分子模拟技术初步

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Outline

- 热力学平均与统计系综
  - 热力学
  - 统计力学
- Monte Carlo模拟
  - Metropolis算法
  - Kinetic MC
- 分子动力学模拟
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  - 分析
- 反应动力学
  - 过渡态搜寻

热力学

- **热力学势**
  - Gibbs自由能：$G=H-TS$
  - Maxwell关系：$\mathrm{d}G=V\mathrm{d}P-S\mathrm{d}T$
- **热力学数据库**

$$H = H^{\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} C_p \mathrm{d}T \qquad S = S^{\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} \frac{C_p}{T} \mathrm{d}T$$

$$C_p = c_1 + c_2 T + c_3 T^2 + \frac{c_4}{T^2}$$

$$G = A_1 + A_2 T + A_3 T \ln T + A_4 T^2 + A_5 T^3 + \frac{A_6}{T}$$

Guggenheim scheme

Good Physicists Have Studied Under Very Active Teachers.

统计平均

- 系综平均

$$\langle A\rangle = \iint A(\mathbf{p}^N, \mathbf{r}^N)\rho(\mathbf{p}^N, \mathbf{r}^N)d^N\mathbf{p}d^N\mathbf{r}$$

- 时间平均

$$A_{ave} = \lim_{\tau\to\infty}\int_{\tau_0}^{\tau} A(\mathbf{p}^N, \mathbf{r}^N)dt$$

- 各态历经假设（ergodic hypothesis）：系综处于平衡态的宏观性质是微观量在足够长时间的平均值，即

$$\langle A\rangle = A_{ave}$$

统计系综

- Microcanonical (NVE)，能量守恒

$$\Omega_{mc} = \underbrace{T_{\text{ions}}}_{E_{kin}} + \underbrace{E[\vec{R}_I, \psi_i, f_i]}_{\text{internal } E} + \underbrace{TS_{ei}[f_i]}_{\text{electr. entropy}}$$

- Canonical (NVT)
- NPT 系综
- Grand canonical (μVT)

Monte Carlo模拟

- MC算法以地中海沿岸Monaco的赌城命名，是一种随机采样技术。
- 关键是根据具体问题，设计合适的采样几率。
- 例如，用MC模拟计算积分，如果能够做变换使得积分核比较平缓，则采样效率较高

$$I = \int_0^1 f(x)dx$$

$$I = \int_0^1 \frac{f(x)}{w(x)} w(x)dx = \int_0^1 \frac{f(x(u))}{w(x(u))} du$$

分子体系

- 计算 $$\langle A\rangle = \frac{\int dr^N e^{-E(r^N)/kT} A(r^N)}{\int dr^N e^{-E(r^N)/kT}} = \int dr^N N(r^N) A(r^N)$$
- 平衡与细致平衡

$$\sum_n N(0)\pi(0\to n) = \sum_n N(n)\pi(n\to 0) \qquad N(0)\pi(0\to n) = N(n)\pi(n\to 0)$$

- 将跃迁分为两步

$$\pi(0\to n) = \alpha(0\to n)\bullet acc(0\to n)$$

$$\alpha(0\to n) = \alpha(n\to 0)$$

$$\frac{acc(0\to n)}{acc(n\to 0)} = \frac{N(n)}{N(0)} = e^{-(E(n)-E(0))/kT}$$

Metropolis算法

- accept几率：

$$acc(0 \to n) = \begin{cases} 1 & N(n)/N(0) \geq 1 \\ N(n)/N(0) & N(n)/N(0) < 1 \end{cases}$$

- 如果某一步移动被拒绝，则需将就构型重新统计一次，否则对两能级系统，能量恒等于算术平均值。
- 在相空间移动时，不能采用固定顺序的移动序列（如先转动，再平动），否则不能满足细致平衡原理

分子动力学

- Ehrenfest MD

$$M_I \ddot{R}_I(t) = -\nabla_I \langle \psi | \hat{H}_e | \psi \rangle \qquad i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_e \psi$$

- Born-Oppenheimer MD

$$M_I \ddot{R}_I(t) = -\nabla_I \min_{\psi_0} \{ \langle \psi_0 | \hat{H}_e | \psi_0 \rangle \} \qquad E_0 \psi_0 = \hat{H}_e \psi_0$$

- Car-Parrinello MD

$$M_I \ddot{R}_I(t) = -\nabla_I \langle \psi | \hat{H}_e | \psi \rangle \qquad \mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^*} \langle \psi | \hat{H}_e | \psi \rangle + \frac{\delta}{\delta \psi_i^*} \{\text{constants}\}$$

