Energy landscapes – past, present and future

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MAX-PLANCK-GESELLSCHAFT

Studying energy landscapes : Why ?

The World

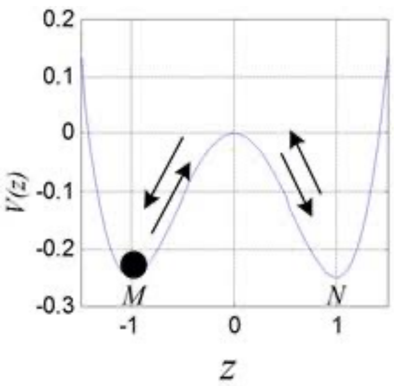
Natural Science

"Never shall the twain meet" ?

(Human) Society / Life / Self-conscious beings

Foundation:
- Laws of physics
- Tools of mathematics
- Substrate of materials

Emergent complexity:
- Chemistry, biology,...
- Engineering



Foundation:
- Rules of evolution
- Tools of psychology
- Substrate of living entities

Emergent complexity:
- Sociology, economy, law,..
- Society

In physics, stable states often look like the extremum of a function, e.g. the energy. Many dynamical / static / stationary states can be described by a point on such an "energy landscape". Do we find similar landscapes in e.g. economics, evolution etc. ?

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- Stable states
- Dynamics and time evolution:
  - Microstates → macrostates
  - Energy as driving potential → forces in the non-living world, phenomenological laws

Energy landscape

- Stable society / ecosystems
- Time evolution:
  - Individual lives → organizations
  - Striving and driving potentials → forces in the living world, rules of societal processes

Cost function / fitness landscape

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"Energy" landscapes:

- Potential energy
- Potential enthalpy
- Free energy
- Cost functions of inverse problems
- Geological landscapes
- Cost functions of (abstract) optimization problems
- Cost function of engineering problems
- Optimal control landscapes

Cost function / fitness landscapes:

- Evolutionary fitness
- Cost function of business plans
- Budgets
- Cost functions of (living being) optimization problems
- Social fitness within groups
- Biological fitness of groups
- Social fitness of groups
- Migration landscape
- Objective functions of control problems in organisms

Pictures of examples from the "world"

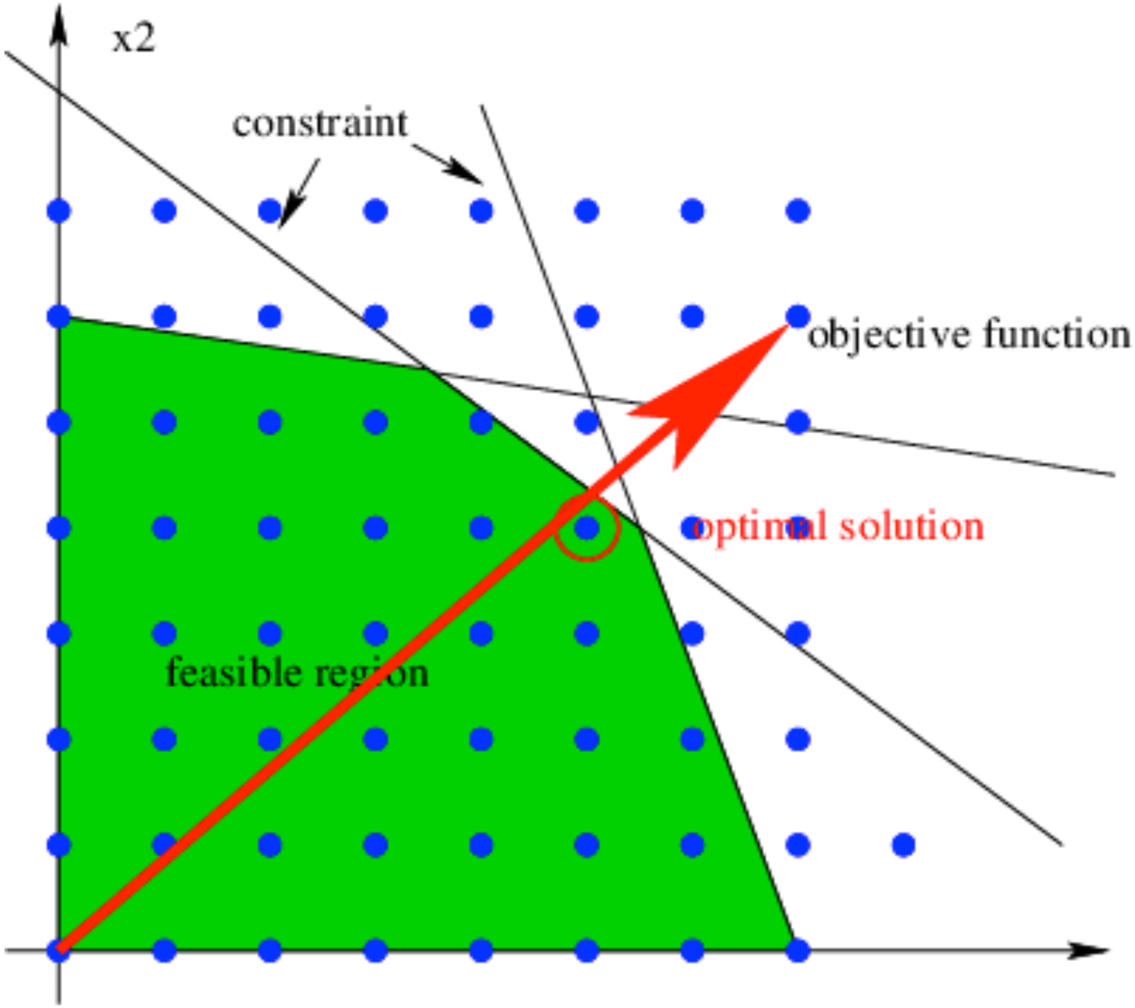
Potential energy landscape made by nature

"Manager fitness" landscape built by humans

History of energy landscapes: Systems (I)

	before 1950 („before“ computers)	1950 - 1980
Physics	Inverse problem data analysis; potential energy (two-well problems); chaotic trajectories; glass transition (1948); diabatic (excited electronic state) energy surfaces (1935)	Spin glass (1970‘s), Coulomb glass (1970‘s), multiple-double-well model for glasses (1972); landscapes „without“ global minimum (1970‘s)
Chemistry	(Minimal degree of freedom) small molecule models (1930‘s); optimal shapes of crystals (1901), defects, isomers (19th)	Landscape paradigm of glass (1969); cis/trans barriers; crystal structure from powder diffraction problem (1960‘s)
Mathe-matics / Computer science	Global optimization problems: Knapsack (1897/1912), Graph partitioning (19th/1966), Sphere packings (17th); Penalty functions to guide/simplify the problem (1943)	Satisfiability problems (1950‘s); Scheduling problem (1966); NP-completeness (1970‘s); Robotics (1961)
Biology / Econo-mics	Travelling Salesman problem (18th/19th/1930‘s/1950‘s); business cost analysis (1940‘s/1950‘s); Pareto optimization (1897)	Protein folding Levinthal paradox (1969); simulated evolution (1950‘s); (evolutionary/design) fitness function (1960‘s/1970‘s)

