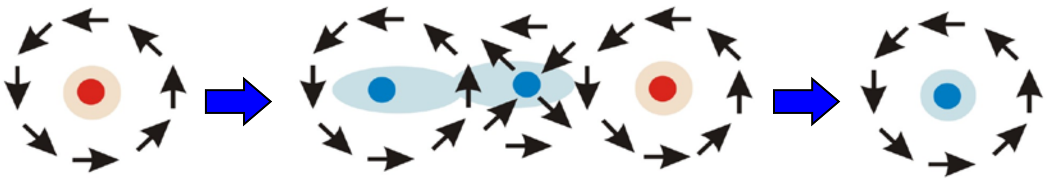
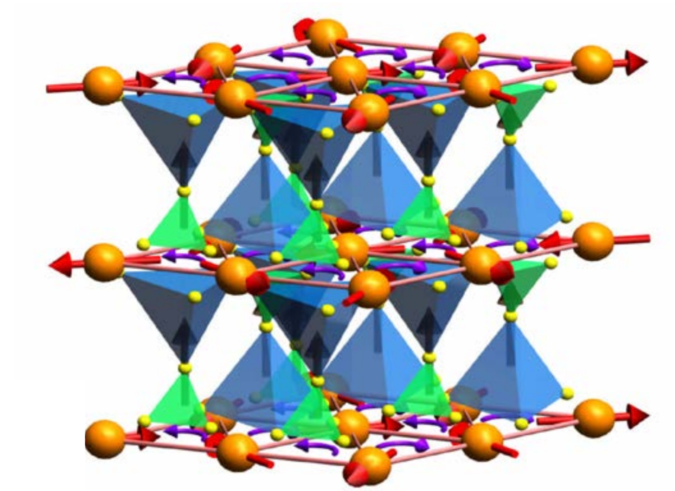
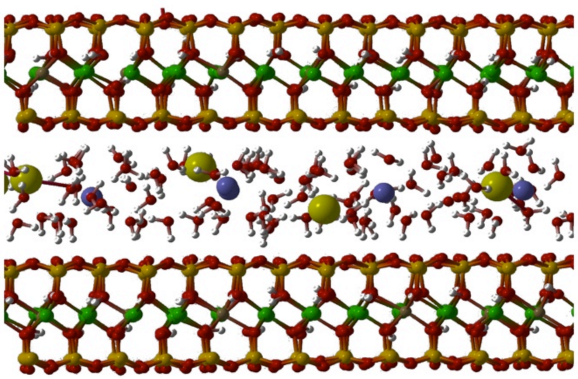
Time and Length Scales in Condensed Matter

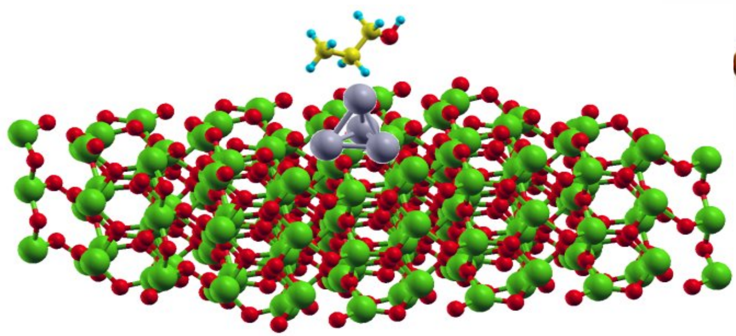
Bruce Patterson
PSI, SwissFEL

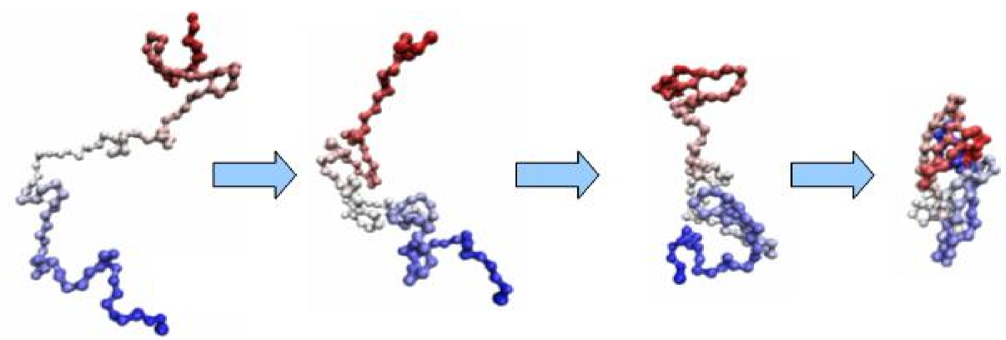
The dance of the atoms

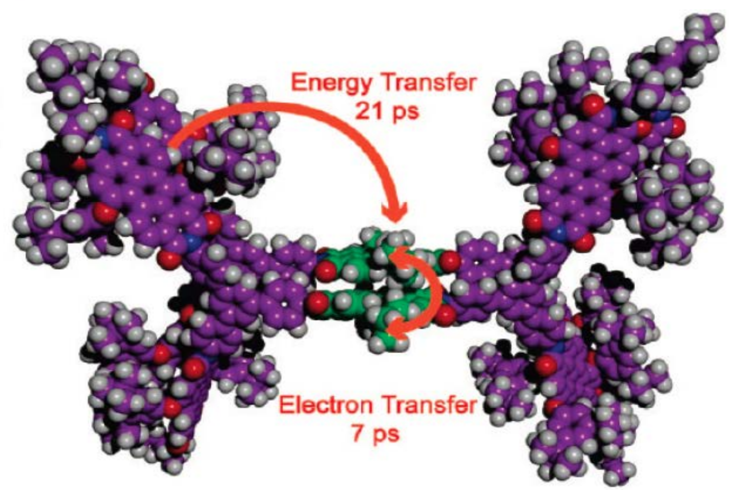












The scientific number system

- Yotta 1‘000‘000‘000‘000‘000‘000‘000‘000 10^{24}
- Zetta 1‘000‘000‘000‘000‘000‘000‘000 10^{21}
- Exa 1‘000‘000‘000‘000‘000‘000 10^{18}
- Peta 1‘000‘000‘000‘000‘000 10^{15}
- Tera 1‘000‘000‘000‘000 10^{12}
- Giga 1‘000‘000‘000 10^{9}
- Mega 1‘000‘000 10^{6}
- kilo 1‘000 10^{3}
- one 1 10^{0}
- milli 0.001 10^{-3}
- micro 0.000‘001 10^{-6}
- nano 0.000‘000‘001 10^{-9}
- pico 0.000‘000‘000‘001 10^{-12}
- femto 0.000‘000‘000‘000‘001 10^{-15}
- atto 0.000‘000‘000‘000‘000‘001 10^{-18}
- zepto 0.000‘000‘000‘000‘000‘000‘001 10^{-21}
- yocto 0.000‘000‘000‘000‘000‘000‘000‘001 10^{-24}

powers of 10

$A = 10^{a}$; $B = 10^{b}$

$A \times B = 10^{(a+b)}$

$A/B = 10^{(a-b)}$

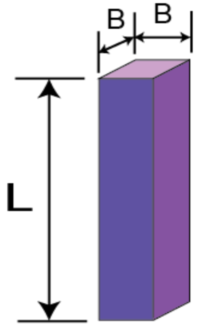
$\sqrt{A} = 10^{(a/2)}$

How big is an atom?

Iron bar:

$L = 30$ cm, $B = 2$ cm $\rightarrow V = 10^{-4}$ m^3

$M = 1$ kg



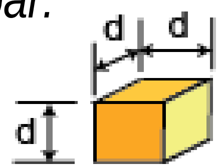
Iron atom:

26 protons + 26 electrons + 30 neutrons

$\rightarrow m = 10^{-25}$ kg

number of atoms in the bar:

$N = M/m = 10^{25}$



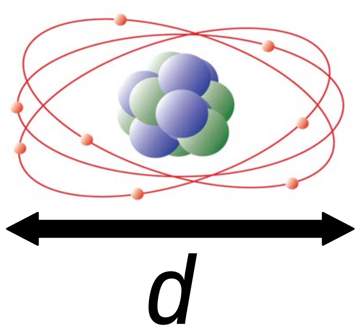
volume per atom:

$v = V/N = 10^{-29}$ m^3 = d x d x d

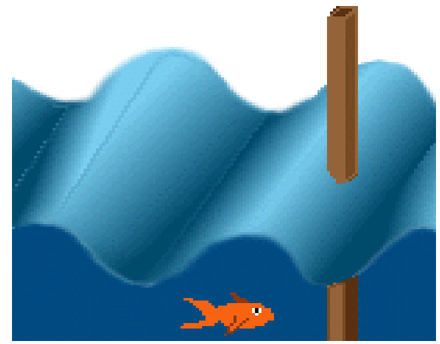
atomic size d:

$d = v^{1/3} = 2 \times 10^{-10}$ m

d = 0.2 nm (nanometer)

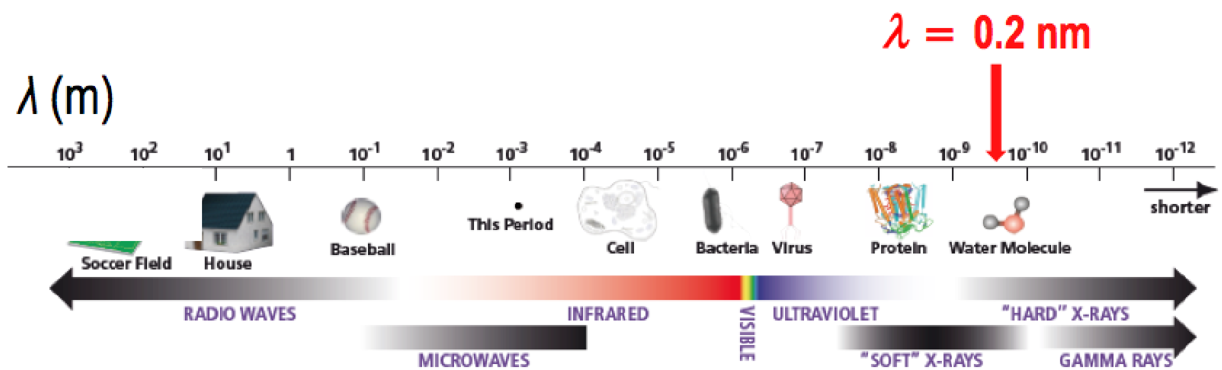


How can we see atoms?



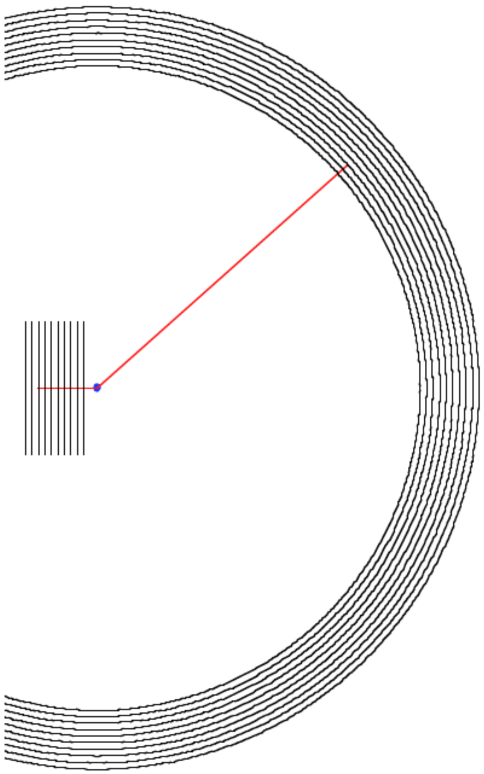
Long waves not influenced by thin rod.

$\rightarrow \lambda \leq d$

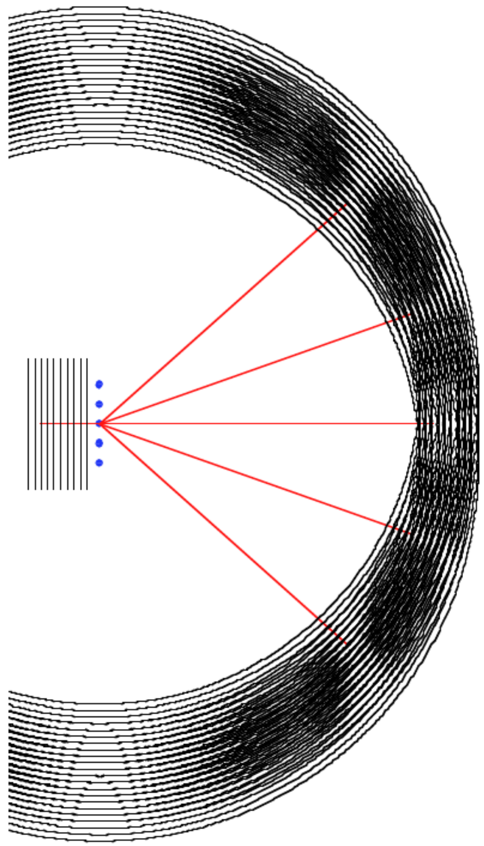


$\rightarrow$ *X-rays*

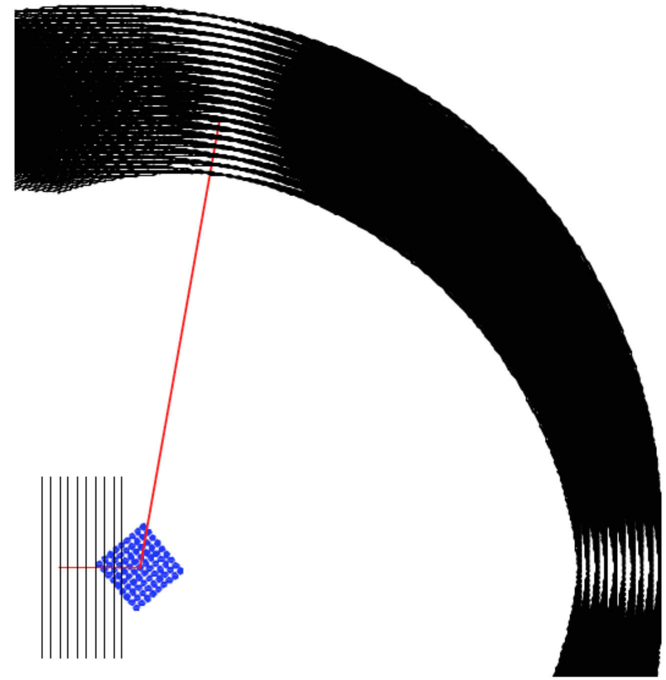
Aside: "seeing" atoms with diffraction



1 atom



5 x 1 atoms



9 x 9 atoms

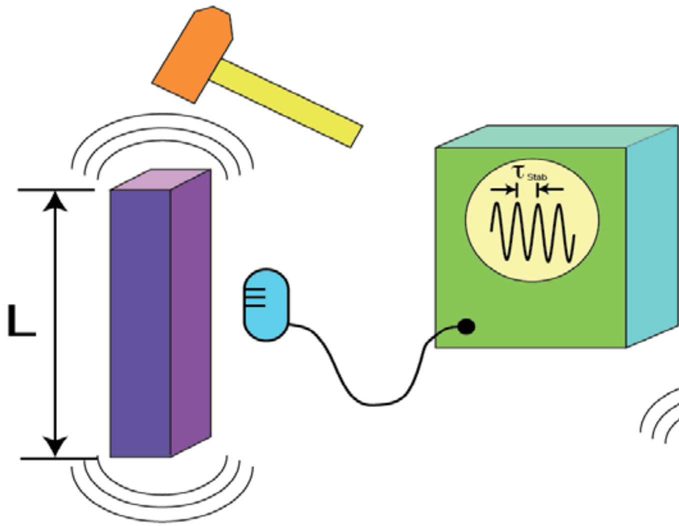
Bragg's Law (1912):
$\lambda = 2d \sin\theta$

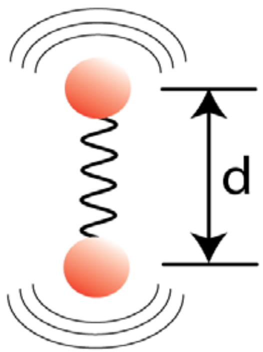
Note: $\lambda < 2d$

How fast do atoms move?

Oscillation period of the bar:

τ_{bar} = 0.12 ms (proportional to L)





L = 0.3 m   d = 0.2 nm

Oscillation period of a molecule:

$\tau_{molecule} = \tau_{bar} \times d/L = 8 \times 10^{-14}$ s

$\tau_{molecule}$ = 80 fs (femtoseconds)

We want to freeze the motion.

➡ *X-ray pulse length < 20 fs*

$$\frac{1}{\tau_{bar}} = \frac{v_{sound}}{2L} = \frac{5000\ \mathrm{m/s}}{2 \times 0.3\ \mathrm{m}}$$

Fermi energy and Schrödinger pressure

Free-electron gas (Sommerfeld 1927)

Density of states (in 3d):

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

Fermi energy:

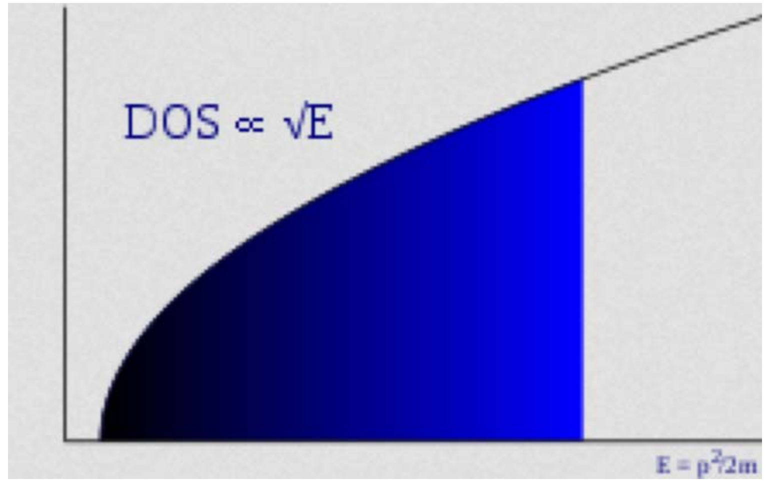
$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Total energy:

$$E_{tot} = \int_0^{E_F} E\, D(E)\, dE = \frac{3}{5} N E_F$$

Schrödinger pressure:

$$P_S = -\frac{dE_{tot}}{dV} = \frac{2}{5}\frac{N}{V}E_F$$



Copper:

$$\frac{N}{V} = 8.5 \times 10^{28}\ \mathrm{m}^{-3}$$

$$E_F = 7.0\ \mathrm{eV}$$

$$P_S = 38\ \mathrm{GPa}$$

Electron and atom velocities

$$v_{electron} \approx v_{Fermi} = \sqrt{\frac{2E_F}{m}}$$

$$v_{atom} \approx v_{sound} = \sqrt{\frac{K}{\rho_M}} \approx \sqrt{\frac{P_S}{\rho_M}}$$

Copper: $\frac{N}{V} = 8.5 \times 10^{28}\ \mathrm{m}^{-3}$

$E_F = 7.0\ \mathrm{eV}$

$\Rightarrow v_{electron} = 1.6 \times 10^{6}\ \mathrm{m/s}$

$P_S = 38\ \mathrm{GPa}$

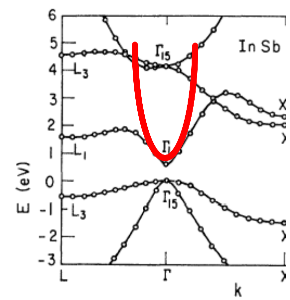
$\rho_M = 9.0 \times 10^{3}\ \mathrm{kg\ m}^{-3}$

$\Rightarrow v_{atom} \approx 2100\ \mathrm{m/s}\ \left(\exp:\ v_{sound} = 4600\ \mathrm{m/s} \approx 5\ \mathrm{nm/ps}\right)$

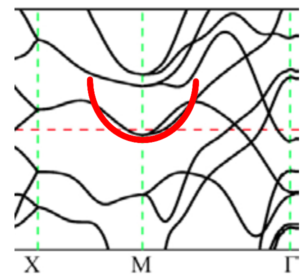
Born-Oppenheimer approximation

Note: Effective electron mass determined by band structure:

$$m^* \equiv \hbar^2 \left(\frac{\partial^2 E_k}{\partial k^2} \right)^{-1}$$



InSb: m*/m=0.014



URu_2Si_2: m*/m≈100

Talk overview

1. Introduction
2. Background concepts
3. Examples of time and length scales
4. Fluctuations
5. Our most critical time scale
6. A biology movie

2. Some background concepts ...

Pump-probe experiment:

How fast do we leave and regain equilibrium?