  - CPMD希望“热核”与“冷电子”之间绝热，电子演化足够靠近BO面，所以不宜处理金属体系。

牛顿运动方程积分

- Verlet算法

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

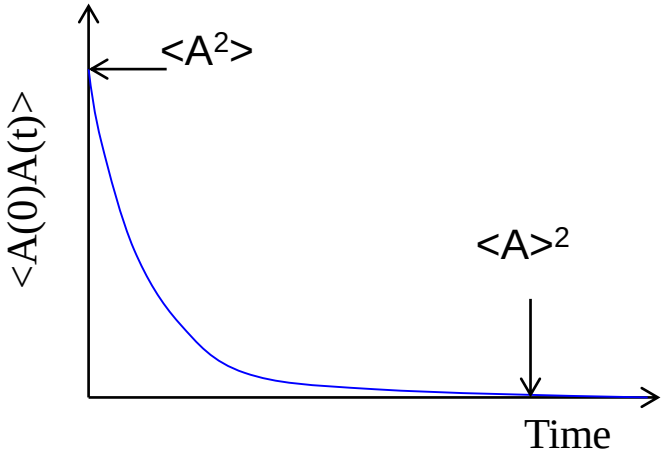
$$r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2$$

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2)$$

- 变种：蛙跳法、速度verlet法、位置verlet法

动力学信息分析

- 关联系数： $C_{xy}=\frac{1}{M}\sum_{i=1}^{M}x_i y_i=\langle x_i y_i\rangle$
- 时间关联系数： $C_{xy}(t)=\langle x(0)y(t)\rangle$
- 吸收光谱强度： $I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dte^{-i\omega t}\langle\mu(0)\mu(t)\rangle$
- 扩散系数： $D=\frac{1}{3}\int_{0}^{\infty}dt\langle v_i(t)v_i(0)\rangle$



温度控制

- Nosé thermostat

$$M_I \ddot{\vec{R}}_I(t) = -\frac{\partial E}{\partial \vec{R}_I(t)} - M_I \ddot{\vec{R}}_I(t) \frac{\dot{s}(t)}{s(t)}$$

$$Q \frac{d(\dot{s}(t)/s(t))}{dt} = -\sum_I M_I |\ddot{\vec{R}}_I(t)|^2 - g k_B T$$

Q mass parameter for the thermostat, determines the response of the heat bath to the uctuations of the ionic system

g number of the ionic degrees of freedom g = 3(N -1)

- characteristic frequency of the thermostat at T: $\omega_T^2 = \frac{2gk_BT}{Q}$
- equilibration between the ions and the heat bath: most effective if ω_T is of the same order of magnitude as the characteristic frequency of the system to which it is coupled.

压力控制

- Parrinello-Rahman dynamics

$$\mathcal{L}(s,h,\dot{s},\dot{h}) = \frac{1}{2}\sum_{i}^{N} m_i \dot{s_i}^t G \dot{s_i} - V(s,h) + \frac{1}{2} W\, Tr(\dot{h}^t \dot{h}) - p_{ext}\Omega,$$

分数　　晶格
坐标　　矢量

$$G = h^t\, h$$

Constrain

- SHAKE algorithm

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i + \sum_{k=1}^{N_c} \lambda_k \nabla_i \sigma_k \qquad \frac{\mathrm{d}}{\mathrm{d}t}\sigma_k(\mathbf{r}_1, ..., \mathbf{r}_N) = 0$$

  - develop a numerical scheme in which the constraint conditions are satisfied exactly as part of the integration algorithm

$$\mathbf{r}_i(\Delta t) = \mathbf{r}_i(0) + \Delta t \mathbf{v}_i(0) + \frac{\Delta t^2}{2m_i}\mathbf{F}_i(0) + \frac{\Delta t^2}{2m_i}\sum_k \lambda_k \nabla_i \sigma_k(0)$$

$$\sigma_l(\mathbf{r}_1(\Delta t), ..., \mathbf{r}_N(\Delta t)) = 0, \qquad l = 1, ..., N_c$$

迭代求解！

自由能计算

- 自由能微扰

$$\langle \mathcal{F}(\mathbf{x}, \mathbf{p}_x) \rangle_1 = \frac{\langle \mathcal{F}(\mathbf{x}, \mathbf{p}_x) \exp(-\beta \triangle U) \rangle_0}{\langle \exp(-\beta \triangle U) \rangle_0}$$