Pictures of examples from the "world"



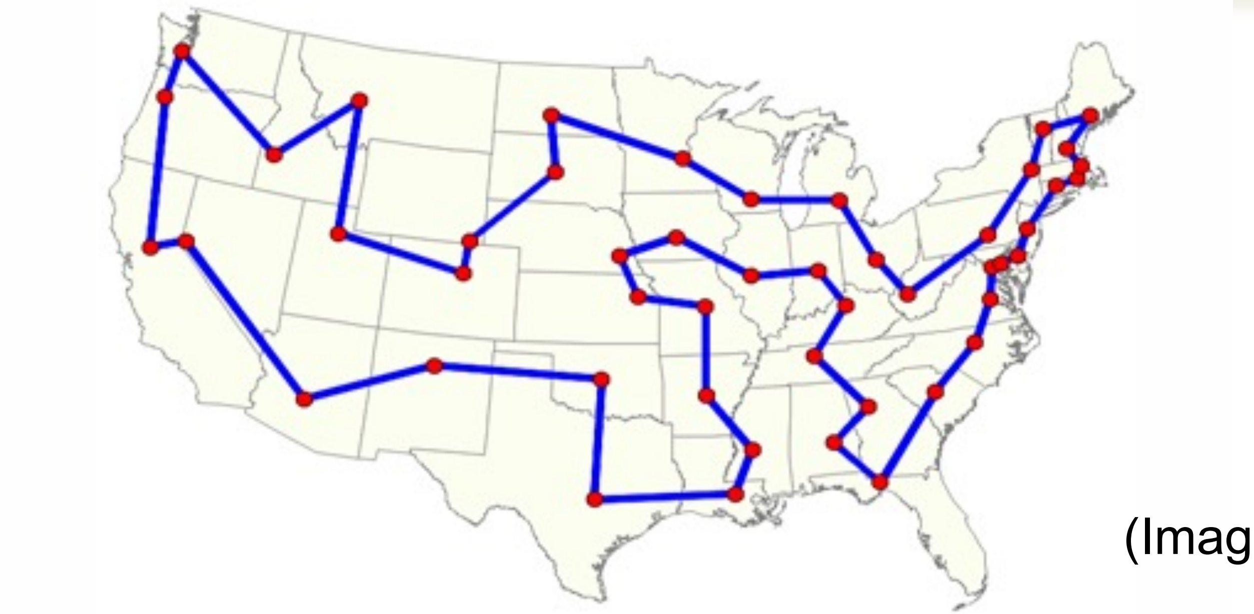
(Image by F. Hüffner)

Business plan combinatorial optimization problem:

$x_1$and x_2 represent small city-cars and SUVs being produced, and the linear objective function is the profit we can make (all lines orthogonal to the red arrow yield the same profit).
Constraints refer to limitations in the production process.

"Corners" should be optimal, but constraints do not hit the corners => non-trivial global optimization problem !

Pictures of examples from the "world"



(Image by R. Allison)

Travelling Salesman Problem:

Find the shortest / fastest route (possibly under additional side conditions) to visit all locations (in a circular route).

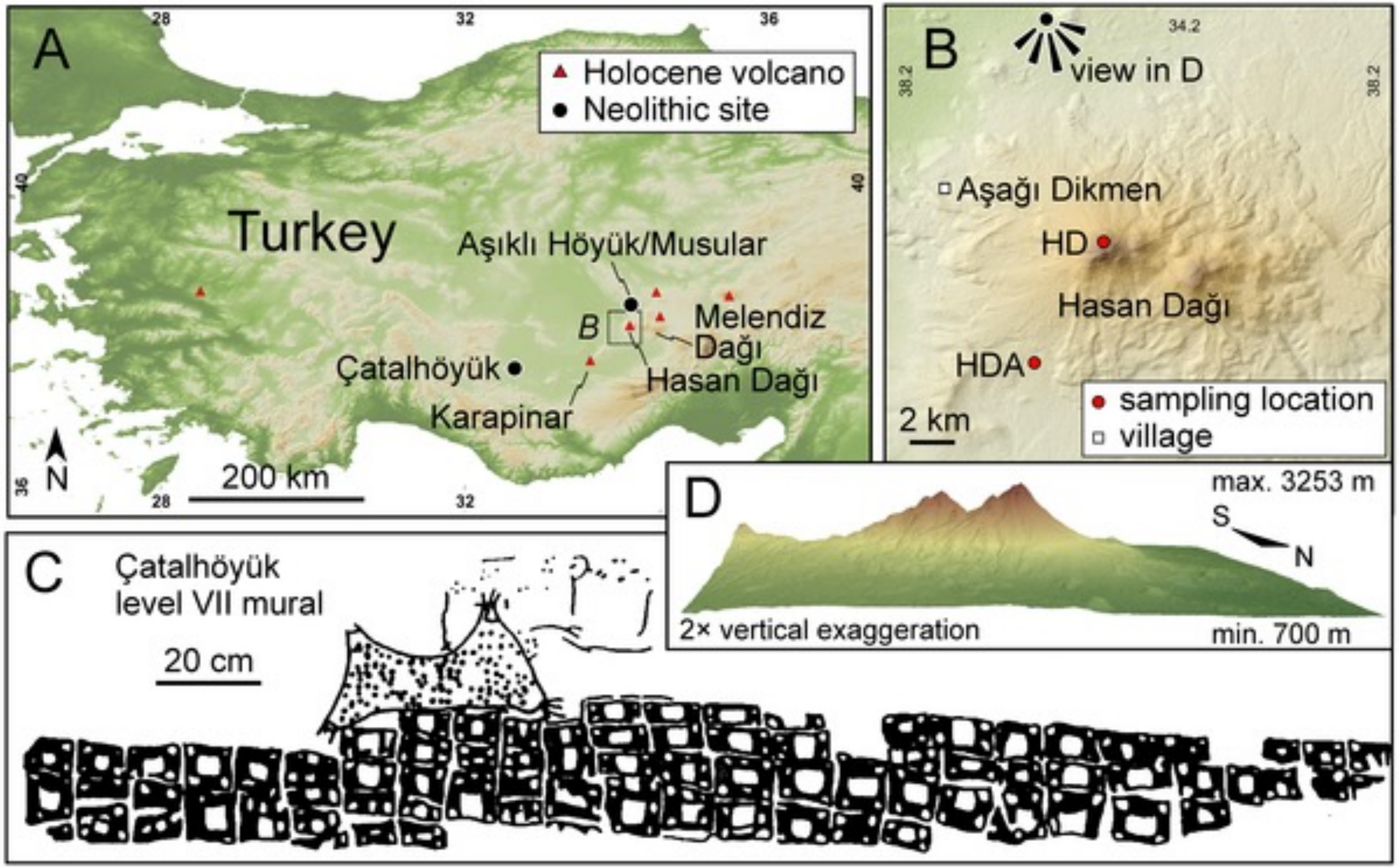
In general, this is a non-trivial so-called NP-complete global optimization problem with a highly complex cost function landscape.