Out-of-equilibrium dynamics of classical and quantum complex systems

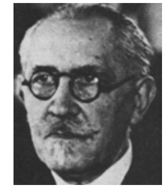
Dynamique hors équilibre de systèmes complexes classiques et quantiques

Leticia F. Cugliandolo

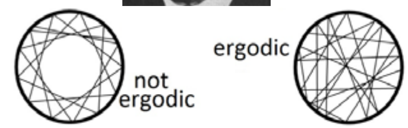
LF Cugliandolo, CR Physique (2013)

Equilibrium dynamics

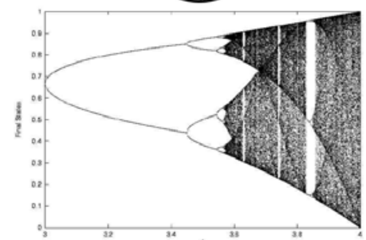
- ***Conservative dynamical system***
  - classical variables (e.g., $\vec{r}_i, \vec{p}_i$) follow deterministic trajectories in phase space.
- ***Grand-canonical ensemble***
  - subsystem interacts with fluctuating bath (Langevin dynamics)
  - exchange of energy and particles

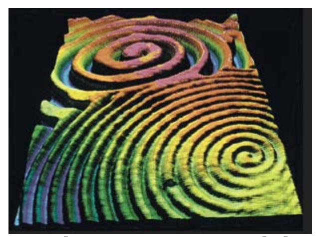


- ***Ergodic hypothesis***
  - all accessible states populated with equal probability

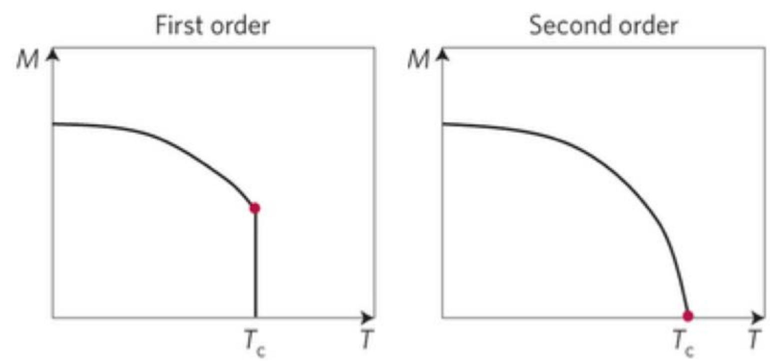


- ***Deterministic chaos***
  - system with non-linear interactions
  - sustained erratic behavior
  - sensitive to initial conditions



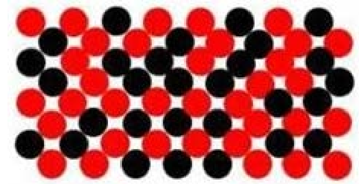


- ***Coherent collective behavior***
  - resulting from strong interactions
  - spatio-temporal patterns
- ***Bifurcation point***
  - qualitative change in trajectories (e.g., phase transitions: order parameter M zero ➔non-zero)
  - first-order (e.g., boiling H_2O)
    - $M(T)$ jumps discontinuously
    - phase coexistence
    - $\frac{\partial G}{\partial T} \to \infty$
  - second-order (e.g., Curie temperature)
    - $M(T)$ continuous
    - $\frac{\partial^2 G}{\partial T^2} \to \infty$
    - spontaneous symmetry breaking

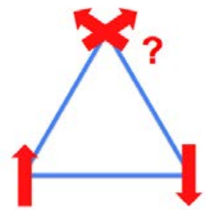


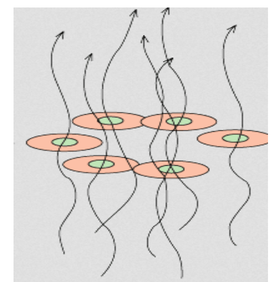
Disorder

- ***Disordered impurities / defects***
  - *quenched*: slower relaxation for impurities than host
  - *annealed*: similar relaxation times for impurities and host
  - *weak quenched disorder*
    - phases unchanged
    - changed dynamics near phase transition (critical exponents)
    - some discontinuities smoothed out



- ***Strong disorder*** (e.g., spin-glasses)
  - competing interactions cause *frustration*



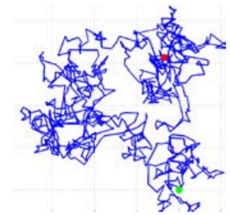


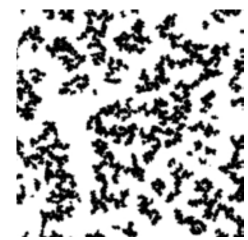
- ***Structural glasses***
  - e.g., granular media (jamming), colloidal suspensions, quickly-cooled silica or polymer melts, type-II SC vortices
  - more later ...

Non-equilibrium dynamics

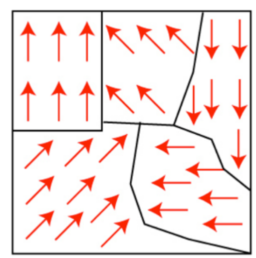
$$\mathbf{J}_{\alpha} = \sum_{\beta} L_{\alpha\beta} \nabla f_{\beta}$$

- *Close to equilibrium*
  - ***Onsager theory***: – linear relation between extensive currents (energy, mass) and intensive gradients (temperature, pressure)
- *Far from equilibrium*
  - ***Brownian motion***: equilibrated velocity, but not position
  - ***interface dynamics***: (crack propagation, fluid invasion of porous media, aggregation, crystal growth)
    - initially thin interface (thermal effects dominate) *roughens* to a thick interface (structural disorder dominates)
    - ageing, memory, avalanches, stochastic creep
  - near phase transition (**critical dynamics**)
    - correlation length diverges (fractal clusters)
    - relaxation time diverges (critical slowing down)



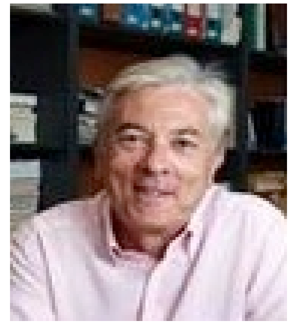


- *Across a phase transition*
  - **first-order**
    - nucleation of *bubbles* of stable phase, which grow at thermally-activated rate
  - **second-order** (symmetry breaking)
    - *domain* patchwork of different symmetries
    - evolution of *self-similar* structures

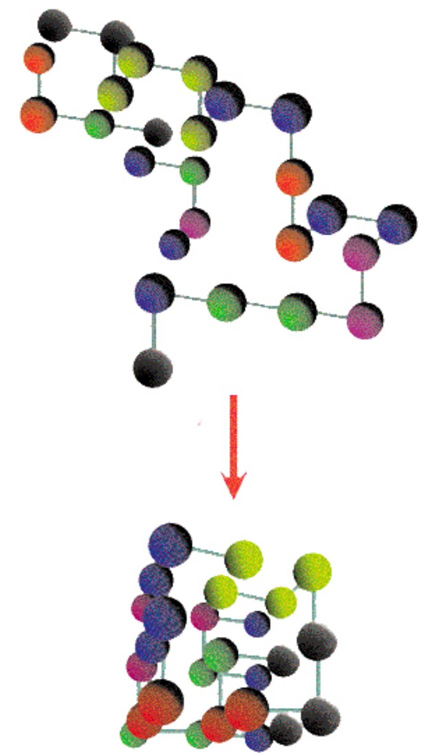


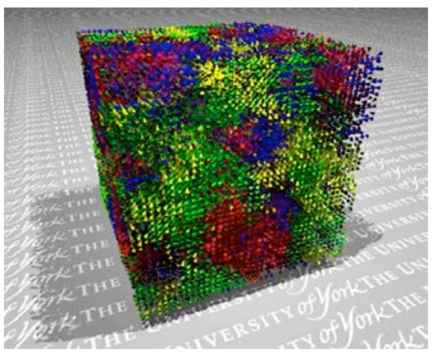
Entropic barriers

- ***Mesoscale Non-equilibrium Thermodynamics (MNET)***
  - extends non-equilibrium thermodynamics (Onsager) to molecular level
  - inherently non-linear interactions
  - small fluctuations play a big role
  - analyze:
    - nucleation and growth
    - active biological transport
    - ...
  - treat ***entropic barriers***

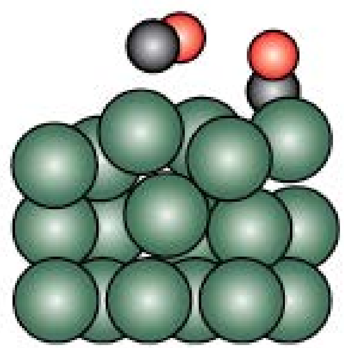


JM Rubi, Energy (2007)





re-magnetization



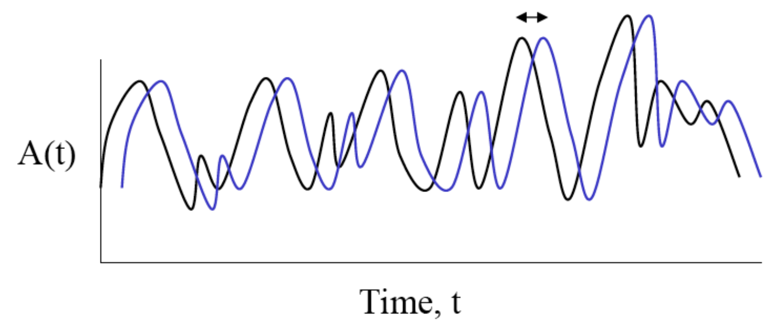
orientational bound state

protein folding

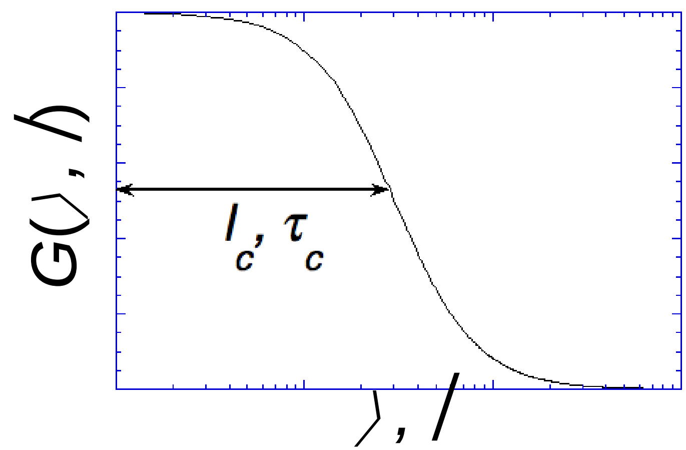
Critical dynamics

Correlation function:

$$G(\vec{\rho},\tau)=\left\langle n(\vec{r}+\vec{\rho},t+\tau)\,n(\vec{r},t)\right\rangle_{\vec{r},t}$$



Correlation length (l_c) and time ($/_c$):

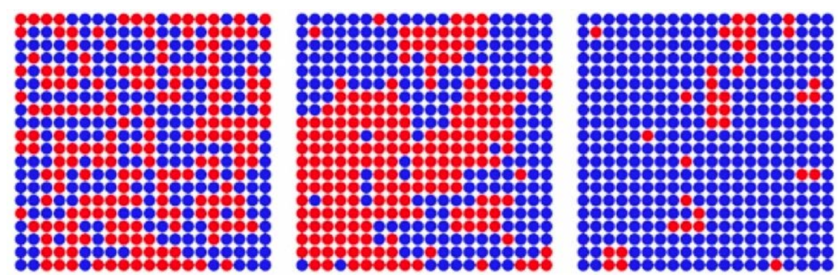


l_c and $/_c$ diverge at $T=T_c$ according to $\dfrac{1}{(T-T_c)^{\alpha}}$

〈 = critical exponent

Scattering function (directly measurable):

$$S(\vec{k},\omega)=\int d\vec{k}\int d\omega\, G(\vec{\rho},\tau)\,e^{i(\vec{k}\cdot\vec{\rho}-\omega\tau)}$$



Diffusion

Fick's law of diffusion: $J_x = -D\dfrac{dn}{dx}$

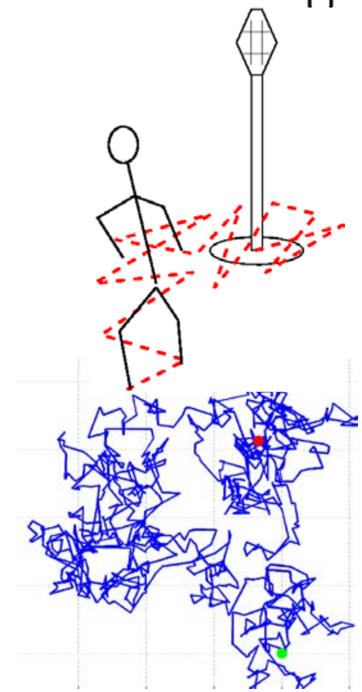
D [m^2/s] = diffusion constant

Interact with a fluctuating bath (Langevin equation)
➔random walk (Brownian motion)

$$W(x,t) \propto e^{-x^2/2\sigma(t)^2} \qquad \sigma(t) = \sqrt{Dt}$$

$\ell(t)$ = diffusion length

Scattering function: $S(k,\omega) \propto \dfrac{1}{1+\omega^2\tau_c^2} \qquad \tau_c = \dfrac{1}{Dk^2}$

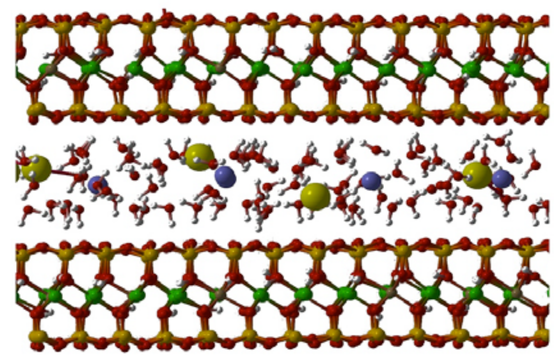


D-values (RT):

air:	10^{-5} m^2/s
water:	10^{-9}
lipids:	10^{-11}
proteins:	10^{-13}
H in Fe:	10^{-13}
Al in Cu:	10^{-26}

Stokes-Einstein: $D = \dfrac{k_B T}{6\pi\eta r}$

Na, Cs diffusion in clay:
$D \approx 10^{-13}$ m^2/s



S Churakov, Sci Env Tech (2013)

The mysterious glass transition

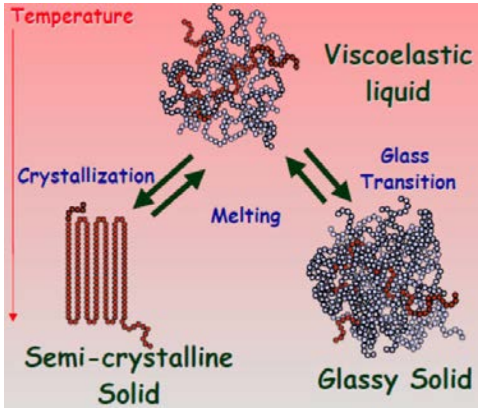
Cool a glassy liquid ➔viscosity increases with Arrhenius law: $\eta \propto e^{\Delta E/k_B T}$

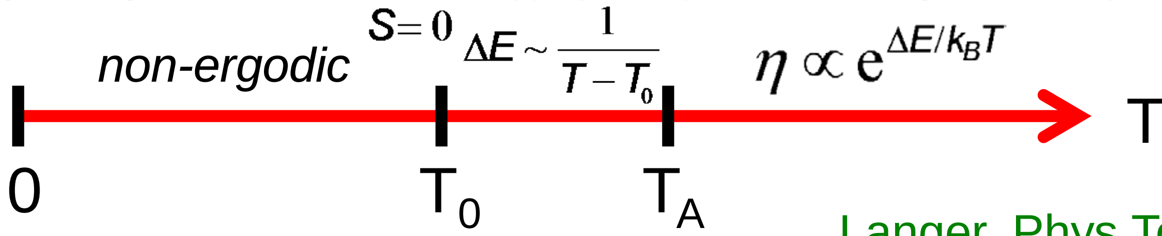
T < T_A: ⊗E grows with decreasing T
implies increasing large cooperative motions (which motions?)

T=T_0: ⊗E becomes infinite
"broken ergodicity"
glassy configuration stuck forever near one state
specific heat measurements ➔entropy = 0 at or near T_0 (significance?)
➔not simply a gradual slowing down as T➔T_0

Questions:
phase transition at T_0?
long- or short-range (jamming) interactions important?
which configurations are accessible and what are transition rates?
(hard to study because of long time scale)

Facit: neither close-to nor far-from equilibrium
requires new physics
perhaps related to biology (always out of equilibrium)





Langer, Phys Today (2007)

Langevin dynamics and the FDT

A particle of mass *M* moves with velocity *v*(*t*), sees viscous damping © and feels a randomly-fluctuating force *A*(*t*):

$$\dot{v}(t)+\gamma v(t)=A(t)$$ ***Langevin equation of motion***

Solution for *t* >> 1/©:

$$v(t)=\int_0^t e^{\gamma(t'-t)}A(t')\,dt'$$

Assume: *A*(*t*) has zero mean ($\langle A(t)\rangle = 0$) and *t*-indep variance ($\langle A(t)A(t')\rangle = A^2\delta(t-t')$).
The steady-state variance of the velocity is then:

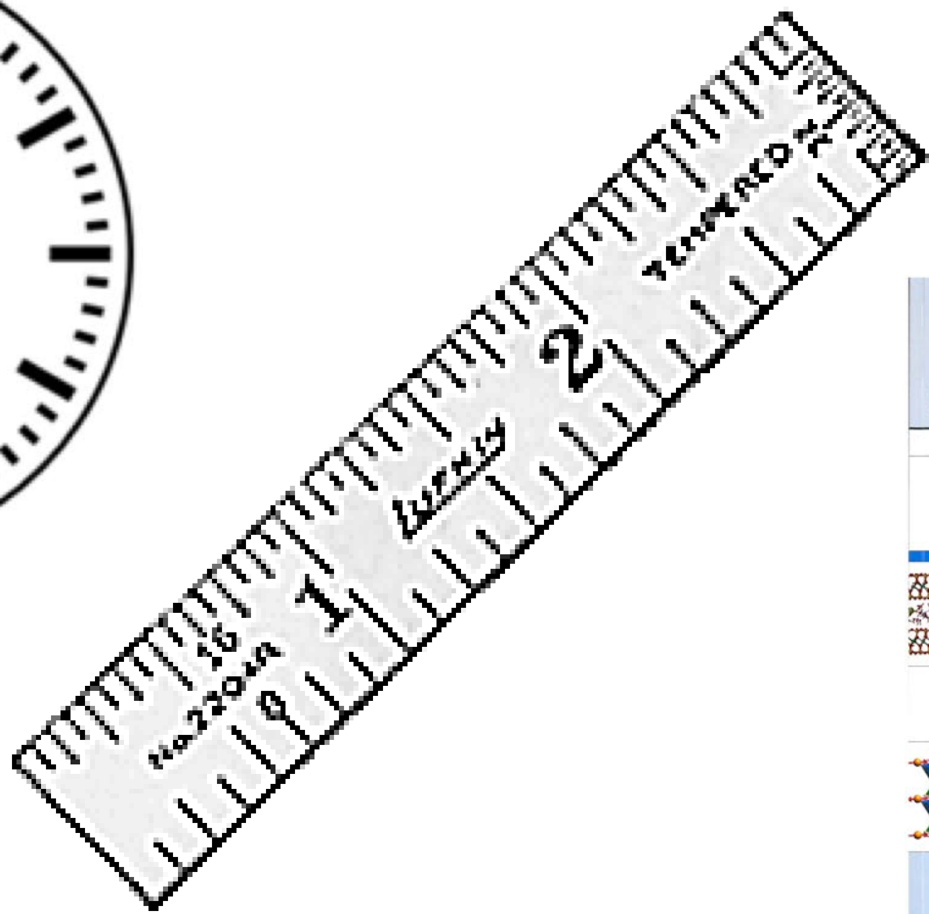
$$\langle v^2(t)\rangle = e^{-2\gamma t}\int_0^t dt'\int_0^t dt'' e^{\gamma(t'+t'')}\langle A(t')A(t'')\rangle$$

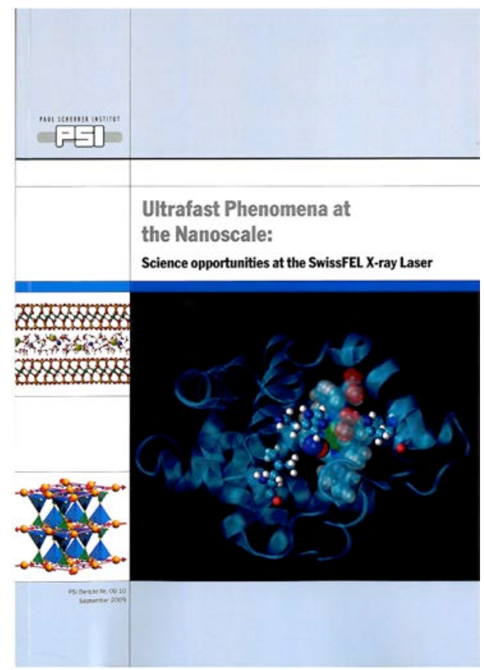
$$=\frac{A^2}{2\gamma}\left(1-e^{-2\gamma t}\right)\to\frac{A^2}{2\gamma}$$

From equipartition: $\frac{1}{2}M\langle v^2\rangle = \frac{k_BT}{2}$, which implies $\boxed{\gamma = \frac{M}{2k_BT}A^2.}$

This fundamental relation between viscous and random forces is a special case of the ***Fluctuation Dissipation Theorem***.

