Four rules of thermodynamic modeling reveal four general Laws of Nature:

Gian Paolo Beretta
Università di Brescia, Italy

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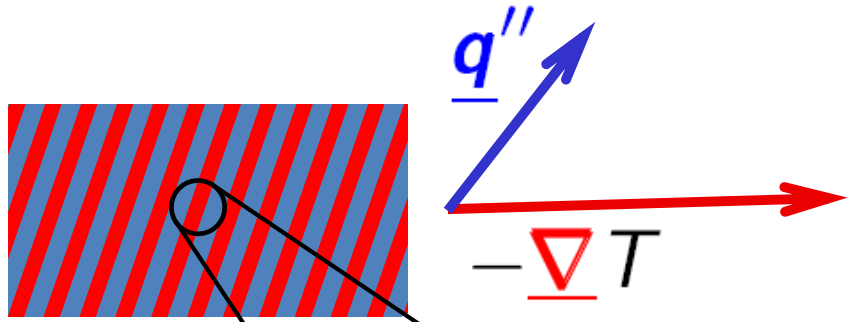
Fourier law in nanostructured anisotropic media



$\underline{q}''$

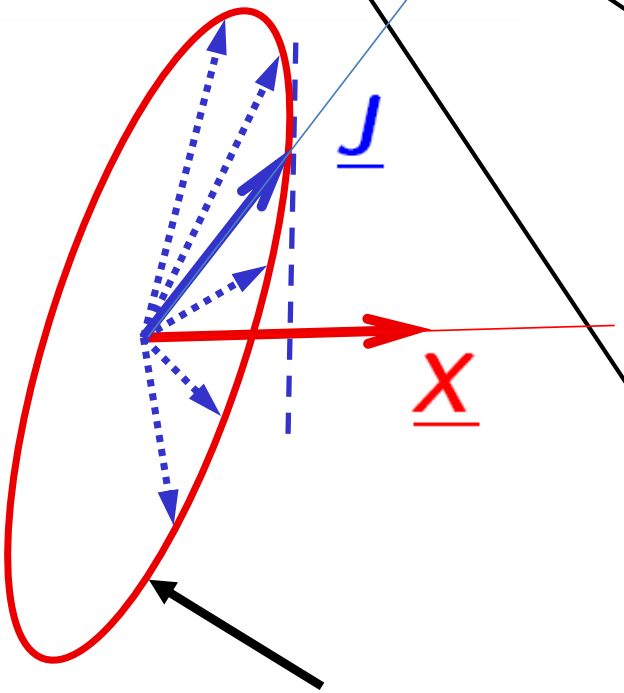
$-\underline{\nabla} T$

$$\underline{X} = \underline{\nabla} \frac{1}{T} = \underline{\nabla} \left(\frac{\partial S}{\partial E} \right)$$

$$\underline{J} = \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla} T = T^2 \underline{\underline{k}} \cdot \underline{X}$$

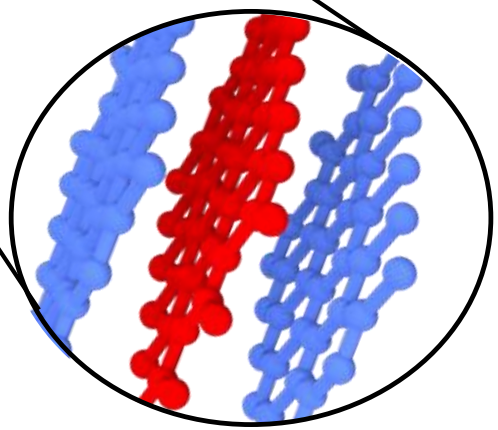
$$\sigma = \underline{J} \cdot \underline{X}$$