History of energy landscapes: Methods (I)

	before 1950 (computers)	1950 - 1980
Landscape represen-tations	Reaction path depictions (1930‘s); small minima+saddle point sets; geographical/town maps (6,500 B.C.); phase diagrams	Purely conceptual as plethora of local minima (1969) or double wells (1972); principal coordinates (1966); dihedral angles state space (1963)
Global optimiza-tion	Exhaustive (isomer) graph enumeration (1927/1937); gradient minimization (1847); linear programming (1827/1939/1947); Verlet integration of differential equations (1791); calculus of variations (17th/18th/19th)	evolutionary algorithms (1960‘s); genetic algorithms (1970‘s); P-completeness of linear programming (1979/1984); branch and bound (1960); optimal control (1950‘s)
Barrier / dynamics studies	Escape from minima and transition between minima via a saddle point via diffusional motion (1940); transition state theory (1935)	Two-minima problems (analytical/numeric); MC/MD simulations (1953/1957)
Density of states	Stat. Mech. / thermodyn. viewpoint; global ergodicity (19th/1913); thermodynamic integration / perturbation (1935/1954)	Global DOS of model systems; umbrella sampling (1976)

Oldest known map of a landscape created by humans

Figure 1. Location of the Çatalhöyük Neolithic site, Hasan Dağı, and other Holocene volcanoes in Anatolia.



(Schmitt AK, Danišík M, Aydar E, Şen E, Ulusoy İ, et al. (2014) Identifying the Volcanic Eruption Depicted in a Neolithic Painting at Çatalhöyük, Central Anatolia, Turkey. PLOS ONE 9(1): e84711. https://doi.org/10.1371/journal.pone.0084711)

https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0084711

History of energy landscapes: Systems (II)

	1980‘s	1990‘s
Physics	Binary LJ glasses (1983); alloy models; (tree) graph models (1985/1988); Stillinger-Weber landscape models for glasses (1981); random energy model (1981)	Analytically solvable graph models (1991); solid solutions; verification of alloy phase diagrams; REM with connections (1997)
Chemistry	Polymer glasses; protein models; prediction from „sequence to structure“; small atomic/nuclear clusters; structural glasses; structure solution of glasses; structure comparison of crystals	Small molecule landscapes; prediction of polymers; folding landscape models; small/medium cluster prediction; determination (1990) / prediction for crystals (1994); optimal lattice occupation in solid solutions; enthalpy landscapes
Mathe-matics / Computer science	Optimal control problems; neural network parameter landscape (1987); analytical models; artificial landscapes for heuristics/counter examples	Robotics path planning landscape (1990); probabilistic landscapes; meta-landscape of ensembles of walkers (for algorithms)
Biology / Economics	Evolution models; resource allocation	Discrete protein landscapes; lock-key protein landscapes; RNA landscapes

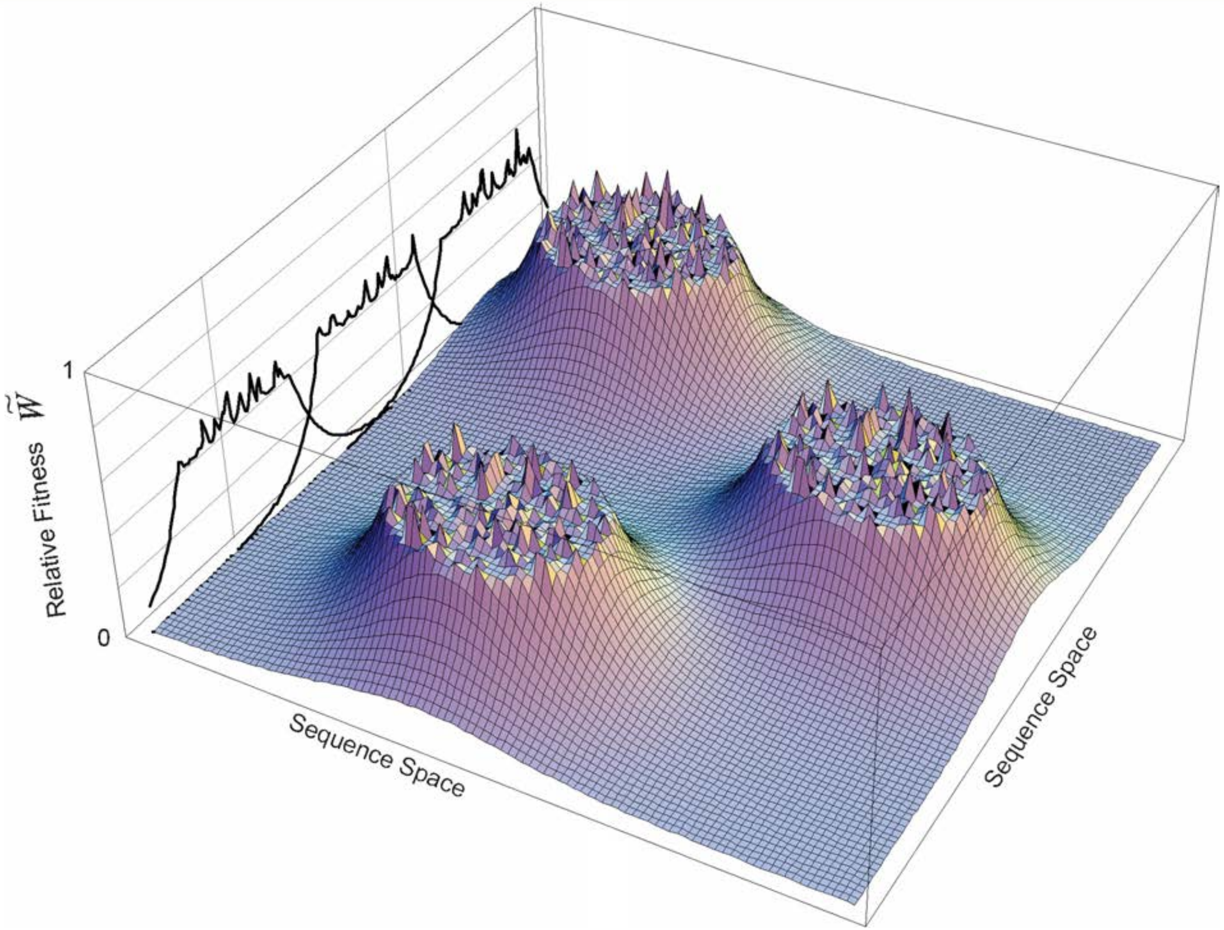
Pictures of examples from the "world"

Fitness function:

In biology, originally defined as the ability of a species to produce descendents.

Nowadays, fitness has been generalized to mean the "quality of a design", etc.