3. Examples of time and length scales

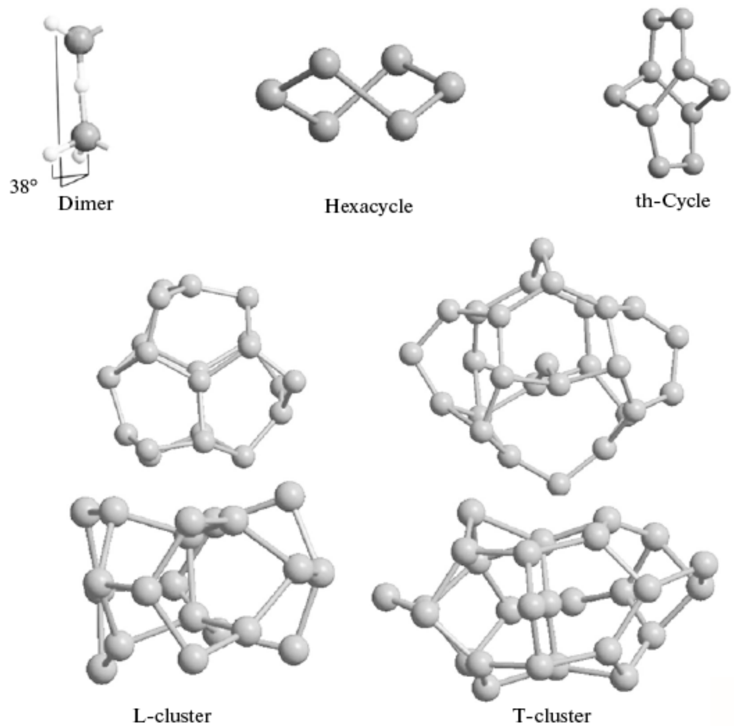




http:psi.ch/swissfel

Water: structure and fluctuations

Nano-structure of water determined by hierarchical hydrogen-bonded clusters



"fractal ice"

Zakharov, Biophys (2012)

Critical points:

gas-liquid: 374º C, 218 bar

low-ρ (low-T) – high-ρ (high-T) ice:

Fluctuations:

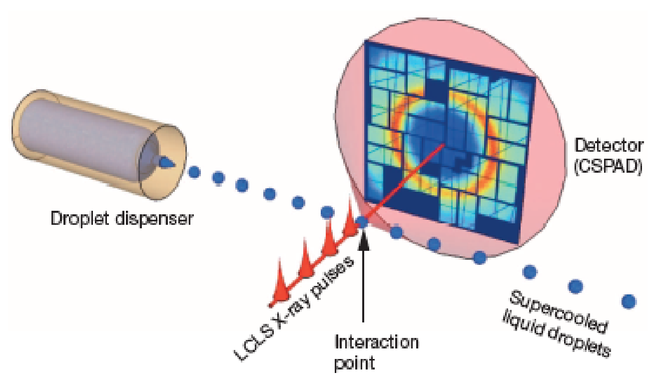
at a wide range of frequencies (~glass)

at low T: slower, but larger amplitude

Interaction with proteins:

7 Å thick hydration shell

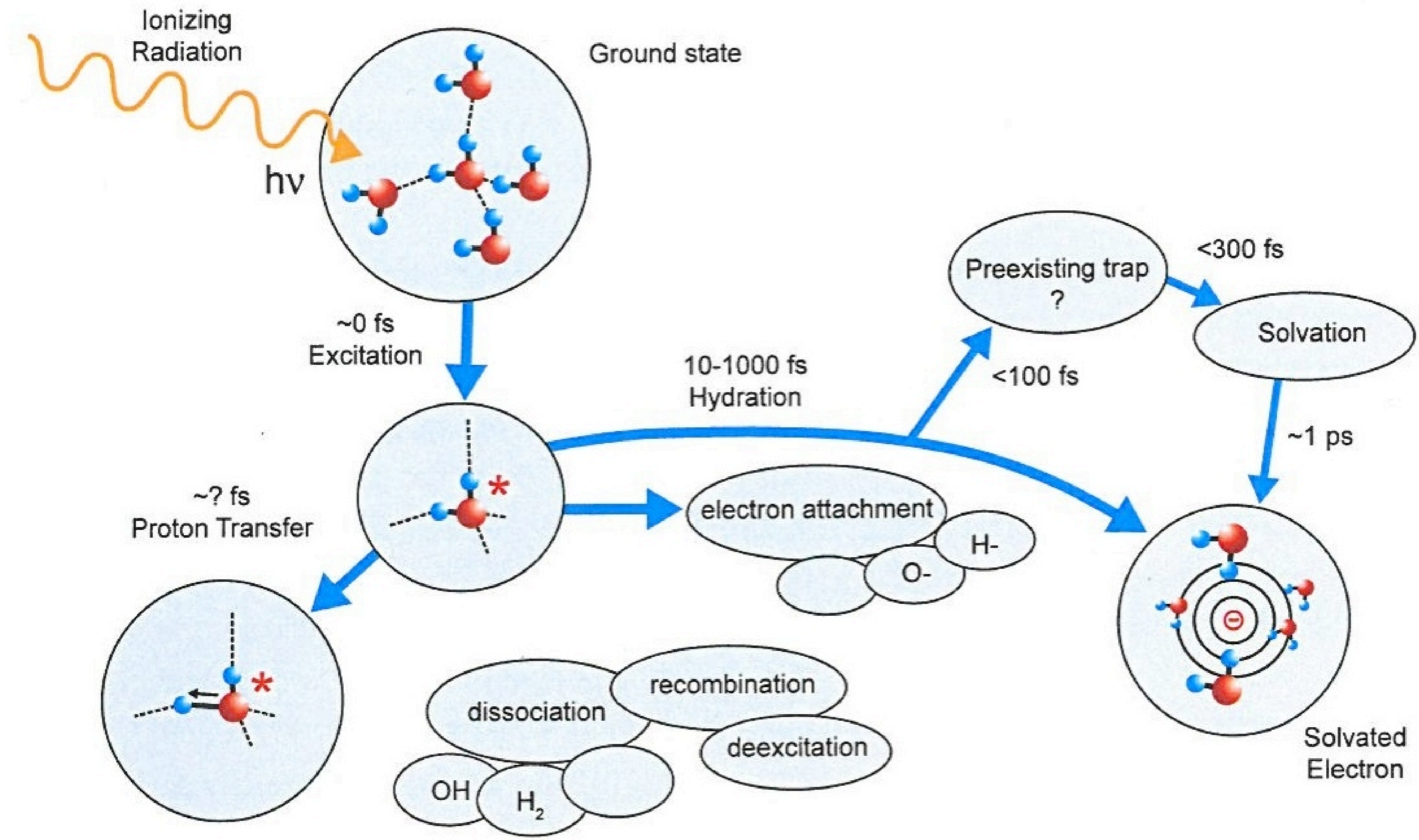
residence time of H_2O molecule: 1-40 ps



Scattering studies of supercooled H_2O at LCLS

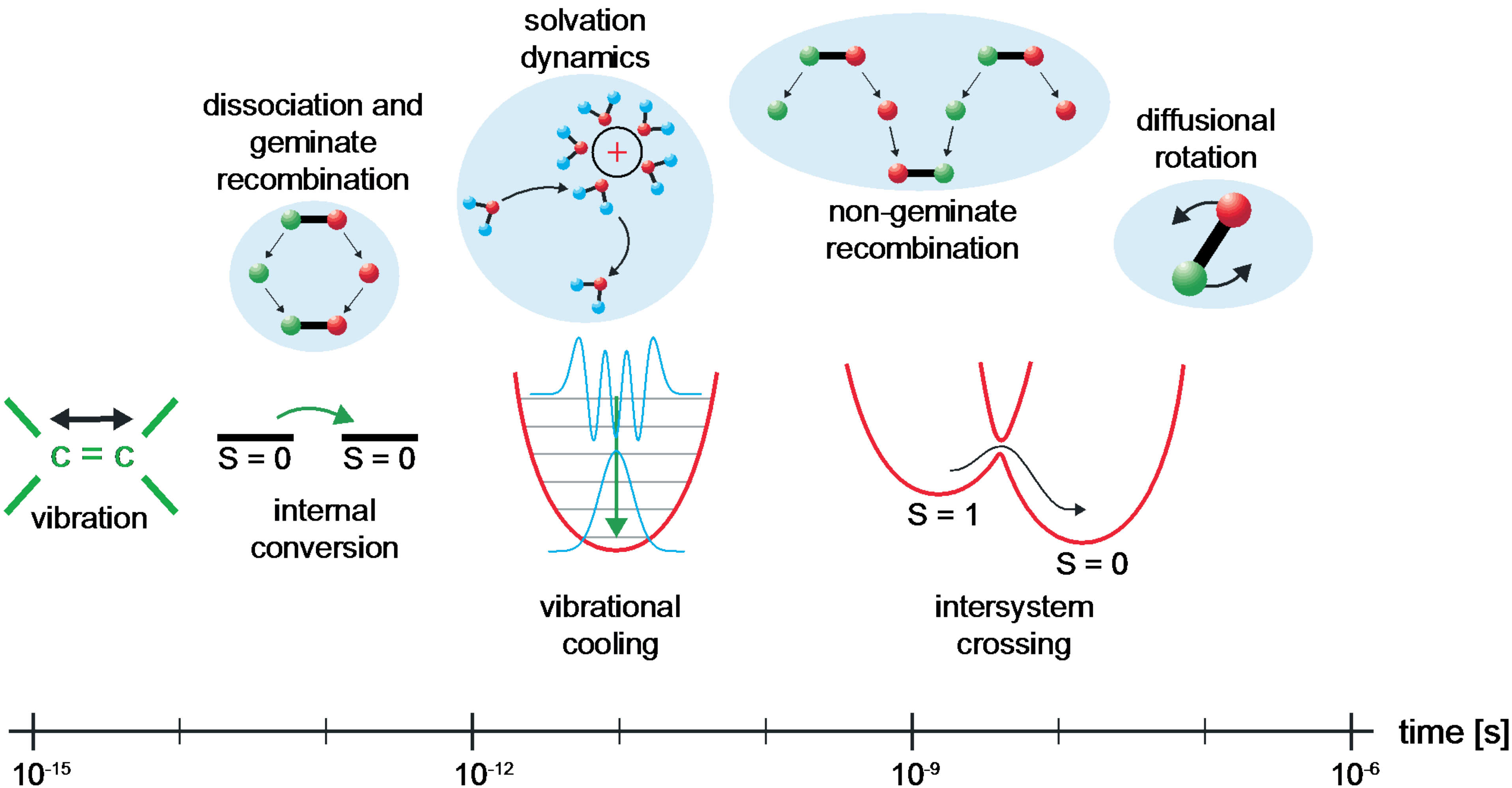
Sellberg, Nature (2014)

Water: *time scales after irradiation*



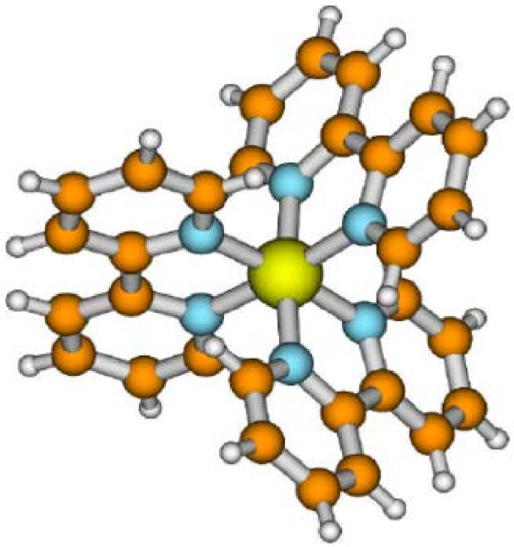
A Nilsson, Stanford (2008)

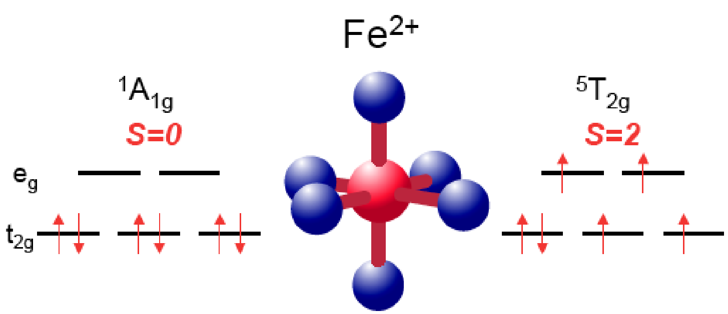
Chemistry: time scales

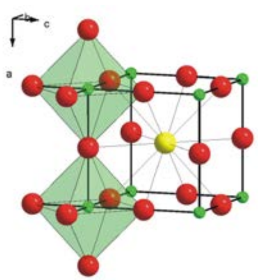


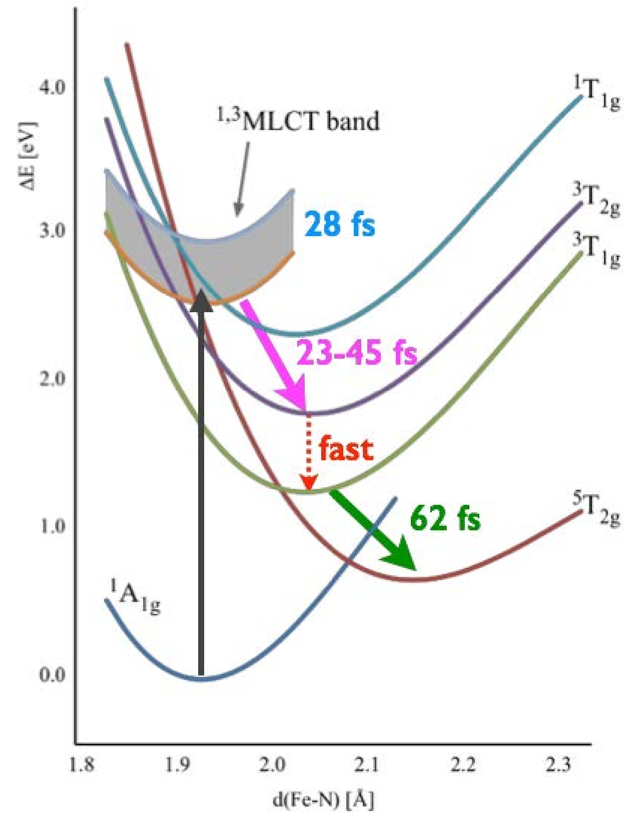
Iron tris-bipyridine: spin cross-over

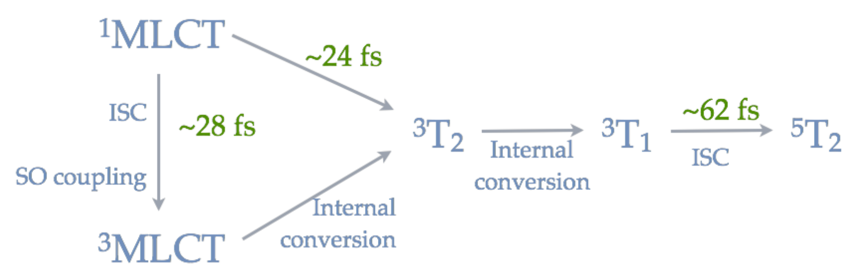
$[Fe^{II}(bpy)_3]^{2+}$





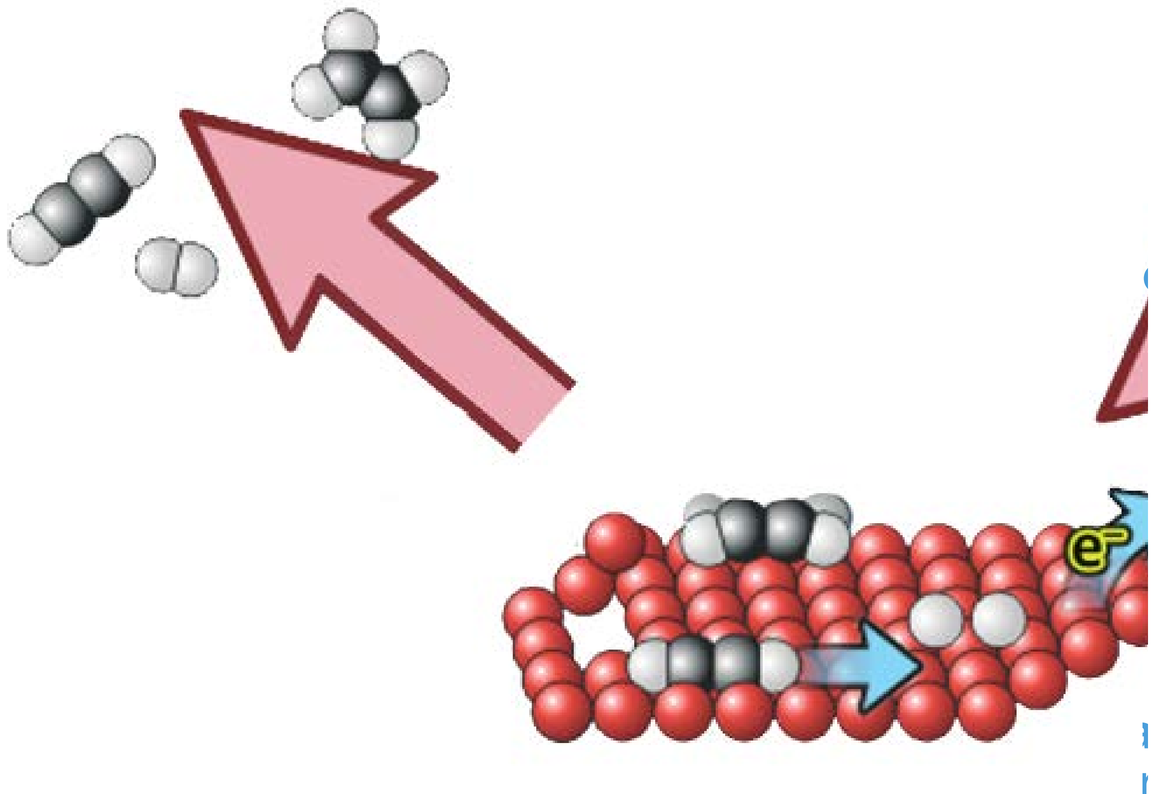






C de Graaf, Chem Eur J (2013)

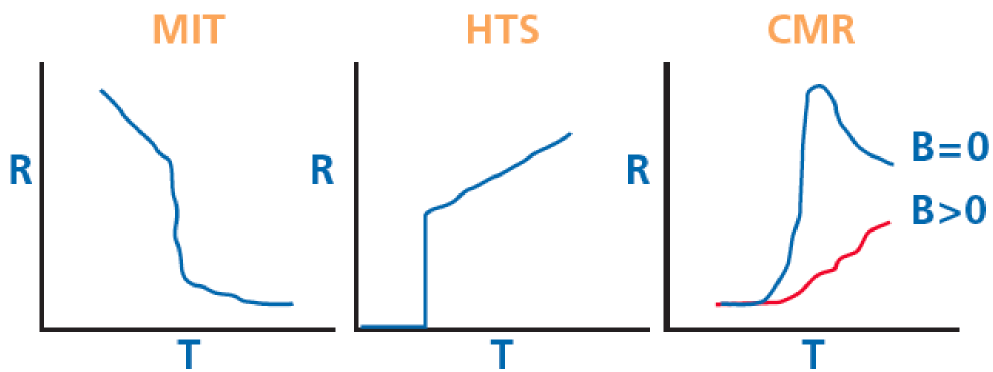
Heterogeneous catalysis: processes



sfer

BNL (2008)

Correlated electrons: degrees of freedom

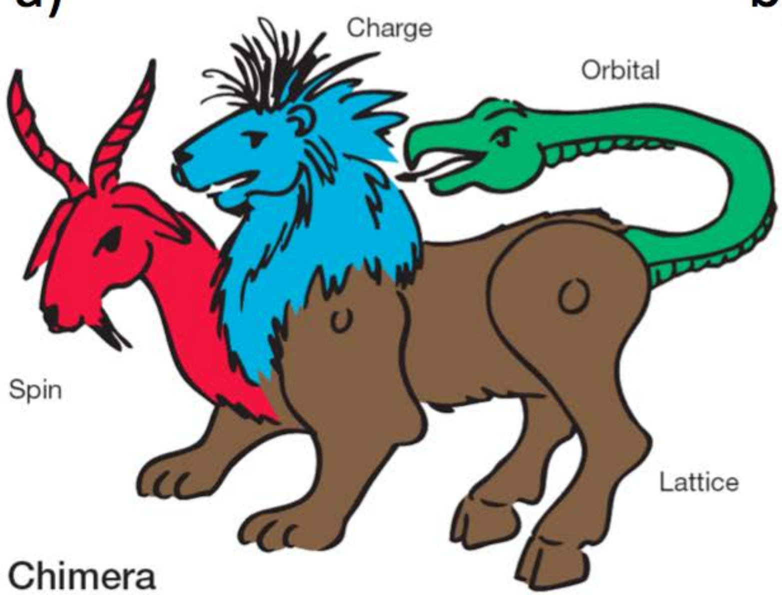


Metal-to-Insulator Transition

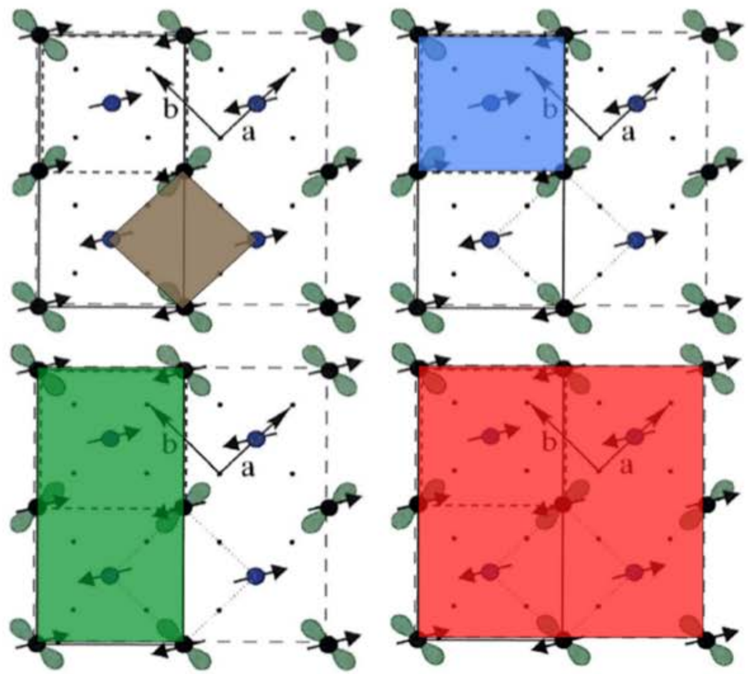
High Temperature Superconductivity

Colossal Magneto-Resistance

a)

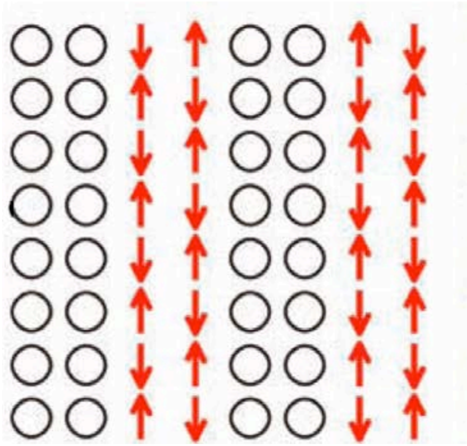


b)

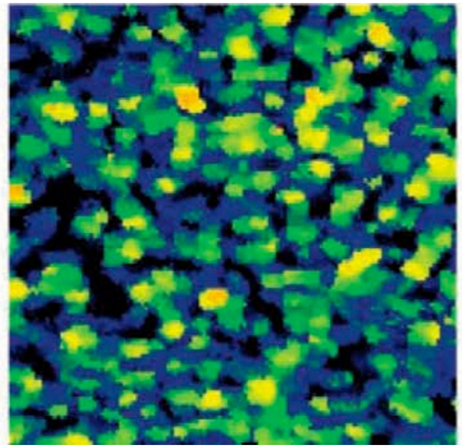


S Johnson, PSI (2008)

