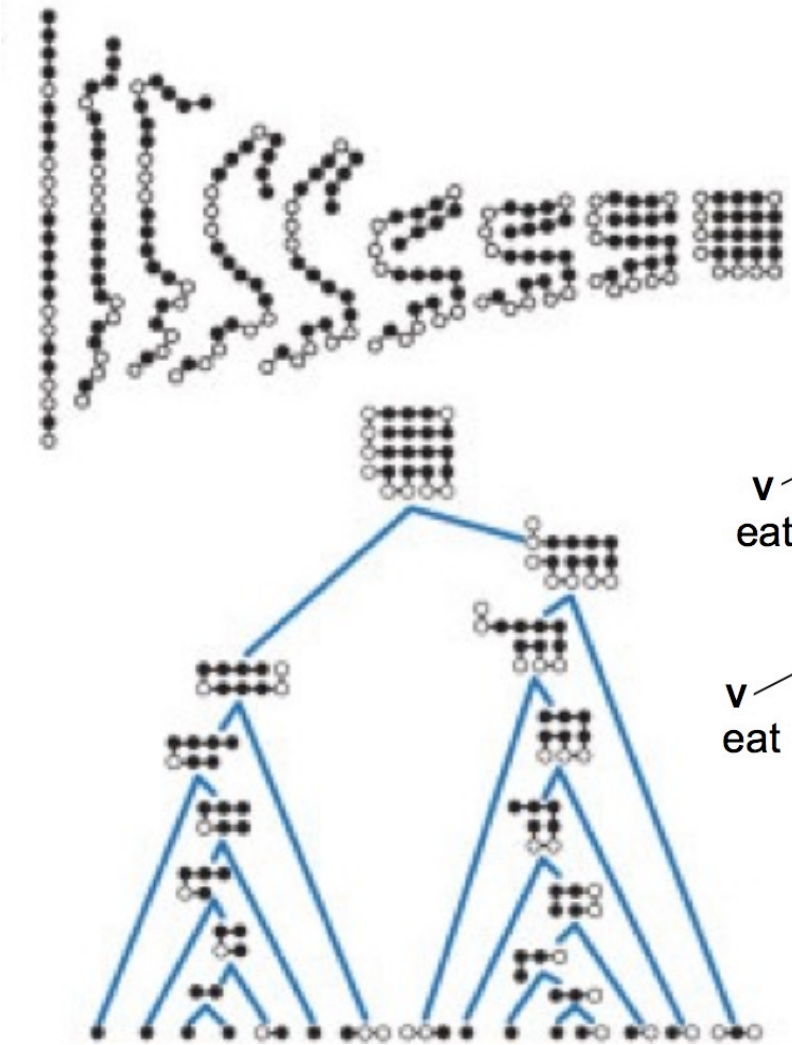
S.B. Ozkan *et al.*, *PNAS* **104**, 11987 ('07)