It is the analogue to the energy or cost function, but we strive to maximize the fitness



(Experimental fitness landscape in protein sequence space; From: Hayashi et al., PLOS ONE 2006)

History of energy landscapes: Methods (II)

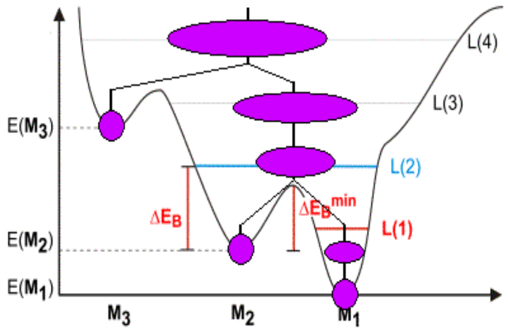
	1980's	1990's	After 2000
Landscape representa -tions	Lumped tree graphs / model tree graphs (1985/1988); Boltzmannised graphs (1989); Markov model dynamics	Local full metagraphs (1993); equilibration trees (1993); probability flows (1999); order parameter plots; tree graphs (1993/1996/1997/1998); MODC (1997); basin-transition matrix (1994)	Characteristic regions (2001); entropic barriers (2003); weighted tree graphs (2005); metastable phase diagrams (2012); G vs. ln(tobs) plots (2015)
Global optimiza-tion	Simulated annealing (1983); taboo searches (1986); jump/bounce algorithms (1988)	Basin hopping (1997), genetic algorithm on minima (1995); deluge algorithm (1990); sequential multi-quench (1995); thermal cycling (1997); many variants of SA; particle swarm optimization (1993); rapidly growing random tree method (1998); machine learning prediction (1992)	T-RRT (2011); ANT algorithm (2013); upgraded NN-based (machine learning) (2019); threshold minimization (2015); hierarchical approaches (both regarding systematics and landscape features)
Barrier / dynamics explora-tion	Saddle point searches (1981); orthogonal path minimization; slowest slides (1986)	Eigenvector following (1991); lid (1993) / threshold (1996); transition path sampling (1997); NEB (1994); „activated" MD (1993/1997); record dynamics (1993)	Metadynamics (2002); prescribed path (2005/2012); pathOpt (2013) ; variants of NEB; hierarchy of transition states (2001)
Density of states	„WHAM" (1989); DOS via width of saddle points / curvature of local minima	Computational alchemy (1990), WHAM (1992); parallel tempering (1992); local DOS and DO minima via lid (1993) / threshold (1996)	Variants of WHAM, ParQ (2007)

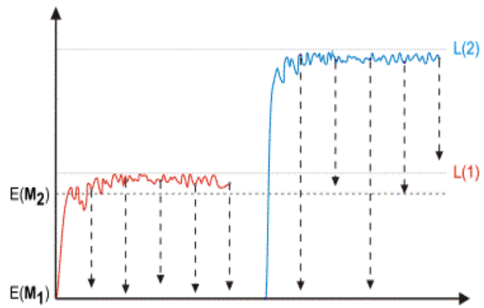
History of energy landscapes: Concepts

	before 1950's	1950 - 1980	1980 - 1990	1990 - 2000	after 2000
Land-scape features	Minima, saddles, energy barriers, reaction paths	Minima and saddle point DOS; order parameters (1950); stable states (1980)	Density of local minima (1989); inherent structures (1982); tree connectivity (1985)	Local density of states beyond single minimum (1993); saddle+minimum network (1993 / 1995); exponential growth-traps (1997 / 1998); locally ergodic regions (1998)	Entropic and kinetic stabilization and barriers (2003 / 2005), characteristic regions (2001); free energy barriers (2016)
Global explora-tion concepts / inspira-tions	Analytics; repeated gradient descent	Systematic (BB) (1960); random (MQ); biology-inspired (EA, GA: 1962 / 1965)	Technology (SA) (1983), analytic (saddle searches) (1981); exhaustive (tabu) (1986)	GO+min (BH, TC, GA-min: 1997 / 1997 / 1995); multi-walker (PSO, demon: 1993 / 1992); motion planning (RRT 1998); bible (deluge 1990); Tree+taboo (Lid 1993); brain (NN 1992)	Stat.mech.+robotics (T-RRT 2011); Lamarck (ANT 2013); NN (machine learning 2008 / 2019); Taboo+order parameter (Metadynamics 2002)
Interpre-tation	Only global minimum counts; robust-ness issue	Multitude of minima are „all“ occupied	Self-averaging (1980/1984); Protein folding funnels (1987); self-similarity (1988)	Probability flow vs. Single walker trajectory: Master-Eq. dynamics (1991 / 1993 / 1997); local free energies (1996); equilibration tree (1993)	Metastable phase diagram (2012); quakes (2003); optimal control of ME dynamics to access regions / minima (2013)
Statistical / dynamics concepts	Thermody namics	Multi-minima system; config. entr. (1965); aging (1978)	Broken ergodicity (1982)	Prob. flows (1993); Local ergodicity (1998), time scale dependence (1993 / 1998); rare events (1997)	Marginal ergodicity (2009); local free energy landscapes (2002 / 2008 / 2014)

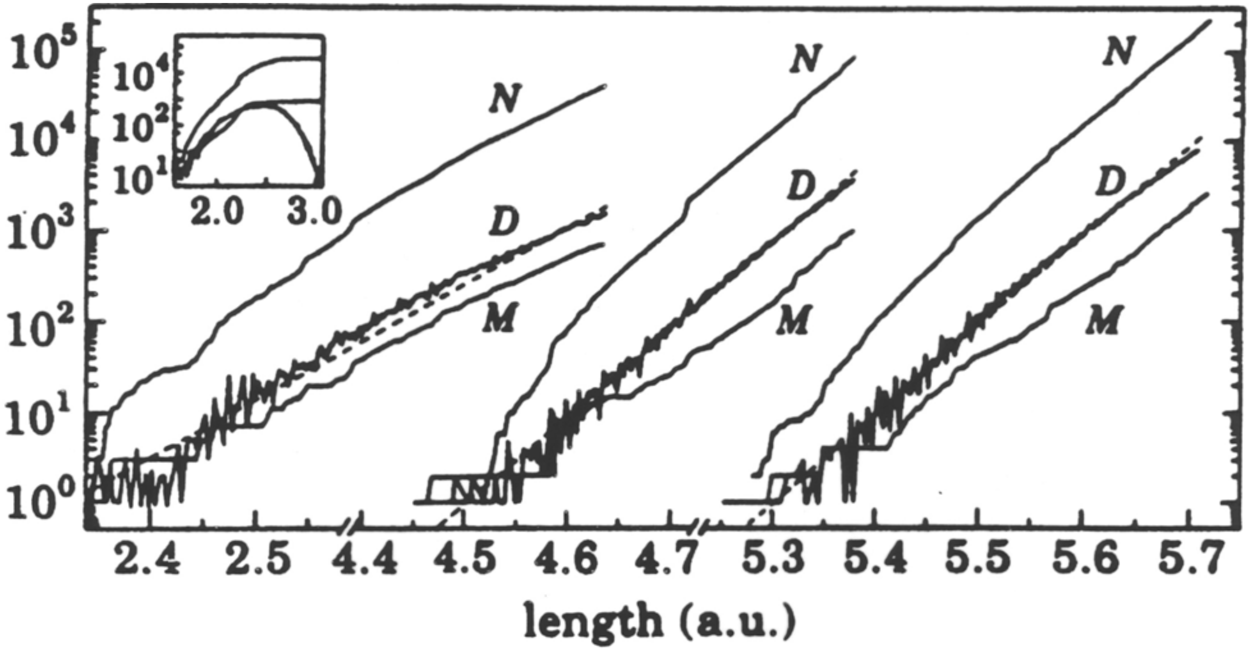
Traveling salesman problem

Sizes of Tour: 8, 20, 32, 36 cities





Lid / Threshold algorithm
(Sibani et al. EPL 1993
Schön, Ber. Bunsenges., 1996)