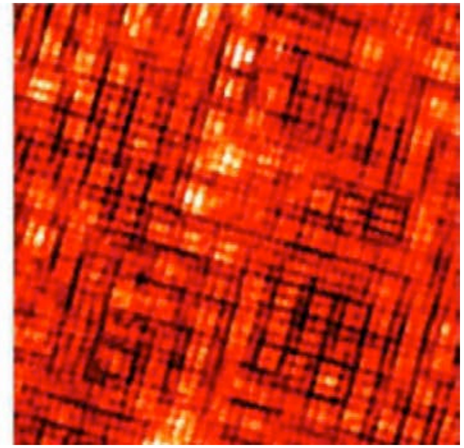
Correlated electrons: fluctuations



charge/spin stripes in cuprate SC

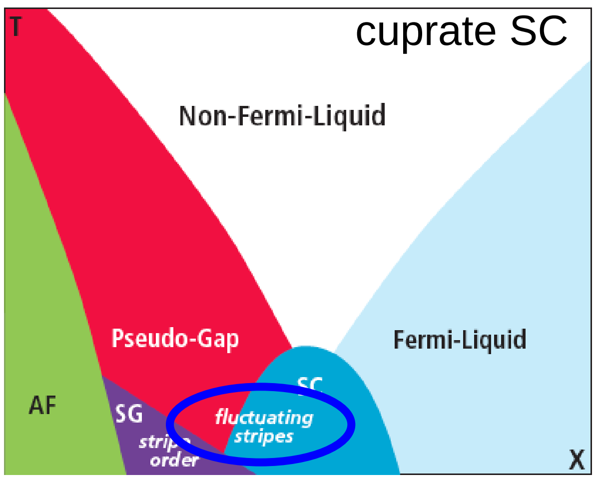


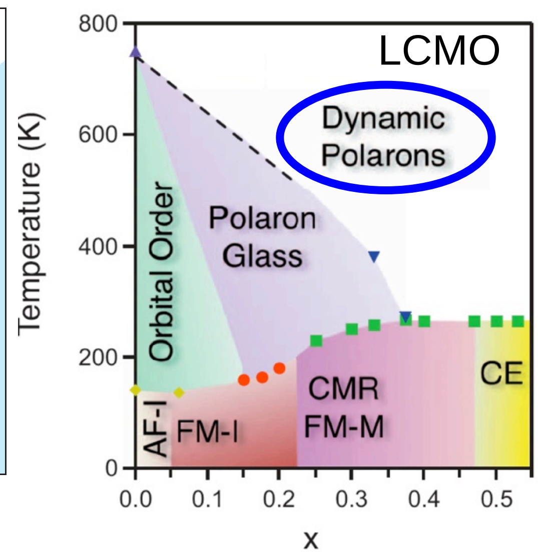
gap variations in BiSCCO

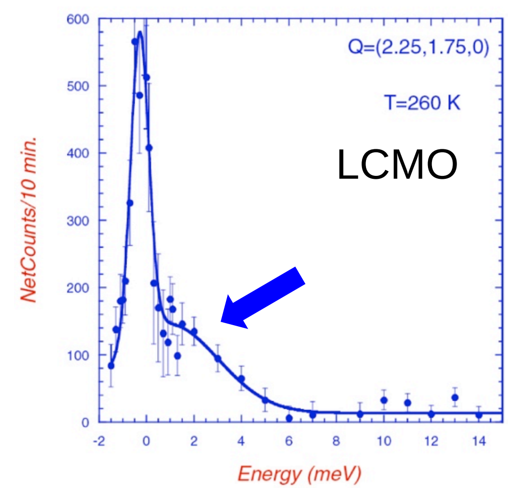


charge-ordered state in Na-doped cuprate

E Dagotto, Science (2005)





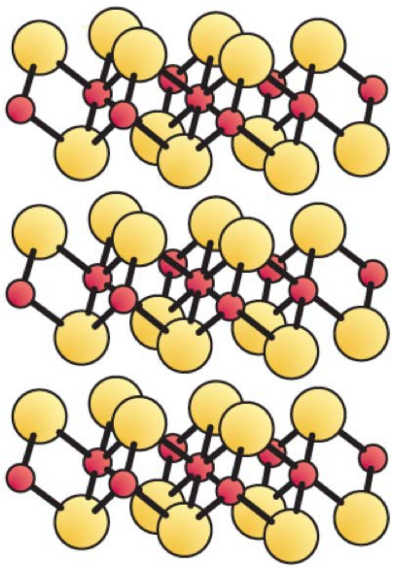


Facit: correlated-electron materials have "electronic liquid-crystal" properties.

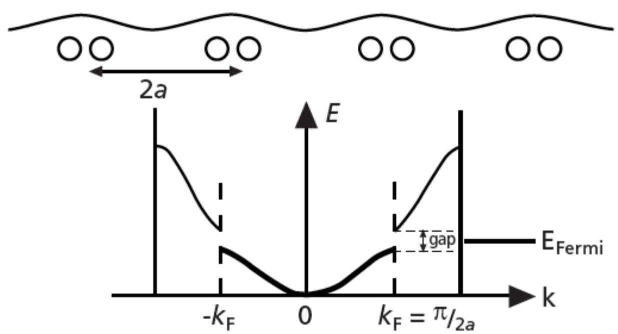
Correlated electrons: time scales

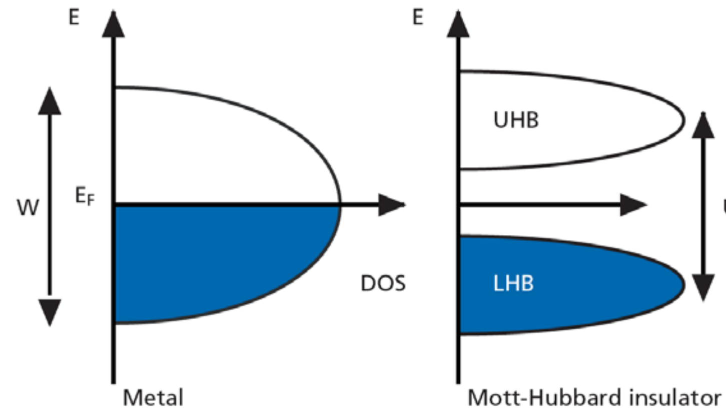
Ultrafast metal-insulator transition in 1T-TaS_2:

1T-TaS_2

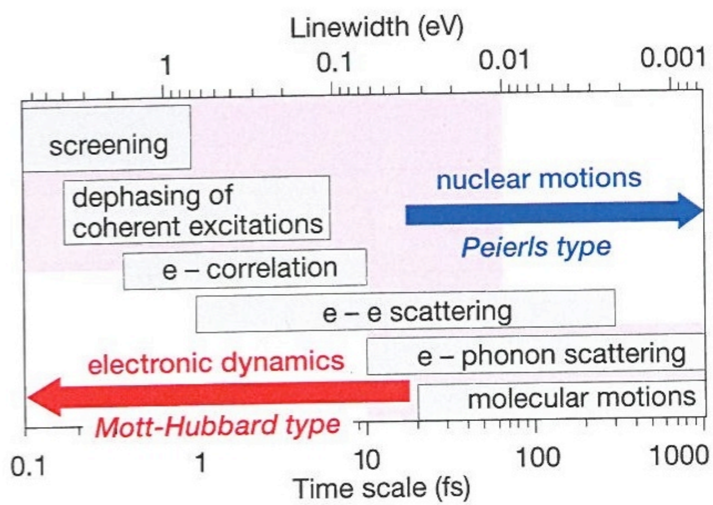


Peierls or ***Mott-Hubbard*** ?





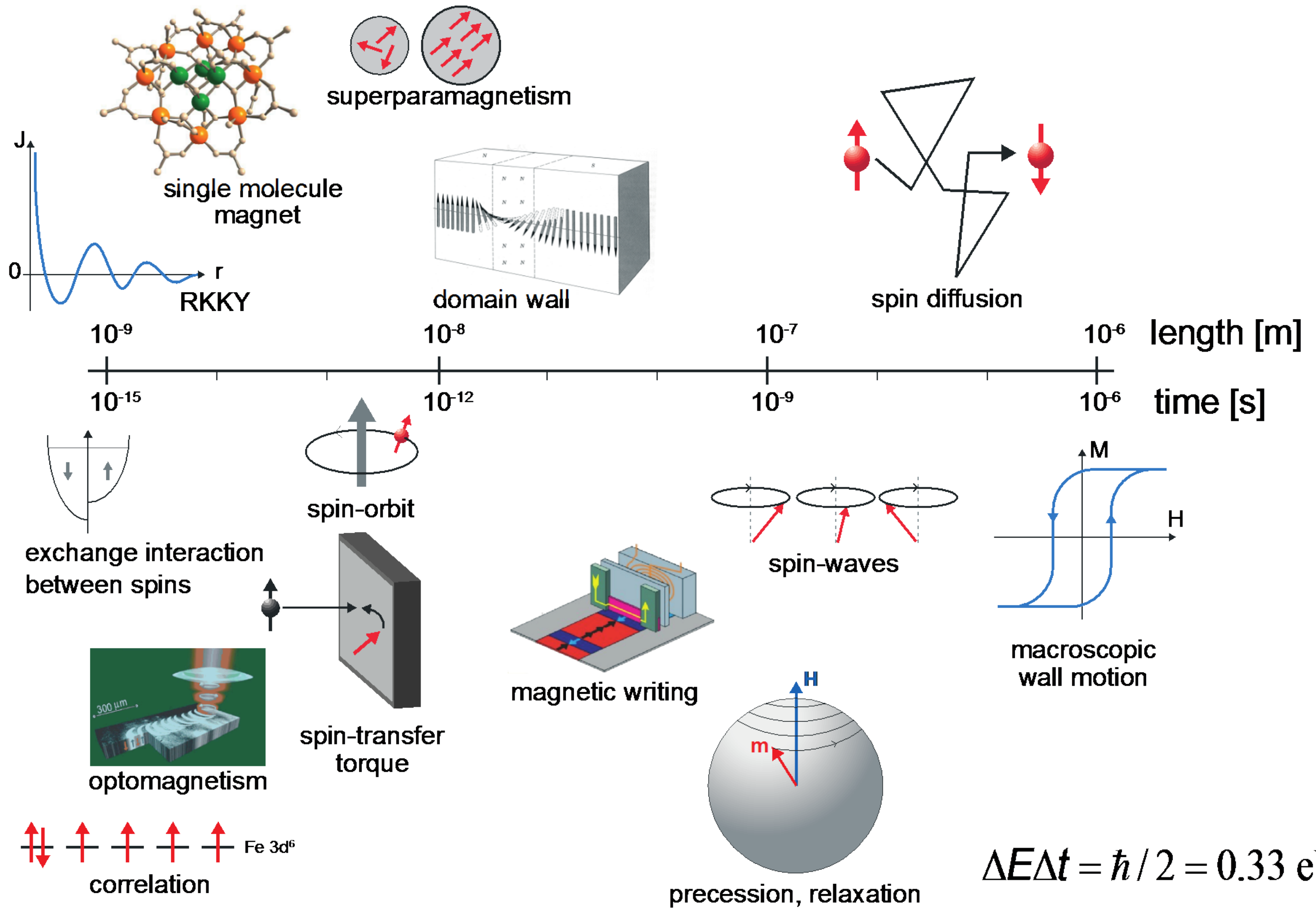
Different time-scales



MIT time scale from pump-probe PES:
< 100 fs
➔ Mott-Hubbard

L Perfetti, NJP (2008)

Magnetism: time and length scales



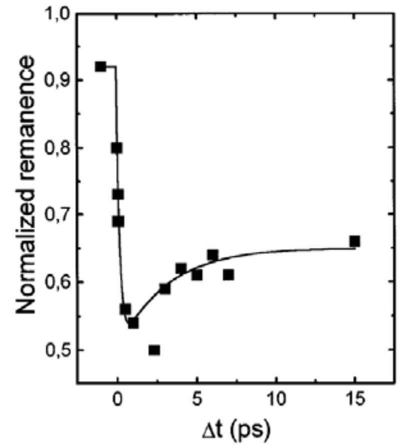
$$\Delta E \Delta t = \hbar / 2 = 0.33 \text{ eV fs}$$

Ultrafast demagnetization

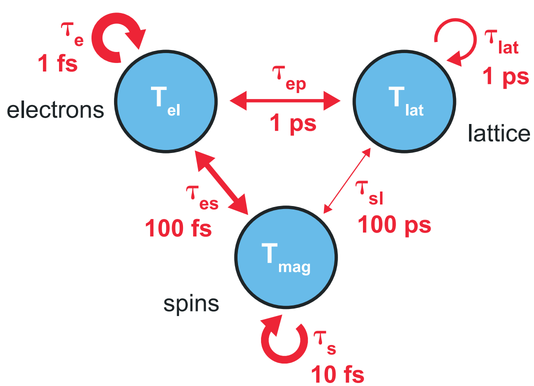
1996: Beaurepaire's discovery (using Magneto-Optic Kerr Effect MOKE)

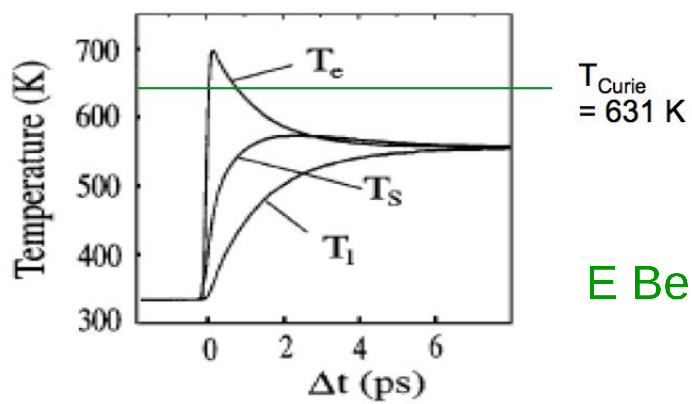
An intense laser pulse

demagnetizes Ni within 200 fs.



Interpretation: "3-temperature model" (ignores angular momentum)

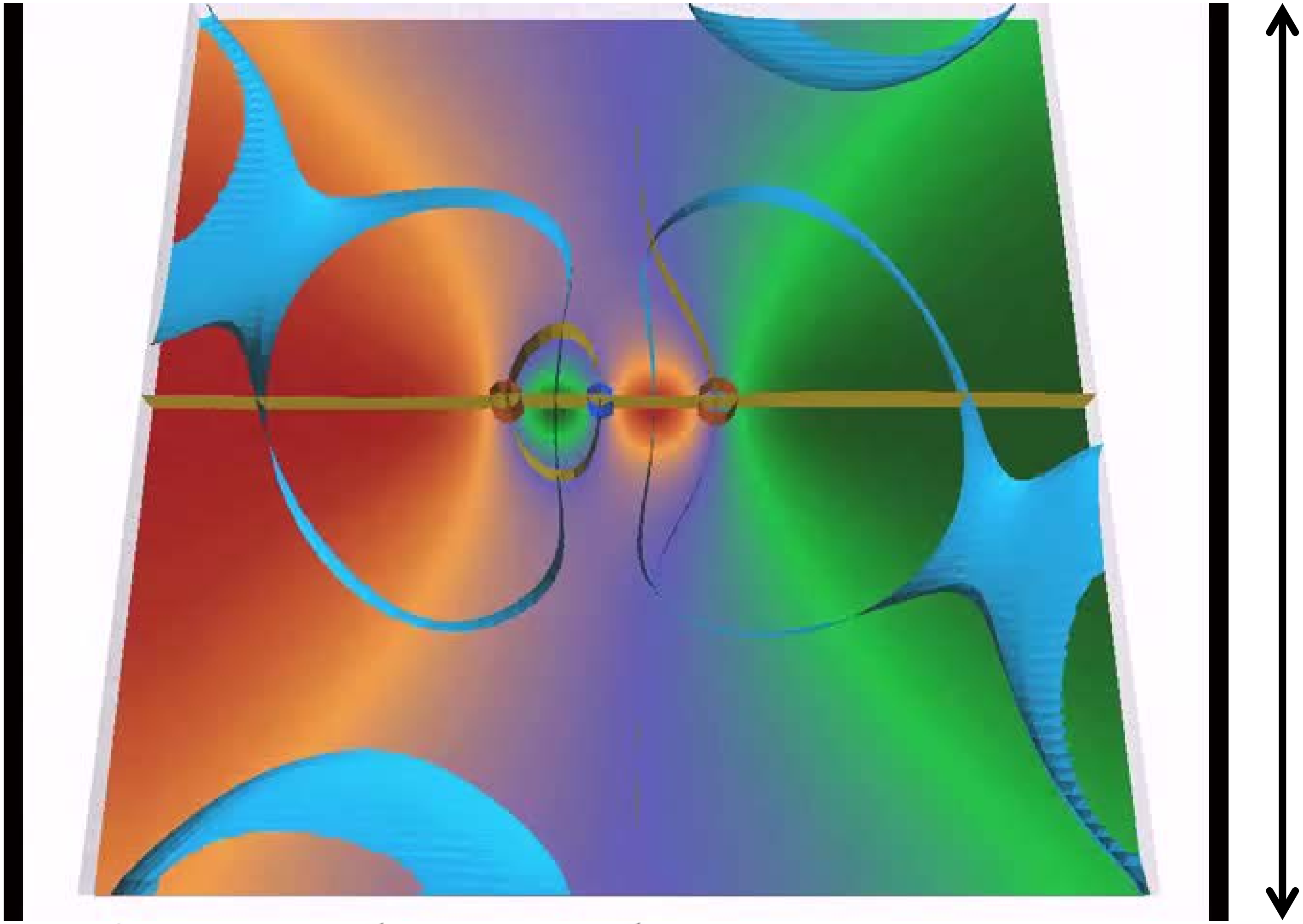




E Beaurepaire, PRL (1966)

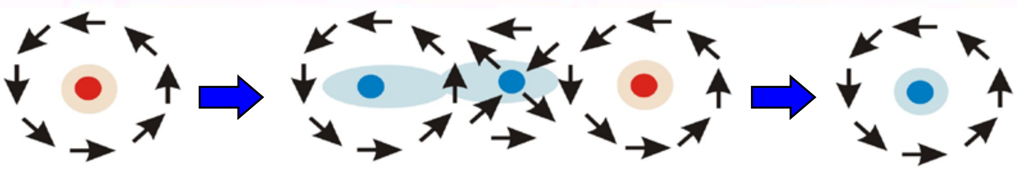
Unresolved question: where does the angular momentum go?

