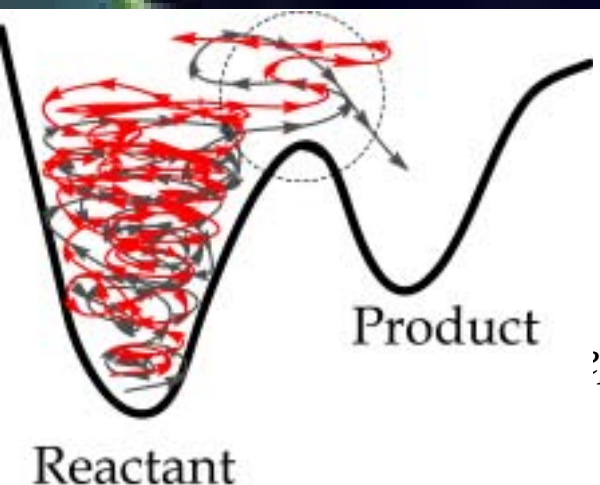
COE SYMPOSIUM on Cross Talk between Chemistry and Planetary Sciences Nov 17 2003

化学反応のダイナミックスとカオス

Cross-Talk between celestial mechanics and chemical reactions



The interplanetary transport network

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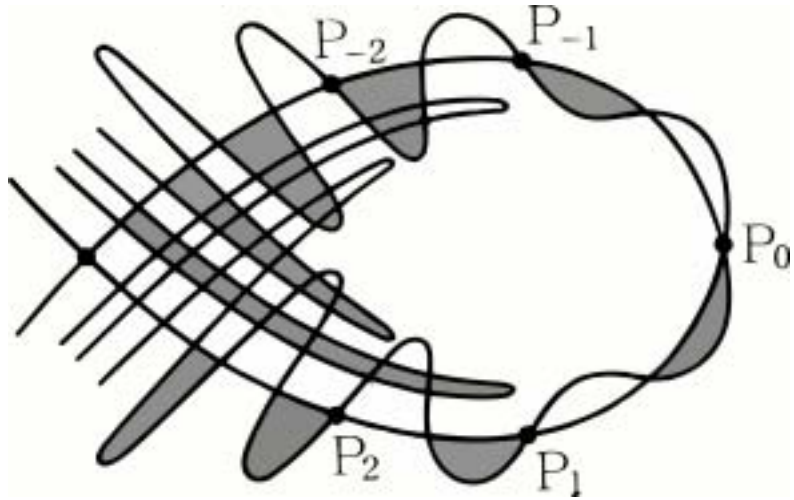
天文学から生まれたカオス

A hypothetical comet of 1857 collides with Earth in this 19th century French cartoon

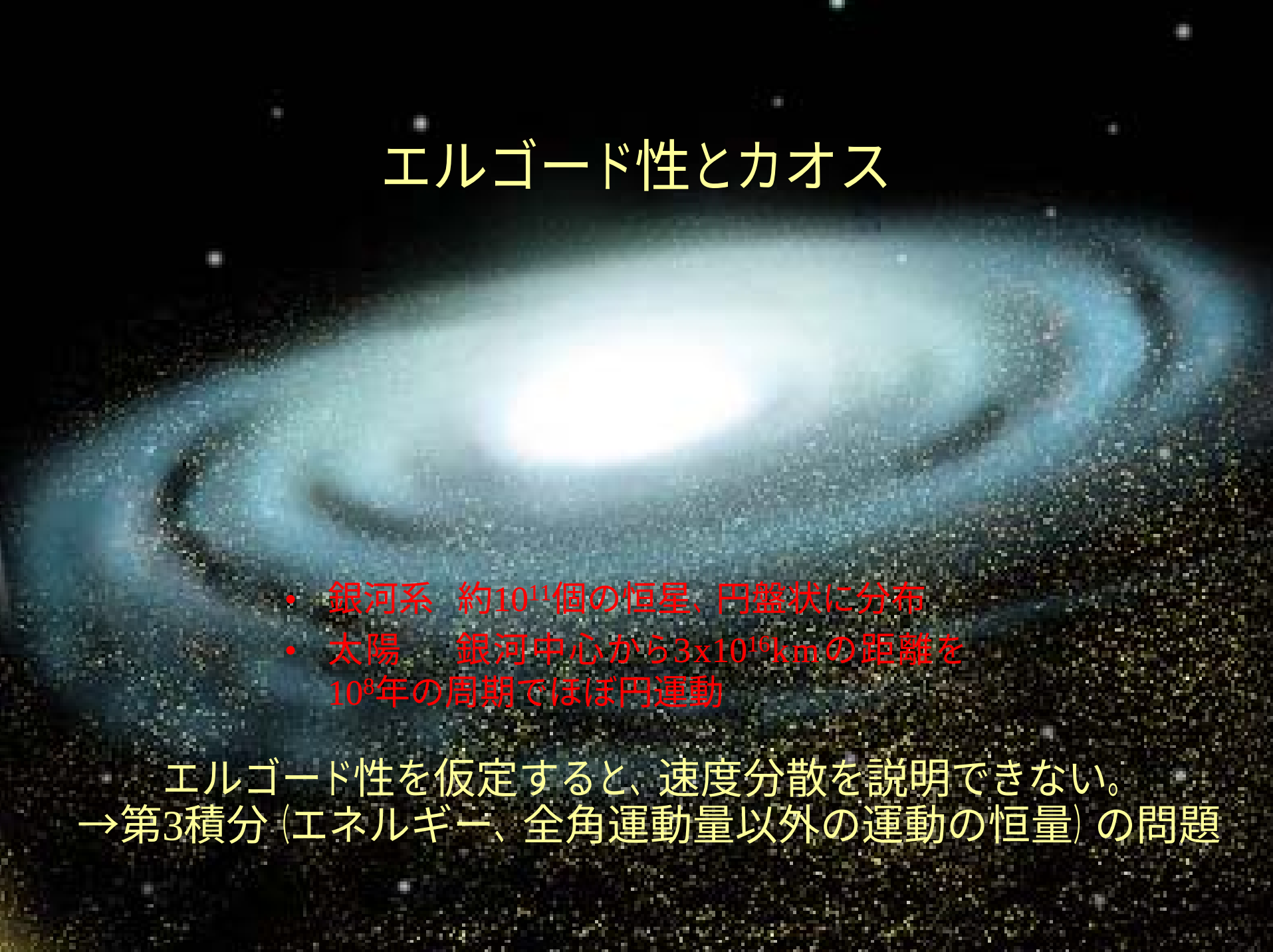
決定論的カオス

天文学者・物理学者
Henri Poincare
(France, 1854-1912)



”(無限の未来に渡って予測を可能とする)決定論的形式(ニュートン力学)に縛られていても、その振舞いは非常に複雑で、事実上未来を一義的に予測することは出来ない”

エルゴード性とカオス



- 銀河系　約10^{11}個の恒星、円盤状に分布
- 太陽　　銀河中心から3×10^{16}kmの距離を10^{8}年の周期でほぼ円運動

エルゴード性を仮定すると、速度分散を説明できない。
→第3積分（エネルギー、全角運動量以外の運動の恒量）の問題

堀源一郎が発明したリー正準変換摂動論と「カオスの発生」

G. Hori, *Pub. Astro. Soc. of Japan* **18**, 287(1966);**19**, 1967(1967);J.R. Cary, *Phys. Rep.* **79**,130(1980)

基準座標(Normal **Mode** coordinate)

$$H=\frac{1}{2}\sum_{j=1}(p_j^2+\omega_j^2 q_j^2)$$

ポテンシャルエネルギー面上の停留点
近傍2次で記述できる領域

always true

$$\frac{d^2 q_k}{dt^2}+\omega_k{}^2 q_k=0 \qquad p_k=\frac{dq_k}{dt}$$

各モードは独立、作用 $J_k=\frac{1}{2\pi}\oint p_k dq_k$

は相空間全域に渡って保存する

標準形座標 (Normal **Form** coordinate)

$$H=\frac{1}{2}\sum_{j=1}(p_j^2+\omega_j^2 q_j^2)$$

$$+\varepsilon^1\sum_{j,k,l}C_{jkl}q_j q_k q_l+\varepsilon^2\sum_{k,l,m}C_{jklm}q_j q_k q_l q_m+\ldots$$

非調和項を包含する領域

not always possib

$$\frac{d^2\bar{q}_k(\mathbf{p},\mathbf{q})}{dt^2}+\bar{\omega}_k{}^2\bar{q}_k(\mathbf{p},\mathbf{q})=0$$

$$\bar{p}_k(\mathbf{p},\mathbf{q})=\frac{\omega_k}{\bar{\omega}_k}\frac{d\bar{q}_k(\mathbf{p},\mathbf{q})}{dt}$$

$\bar{J}_k=\frac{1}{2\pi}\oint\bar{p}_k(\mathbf{p},\mathbf{q})d\bar{q}_k(\mathbf{p},\mathbf{q})$ が保存する領域では、

調和振動子類似の独立したモードが位相空間上に存在する

カオスの発生＝small-denominator problem

$$\left| \sum_{k=1}^{M} n_k \omega_k(\mathbf{J}) \right| \approx 0$$

M: 自由度の数
n_k: 任意の整数
w_k: 作用Jの連続微分可能関数であるk番目の振動数

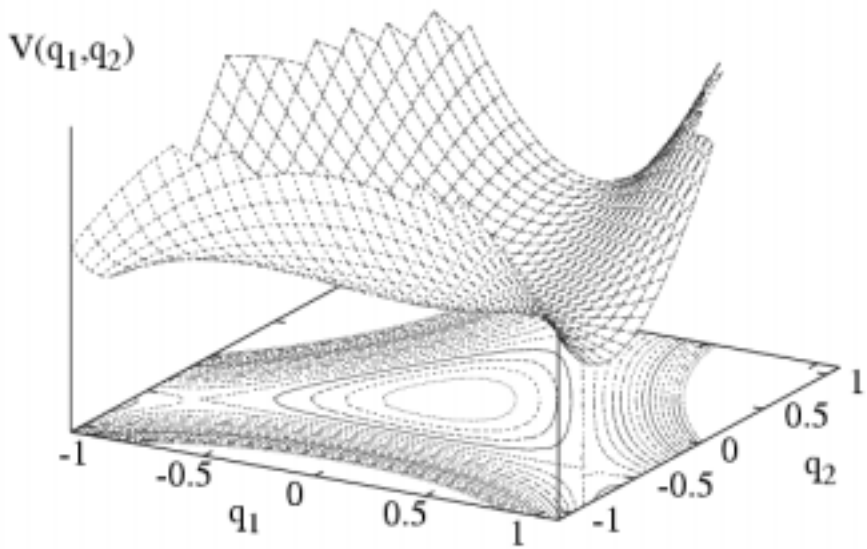
の左辺の和が、摂動計算の過程で各項の分母に現れる。
一般に非線形性が強い領域では左辺を限りなく小さくする整数の組が沢山存在する