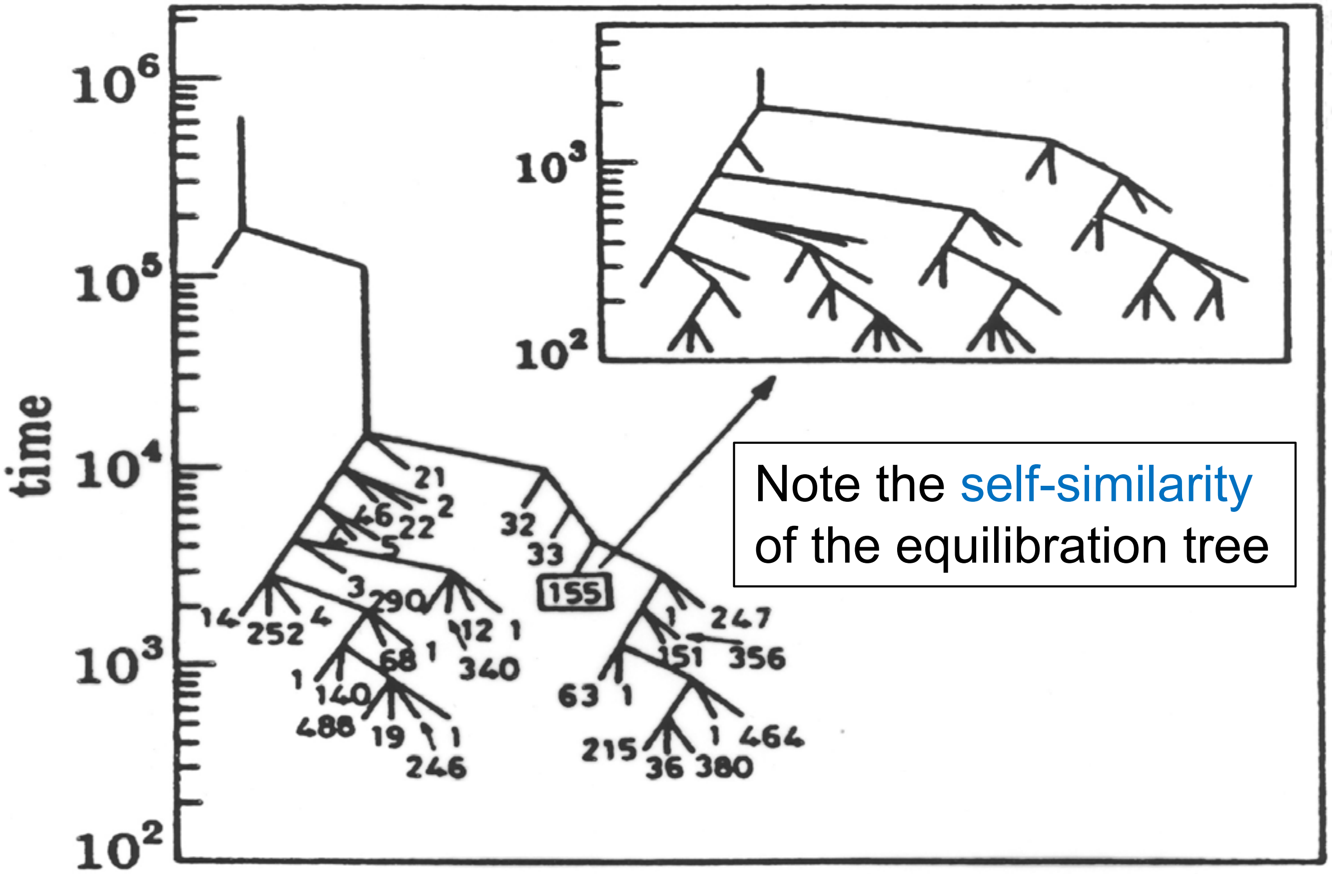


N(L) = number of accessible states
M(L) = number of accessible minima
D(E;L) = density of states in pocket

(Sibani et al., Europhys. Lett. 1993)

Equilibration tree (pocket on 32-city landscape)

Paolo Sibani
1954 - 2023



Note the self-similarity of the equilibration tree

Measure probability flows on the landscape and register, when two minima / states achieve relative equilibrium:
The ratio of their occupation probabilities stays constant for observation times larger than the equilibration time (which is actually defined via this criterion !)

(Sibani et al., Europhys. Lett. 1993)

Looking to the future

A1) Generalized landscape in physics/chemistry - interaction with the environment

A2) Time dependence of energy landscapes

A3) Variation of particle number -> "meta"-landscape including variable number of atoms in the state space (Hilbert-Fock space would be QM analogue) (and also chemical potential parameters)