Magnetic vortex switching



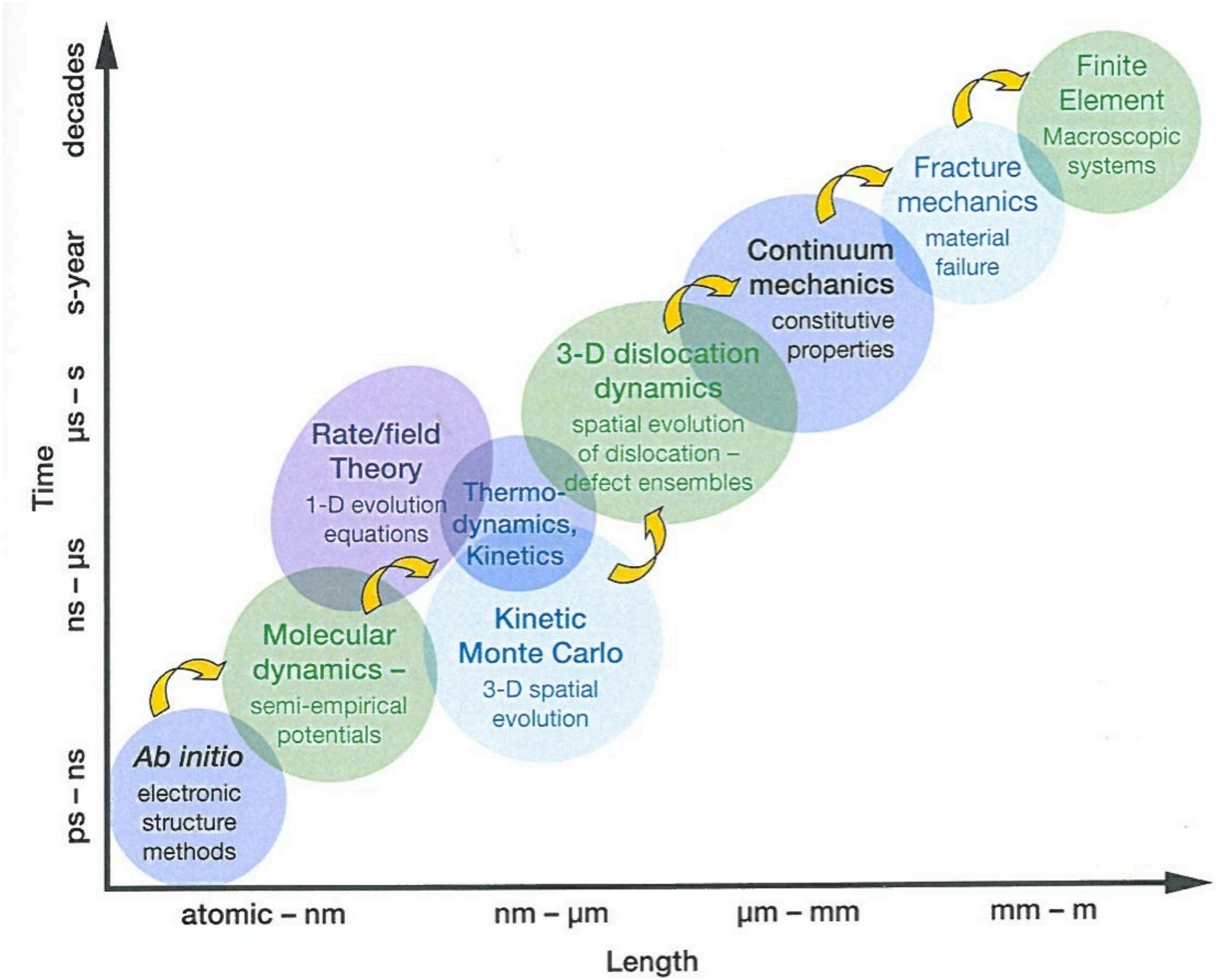
500 nm

total time:
50 ps



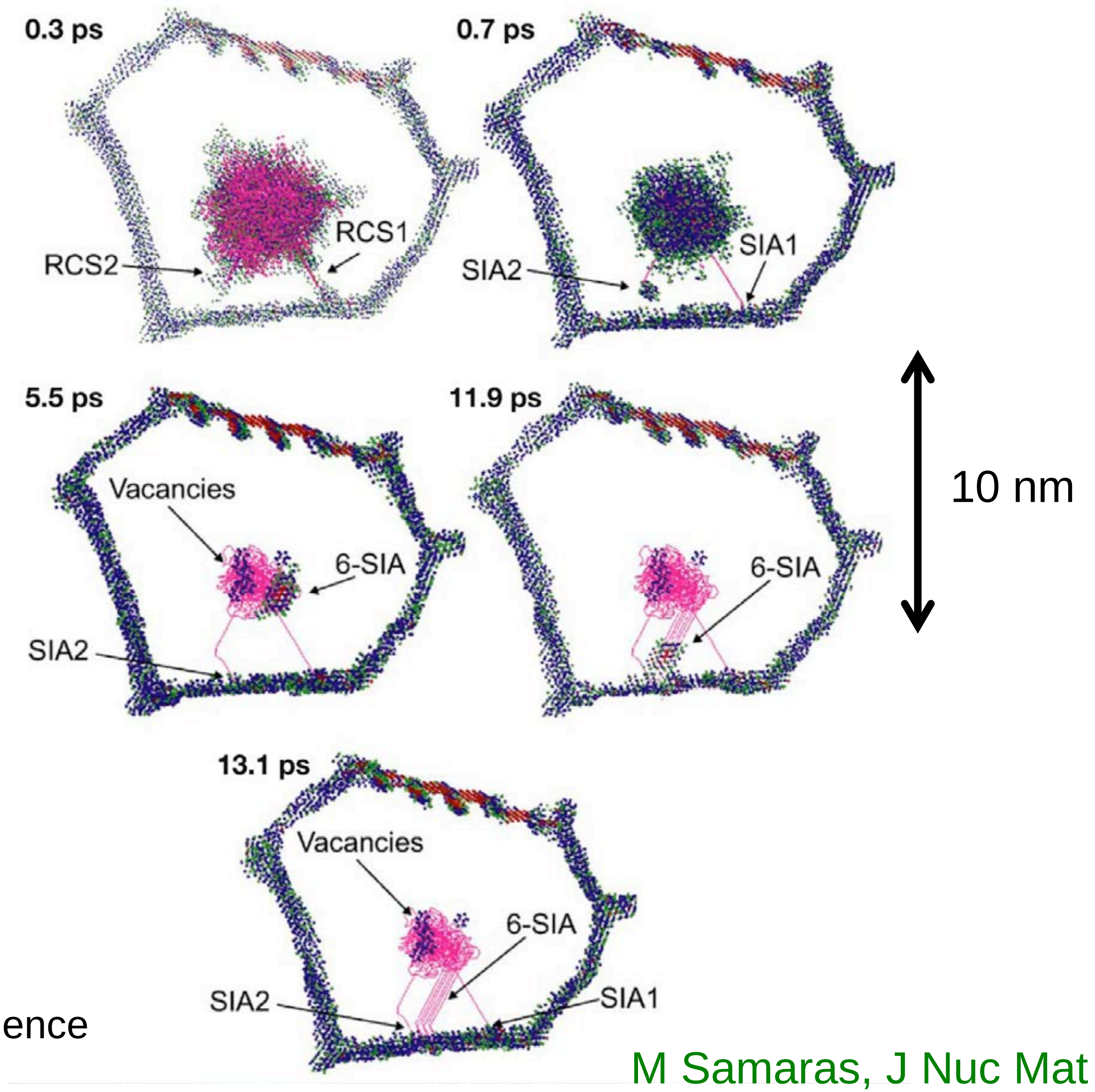
R Hertel, Jülich, (2008)

Materials modeling: time and length scales



BD Wirth, J Nuc Mat (2004)

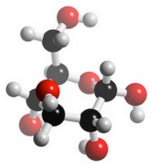
Radiation defect cascade



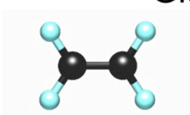
nanocrystalline Ni
5 keV knock-on event
SIA: self-interstitial atom
RCS: replacement collision sequence

M Samaras, J Nuc Mat (2003)

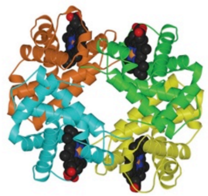
Biology: time and length scales



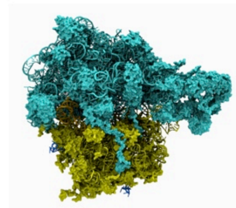
Glucose



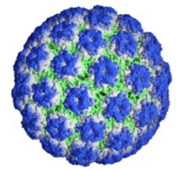
C-C bond



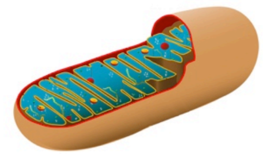
Hemoglobin



Ribosome



Virus



Mitochondria

Bacteria

Erythrocyte

length [m]	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}
time [s]	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}

bond vibration

photodissoc. of CO from heme

trans-membrane electron transfer

methyl rotation

side-chain rotamers

trans-cis photoisomerization

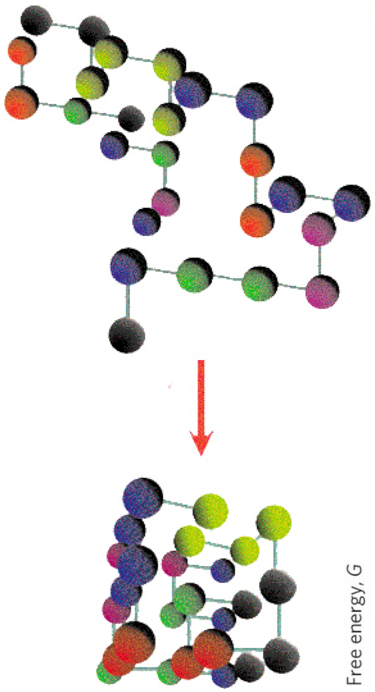
loop motion

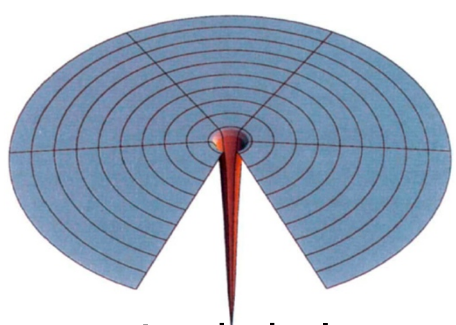
fast de-caging

large domain motions

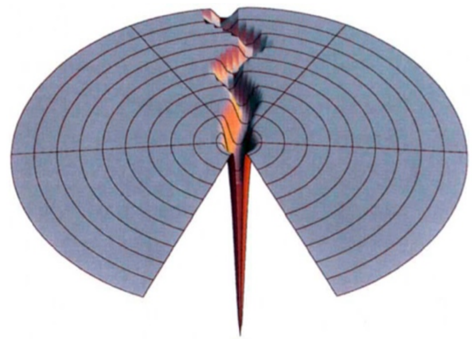
http://w3.dbb.su.se/~barth

Protein folding: energy landscapes

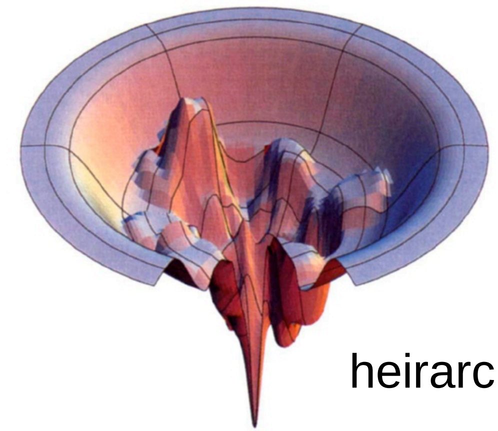




Levinthal
golf course

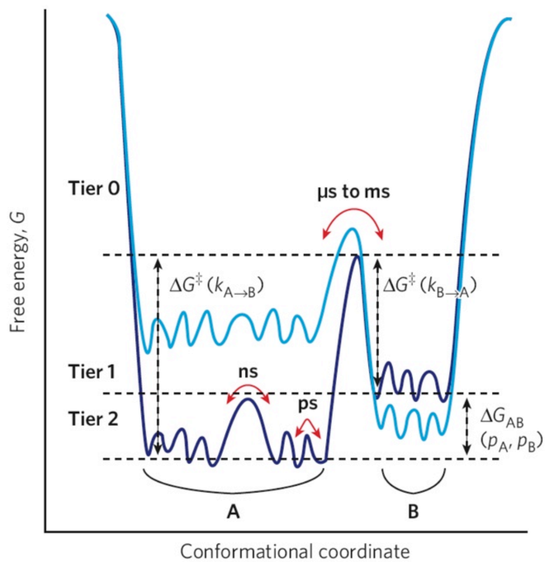


gully



heirarchy

KA Dill, Nat Str Bio (1997)



K Henzler-Wildman, Nature (2007)

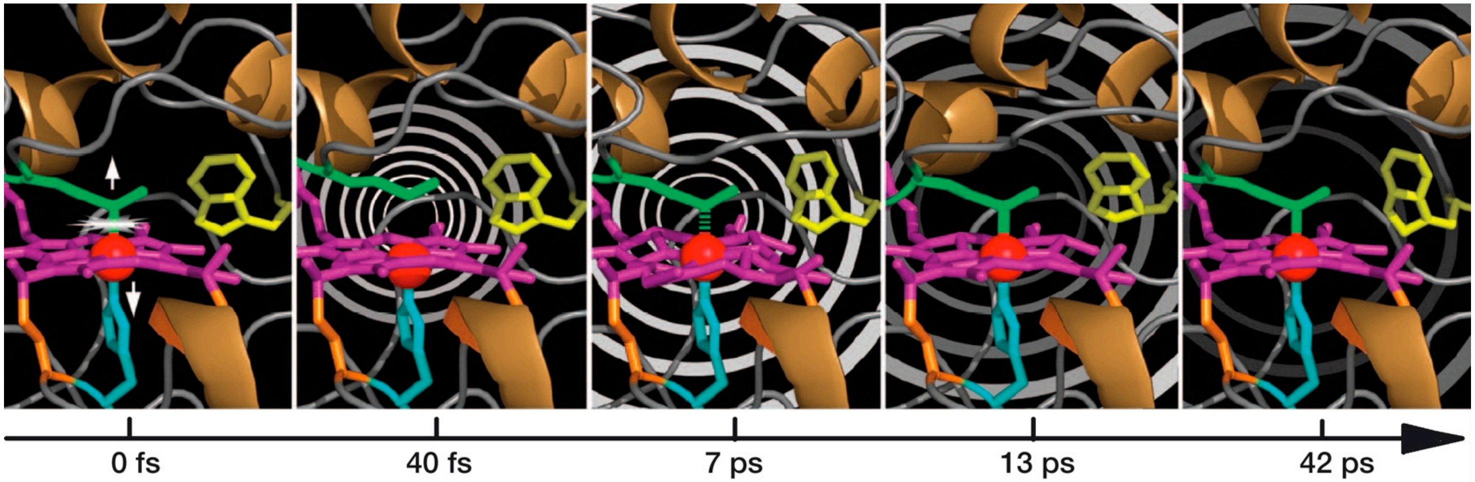
Class	Type of Motion	Approximate Range Amplitude (nm)	Approximate Range Time (s)	
1	Vibrations and oscillations of individual atoms and groups	0.2	10^{-15}–10^{-12}	fs-ps
2	Concerted motions of structural elements, like α helices and groups of residues	0.2–1	10^{-12}–10^{-8}	ps-ns
3	Motions of whole domains; opening and closing of clefts	1–10	$\geq 10^{-8}$	ns-ms

Faster processes need higher resolution

Lehninger, Principles of Biochemistry (2008)

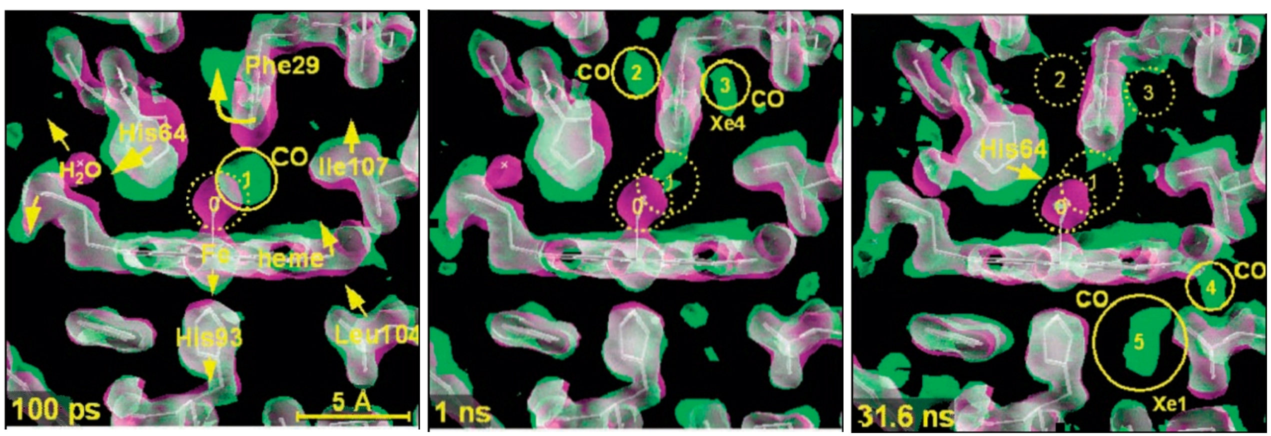
"Protein quake": time scales

Cytochrome: heme-ligand bond breaking



C Zang, J Am Chem Soc (2009)

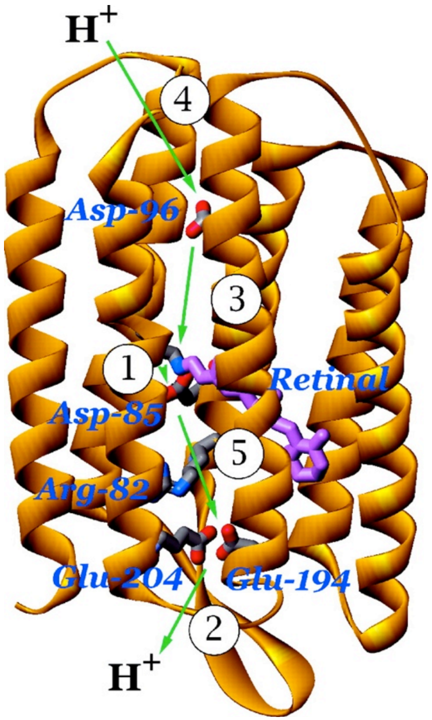
Myoglobin: photo-detachment of CO

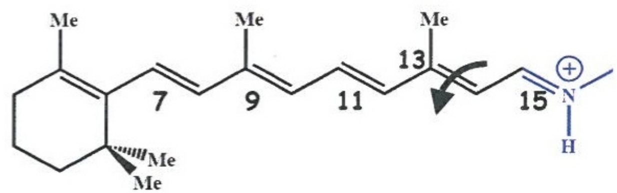


(time-resolved Laue diffraction)

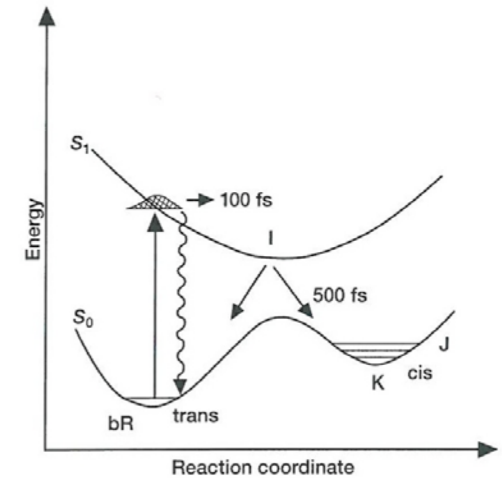
F Schotte, Science (2003)

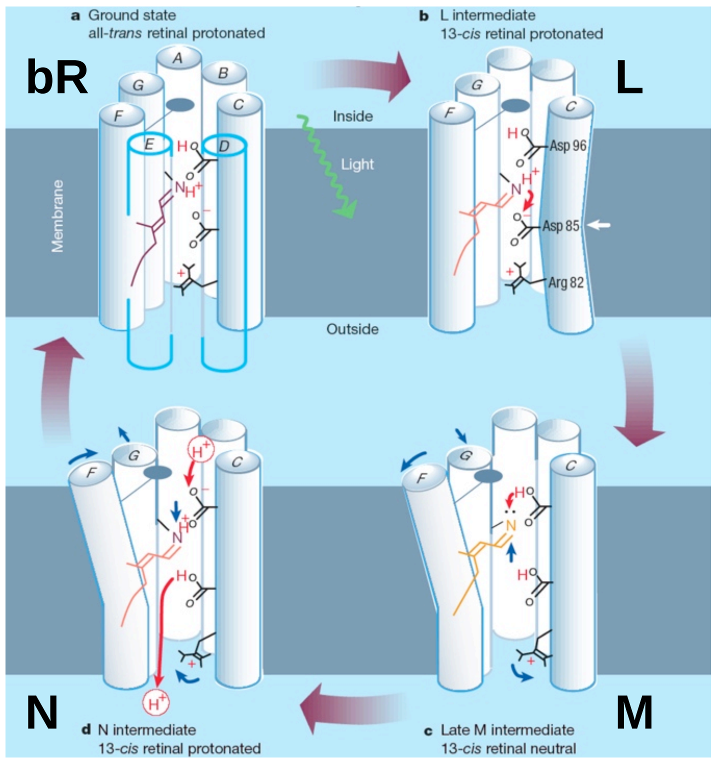
Bacteriorhodopsin: time scales

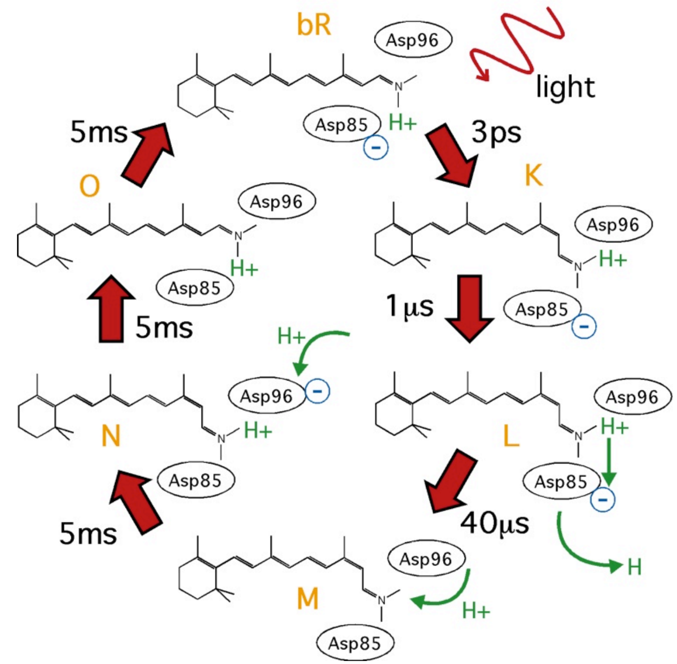




retinal: I➔J
(500 fs)







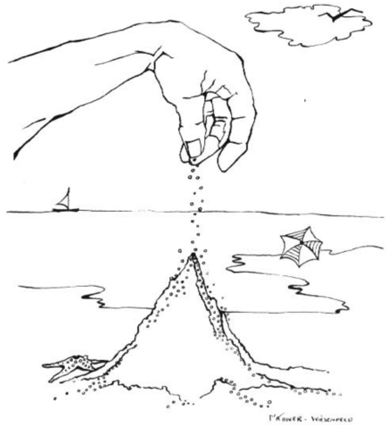
W Kuhlbrandt, Nature (2000)

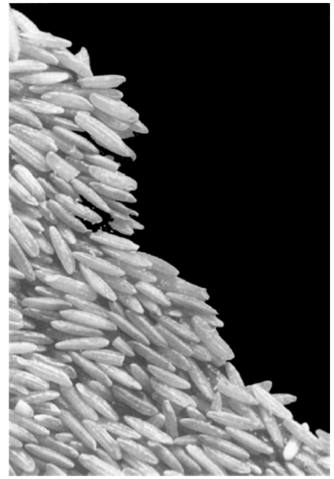
4. Fluctuations in time and space

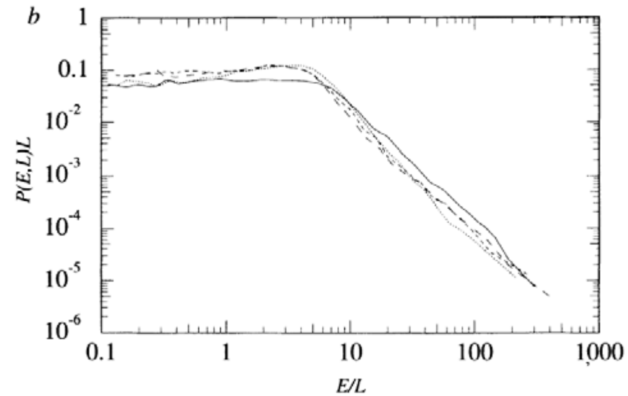
- power-law distributions
- 1/f noise
- self-similarity
  - quasicrystals and Penrose tiling
  - fractals
  - aggregation
- self-organized criticality

Power-law fluctuations

Sandpile avalanches

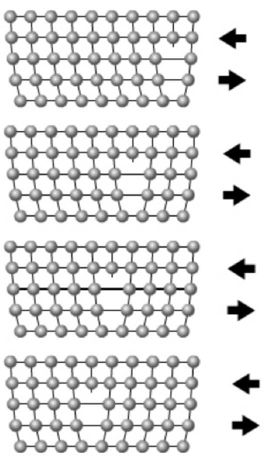


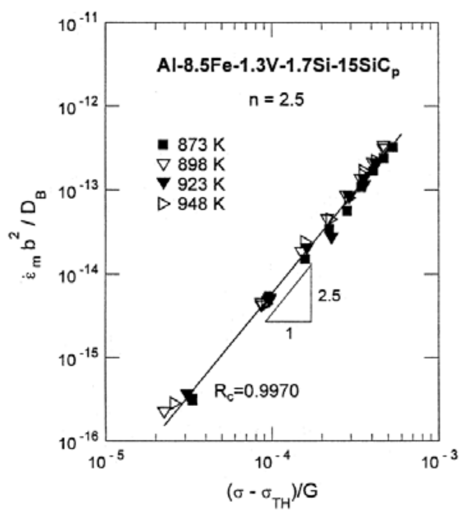




Frette, Nature (1996)