→摂動計算は発散する。

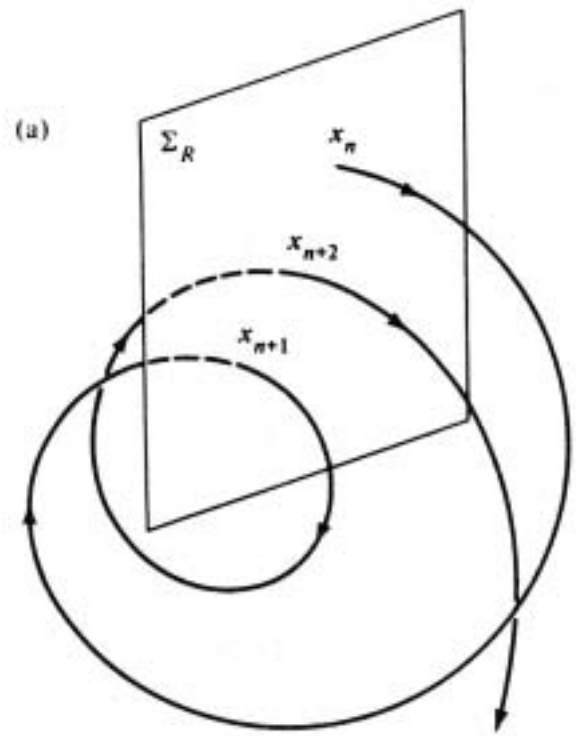
~~$H(\mathbf{J},\boldsymbol{\theta}) \longrightarrow \overline{H}(\mathbf{J})$~~

銀河系内の円軌道に近い星の運動を記述する「簡単かつ十分に複雑な」Henon-Heilesモデル (1960)

$$H = \frac{1}{2}(p_x{}^2 + p_y{}^2) + \frac{1}{2}(x^2 + y^2) + x^2 y - \frac{1}{3}y^3$$

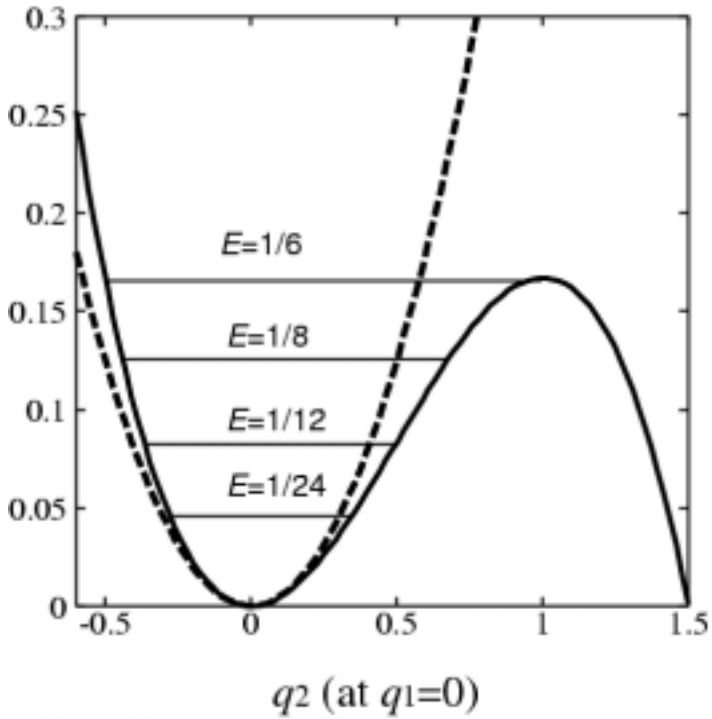


Henon-Heiles ポテンシャル

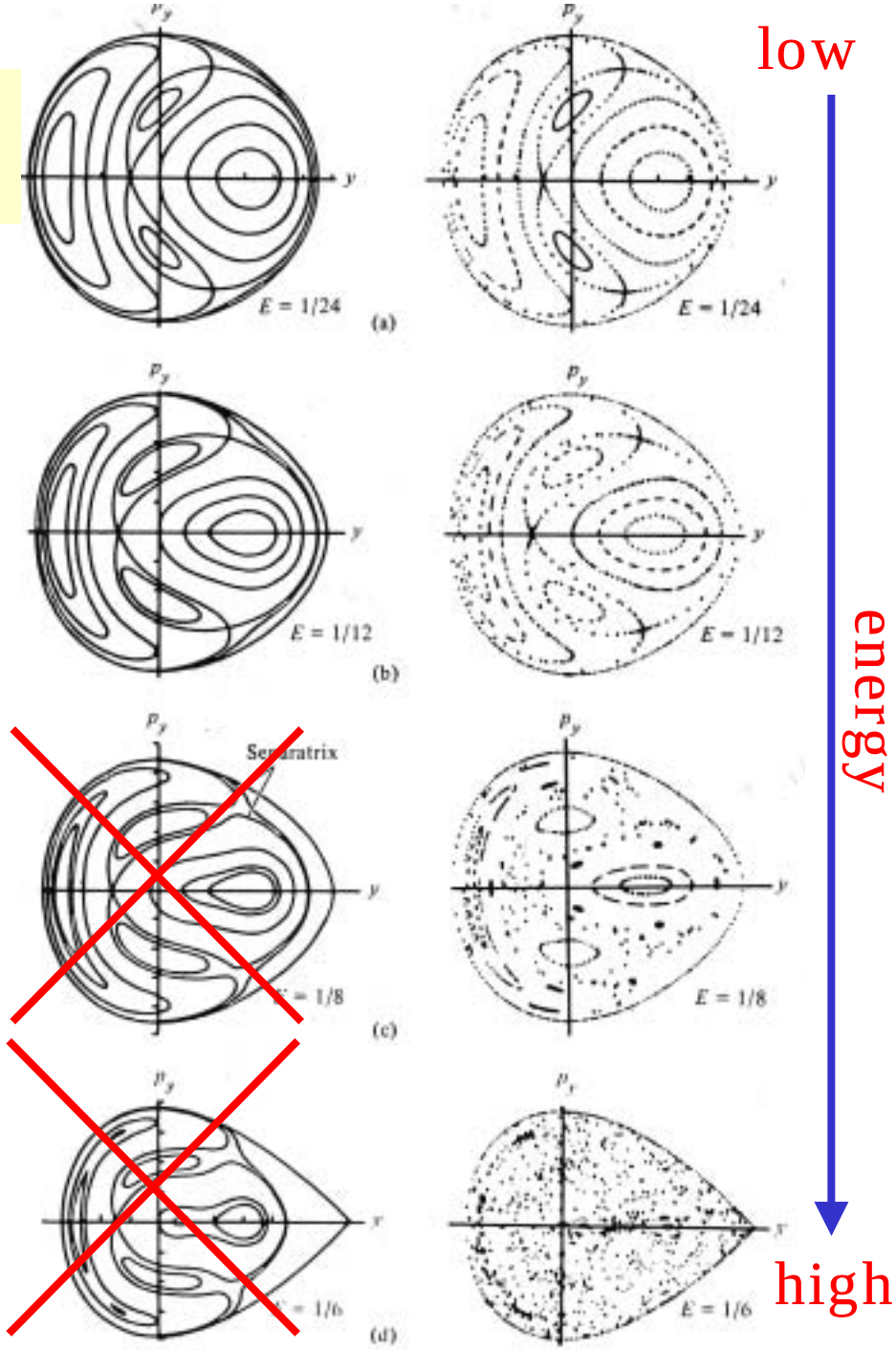


相空間上のポアンカレ断面

ポアンカレ断面にみるエネルギー増加に伴う第3積分（近似的曲線群）の消失



左図:右図＝正準変換摂動計算によるポアンカレ断面：実軌道によるポアンカレ断面

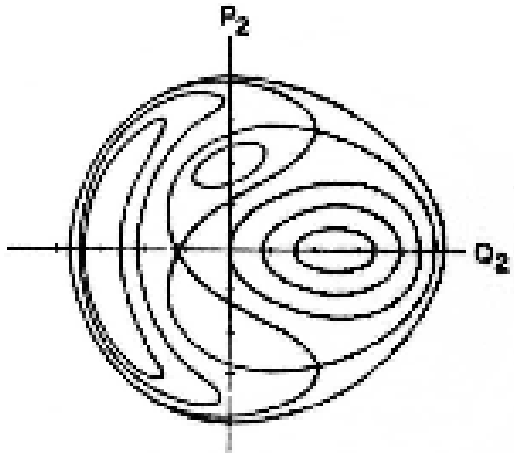


化学反応ダイナミックスとカオス

Henon-Heilesモデルの低エネルギー領域では運動の恒量が存在する

→太陽系、銀河系における第3積分に相当

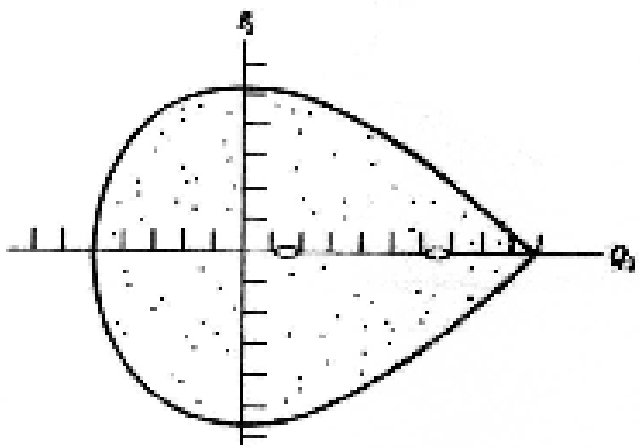
→正準変換摂動理論が役立つ



(峠を越えて異なる平衡状態へ到達しなければならない) 化学反応が生起する高振動エネルギー領域

→第3積分が存在せず、強カオス領域

→ 運動がエルゴード的であることを示唆する



→正準変換摂動理論は化学反応ダイナミックスを理解する上で役に立たない？

従来の化学反応理論の基本仮定

ちなみに、化学反応速度論の開祖は

1889年　Svante August Arrhenius
化学者･天文学者（1903年ノーベル化学賞）

Arrheniusの式　$k(T)=A\exp(-E_{act}/RT)$

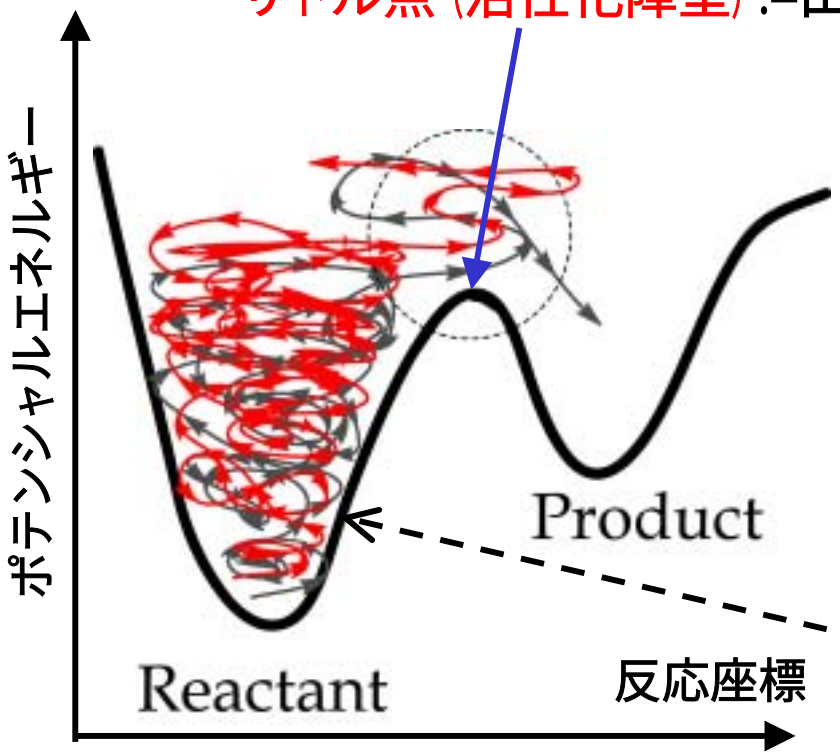
温度依存性は主に指数部によって決まり、前指数因子Aは温度依存性小

(1)　局所平衡仮説

遷移状態を探し当てるプロセスはエルゴード過程

(Eyring, Polanyi, Wigner 1935)