$$\underline{\underline{G}} = \underline{\underline{k}}^{-1}$$



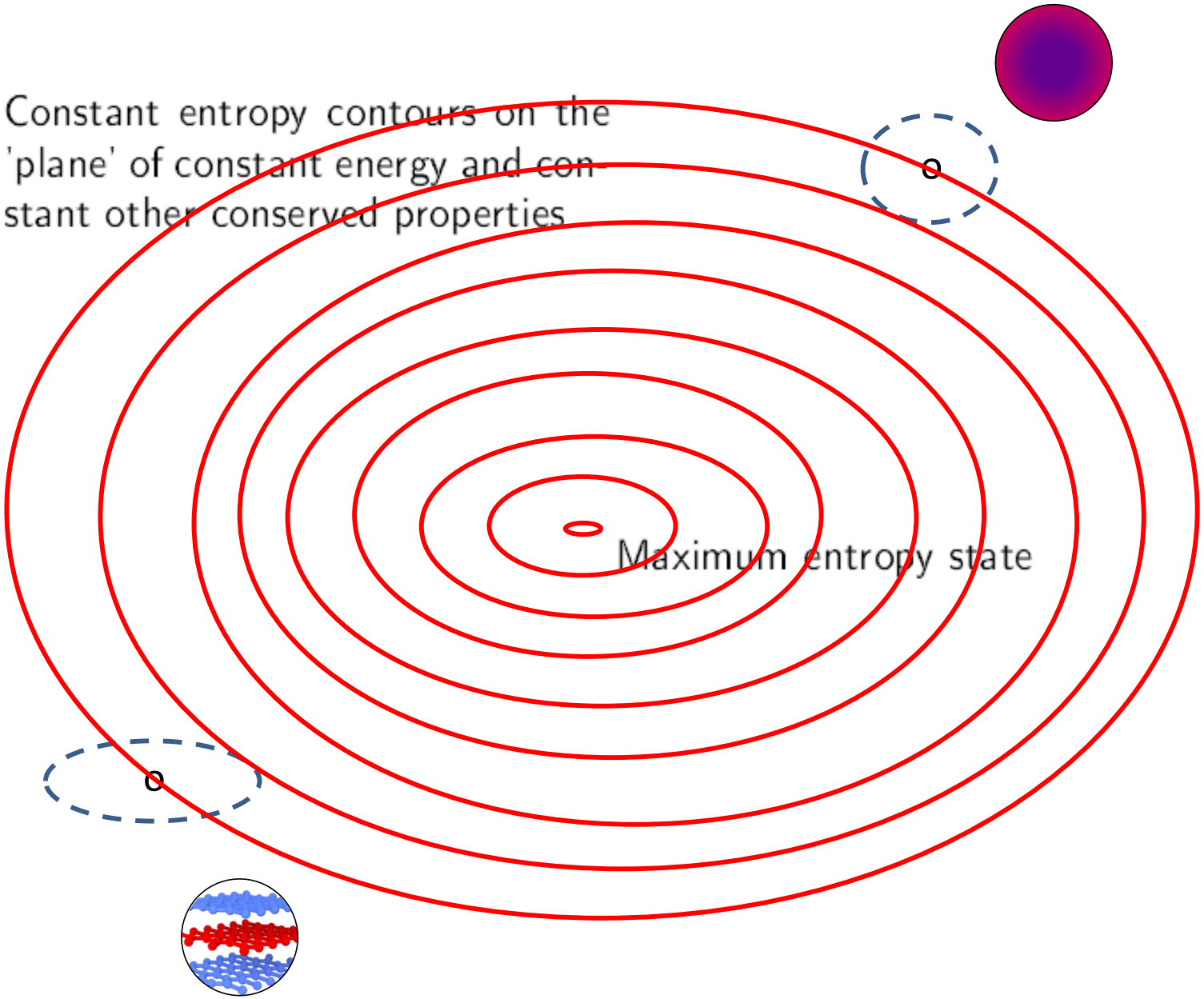
$\underline{J}$

$\underline{X}$



$$\underline{J} \cdot \underline{\underline{G}} \cdot \underline{J} = \text{const}$$