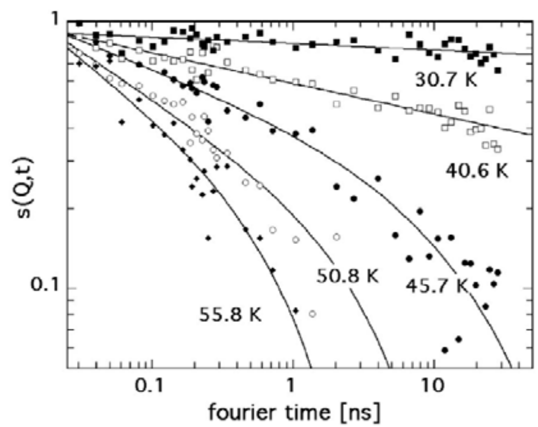
Creep rate





Cadek, Mat Sci Eng (2002)

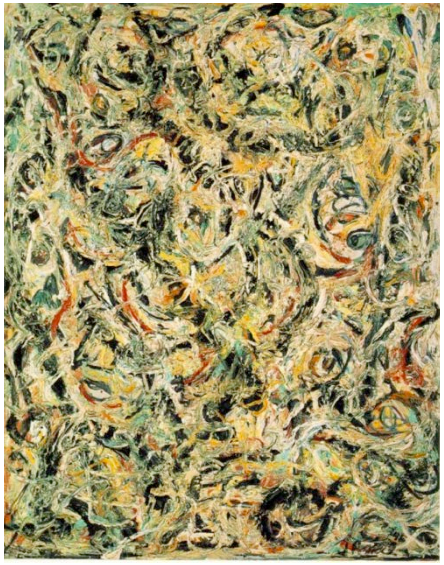
Spin glass:
power-law relaxation



n-spin echo experiments near T_{glass} in $Au_{0.86}Fe_{0.14}$

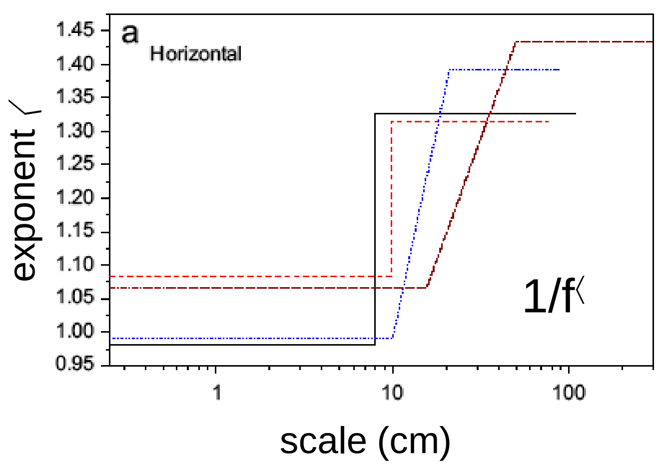
Pappas, PRB (2003)

1/f noise in art and music



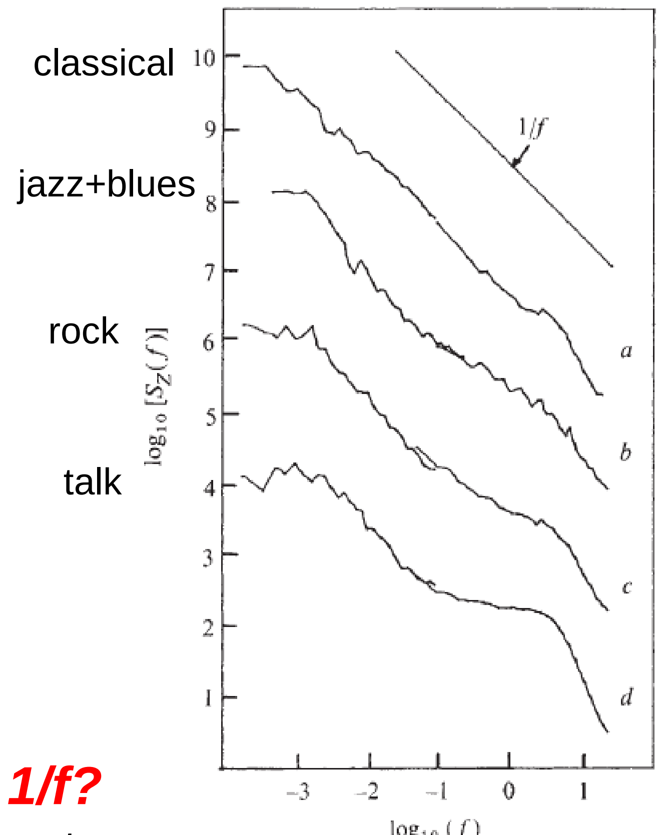
Jackson Pollack paintings
Eyes in the Heat (1946)

J Alvarez, Physica A (2008)



Musical pitch variations

Voss+Clarke, Nature (1975)

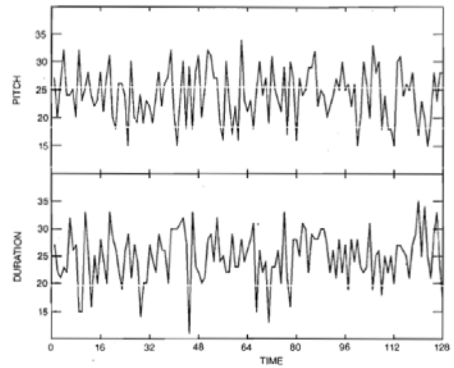


What is special about 1/f?

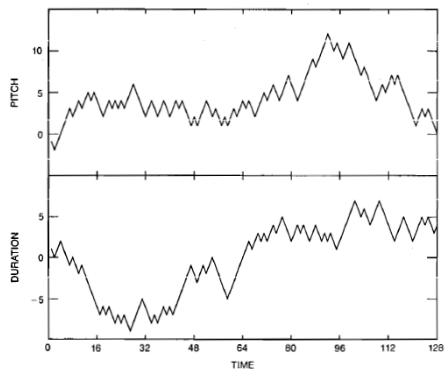
- balance surprise and monotony

Which is more pleasing?

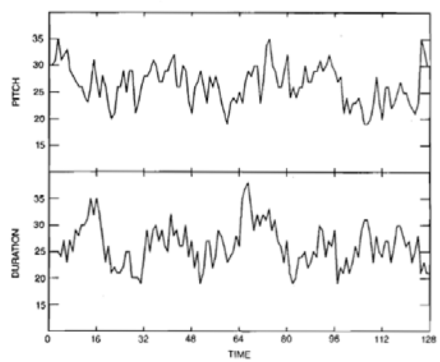
1/f⁰ "white"



1/f² "Brown"



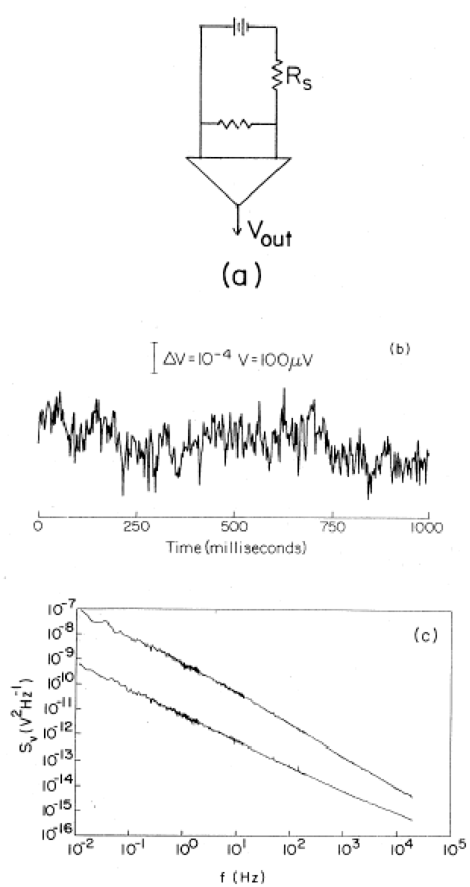
1/f¹ "self-similar"



M Gardner + RF Voss, Sci Am (1978)

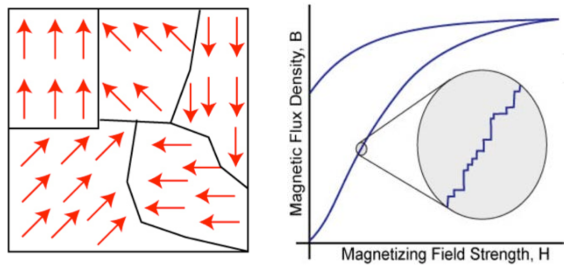
1/f in condensed matter

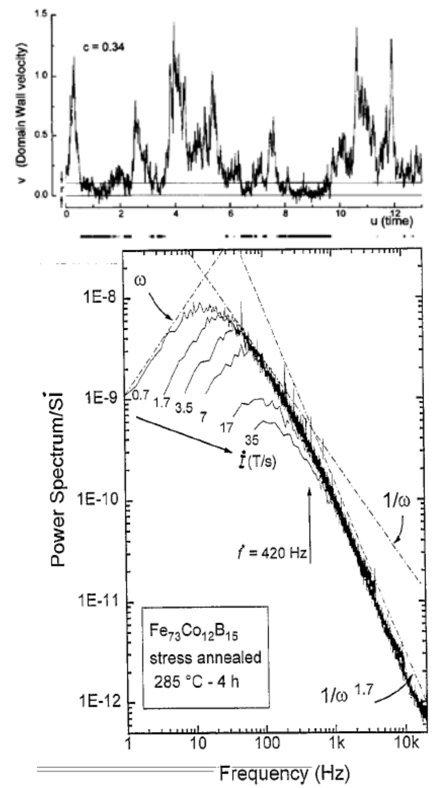
Resistor voltage



Pellegrini, PRB (1983)

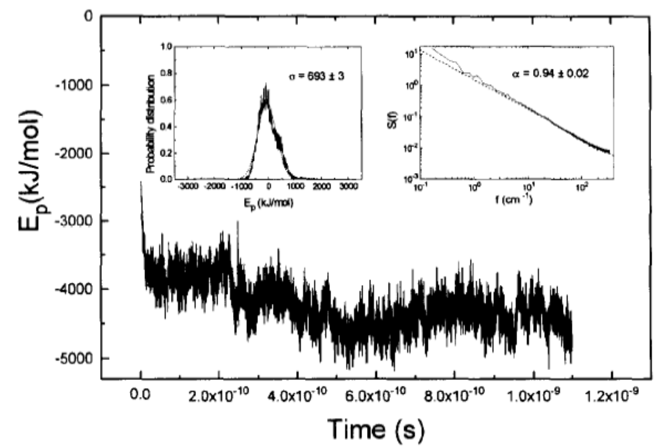
Barkhausen magnetization jumps





Durin, J Mag Mag Mat (1996)

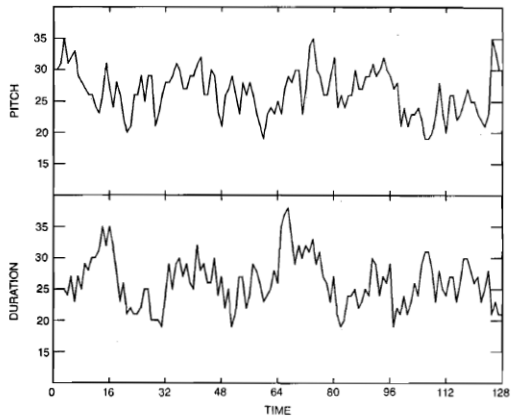
Simulated protein energy fluctuations



Bizzarri, Phys Lett (1997)

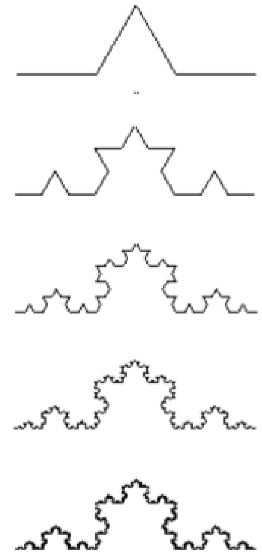
Requirement:
escape from a distribution of traps

Self-similarity

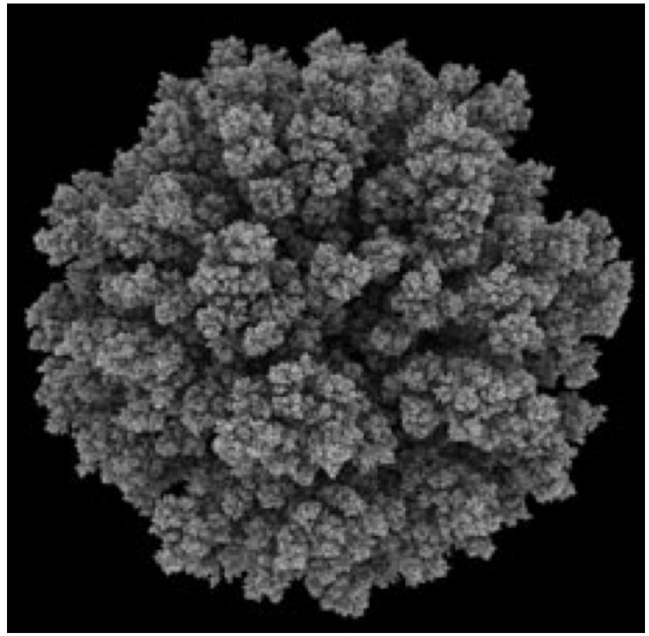


1/f noise is is self-similar

➔familiarity in art and music

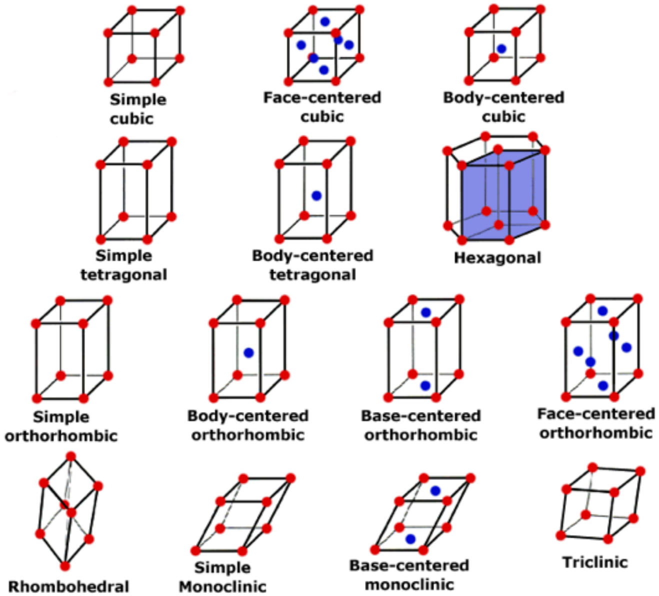


"fractal"

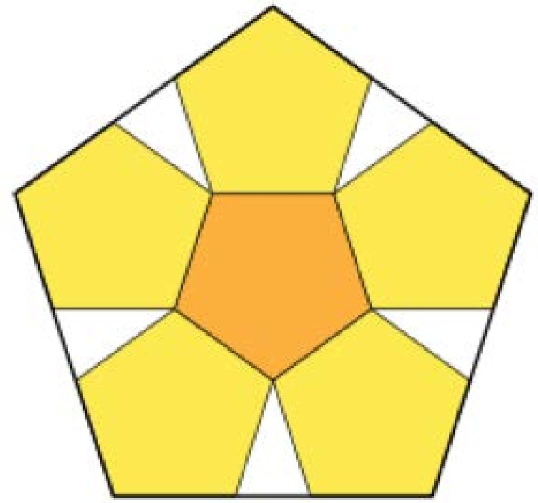


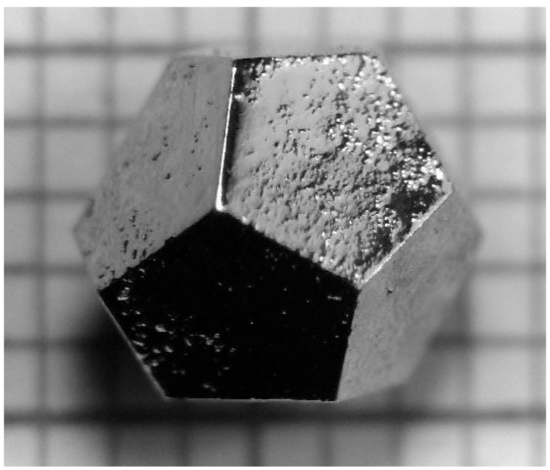
Crystals and quasicrystals

The 14 Bravais lattices

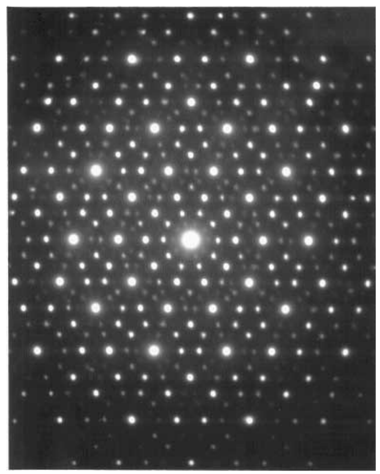


Only 2, 3, 4 and 6-fold axes possible





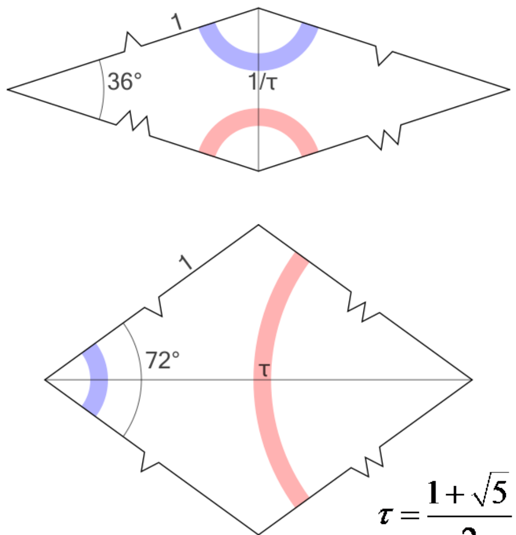
Ho-Mg-Zn



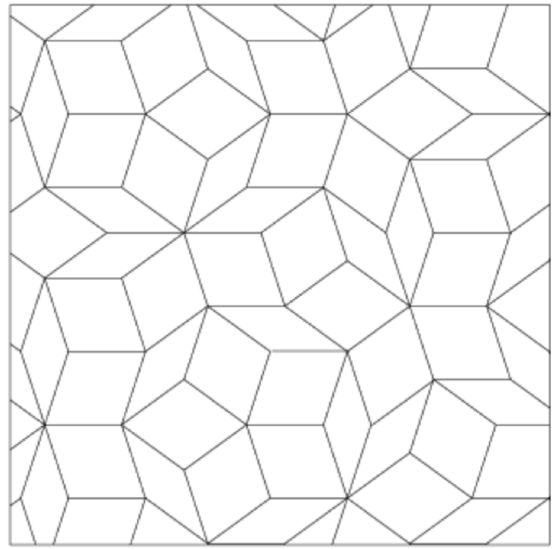
Al-Mn

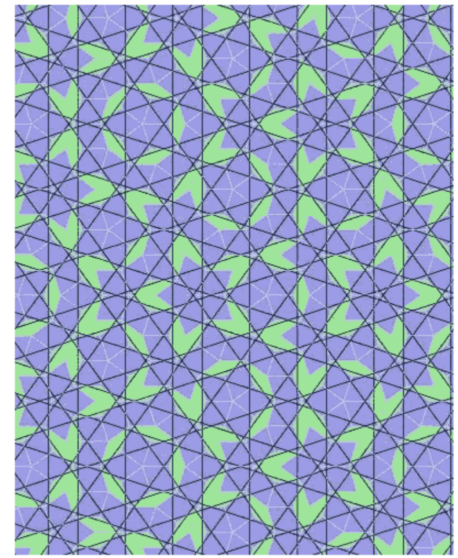
Schechtman, PRL (1984)

Penrose tiling

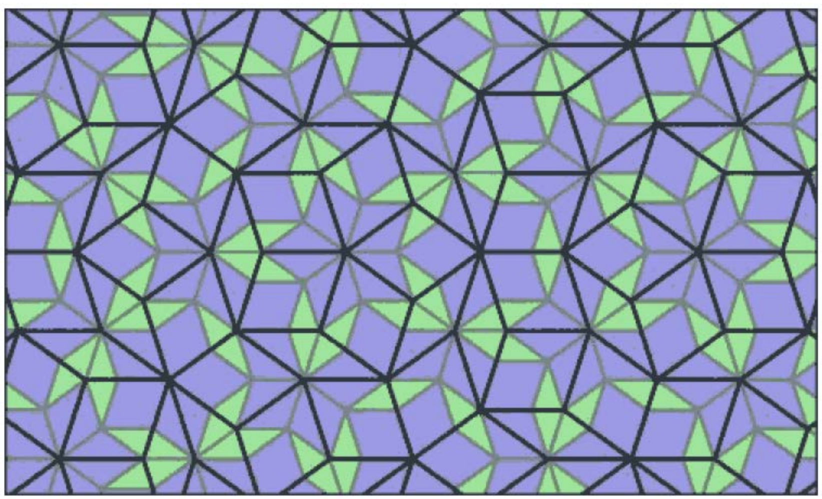


$$\tau = \frac{1+\sqrt{5}}{2}$$

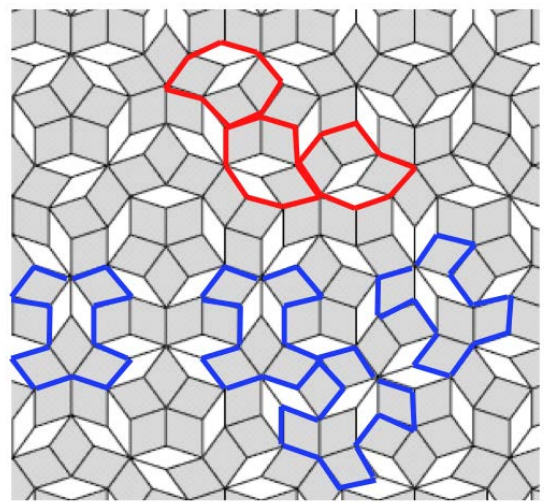




2 tiles with (local?) matching rules ➔aperiodic tiling ... but with diffracting planes ...