サドル点 (活性化障壁) :=山の峠



遷移状態、ボトルネック:=拡張概念、「そこ」を越えたら必ず向こうの山の麓 (product) へ辿りつける“場所”

遷移状態を探し当てるまでに、系は与えられたエネルギーのもとで許される相空間をエルゴード的に経巡る

と仮定する

配位空間描像

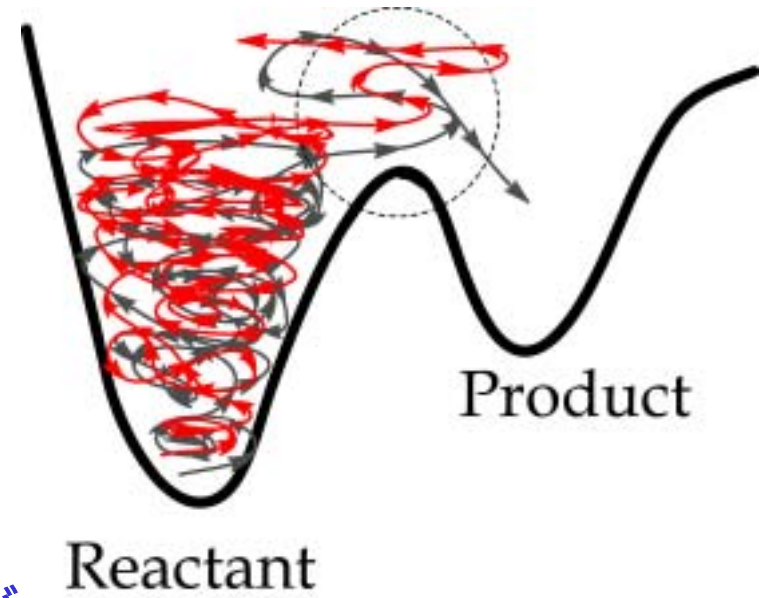
(2) 非再交差仮説

遷移状態を一旦通過した軌道は再び
遷移状態を横切ることなく、生成系へと至る

(Eyring, Polanyi, Wigner 1935)

実際の古典軌道計算によると

サドル(峠)を何度も横断した挙句の果てに、
反応系(reactant)に戻ったり、
生成系(product)へ辿りつく
軌道群が多数存在する

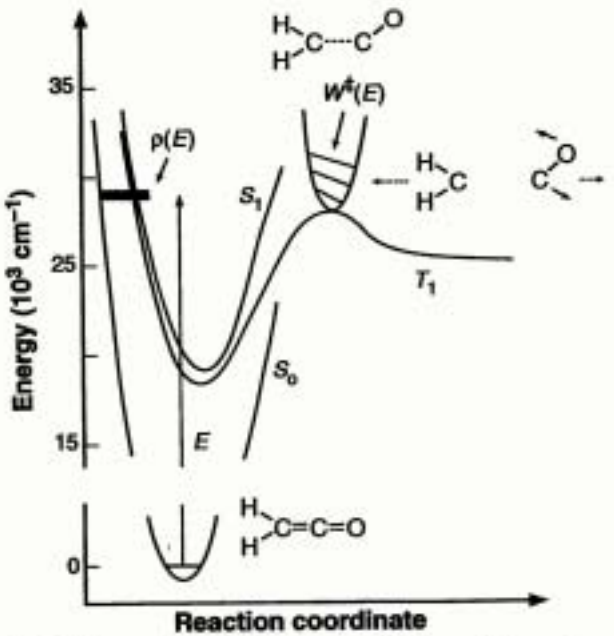


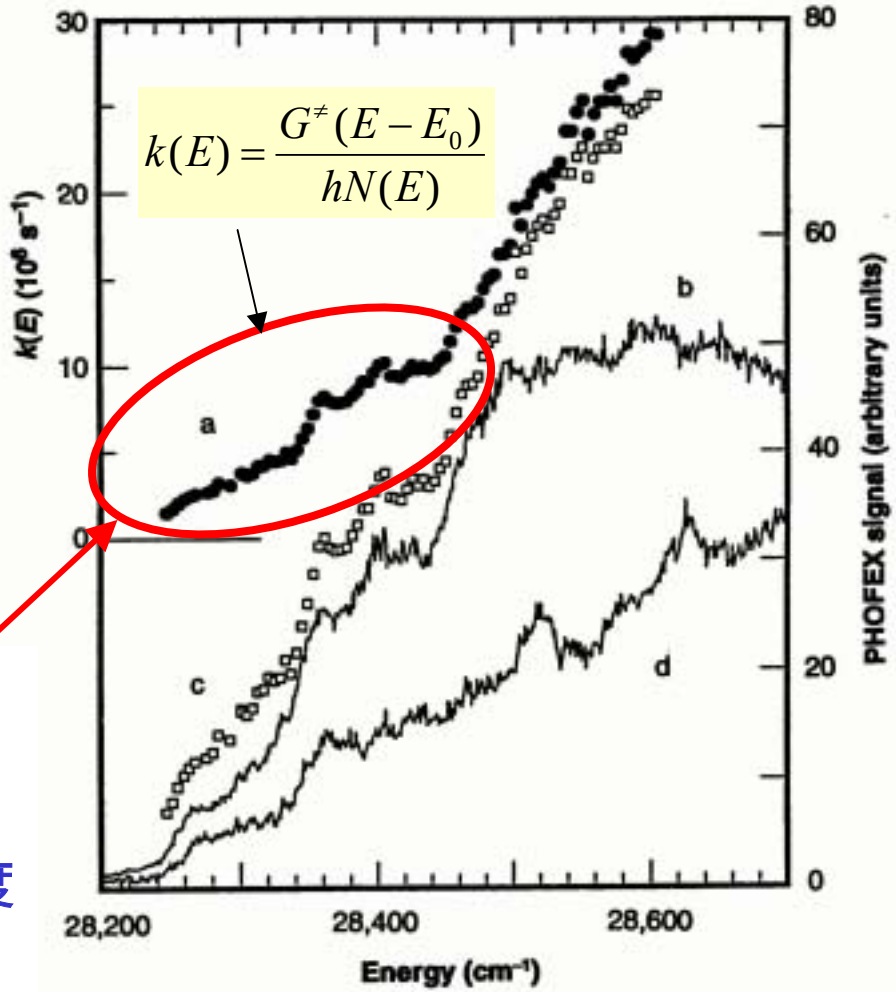
1935年以降の未解決問題

どのような状況下で再交差を与えない遷移状態が
存在し得、恣意性なく見出すことが出来るのか？

遷移状態分子分光

E.R.Lovejoy, S.K.Kim and C.B.Moore, *Science* **256**, 1541 (1992)





遷移状態領域における運動の可積分性に関する実験的証拠
良い量子数の存在→非反応自由度の作用は保存

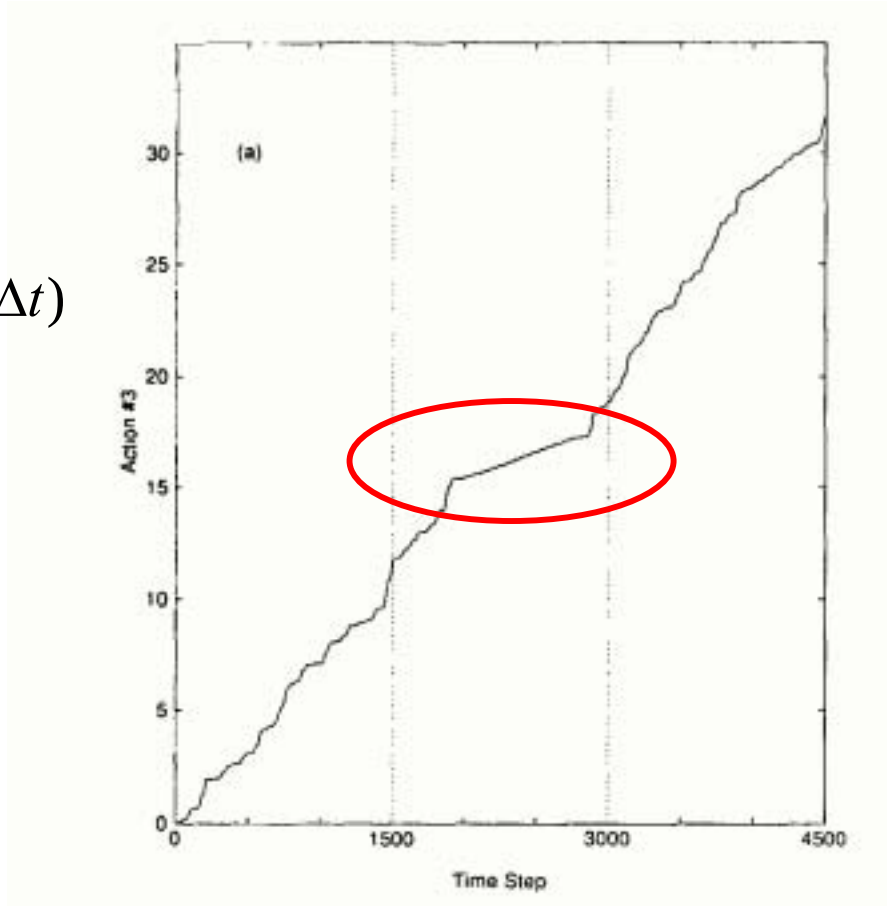
Rudolph A.Marcus, *Science* **256**, 1523 (1992)

LJ_3〜LJ_7クラスター構造転移における作用変数の保存性

Hinde&Berry *J.Chem.Phys.* **99**, 2942 (1993)

- LJ_3クラスターの遷移過程

$$I_j(n\Delta t) = \sum_{k=1}^{n} p_j(k\Delta t)\Delta q_j(k\Delta t)$$



作用がサドル領域で局所的に保存している

ただし、6原子クラスター以上のサイズでは明確に観測されなかった

カオスのなかに隠された、再交差を与えない真の遷移状態
リー正準変換摂動理論の化学反応への適用

Dynamical hierarchy in transition states: Why and how does a system climb over the mountain?