Steepest Entropy Ascent with respect to a Metric



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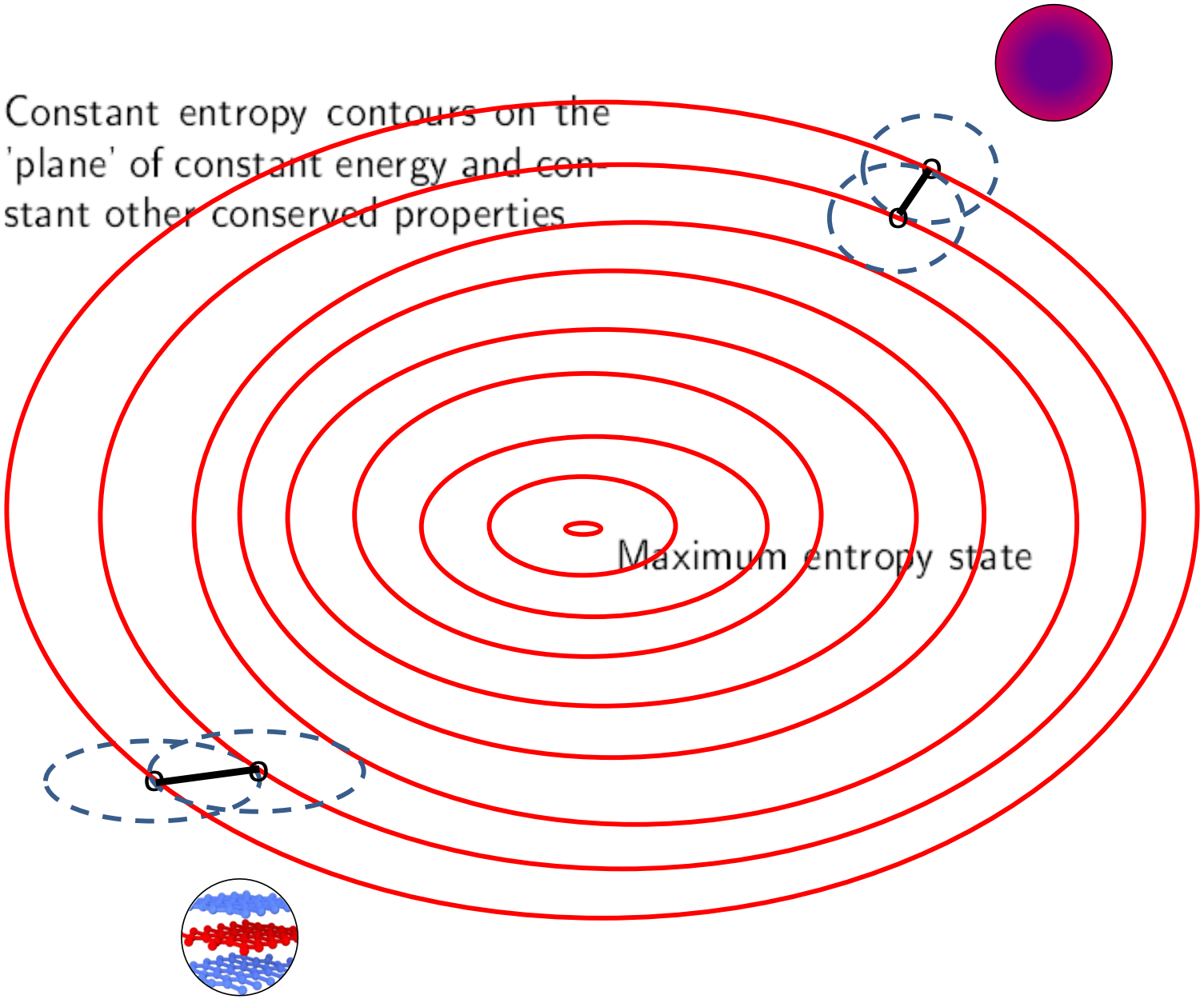