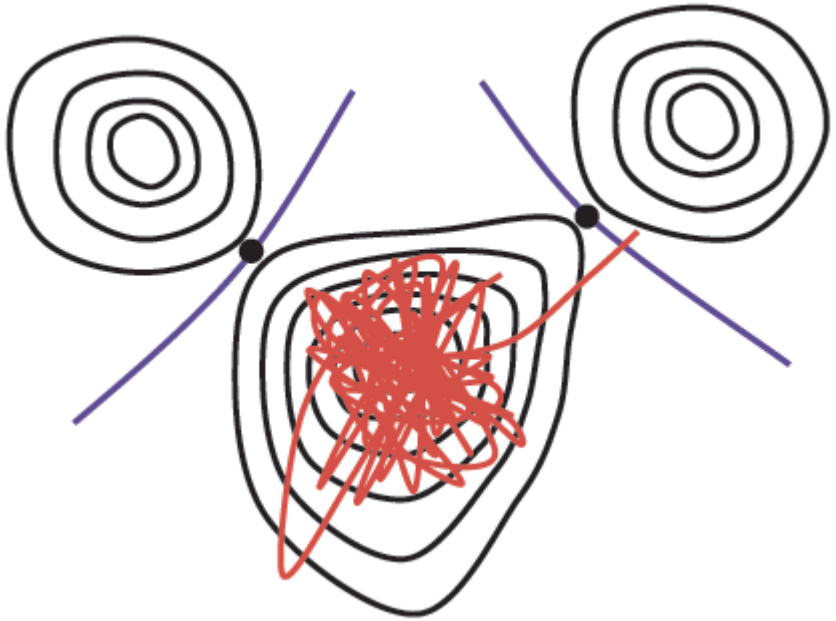
- 热力学积分

$$\Delta A_{a \to b} = \int_{\lambda_a}^{\lambda_b} \langle \frac{\partial \mathcal{H}(\mathbf{x}, \mathbf{p}_x; \lambda)}{\partial \lambda} \rangle_\lambda \mathrm{d}\lambda$$

Potential of mean force

稀有事件

- 稀有事件存在时对整个相空间均匀采样变得困难。

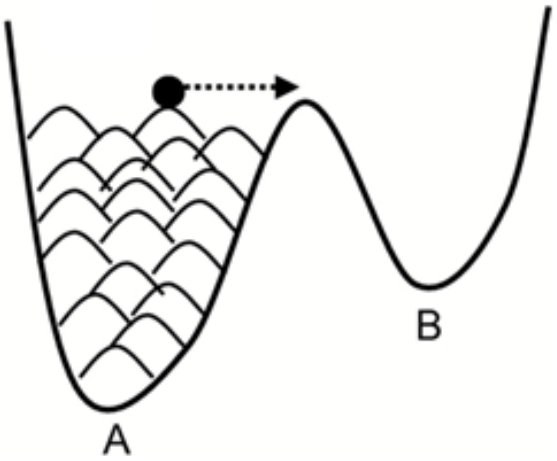


Biased sampling

- 伞形采样
- Metadynamics

$$\hat{F}(\mathbf{s}) = -\frac{1}{\beta}\ln N(\mathbf{s}) - V(\mathbf{s})$$

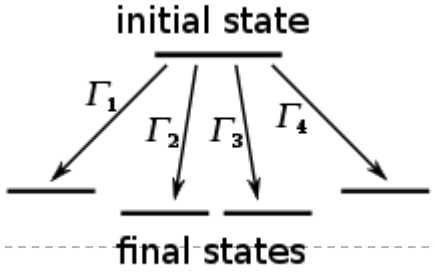
$$V(\mathbf{s},t) = \int_0^t \mathrm{d}t'\omega \exp(-\sum_i^d \frac{\mathbf{s}_i(\mathbf{r}) - s_i(\mathbf{r}(t')^2)}{2\sigma_i^2})$$

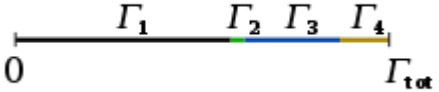


Kinetic MC

- simulating the time evolution of a system where some processes can occur with known rates r

1. Calculate the cumulative function $R_i = \sum_{j=1}^{i} r_j$
2. Get a uniform random number $u \in (0,1]$
3. Carry out event *i* with $R_{i-1} < uR_N \leq R_i$
4. Get a new uniform random number $u' \in (0,1]$
5. Update the time with $t = t + \Delta t$, where $\Delta t = R_N^{-1} \ln(1/u')$
6. Recalculate all rates and update even list.
7. Return to step 1.