Tamiki Komatsuzaki* and R. Stephen Berry†‡

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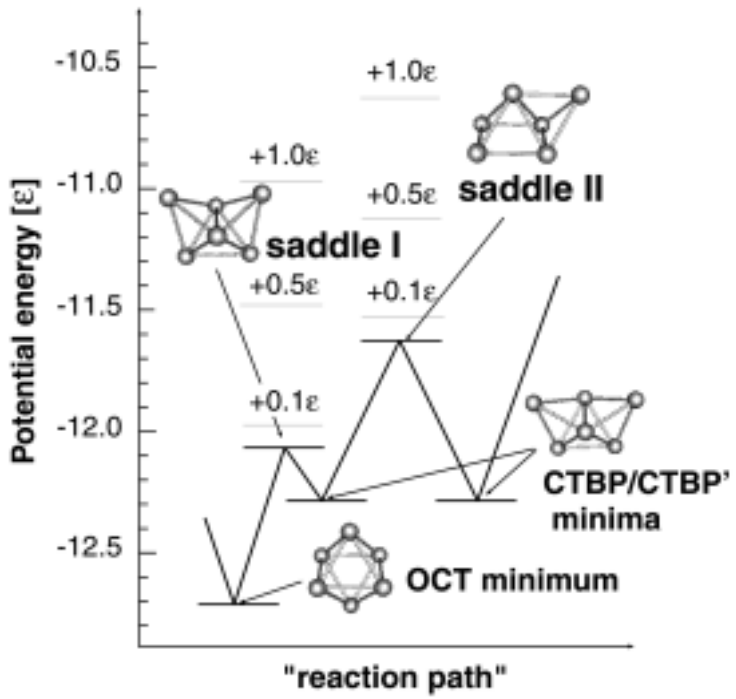
Edited by Rudolph A. Marcus, California Institute of Technology, Pasadena, CA, and approved April 12, 2001 (received for review December 28, 2000)

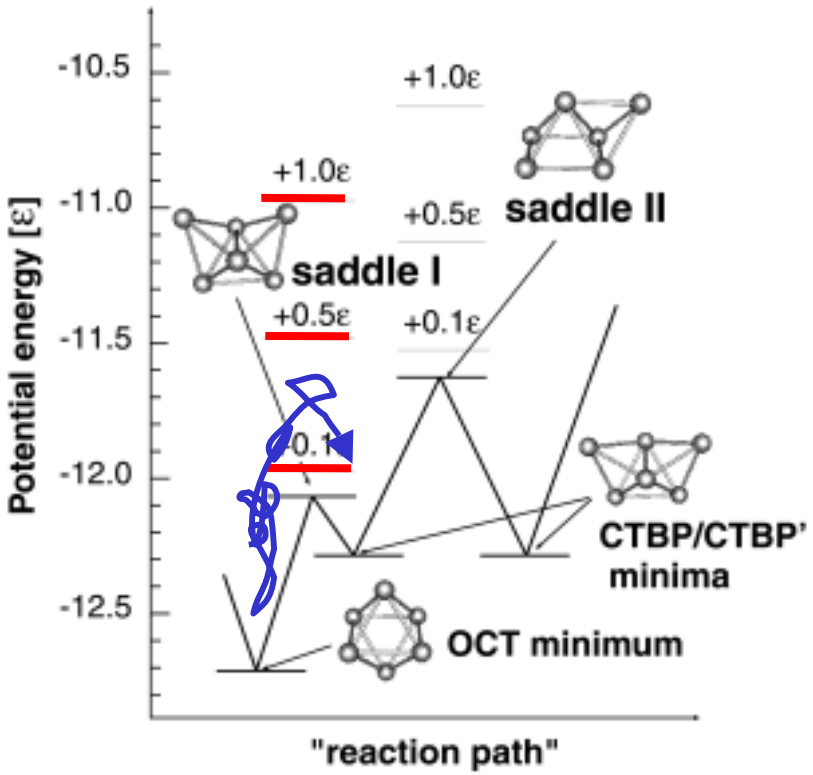
How a reacting system climbs through a transition state during the course of a reaction has been an intriguing subject for decades. Here we present and quantify a technique to identify and characterize local invariances about the transition state of an *N*-particle Hamiltonian system, using Lie canonical perturbation theory combined with microcanonical molecular dynamics simulation. We show that at least three distinct energy regimes of dynamical behavior occur in the region of the transition state, distinguished by the extent of their local dynamical invariance and regularity. Isomerization of a six-atom Lennard–Jones cluster illustrates this: up to energies high enough to make the system manifestly chaotic, approximate invariants of motion associated with a reaction coordinate in phase space imply a many-body dividing hypersurface in phase space that is free of recrossings even in a sea of chaos. The method makes it possible to visualize the stable and unstable invariant manifolds leading to and from the transition state, i.e., the reaction path in phase space, and how this regularity turns to chaos with increasing total energy of the system. This, in turn, illuminates a new type of phase space bottleneck in the region of a transition state that emerges as the total energy and mode coupling increase, which keeps a reacting system increasingly trapped in that region.

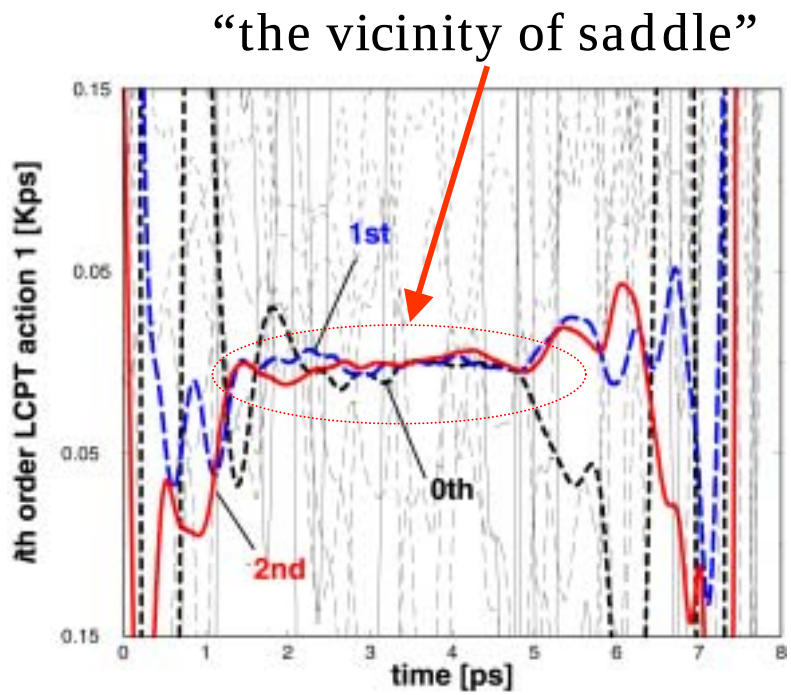


Proceedings of National Academy of Sciences USA (2001) **98**,7666-7671

Isomerization Reactions in Ar_6

代表的な交差軌道に沿って、作用変数の時間依存性を調べる(E=0.5ε)

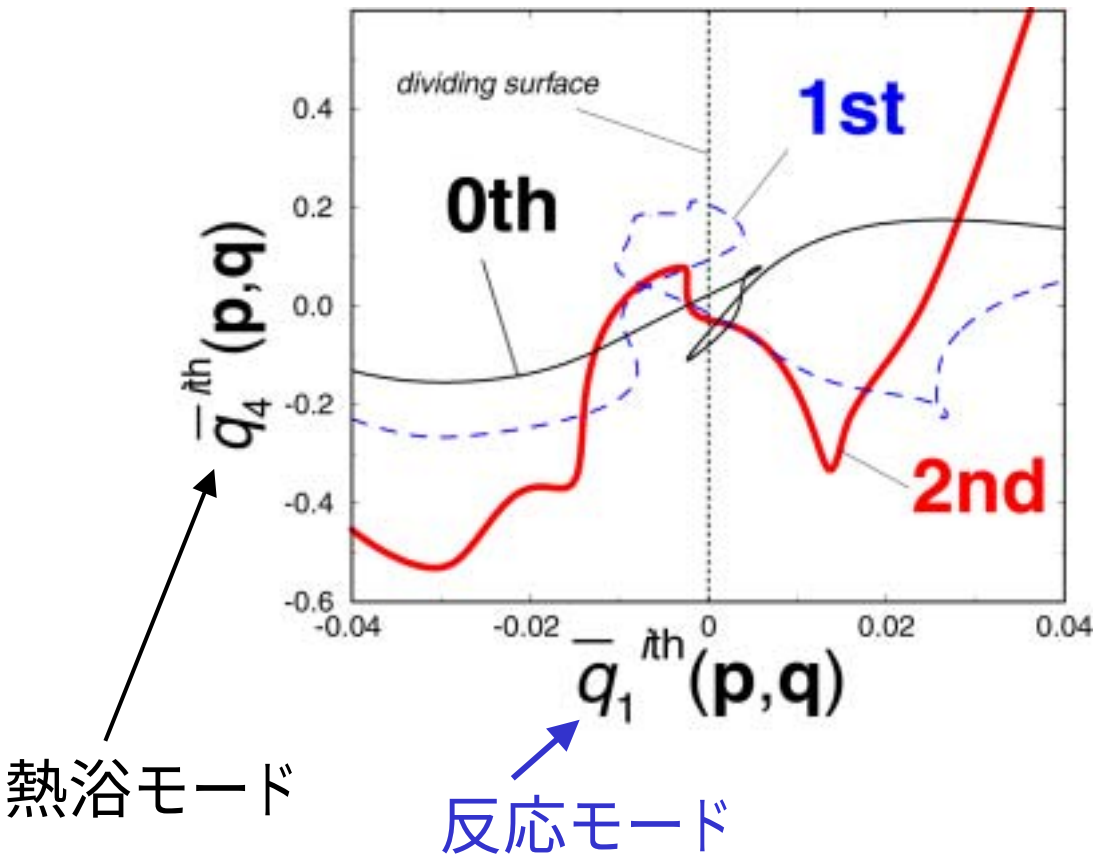




相空間上の反応座標1に沿った、作用変数 $(\bar{J}_1)_i(\mathbf{p}(t),\mathbf{q}(t))$ だけは、鞍部領域において近似的に保存している

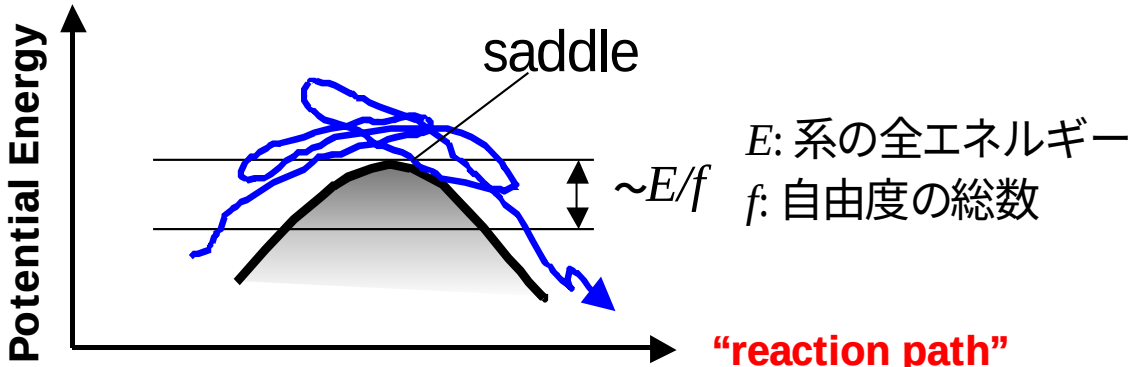
$$\frac{d^2\bar{q}_1(\mathbf{p},\mathbf{q})}{dt^2}+\bar{\omega}_1{}^2\bar{q}_1(\mathbf{p},\mathbf{q})\approx 0$$