A4) Inclusion of diabatic/adiabatic energy surfaces

Extended energy landscapes:
Possible / feasible (?) directions

Interactions with the environment*: Themodynamic boundary conditions

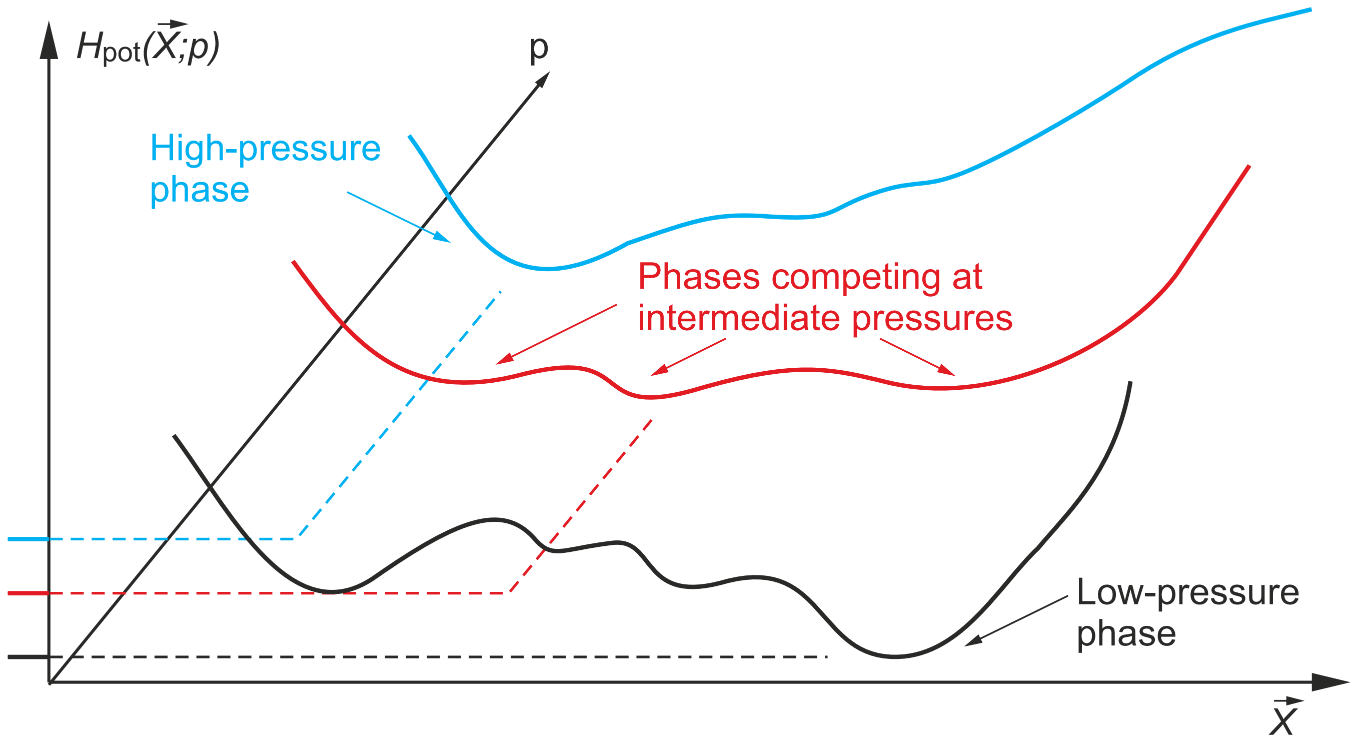
a) Static quantities:
   Pressure, electric/magnetic fields, stresses
   Applied electric potential difference
   Applied temperature difference
   Applied chemical potential difference
b) Enforced currents:
   Electric current
   Thermal current
   Particle current
c) Temperature
d) …

Note: Often requires to connect microstates with continuum approximation variables

(* JCS, J. Innov. Mater. Extreme Conditions, 2021)

Extended energy landscapes: Possible / feasible (?) directions

Shape of the energy landscape (here: potential enthalpy) as function of pressure



Extended energy landscapes:
Possible / feasible (?) directions

Time-dependent energy landscapes*

a) slow (adiabatic) evolution
b) periodic variation
c) random/chaotic variation about an average landscape
d) discrete jumps of landscape
e) monotonic variation

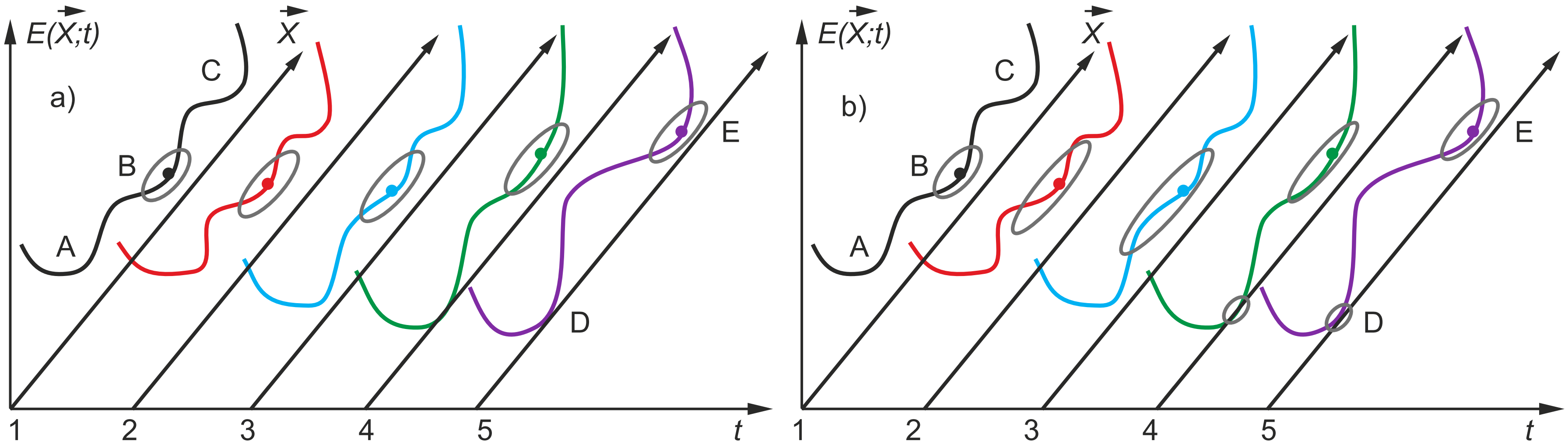
(* JCS, J. Innov. Mater. Extreme Conditions, 2021)

Extended energy landscapes:
Possible / feasible (?) directions

Shape of the energy landscape as function of time*, together with the evolution of the occupation probability when starting in region B

Left: slow (adiabatic) variation with time; Right: fast (sudden, abrupt) variation in time

Note: Same overall change, but the time intervals between equivalent shapes are different !



Looking to the future

B1) Landscapes for systems in the continuum approximation

B2) Energy landscapes on the mesoscopic level - suitability for finite systems or for qualitative discussions or for continuum properties like conductivities