过渡态理论

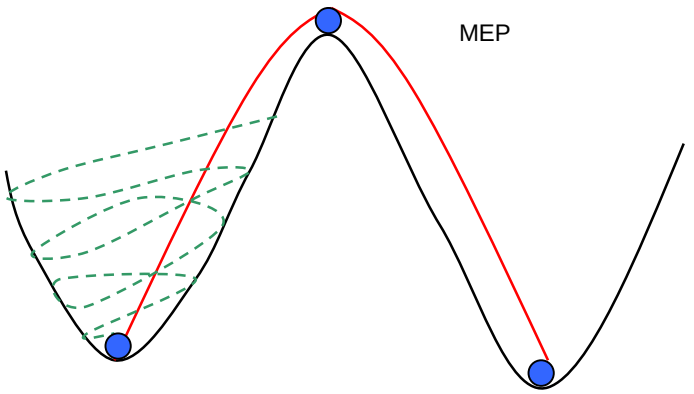
- 对于反应 $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A'$，认为其存在过渡态$A^{\neq}$，使得反应历程为：

$$A \rightleftharpoons A^{\neq} \xrightarrow{k_{\neq}} A'$$

- 化学反应速率

$$k_1 = k_{\neq} \frac{[A^{\neq}]}{[A]} = k_{\neq} e^{-(G_{\neq} - G_A)/k_B T}$$

- 变分过渡态理论



过渡态搜寻

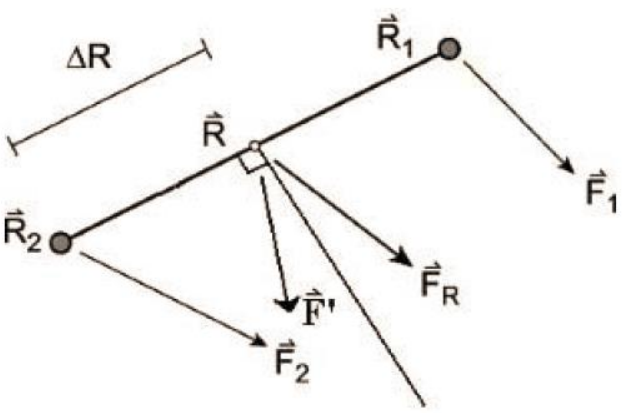
- 基于初始猜想
  - Constrained Minimization：固定反应坐标R（如需断开的化学键键长）优化其他自由度。R的取值通常需要通过手动扫描得到，也可对特定的优化算法发展自动逼近真实过渡态对应的R
  - Eigenvector following：手动构造初始过渡态模型，当优化算法给出Hessian或其近似时，跟随最大的负二次微分。
  - Dimer method：构造两个相近的构型，从初始位置和初始方向沿能量高的方向走，通过“转动”二聚体来寻找最小曲率（最终为负）的方向。

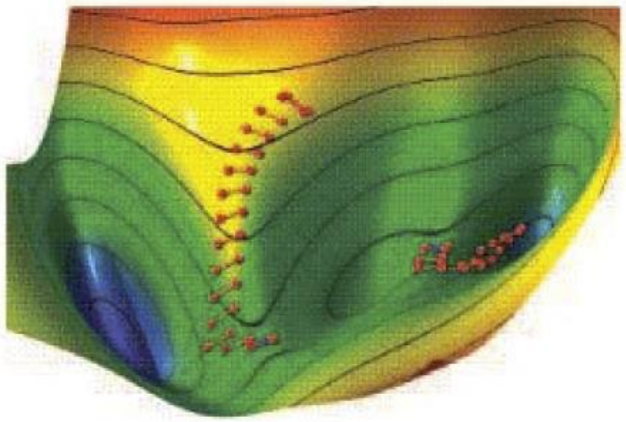
过渡态搜寻

- 基于反应物产物
  - Synchronous Transit (LST/QST)：在两个稳定构型间做几何插值，计算能量（或沿垂直方向优化构型），查找能量最高点。
  - Nudged elastic band：每个映像上的力垂直反应路径；采用一个人为的弹性力来使映像沿反应路径分开。