前述の軌道を配位平面q_k-q_jおよび相平面へまとめて投影してみよう　(E=0.5ε, Saddle I)



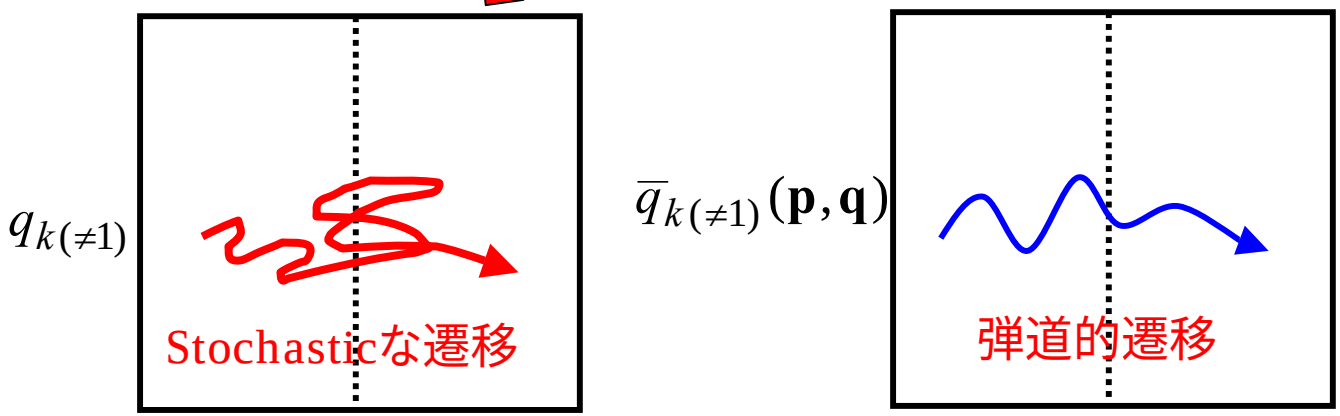
配位空間上に定義した“遷移状態”は再交差しているが、相空間上の遷移状態は1回交差であり、相空間上の反応座標に沿った軌道も弾道的である

再交差運動の動的描像（確率過程的か弾道的か）が視点に依存する！



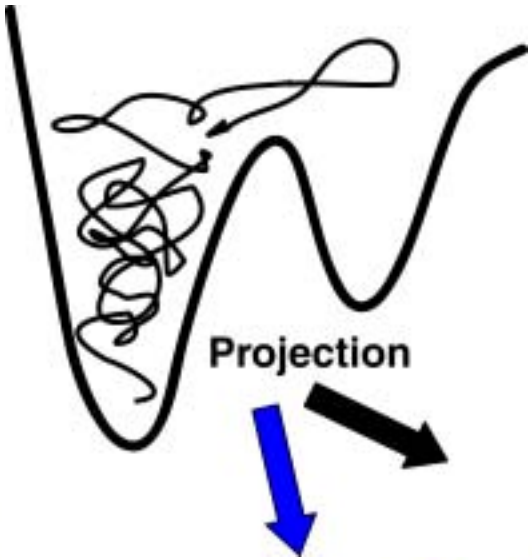
投影

もし$\bar{q}_F(\mathbf{p},\mathbf{q})$に関する作用が系の終状態を決定するのに十分長時間保存する場合

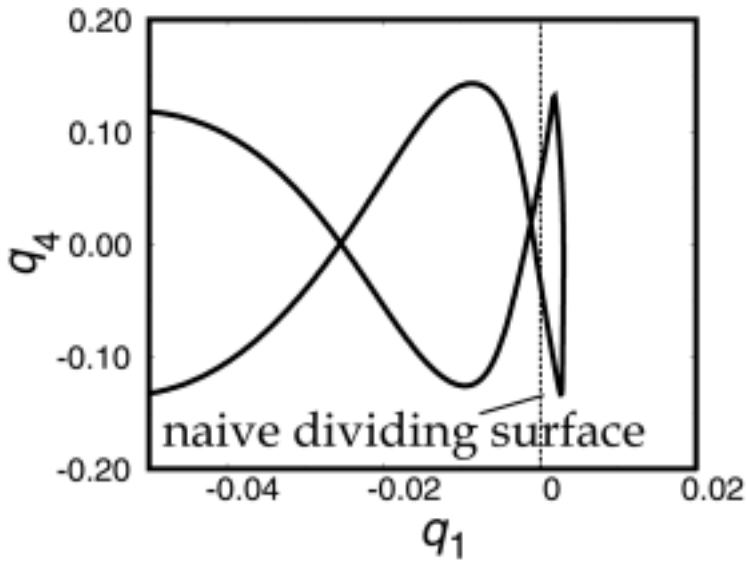


配位空間描像　　相空間描像

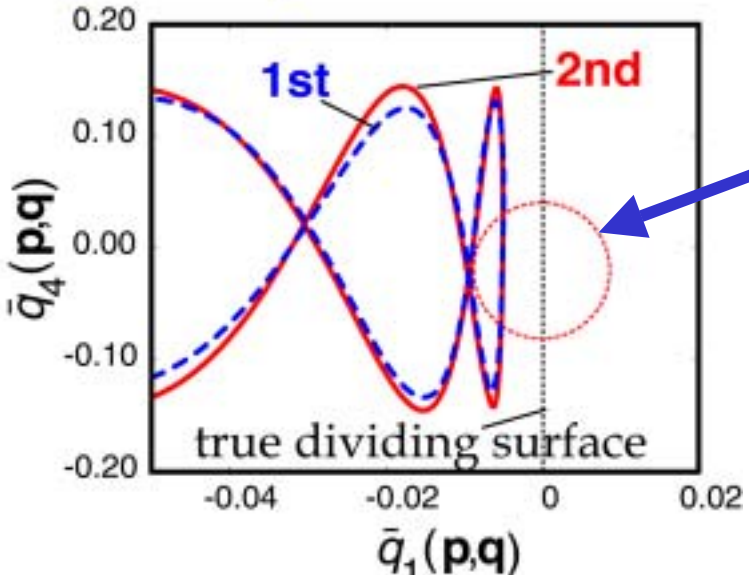
なぜ系は活性化障壁を越え得るのか？



Onto the normal coordinates



Onto the phase space coordinates



系は遷移状態領域に侵入する際に、
相空間上の反応方向の入射運動量が

$$\overline{p}_1\left(\mathbf{p}(0),\mathbf{q}(0)\right) \geq \left|\overline{\omega}_1\right| \overline{q}_1\left(\mathbf{p}(0),\mathbf{q}(0)\right)$$

の条件を満たす場合に反応が生起する

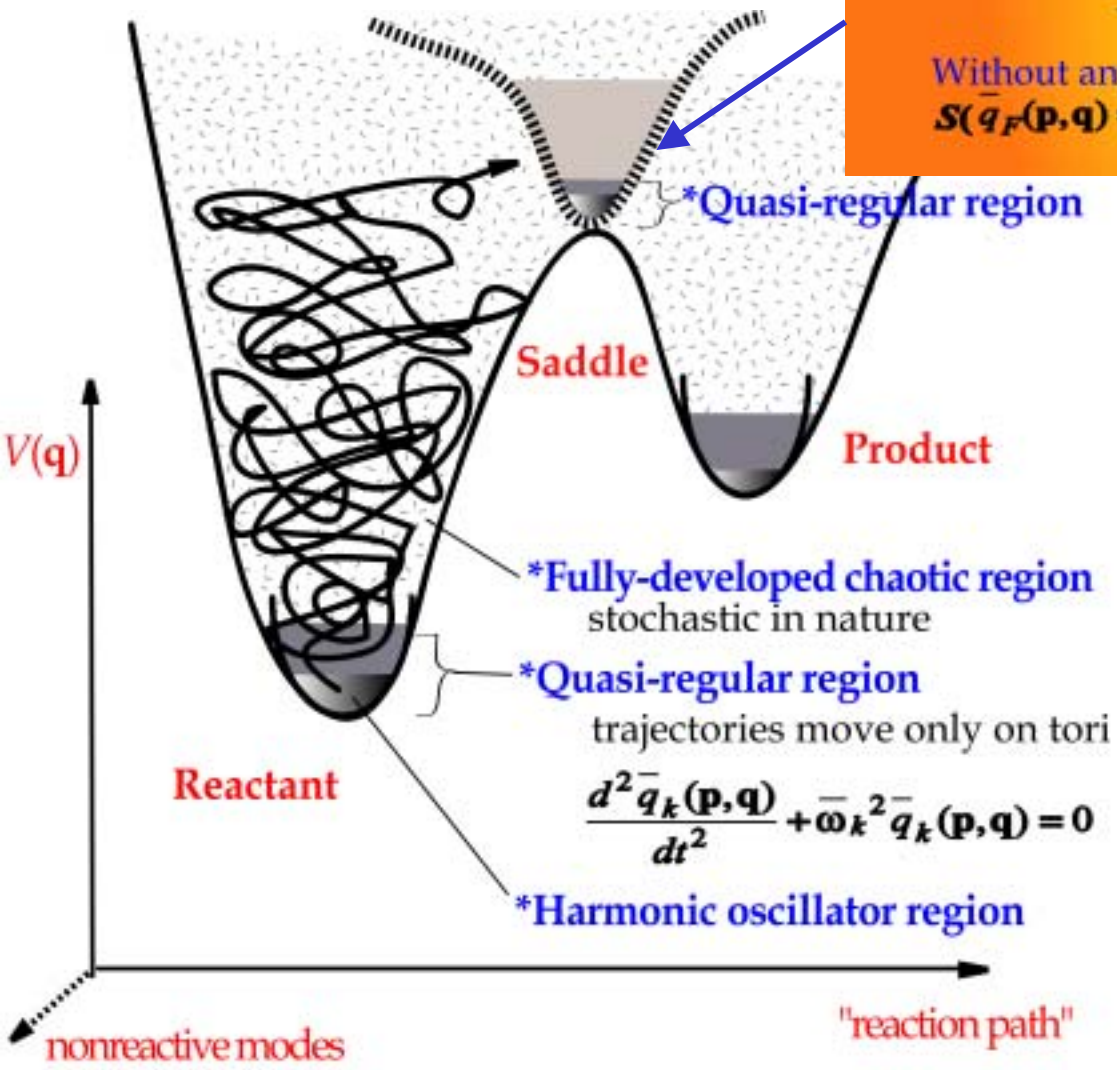
サドル領域の階層的規則性

***Semi-chaotic region**

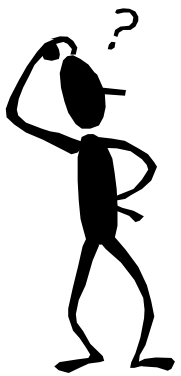
almost of all nonreactive modes are chaotic,
but the reactive mode is still regular.

$$\frac{d^2\bar{q}_F(\mathbf{p},\mathbf{q})}{dt^2} + \bar{\omega}_F{}^2\bar{q}_F(\mathbf{p},\mathbf{q}) = 0$$

Without any artifact, a no-return dividing surface
$S(\bar{q}_F(\mathbf{p},\mathbf{q}) = 0)$ exists!