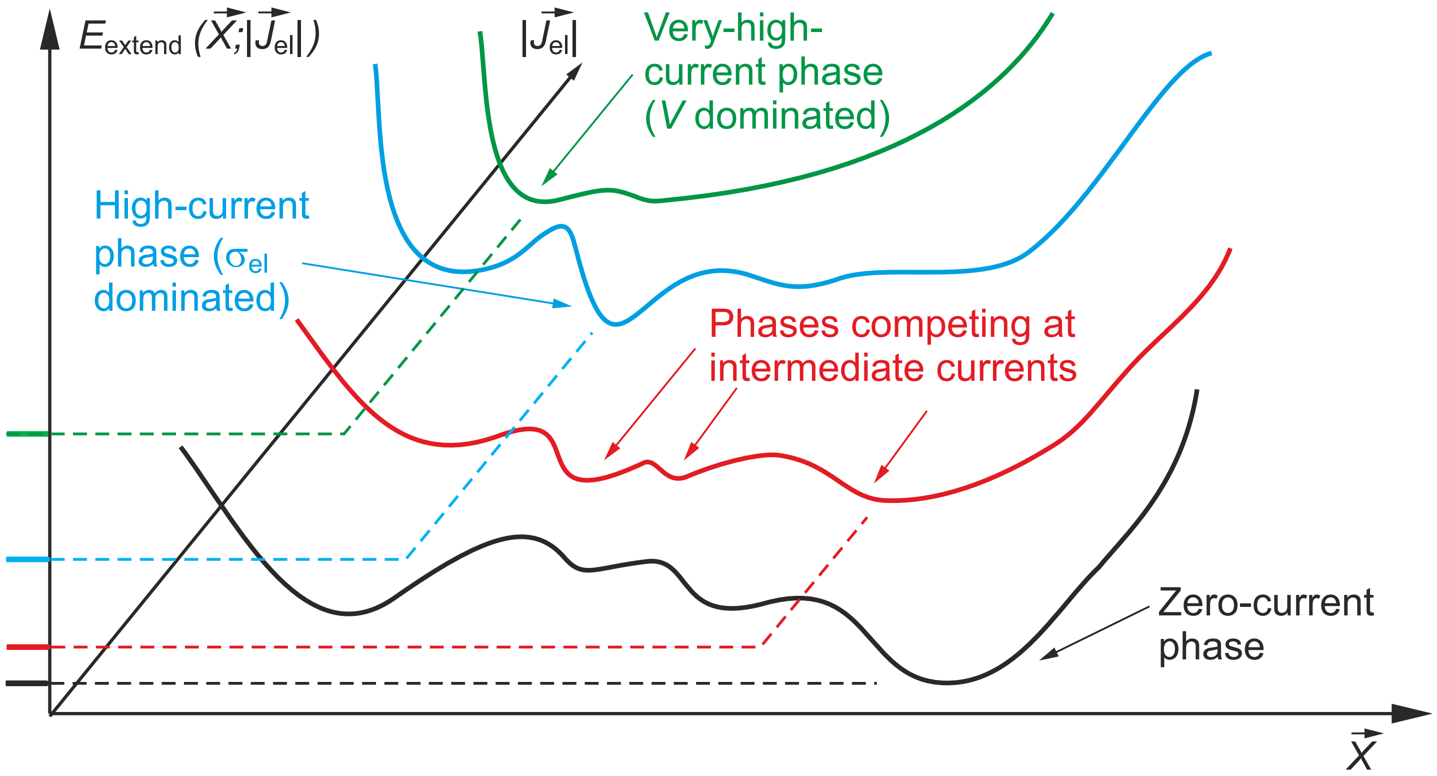
B3) Applications in spatially macroscopic systems (macroscopic gradients, phase equilibria, phase boundaries); realism of finite-size systems; realism of applied (external) thermodynamic parameters such as temperature/pressure/chemical potential

B4) Order parameter landscapes: globally defined on tobs -> infinity but for variable control parameters; defined for finite systems and times and spatial inhomogeneities; for characterization of minima basins/regions with and without demanding local ergodicity

B5) Spatial distribution of temperatures on an energy landscape (T(X) like continuum approximation variable ?); does temperature definition require local equilibrium/ergodicity - usually define local ergodicity for fixed given temperature; in microcanonical ensemble, T is a local variable that requires time to become established, ie., it needs local ergodicity to make sense; temperature is ill-defined for small isolated systems like molecules/clusters

Extended energy landscapes:
Possible / feasible (?) directions

Shape of the energy landscape (inspired by thermodnamics) as function electric current



Looking to the future

C1) Probability flows between landscape regions and their interpretation and realization in a master equation treatment and lumped model description of the landscape; to what extent does a ME represent the evolution of a chemical system that does not fulfill the self-averaging hypothesis, i.e, the system is an individuum but the probability flow deals with an ensemble ?

C2) Probability flow at constant temperature (canonical ensemble) vs. constant energy (microcanonical ensemble)

Looking to the future

D1) Return of the "noise limit" (often used as a noise temperature that indicates that we should not take the results of the landscape study down to T = 0) of energy landscape accuracy and solution accuracy: "real" noise incorporated in the landscape definition, due to limitations on cost function evaluation, due to lack of information on the system, due to finite process times in applications, i.e., "real" noise (external fluctuations of parameters of the landscape or of the thermodynamic parameters); noise due to limitations of the cost function evaluations; noise due to lack of information on the system or specific parameter values of the cost function (i.e., the model is okay, but we do not have the proper empirical / measurement parameters); noise due to finite process times in applications such that we cannot be assured that we follow the ideal noise-less landscape during the process

D2) Limitations of energy landscapes and their concepts: time variation of external conditions; quantum mechanical entanglement of states; meaningfulness of thermodynamic parameters in finite (especially small) systems, e.g., temperature/pressure (what about a cluster in vacuum, i.e., proper way to include volume in the problem)