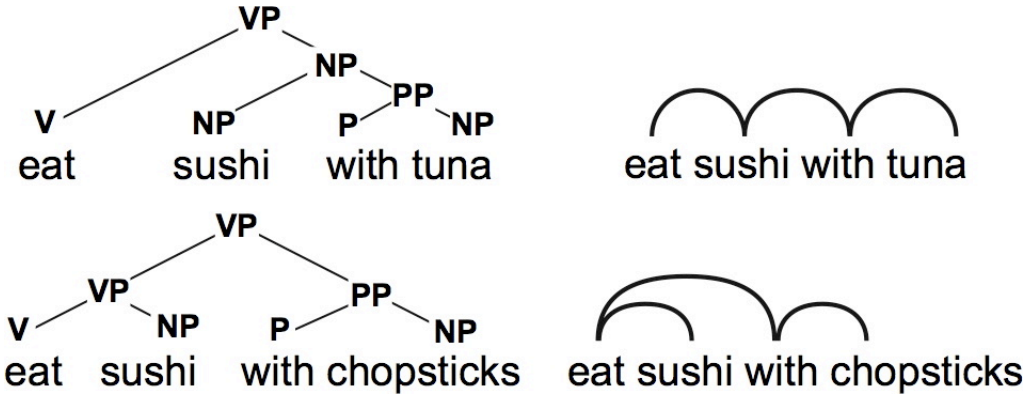
Parsing Protein-Folding Routes

Computational linguistics

(1) Formal grammar to describe protein-folding routes

(2) Dynamic programming for an efficient algorithm for the folding routes

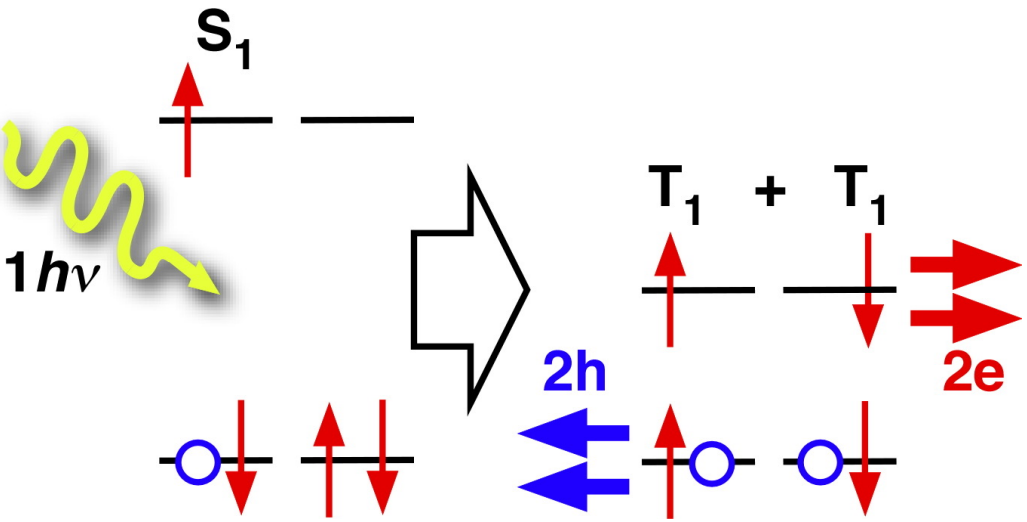


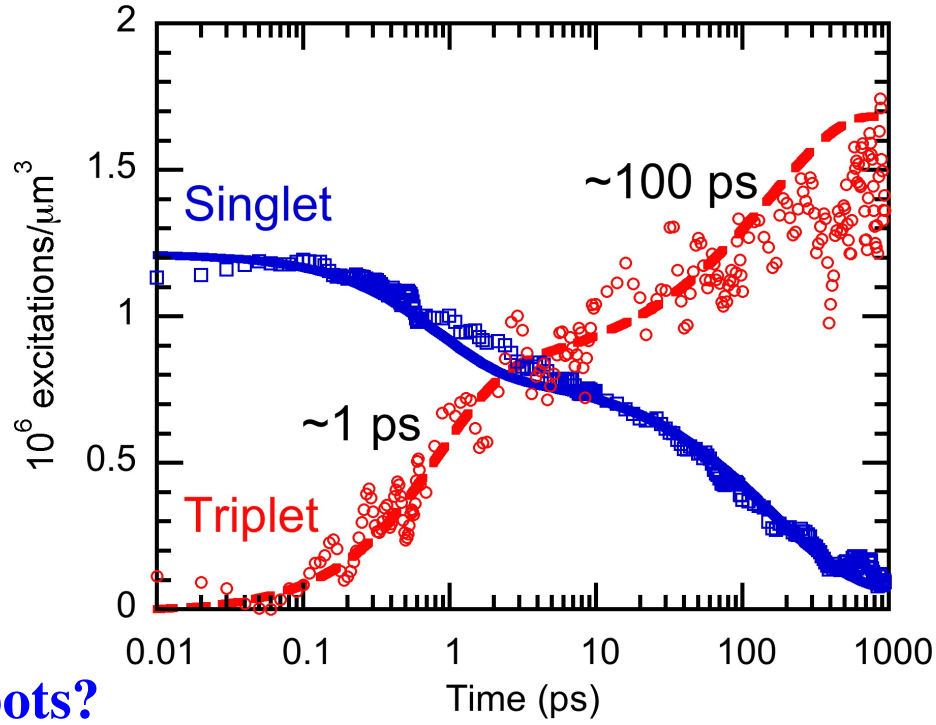


K. A. Dill *et al*., *Polymer* **48**, 4289 ('07)
W. Dyrka *et al*., *Alg. Mol. Biol*. **8**, 31 ('13)

Singlet Fission in Amorphous DPT