なぜ高次元カオスを呈する高エネルギー領域に至るまで、相空間上の反応方向の作用だけは鞍部領域において保存するのか？



小さい分母の問題

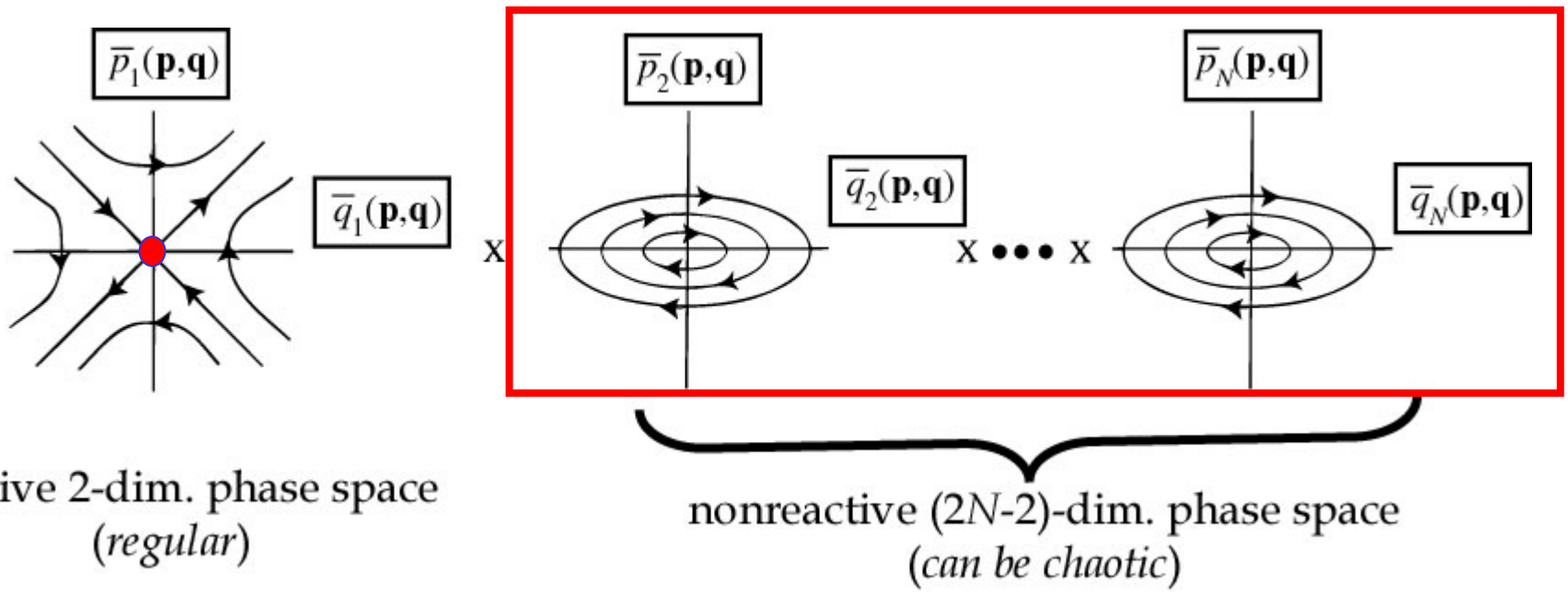
$$\left|\sum_{k=1}^{M} n_k \omega_k\right| = \left|-n_1|\omega_1| i + \sum_{k=2}^{M} n_k \omega_k\right| \geq |\omega_1| > 0$$

$$\omega_1 \in \Im \quad \omega_k \in \Re$$

は反応性の双曲型モードを包含する場合は出現し得ない

最初に指摘した論文：R. Hernandez & W.H. Miller, *Chem. Phys. Lett.* **214**, 129(1993)
最初に利用した論文：T. Komatsuzaki & M. Nagaoka, *J. Chem. Phys.* **105**, 10838(1996)
数学的な記述：
S. Wiggins, L. Wiesenfeld, C. Jaffe & T. Uzer, *Phys. Rev. Lett.* **86**, 5478(2001)
T. Uzer, C. Jaffe, J. Palacian, P. Yanguas & S. Wiggins, *Nonlinearity* **15**,957(2002)
T. Komatsuzaki & R. S. Berry, *Adv. Chem. Phys.* **123**, 79-152 (2002)

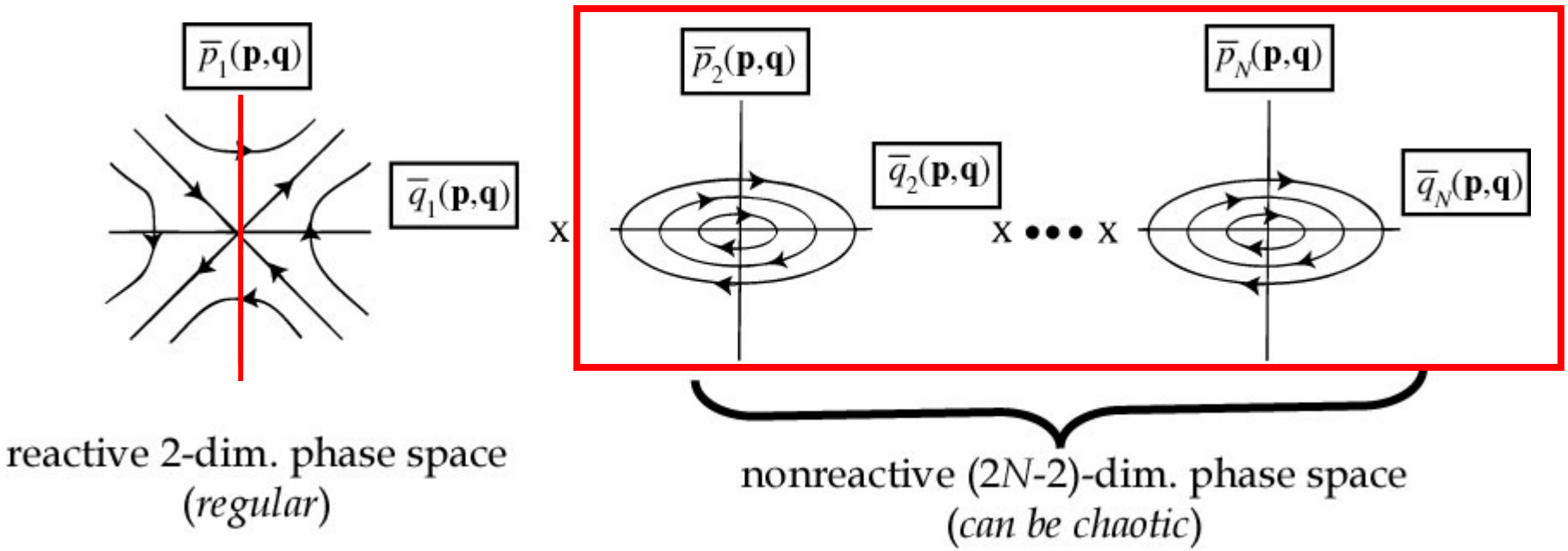
NHIM:= (2N-3) dim. Invariant manifold



$$M_E^{2N-3} = \left\{(q_1,\cdots,q_N,\ldots,p_1,\ldots p_N)\middle|\,\overline{p}_1(\mathbf{p},\mathbf{q}) = \overline{q}_1(\mathbf{p},\mathbf{q}) = 0; E\right\}$$

Our Definition of Phase Space TS

T.Komatsuzaki & R.S. Berry, *J. Chem. Phys.* **110**,9160 (1999)



(2*N*-2)-dim. manifold $\left\{(\mathbf{p},\mathbf{q})\middle|\overline{q}_1(\mathbf{p},\mathbf{q})=0;E\right\}$

not-invariant

Statistical Theory of Asteroid Escape Rates

Charles Jaffé,[1,2,3] Shane D. Ross,[1,2] Martin W. Lo,[1,2] Jerrold Marsden,[1] David Farrelly,[4] and T. Uzer[1,5]

[1]*Control and Dynamical Systems Division 107-81, California Institute of Technology, Pasadena, California 91125*

[2]*Navigation and Flight Mechanics, Jet Propulsion Laboratory, Pasadena, California 91109-8099*

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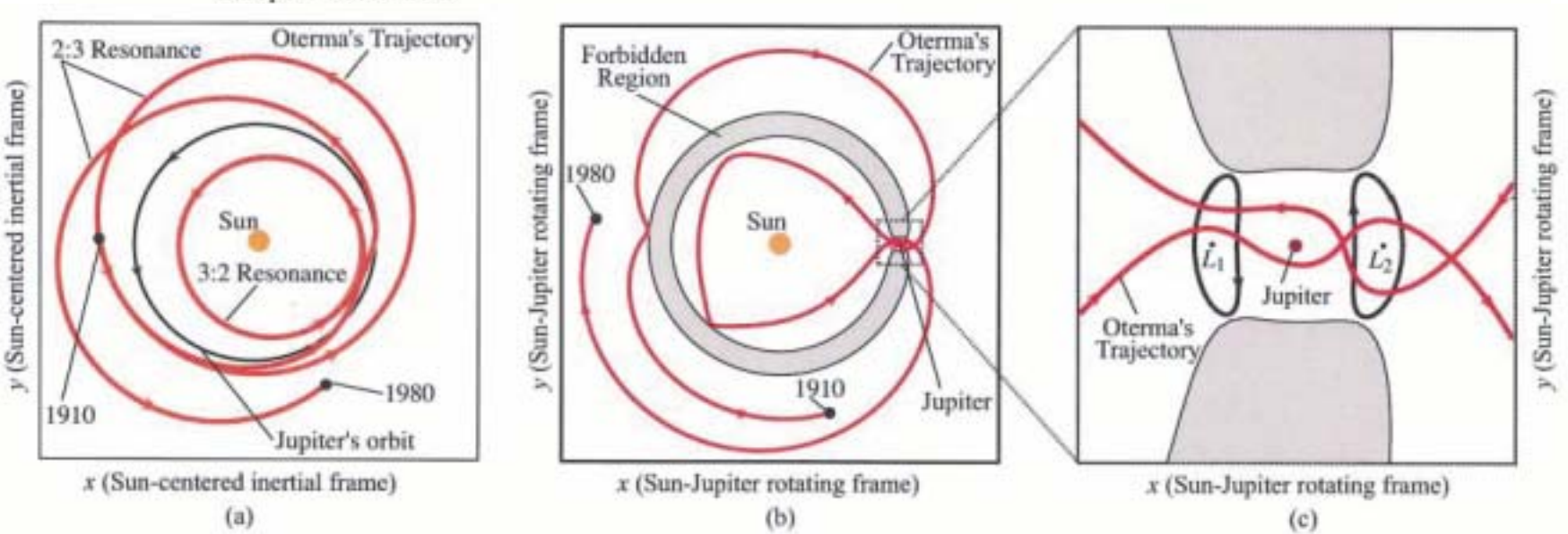
Transition states in phase space are identified and shown to regulate the rate of escape of asteroids temporarily captured in circumplanetary orbits. The transition states, similar to those occurring in chemical reaction dynamics, are then used to develop a statistical semianalytical theory for the rate of escape of asteroids temporarily captured by Mars. Theory and numerical simulations are found to agree to better than 1%. These calculations suggest that further development of transition state theory in celestial mechanics, as an alternative to large-scale numerical simulations, will be a fruitful approach to mass transport calculations.