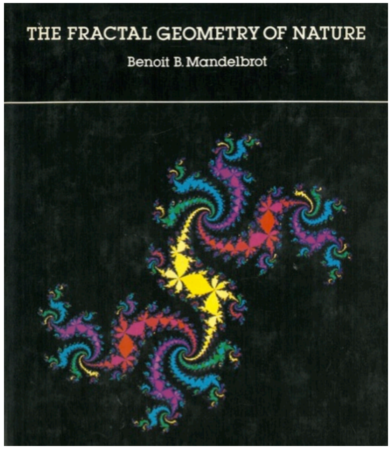


... self-similarity (inflation) ...

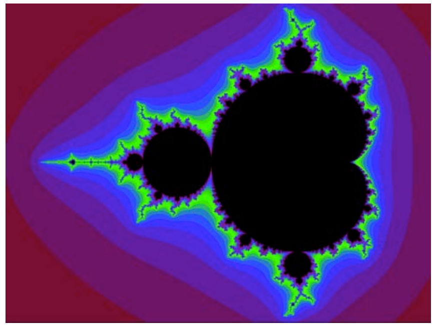


... and "Penrose recurrence".

Fractals



Mandelbrot, Freeman (1977)



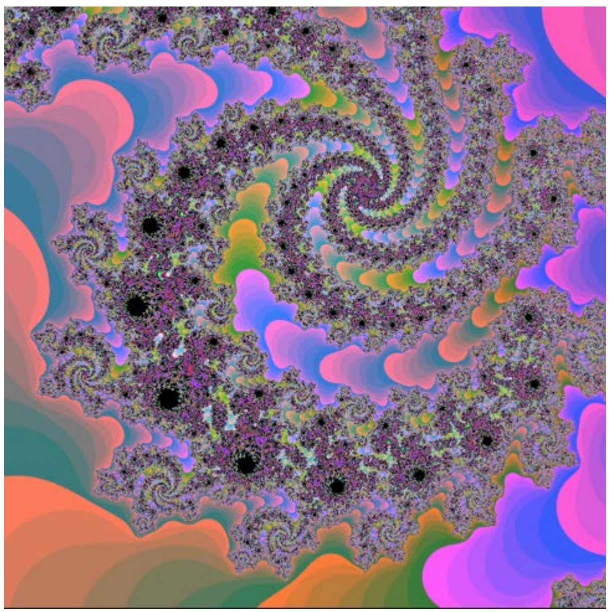
How long is the coast of England?

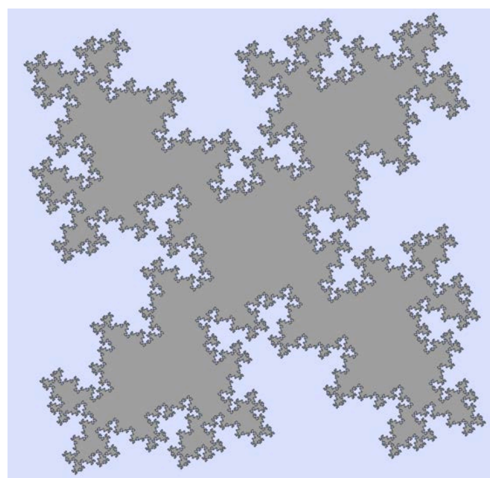
s = 200 km
L=2400 km

s = 50 km
L=3400 km

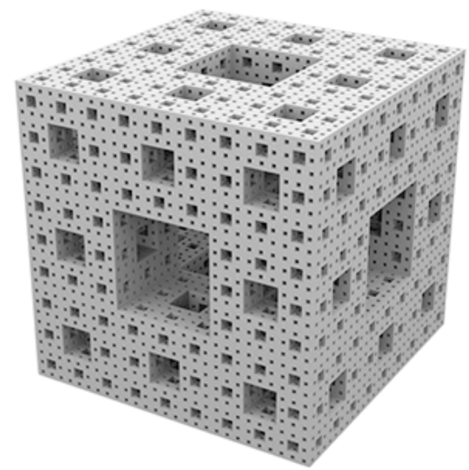
$$L(s) \propto s^{1-D}$$

Fractal dimension D=1.25



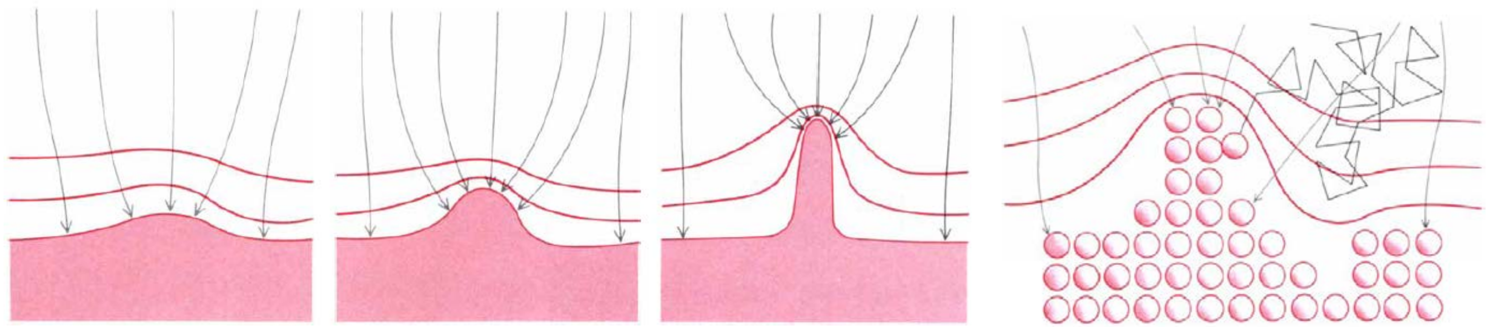


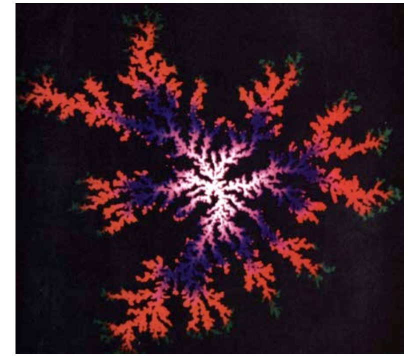
Koch island D=1.25



Menger sponge D=2.73

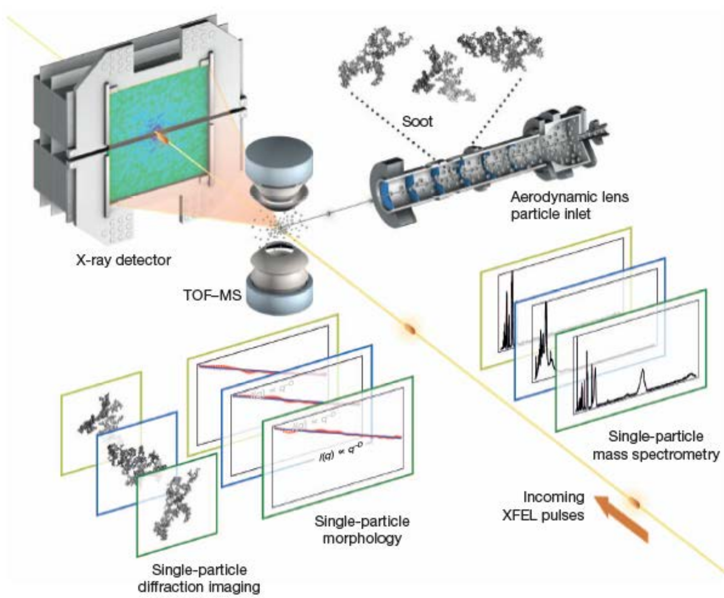
Diffusion-limited aggregation

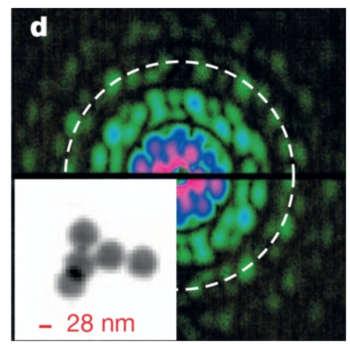


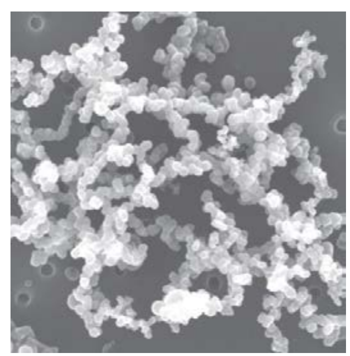


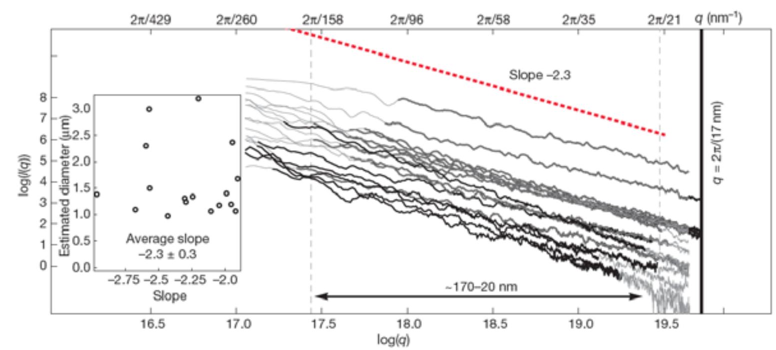
Sander, Sci Am, (1986)

Soot particles in flight
X-ray scattering (at LCLS XFEL)









$$I(q) \propto q^{-D}$$

D=2.3±0.3

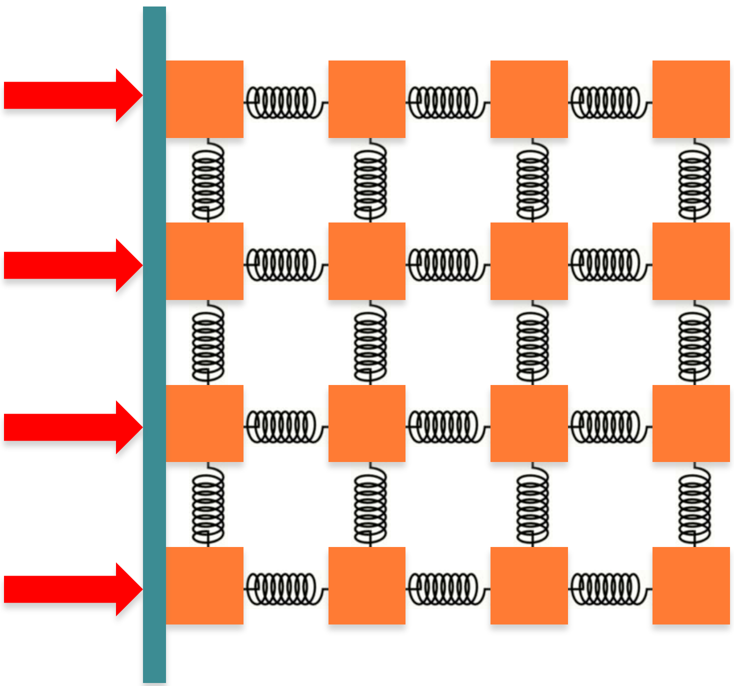
Loh, Nature, (2002)

Self-organized criticality

Self-Organized Criticality: An Explanation of $1/f$ Noise

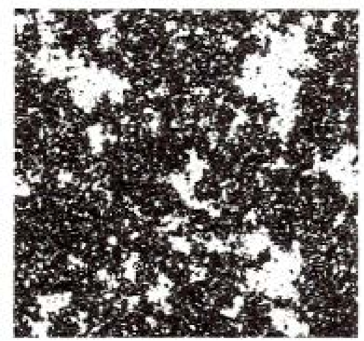
Per Bak, Chao Tang, and Kurt Wiesenfeld
Physics Department, Brookhaven National Laboratory, Upton, New York 11973
(Received 13 March 1987)

We show that dynamical systems with spatial degrees of freedom naturally evolve into a self-organized critical point. Flicker noise, or $1/f$ noise, can be identified with the dynamics of the critical state. This picture also yields insight into the origin of fractal objects.



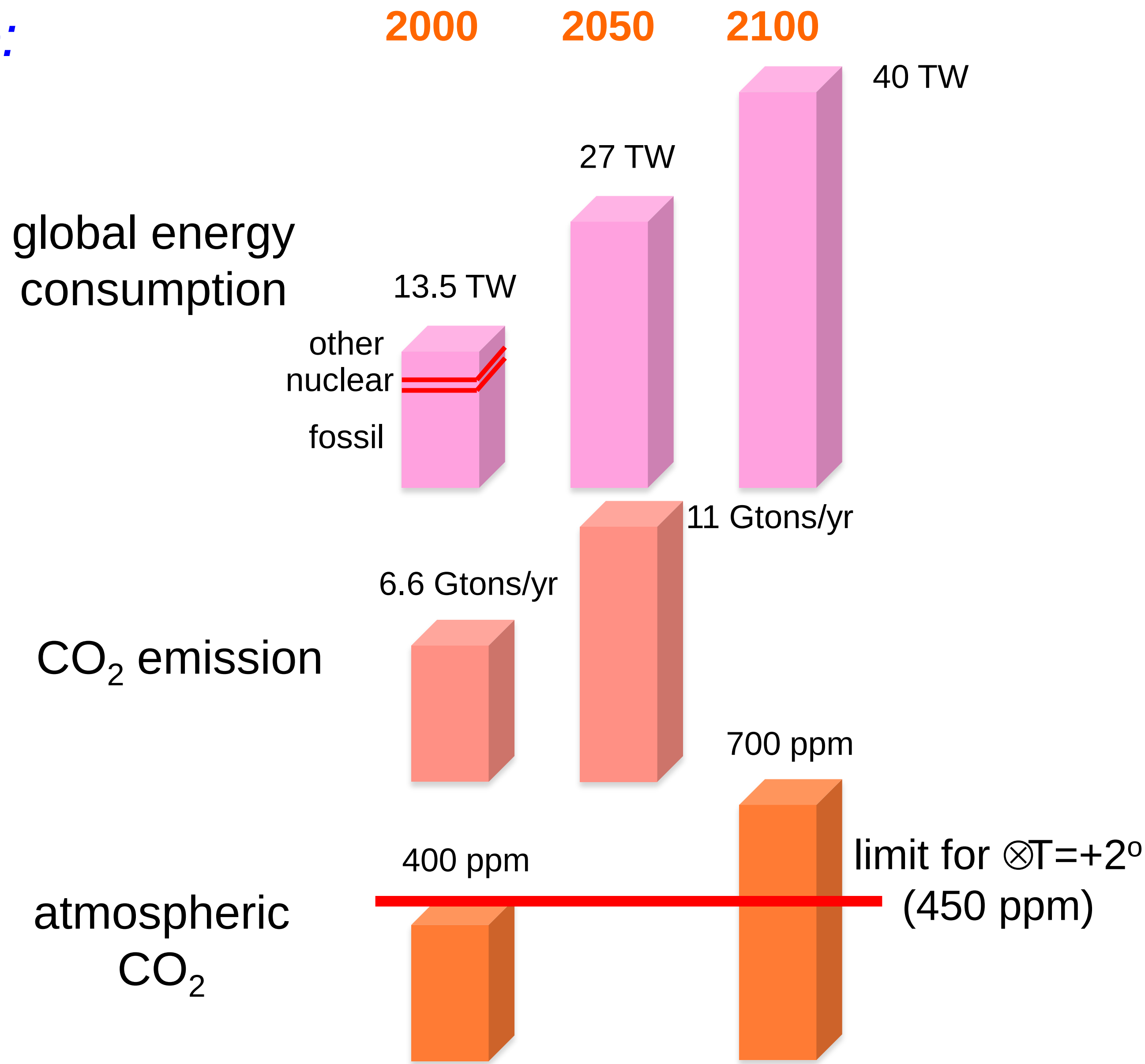
Frictional sliding-block "earthquake" model:

Continue to push:
- critical situation reached (SOC)
- power-law probability distribution of quakes
- 1/f noise spectrum
- fractal distribution of local strains



5. Climate dilemma: time scale = 36 years

If we continue status quo:



Needed: 10 TW C-free energy by 2050

options:

1) nuclear fission

➔ 1 GW plant/1.6 days for next 45 years

➔ exhaust ^{235}U in 10 yrs

2) CO_2 capture / storage

➔ store 1 x Lake Superior / yr; leakage < 1%/yr

3) solar

10 TW @ 10% ➔need 350 x 350 km^2

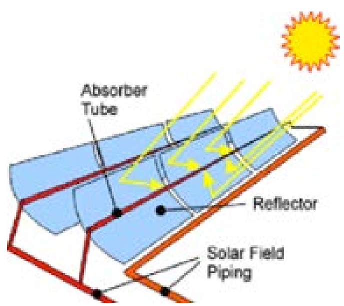
a) PV

➔ must reduce cost by factor 15

➔ pumped storage for US:

5000 Hoover Dams / day

b) solar thermal – worth considering



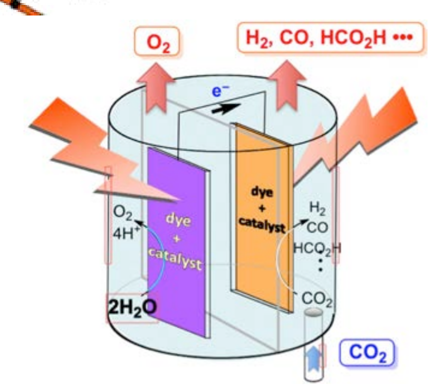
c) biomass

conversion efficiency <1%

➔ use *all* arable land not used now for food

d) liquid solar fuels (*e.g.*, methanol)

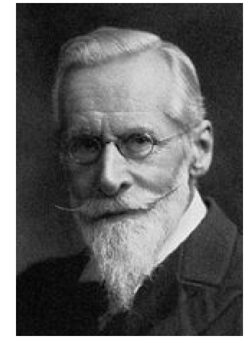
➔ *Understand photocatalysis at atomic time and length scales!*



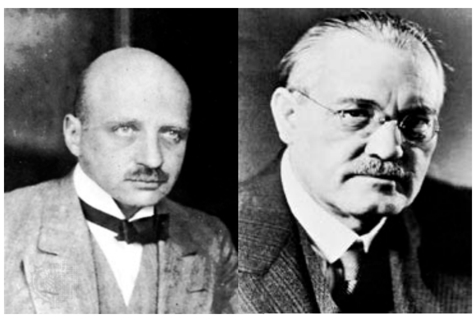
Lewis + Nocera, PNAS (2006)

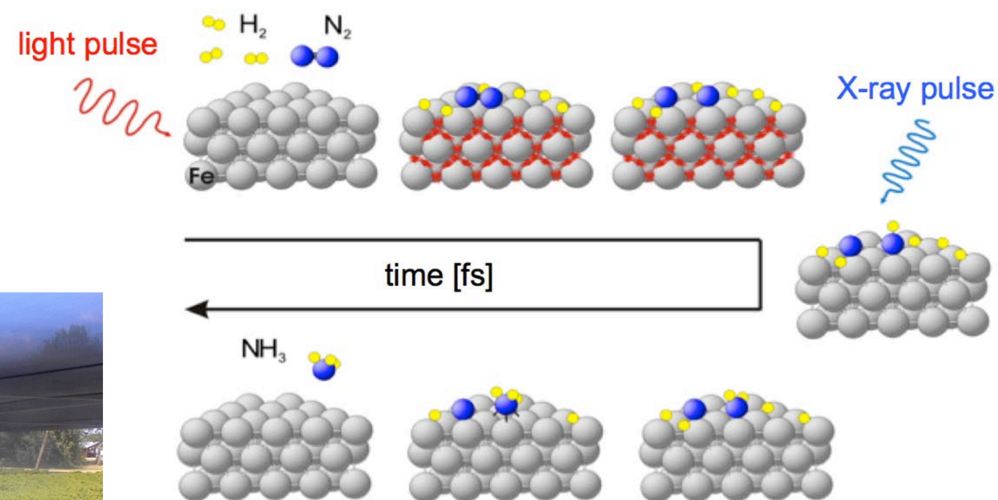
Crookes' address

British Academy of Science, Fall 1898, Bristol, England:



- "All civilized nations stand in deadly peril".
- Lack of fixed nitrogen fertilizer to feed growing population.
- Not taken seriously then by majority of Englishmen.
- 30 years later, Haber-Bosch process discovered and industrially developed.
- Now feeds 1/3 of global population.