- **Photo-current doubling by splitting a singlet exciton into 2 triplet excitons**
- **Singlet fission (SF) in mass-produced disordered organic solid → efficient low-cost solar cells**
- **Exp'l breakthrough: SF found in amorphous diphenyl tetracene (DPT)**
- **Ultrafast transient absorption measurements identified *two time-scales* (1 & 100 ps) for exciton population dynamics**
- **Hypothesis: Existence of *SF hot spots*** [S. T. Roberts *et al.*, *JACS* **134**, 6388 ('12)]

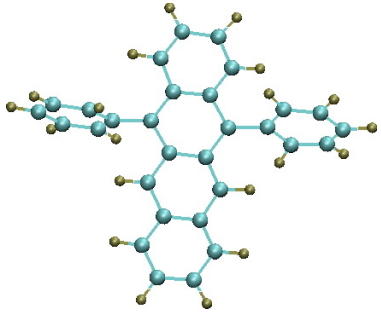




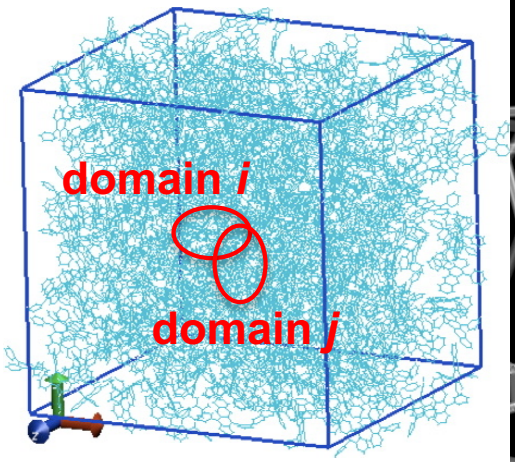
- **Problem: *Molecular origin* of SF hot spots?**

Divide-Conquer-Recombine KMC

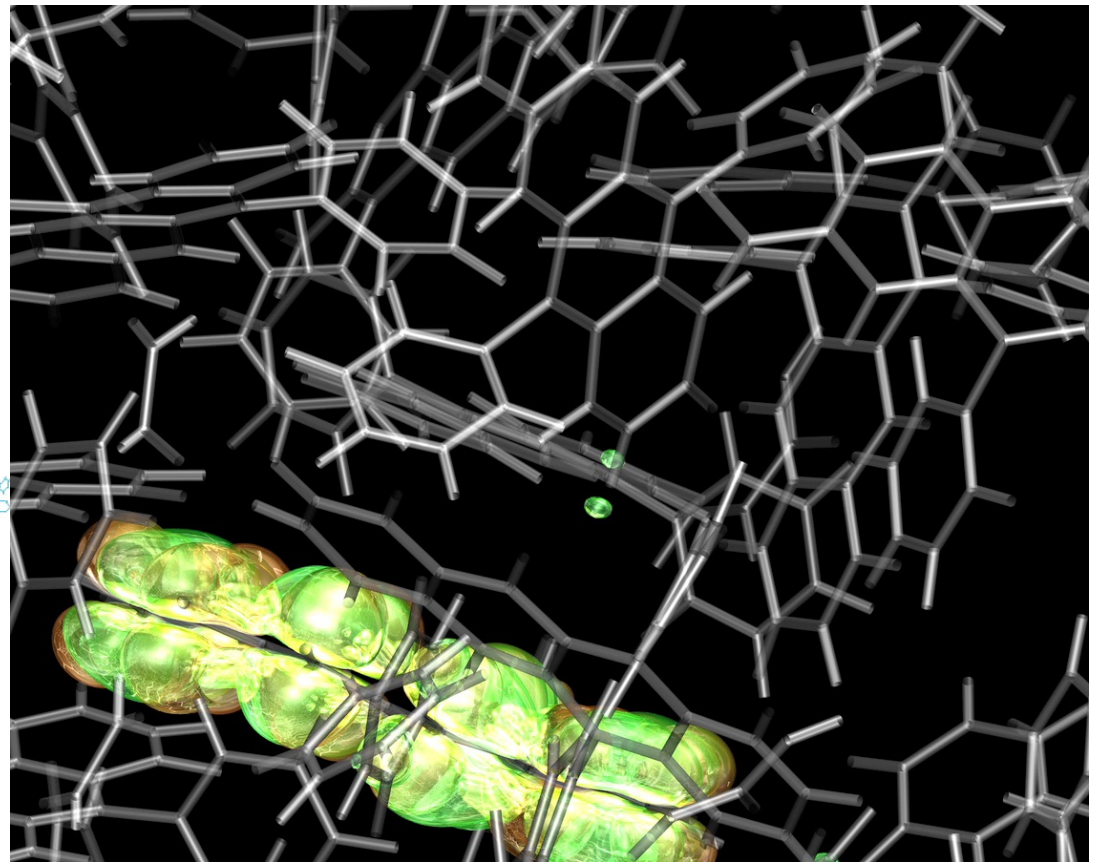
- **Move up from molecules to microstructures**
- **Challenge: Unprecedented 10^4-atom NAQMD simulation**
- **Computational approach: Divide-conquer-recombine (DCR) NAQMD**