Phys. Rev. Lett. **89**,11101 (2002)

A S_N2 Reaction That Avoids Its Deep Potential Energy Minimum

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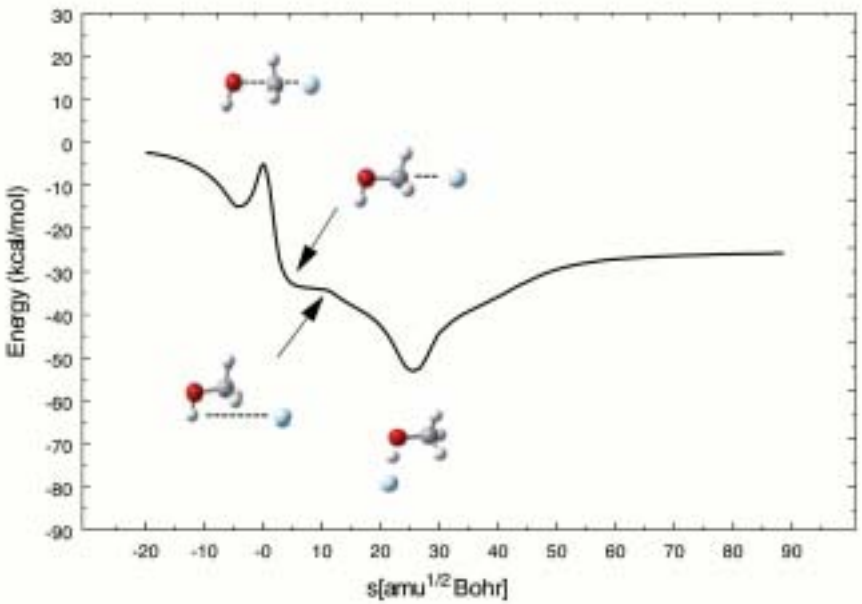
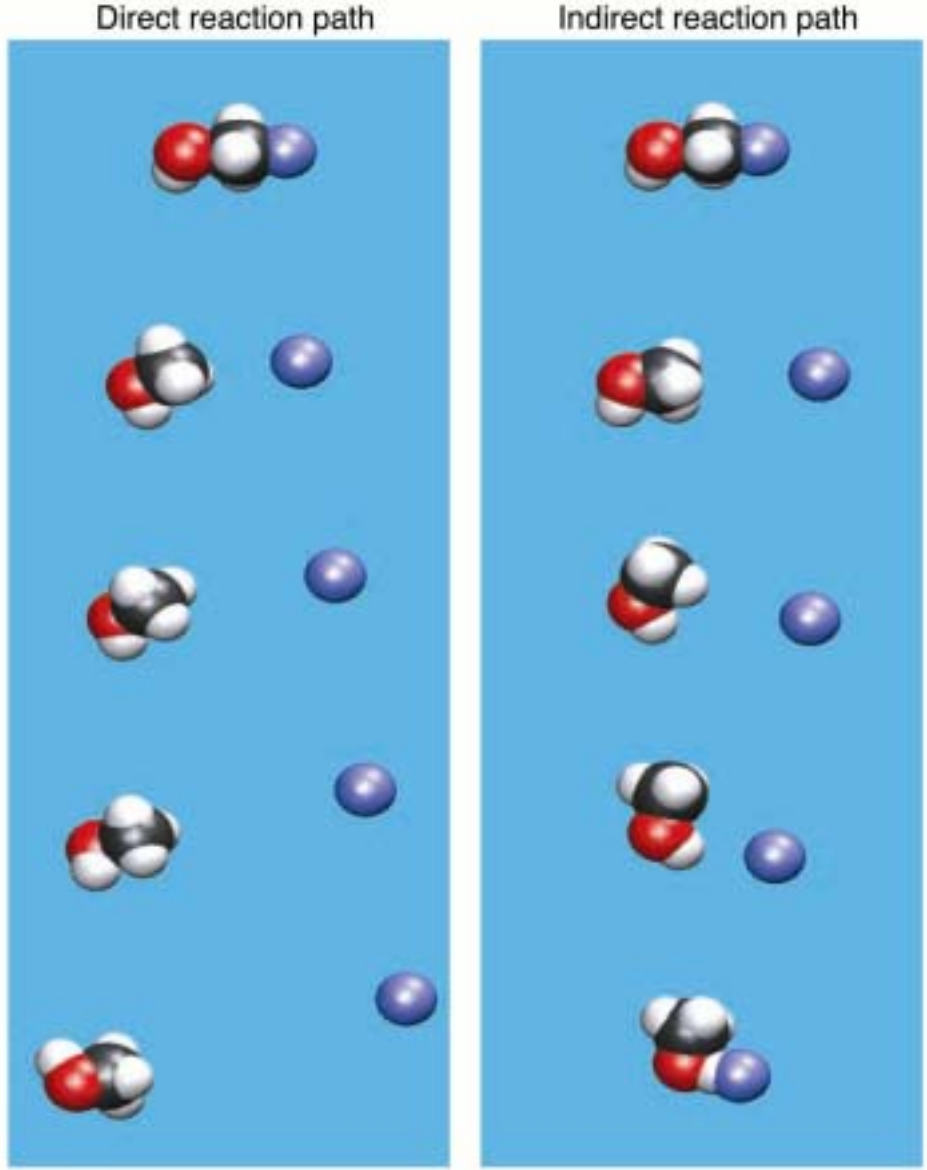
Chemical dynamics trajectory simulations were used to study the atomic-level mechanisms of the $OH^- + CH_3F \rightarrow CH_3OH + F^-$ S_N2 nucleophilic substitution reaction. The reaction dynamics, from the $[OH\cdots CH_3\cdots F]^-$ central barrier to the reaction products, are simulated by ab initio direct dynamics. The reaction's potential energy surface has a deep minimum in the product exit channel arising from the $CH_3OH\cdots F^-$ hydrogen-bonded complex. Statistical theories of unimolecular reaction rates assume that the reactive system becomes trapped in this minimum and forms an intermediate, with random redistribution of its vibrational energy, but the majority of the trajectories (90%) avoided this potential energy minimum and instead dissociated directly to products. This finding is discussed in terms of intramolecular vibrational energy redistribution (IVR) and the relation between IVR and molecular structure. The finding of this study may be applicable to other reactive systems where there is a hierarchy of time scales for intramolecular motions and thus inefficient IVR.





Science **296**,875(2002)

Chemistry of cyano-polyenes

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FORMATION OF NITRILES IN THE INTERSTELLAR MEDIUM VIA REACTIONS OF CYANO RADICALS, CN($X\,^2\Sigma^+$), WITH UNSATURATED HYDROCARBONS

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$$\mathrm{CN}(X\,^2\Sigma^+) + \mathrm{C_2H_2}(X\,^1\Sigma_g^+) \rightarrow \mathrm{HCCCN}(X\,^1\Sigma^+) + \mathrm{H}(^2S_{1/2}), \quad (5)$$

$$\mathrm{CN}(X\,^2\Sigma^+) + \mathrm{C_2H_4}(X\,^1A_g) \rightarrow \mathrm{C_2H_3CN}(X\,^1A') + \mathrm{H}(^2S_{1/2}). \quad (6)$$

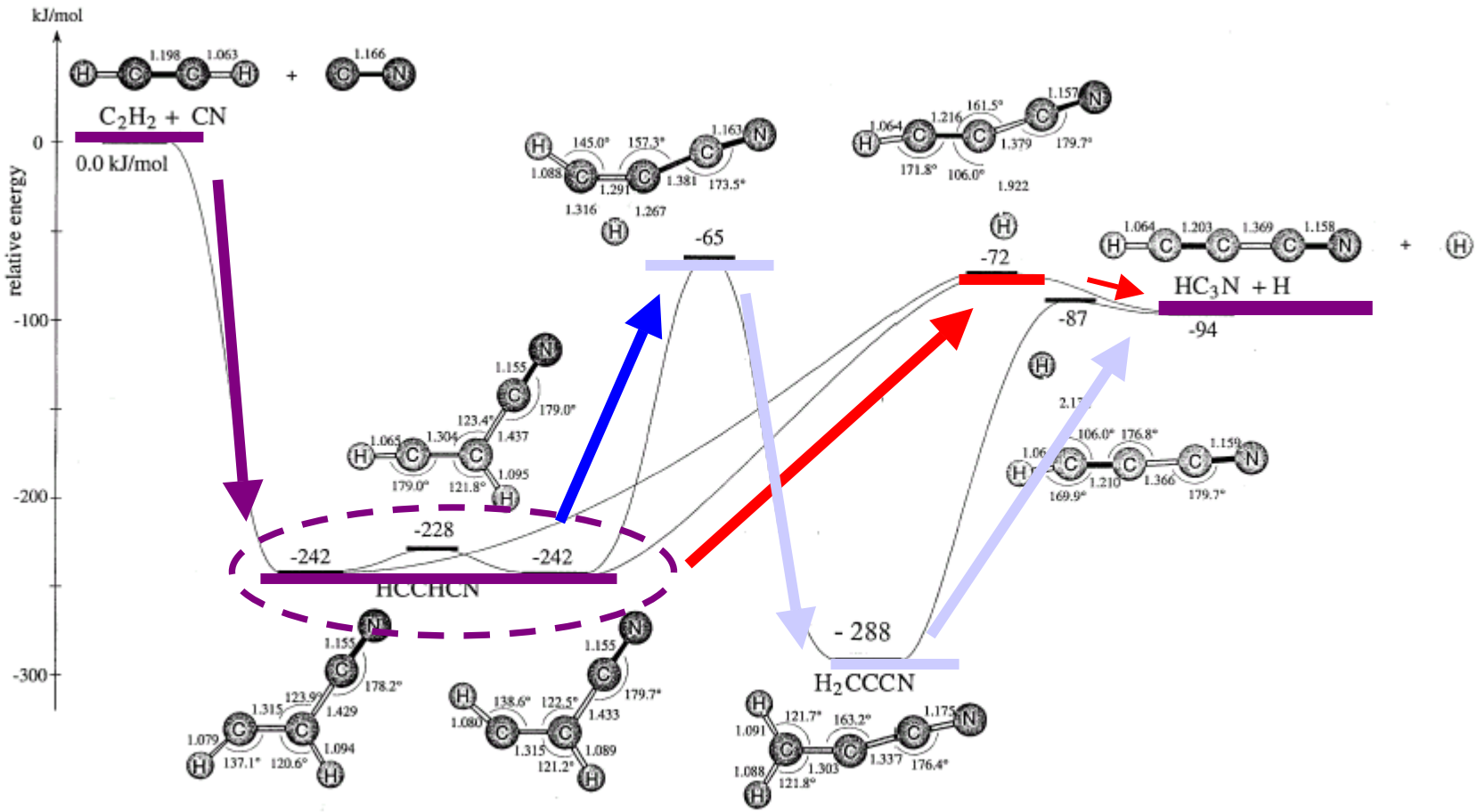
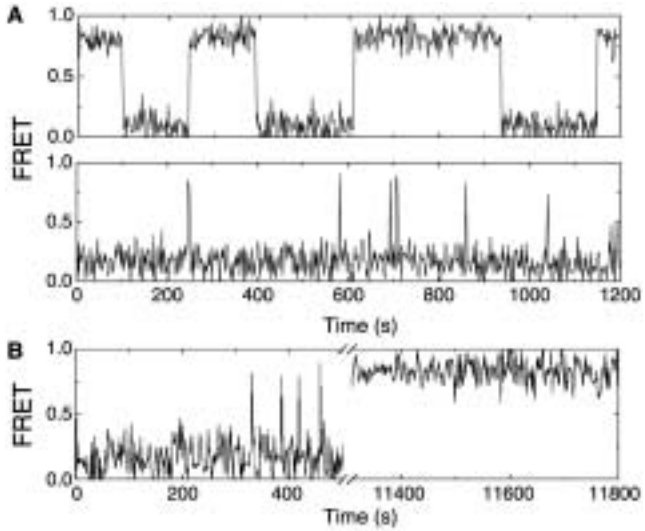