Dimer方法

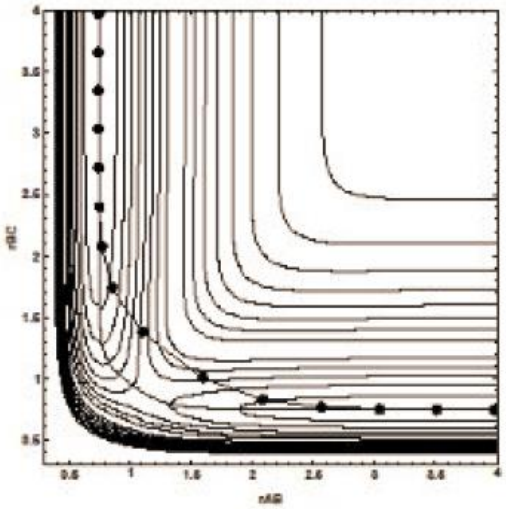
- Dimer方法每一步包括平移和旋转两步
- 旋转：沿中点旋转直至总能最小，对应于曲率最小的方向。
- 平移：根据受力F‘移动。F’等于将F(R)平行于Dimer方向力的分量符号反转。Dimer方向以受力相反方向移动，而其它方向顺着受力方向移动。



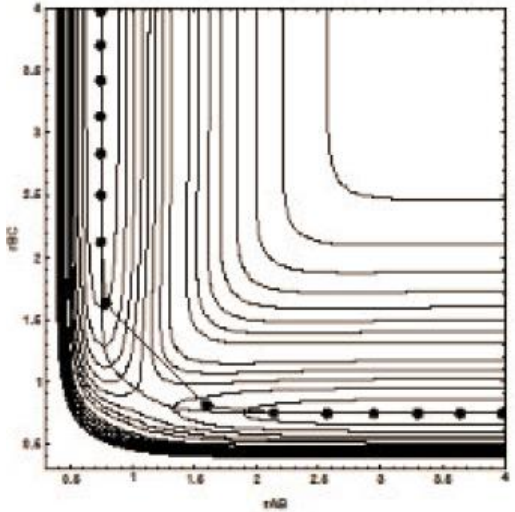


NEB

- Plain elastic band



Corner Cutting

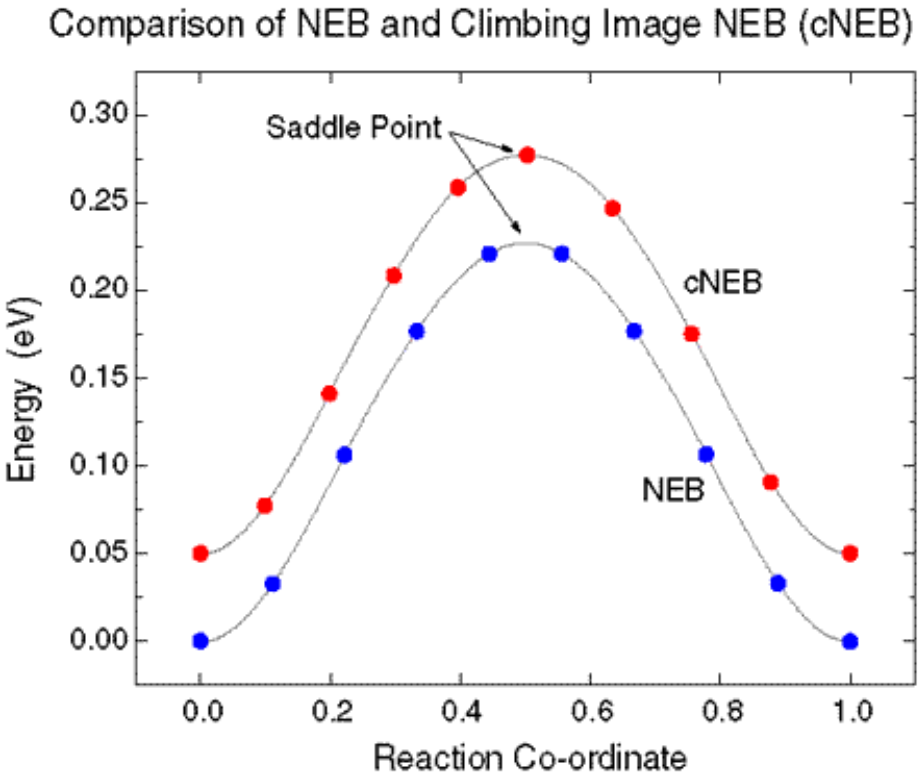


Sliding Down

- Nudged Elastic Band
  - 切线方向受力等于弹簧力在这个方向分量
  - 垂直于路径切线方向的受力等于势能力在此方向上分量

CI-NEB

- The highest energy image does not feel the spring forces along the band. Instead, the true force at this image along the tangent is inverted.



上机实践

- 简单有机反应过渡态
  - NEB
  - CI-NEB
  - dimer
- 小分子构象统计采样