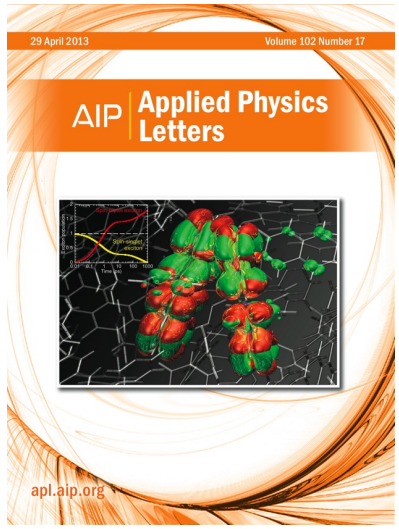


DPT molecule



Amorphous DPT





Quasi-electron

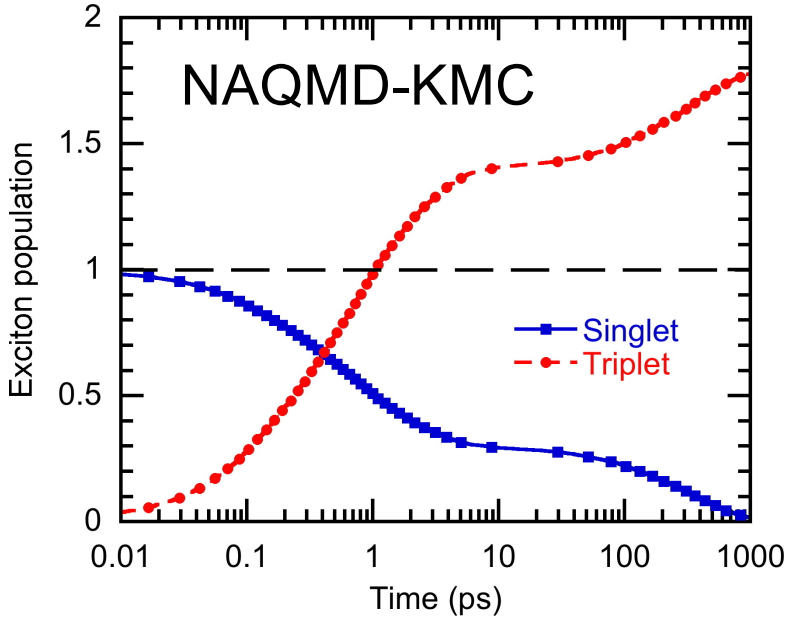
Quasi-hole

- **DCR-NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT**

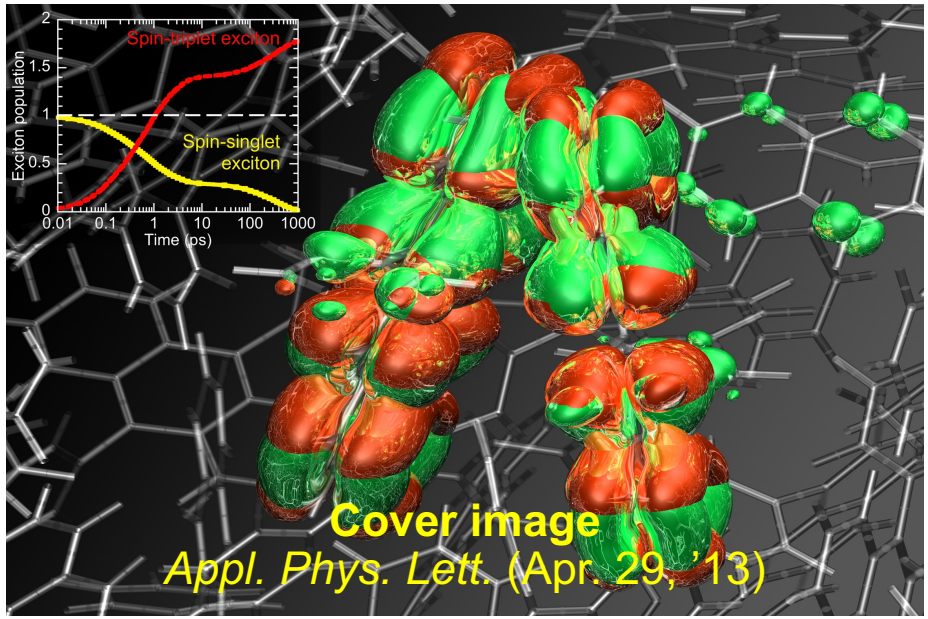
F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14)

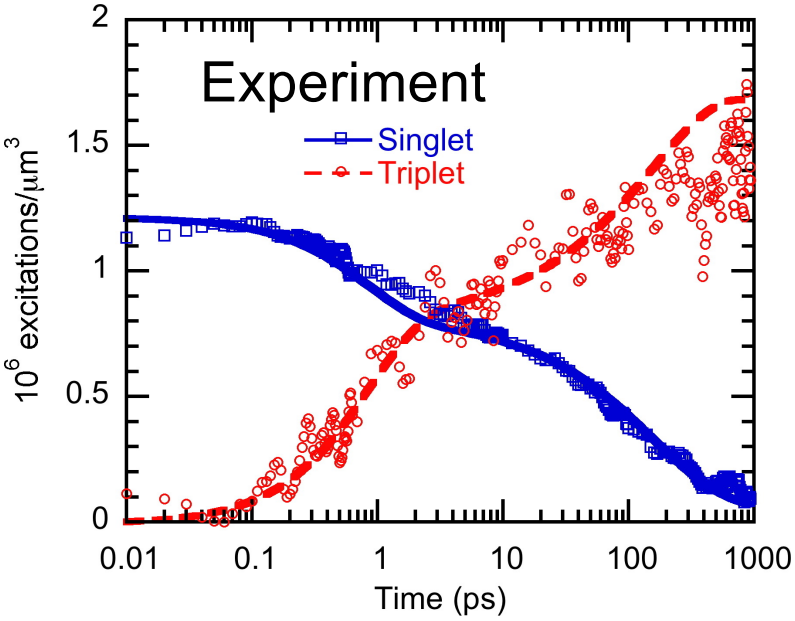
NAQMD-informed Kinetic Monte Carlo

- **NAQMD-KMC exciton population dynamics reproduces the experimentally observed two time scales (~ 1 & 100 ps) in amorphous DPT**



W. Mou *et al.*,
APL **102**, 173301 ('13)





S. T. Roberts *et al.*,
JACS **134**, 6388 ('12)