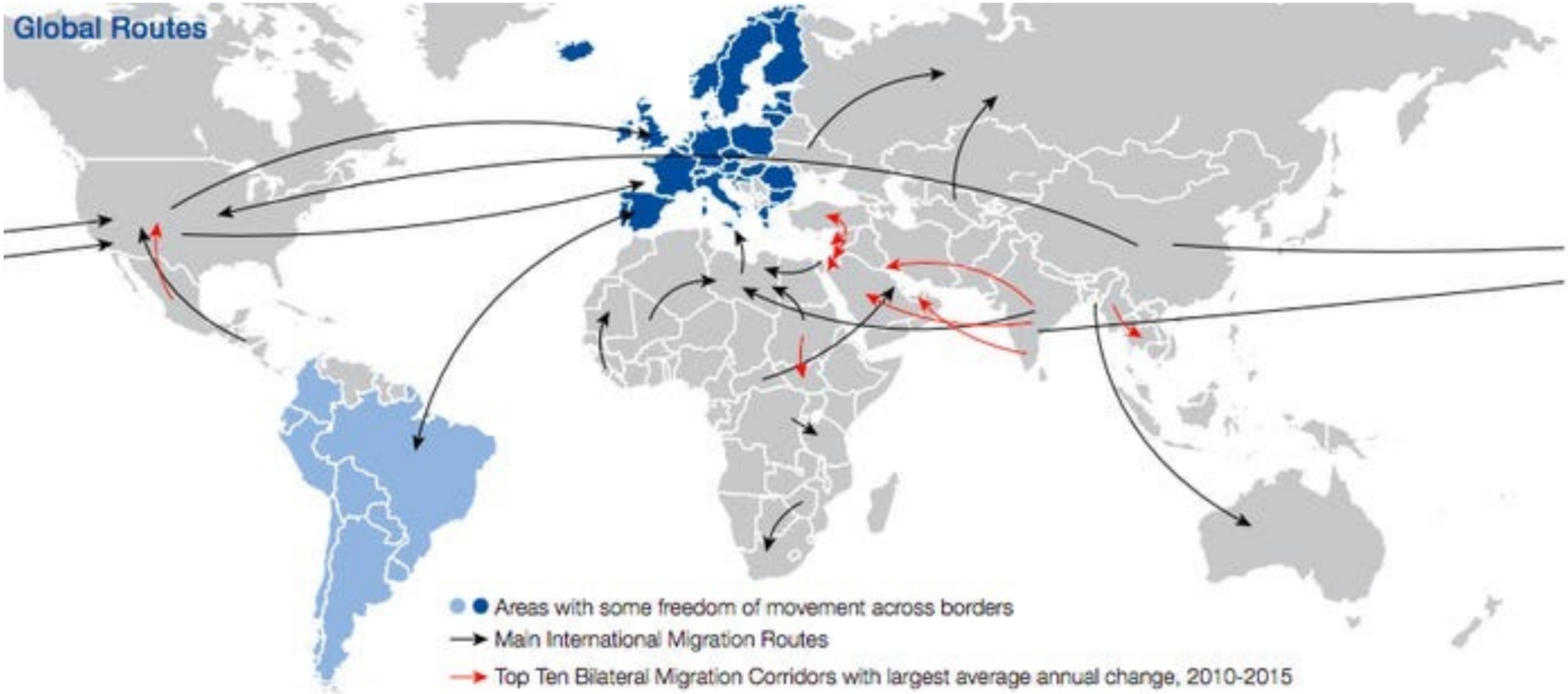
Looking to the future

E1) Application to "humanities" problems beyond those in economics: migration between countries, movement between political parties or cultures, variation of "motivation = cost", evolution of memes/attitudes analogous to biological evolution, optimal distribution of limited (health) resources,... : various kinds of migration landscapes - people between countries, political parties, cultures, religions, ...; variations of the "motivation = cost" for such a migration, evolution of memes and other social attitudes; optimal distribution of limited resources (e.g., for health treatments, etc.)

E2) Applications in biology: "classical evolution" (fitness function); spatio-temporal evolution; migration of animals; cost function construction and evolution of ecosystems (what is the "right" fitness function ?); evolution with periodic disturbances

E3) Landscapes of optimal control problems

Pictures of examples from the "world"



Looking to the future

F1) What corresponds to temperature in the context of landscapes where the state space does not incorporate physical/chemical degrees of freedom ? Is there more than its use as a control parameter in the context of global optimizations ?
For example: rates (of mutations, innovations, ...), interest rates in economics (check with econophysics), ...

F2) Consider thermo-economics as an inspiration to address the issue of free energies in non-physics/chemistry systems, which deal with various cost function landscapes. Again this might depend on the question what we consider a temperature, and perhaps there might be several types of temperatures ? Start with microcanonical ensemble picture of the cost function and its (local) entropy, to define a temperature ?
Problem: Why would we be interested in a system that remains at constant energy throughout its time-evolution (outer space, perhaps ?) ; we might also have a lot of external time-varying parameters being involved !

Looking to the future

G1) Dimensionality of state space, such as fractal state spaces

G2) Topological features of landscapes

G3) Landscape in curved space-time

G4) Landscapes that take into account the quantum nature of the state space

G5) Energy landscape of photonic systems; landscapes based on reciprocal space as state space ?

What is the Energy Landscape in Quantum Mechanics ?

	Classical system	Classical system with QM energy (of electrons)	QM Eigenstate system with QM eigen-energy	QM General state system with QM energy expectation
State space	$\vec{X} = (\vec{R}, \vec{P}) \in \mathbb{R}^{6N}$	$\vec{X} = \vec{R} \in \mathbb{R}^{3N}$	$\vec{X} = \vert\phi_i\rangle \in \{\vert\phi_k\rangle\}$; $H_{op}\vert\phi_i\rangle = E_i\vert\phi_i\rangle$	$\vec{X} = \vert\psi\rangle = \sum_k a_k \vert\phi_k\rangle$; $a_k \in \mathbb{C}$ and $\sum_k \vert a_k\vert^2 = 1$
Energy $E(\vec{X})$	$E_{kin}(\vec{P}) + E_{pot}(\vec{R})$	$E_0(\vec{R})$	$\langle\phi_i\vert H_{op}\vert\phi_i\rangle = E_i$	$\langle\psi\vert H_{op}\vert\psi\rangle = \sum_k E_k \vert a_k\vert^2$
Distinct states $\vec{X}$	Yes	Yes	Yes: $\langle\phi_i\vert\phi_j\rangle = \delta_{ij}$	No: $\langle\psi_i\vert\psi_j\rangle \neq \delta_{ij}$
Physical neighborhood $\mathcal{N}(\vec{X})$	Well-defined	Well-defined	Not really well-defined	Well-defined, perturbatively
MD/SE evolution	Yes	Within limits (BOA); extend to diabatic	Not really	Yes
MC evolution	Yes	Yes	Yes	Not really
Problems	Not QM	Not fully QM	No evolution of wave function; correspond to measurement and wave function reset	Probabilistic energy; wrong stat. mech. averages; what is a time average of $\vert\psi\rangle$

Looking to the future

H1) Energy landscapes and machine learning/neural networks: complementarity and replacement; can the dynamics be captured by machine learning ?

Disclosure: This presentation was <u>not</u> prepared using ChatGPT

Some useful literature can be found in:

JCS, “Energy landscapes in inorganic chemistry” in:
Comprehensive Inorganic Chemistry III, (2023), Chapter 3.11,
pp. 262 - 392

DOI: 10.1016/B978-0-12-823144-9.00127-8

Energy landscape workshops - history

Workshops in Telluride strongly related to energy landscapes:

1985: "Phase Transactions in Small Clusters"
1986: "Simulated Annealing"
1988: "Clusters"; "Finite Time Thermodynamics and Simulated Annealing"
1989: "Atomic an Molecular Clusters"; "Simulated Annealing Algorithms and Geometric Thermodynamics"
1990: "From Clusters to Bulk Matter"
1991: "Large Clusters and Nanometer Particles"
1993: "Clusters"; "Thermodynamics and Statistics of Complex Systems"
1995: "Clusters"; "Thermodynamics of Landscapes and Trapping"
1996: "Stochastic Optimization"
1997: "Topographies and dynamics on complex potential surfaces"
1999: "Rugged Energy Landscapes"; "Energy Landscapes"
2001: "Cartography of complex energy landscapes"
2003: "Energy landscapes: Structure, Dynamics and Exploration Algorithms"
2005: "Energy landscapes: Dynamics and Optimization"
2007: "Energy Landscapes: Negotiating the Black Diamonds"
2010: "Characterizing Landscapes: From Biomolecules to Cellular Networks"
2011: "Energy landscapes: Structure and Dynamics"; "Exploring Energy Landscapes: From single molecules to mesoscopic models"
2012: "Characterizing Landscapes: From Biomolecules to Cellular Networks"
2013, **2015, 2017, 2022**: "Energy landscapes: Structure, Dynamics and Exploration Algorithms"

Workshops on energy landscapes away from Telluride:

2000 (Germany), **2007** (Italy), **2008** (Switzerland), **2010** (Germany), **2012** (Austria), **2014** (UK), **2016** (France), **2017** (India), **2018** (Greece), **2019** (Serbia), **2023** (France)

Energy landscape workshops history

R. Stephen Berry
(1931 – 2020)

- *Essentially all workshops related to energy landscapes were organized by Steve or his scientific children (students, post-docs) and/or grandchildren*

- *After ca. 10 years, energy landscapes were realized to be not only tools for studying various topics in science but also entities worthy of investigating per se, thus leading to the creation of dedicated landscape workshops*

Thanks to all contributors over the past 35 years!

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