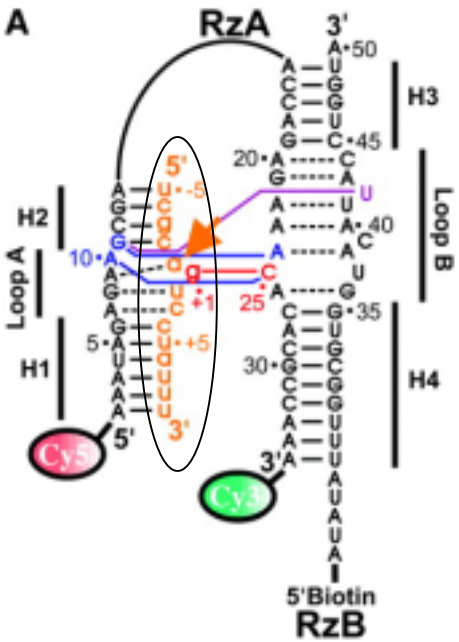
FIG. 1.—Schematic representation of the C_3H_2N potential energy surface relevant in the CN + C_2H_2 reaction. Adapted from Huang et al. (2000). Important bond distances are given in angstrom units and bond angles in degrees.

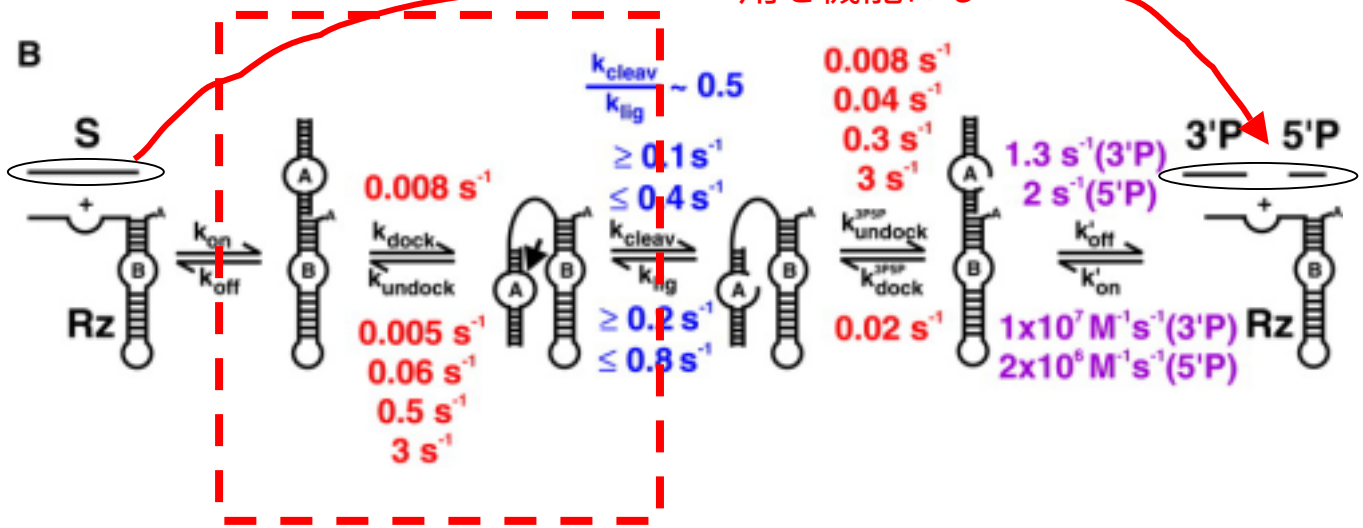
蛋白質フォールデングを始めとする
生体高分子系の構造転移の長時間記憶の解明



リボザイムのdocked state-undocked state間遷移に観測される長時間分子記憶 Zhuang, Kim, Pereira, Babcock,Walter & Steven Chu *Science* **296** 1473(2002)

他のリボザイムを分解する触媒作用を機能にもつ

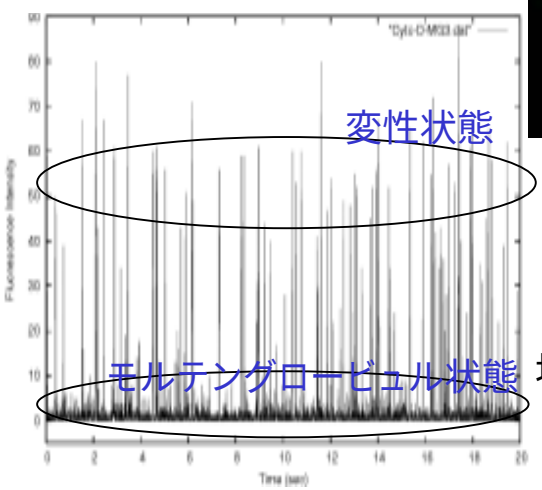




力学系理論に基づく時系列解析理論

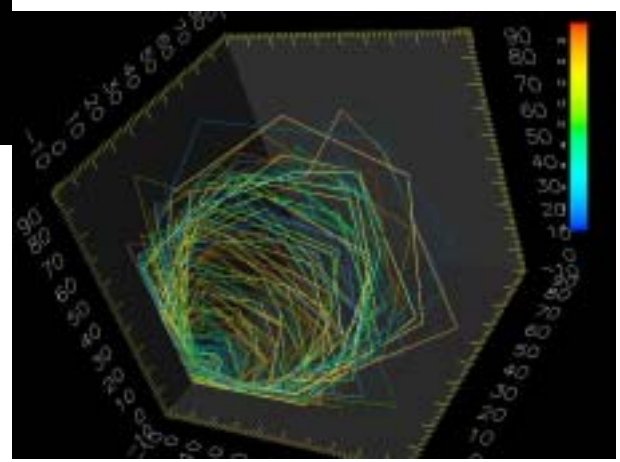
- 一見ランダムに見れる時系列データから集団自由度の動力学的特性を摘出･解析する方法･概念の建設
- 集団的カオスの形成、集団自由度の組替えのメカニズムの検出

シトクロムcの1分子計測時系列



埋め込み解析による
状態空間の構成

3次元遅延座標系への投影図



シトクロムcのFRETの時系列情報から再構成された状態空間の動的構造
Komatsuzaki、Ishii *et al*, 未発表

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Chaos-assisted capture of irregular moons

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It has been thought[1–3] that the capture of irregular moons—with non-circular orbits—by giant planets occurs by a process in which they are first temporarily trapped by gravity inside the planet's Hill sphere (the region where planetary gravity dominates over solar tides[4]). The capture of the moons is then made permanent by dissipative energy loss (for example, gas drag[3]) or planetary growth[2]. But the observed distributions of orbital inclinations, which now include numerous newly discovered moons[5–8], cannot be explained using current models. Here we show that irregular satellites are captured in a thin spatial region where orbits are chaotic[9], and that the resulting orbit is either prograde or retrograde depending on the initial energy. Dissipation then switches these long-lived chaotic orbits[10] into nearby regular (non-chaotic) zones from which escape is impossible. The chaotic layer therefore dictates the final inclinations of the captured moons. We confirm this with three-dimensional Monte Carlo simulations that include nebular drag[3,4,11], and find good agreement with the observed inclination distributions of irregular moons at Jupiter[7] and Saturn[8]. In particular, Saturn has more prograde irregular moons than Jupiter, which we can explain as a result of the chaotic prograde progenitors being more efficiently swept away from Jupiter by its galilean moons.

Figure 1a and b shows surfaces of zero velocity[4] at two energies for the 3D Sun–Jupiter system, together with the Hill sphere. Surfaces of zero velocity limit the motion in the rotating frame, and so serve to define an energetically accessible 'bubble' that may intersect the Hill sphere[4]. At both energies in Fig. 1, the two Lagrange saddle points, L_1 and L_2, are 'open', and act as gateways between the interior energy bubble and heliocentric orbits[2,4]. Figure 1c and d shows orbital inclination distributions[4], $i = \cos^{-1}(h_z/|\mathbf{h}|)$, of test particles as they pass through the Hill sphere at the same two energies (see Methods). The key finding is that at energies slightly above the Lagrange points, only prograde orbits can enter (or leave) the capture zone. At higher capture energies, the distribution shifts to include both senses of h_z. The statistics of inclination distributions will, therefore, be expected to depend strongly on energy, that is, the geometry of how (and if) the curves of zero velocity intersect the Hill sphere.

Figure 2 portrays the structure of phase space in the planar limit ($z = p_z = 0$) in a series of Poincaré surfaces of section[9] (SOS) at four energies. At the lowest energy (Fig. 2a), many of the prograde orbits are chaotic, whereas all the retrograde orbits are regular[9]. Because incoming orbits cannot penetrate the regular Kolmogorov–Arnold–Moser (KAM) regions[9], prograde orbits must remain prograde. Although KAM tori in 3D cannot 'block' trajectories in this manner, orbits can only enter nearly integrable volumes of phase space by Arnold diffusion, which, by the Nekhoroshev theorem, is expected to occur exponentially slowly[9,10]. In essence, the chaotic layer selects for the sense of the angular momentum of incoming and outgoing particles.

After L_2 has opened up (Fig. 2b), the chaotic 'sea' of prograde orbits quickly 'evaporates', except for a thin, advancing front of chaos which clings to the KAM tori, buffering them from the expanding basin of direct scattering. With increasing energy, this