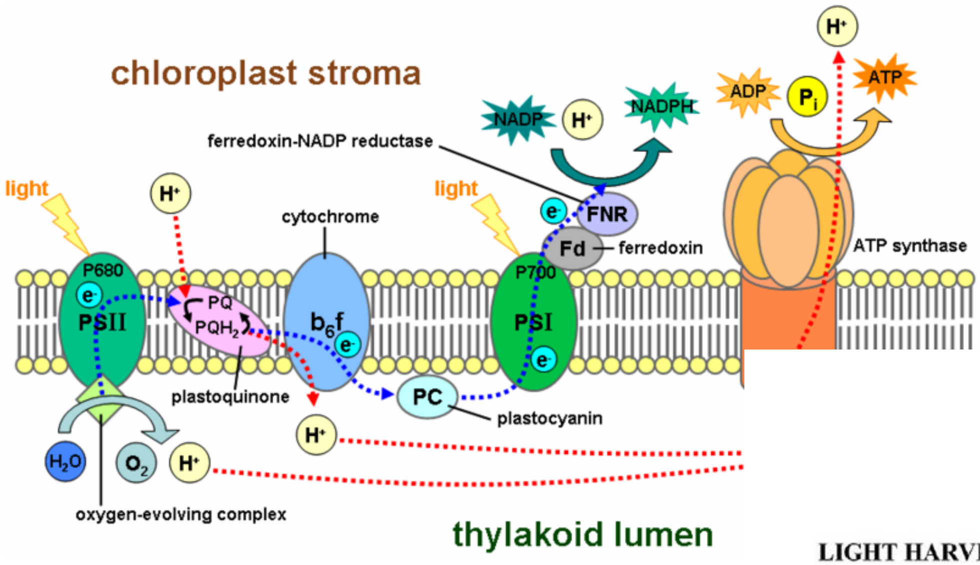
Th Hager, "The Alchemy of Air" (2008)

Photosynthesis

Natural photosynthesis:

ca 1% efficient

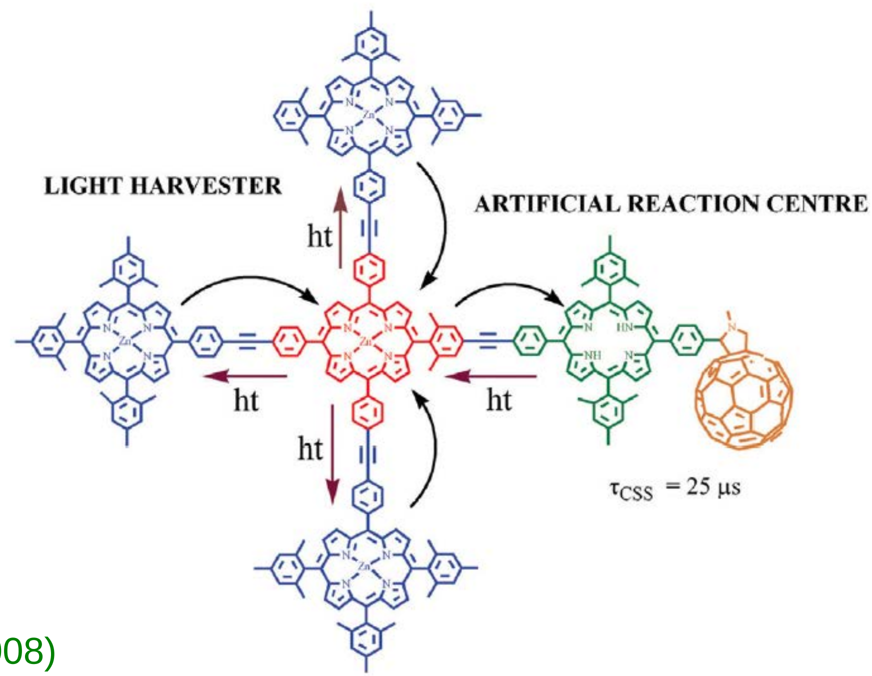
UV damage ➔ plants must replace all photosensitive molecules every 30 min!!



Artificial photosynthesis:

needs sophisticated molecular engineering

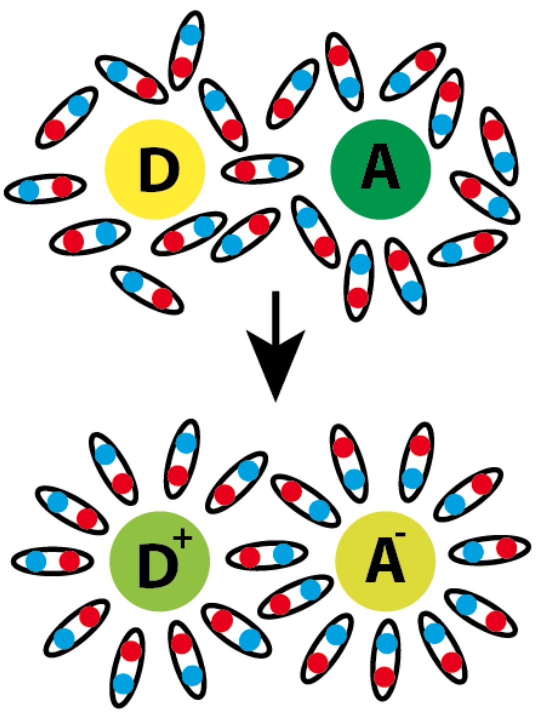
important step: electron (and hole) transfer



Benniston, Mat Today (2008)

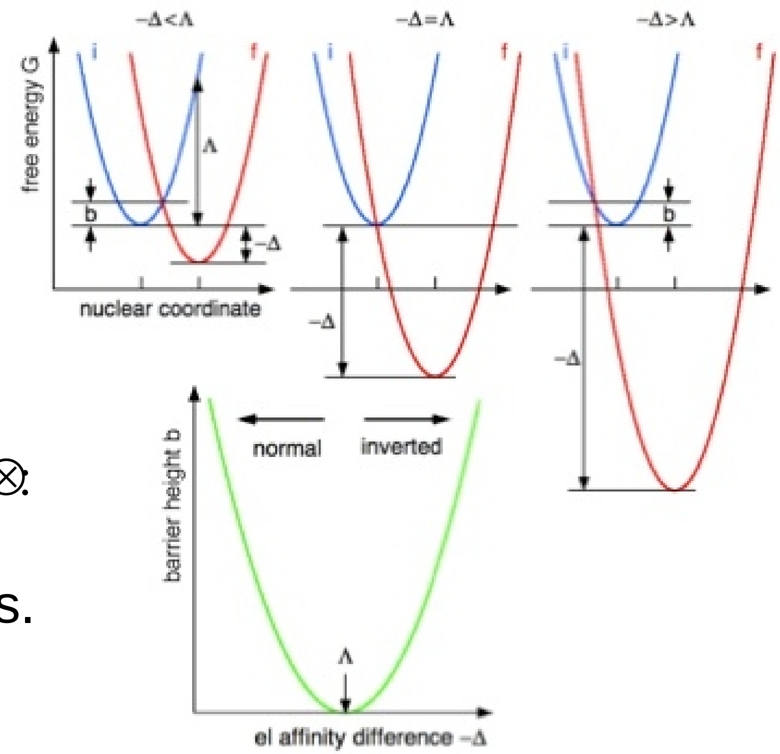
Marcus theory: electron transfer

- RA Marcus, Nobel Prize (Chemistry, 1992)
- Quantify electron transfer from donor (D) acceptor (A) in a polar solvent.
- Define "nuclear coordinate" corresponding to solvent polarization.
- Assume parabolic potentials.
- Barrier height *b vs* electron affinity difference ⊗:



$$b = \frac{(\Delta + \Lambda)^2}{4\Delta}$$

Inverted regime at large –⊗: essential to inhibit back-reactions in photosynthesis.



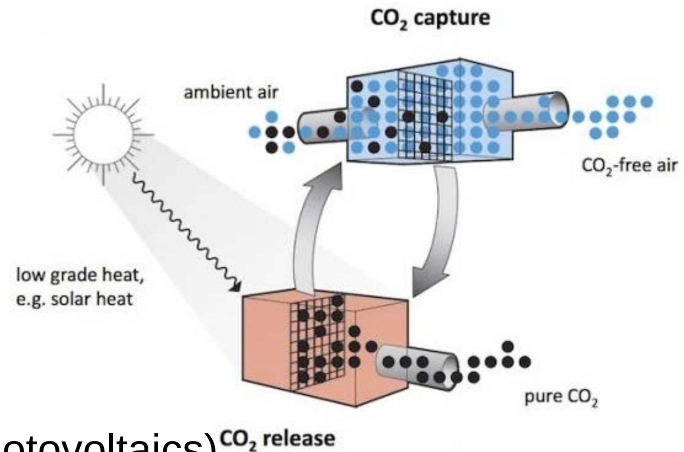
Marcus, J Chem Phys (1956)

Liquid solar fuels

Goal: $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$

Requires:

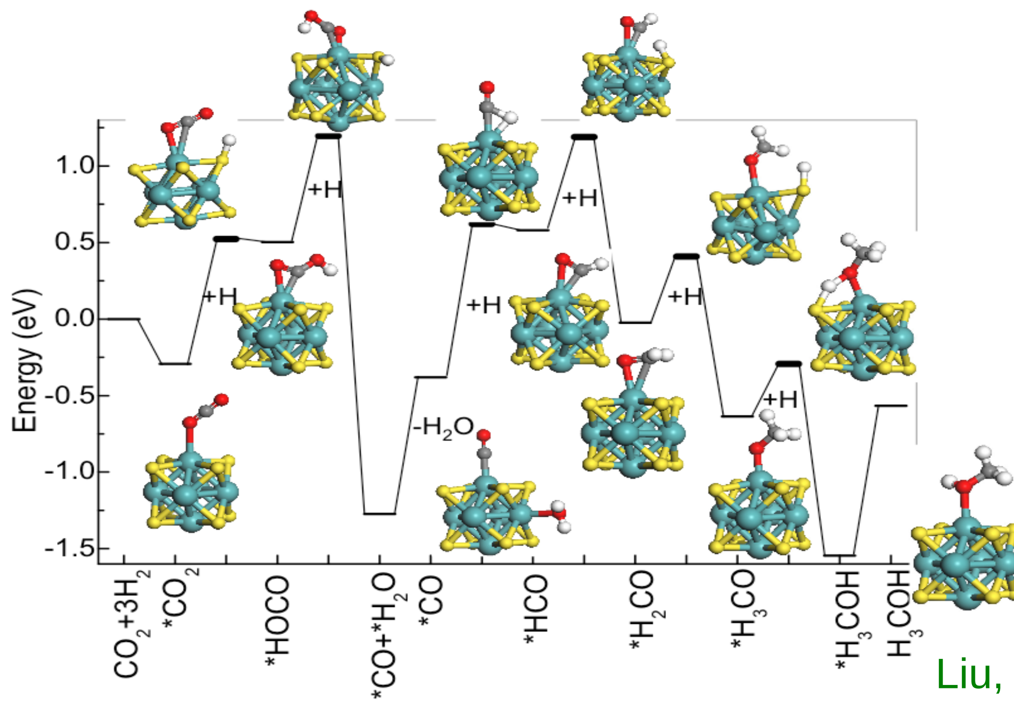
extracting CO_2 from atmosphere
(absorb on KOH, <$100 / ton)



ClimeWorks,
ETH/EMPA

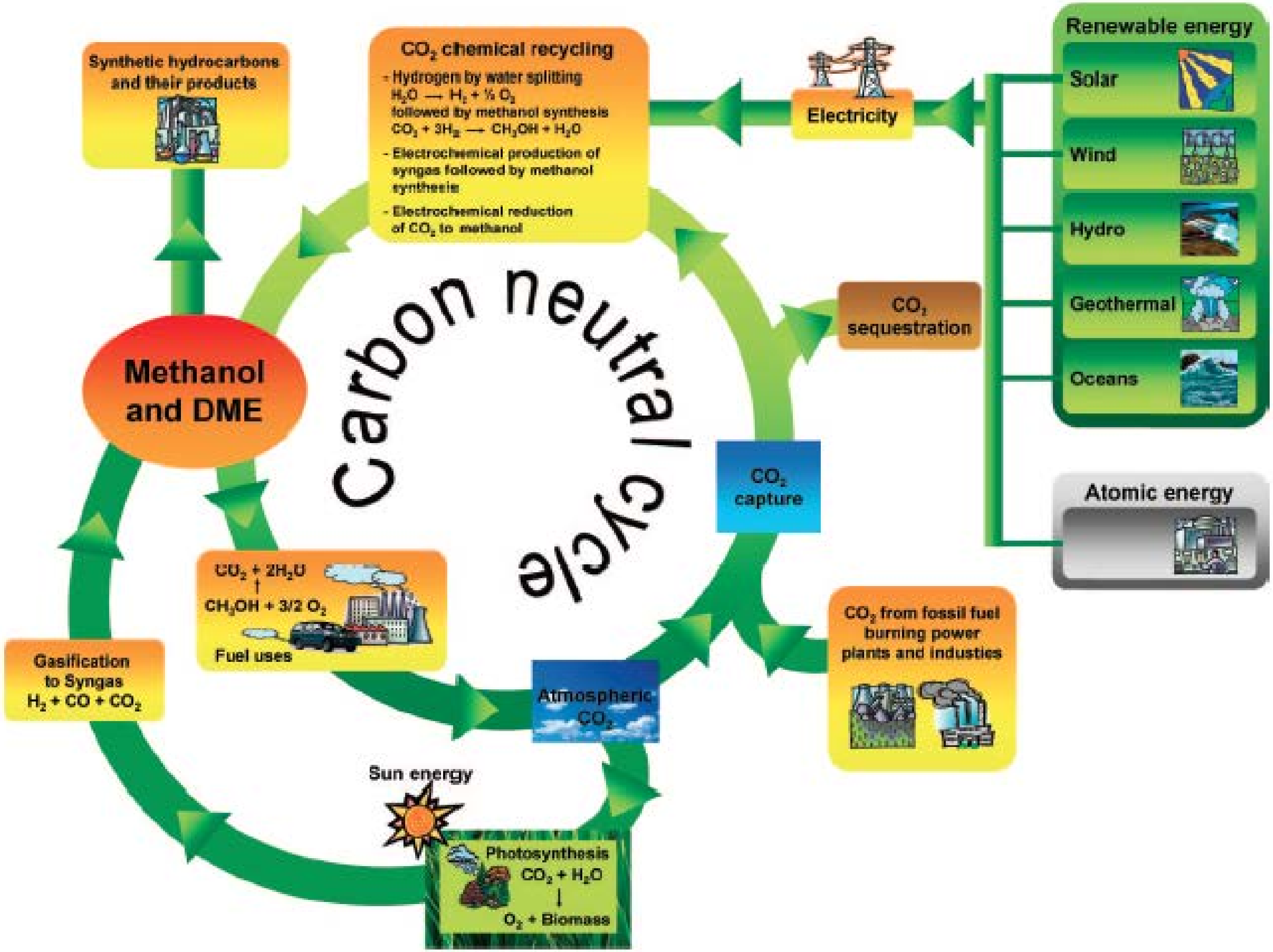
electro-hydrolysis to split water (use photovoltaics)
catalytic hydrogenation of CO_2 to produce methanol

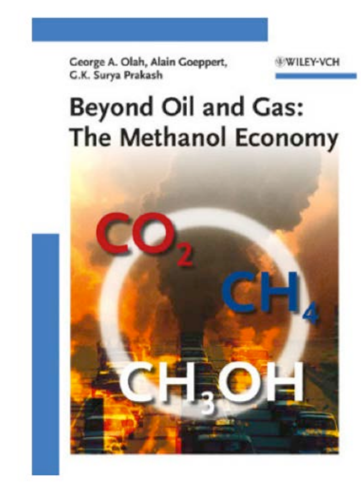
possible catalyst:
Mo_6S_8 clusters



Liu, J Phys Chem (2010)

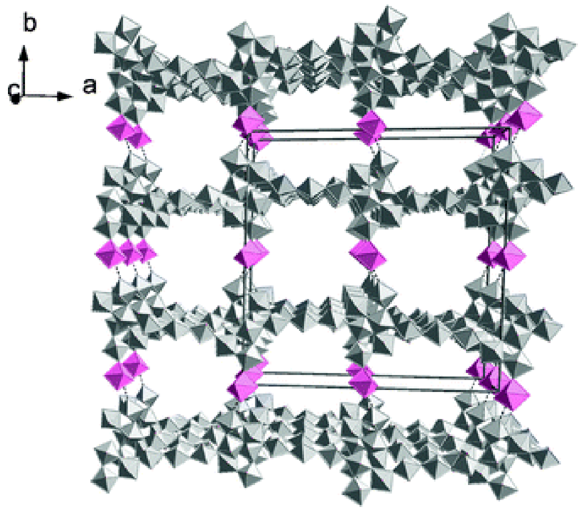
The methanol economy



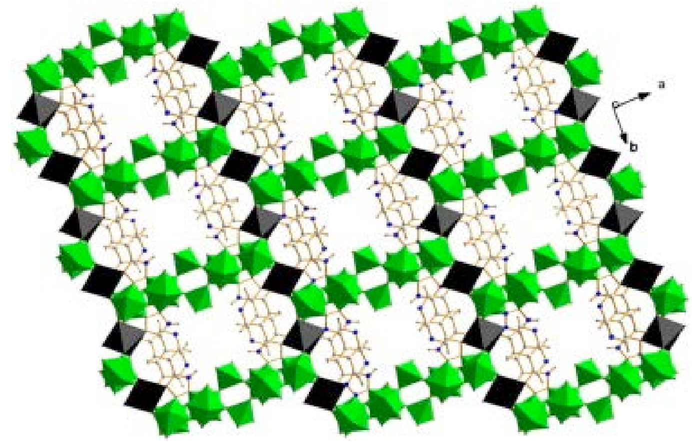


G Olah, J Org Chem (2009)

Metal-organic frameworks (MOF)



YG Li, Chem Comm (2007)

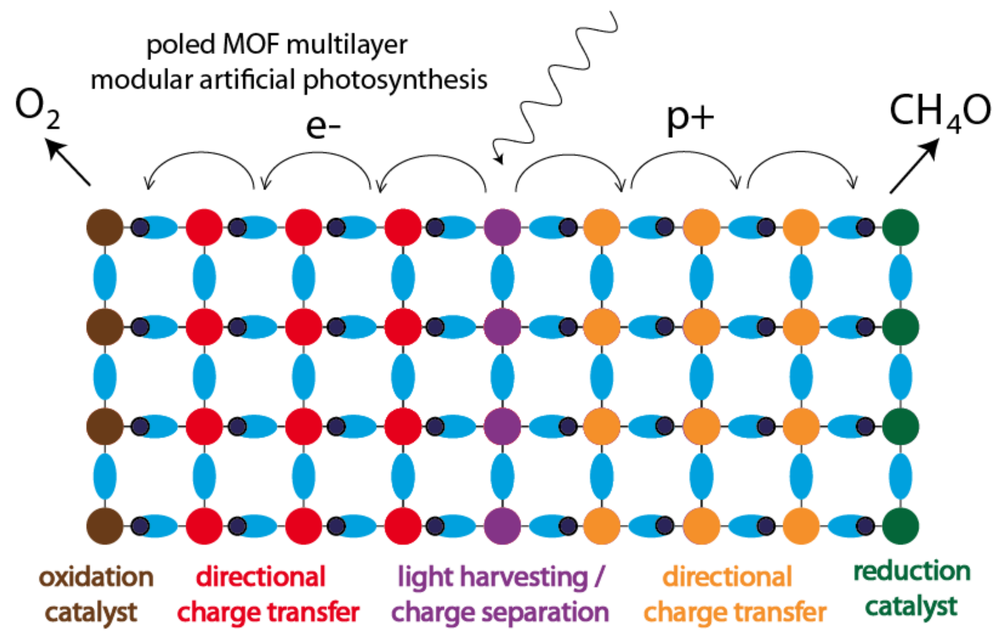


MX Yang, Inorg Chem Comm (2011)

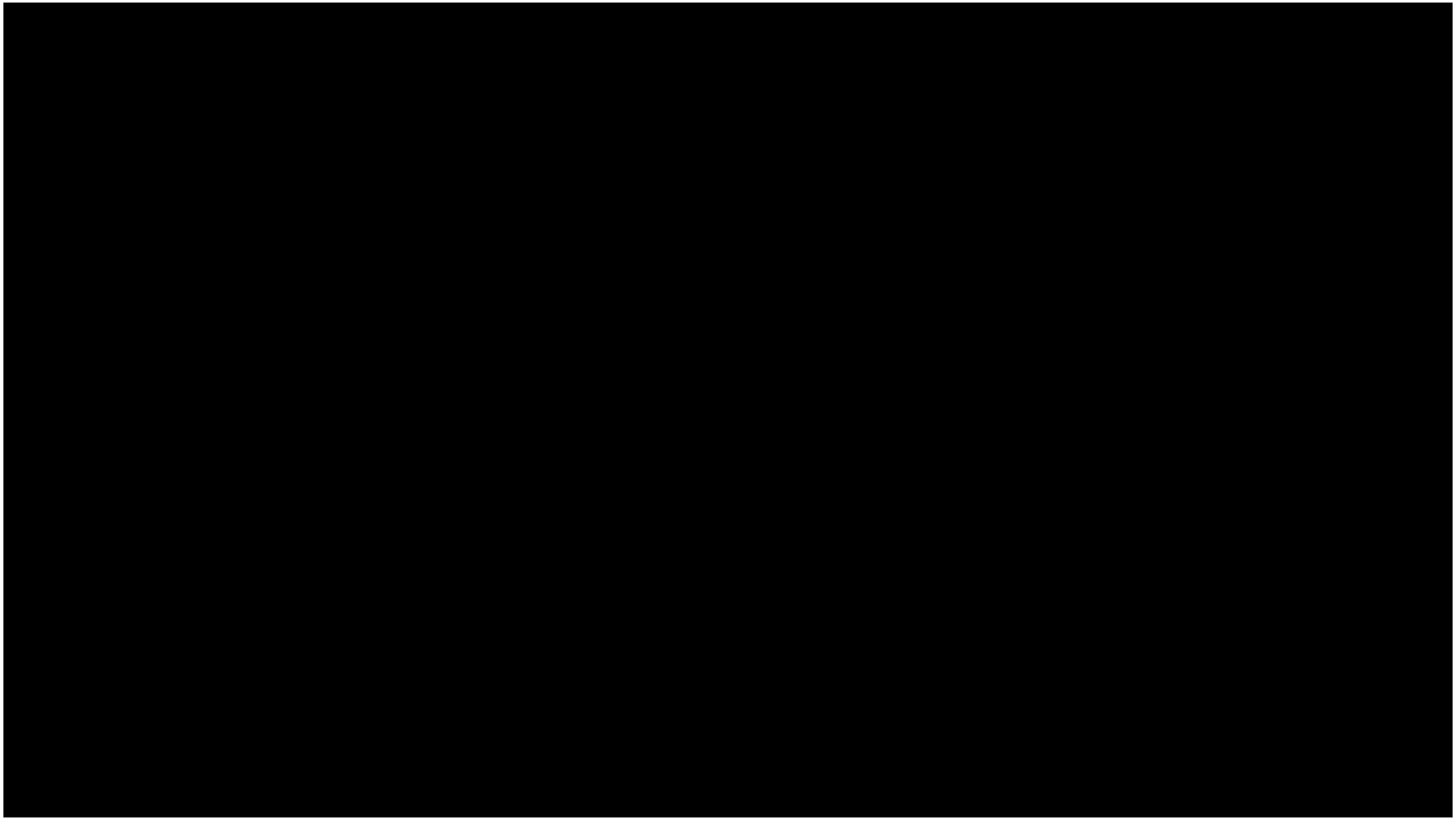
advantages
- flexible chemistry
- highly porous
- combines heterogeneous and homogeneous catalysis

disadvantage
- poor stability

BP's dream: heterostructure MOF
"REDOX junction"



6. The life of the cell



time-lapse factor: ~10^6

Harvard Biovisions (2009)

Thank you for your attention.