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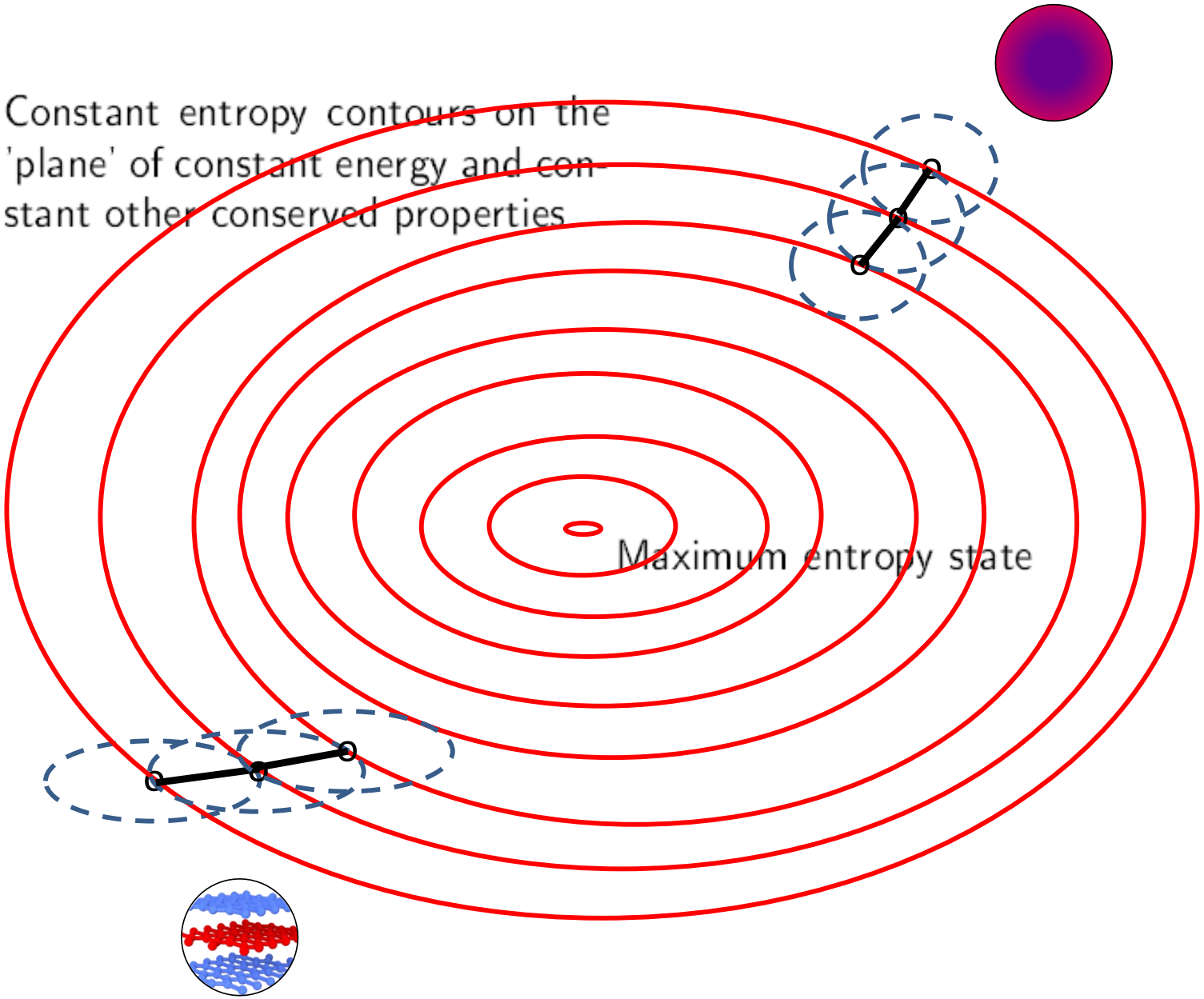

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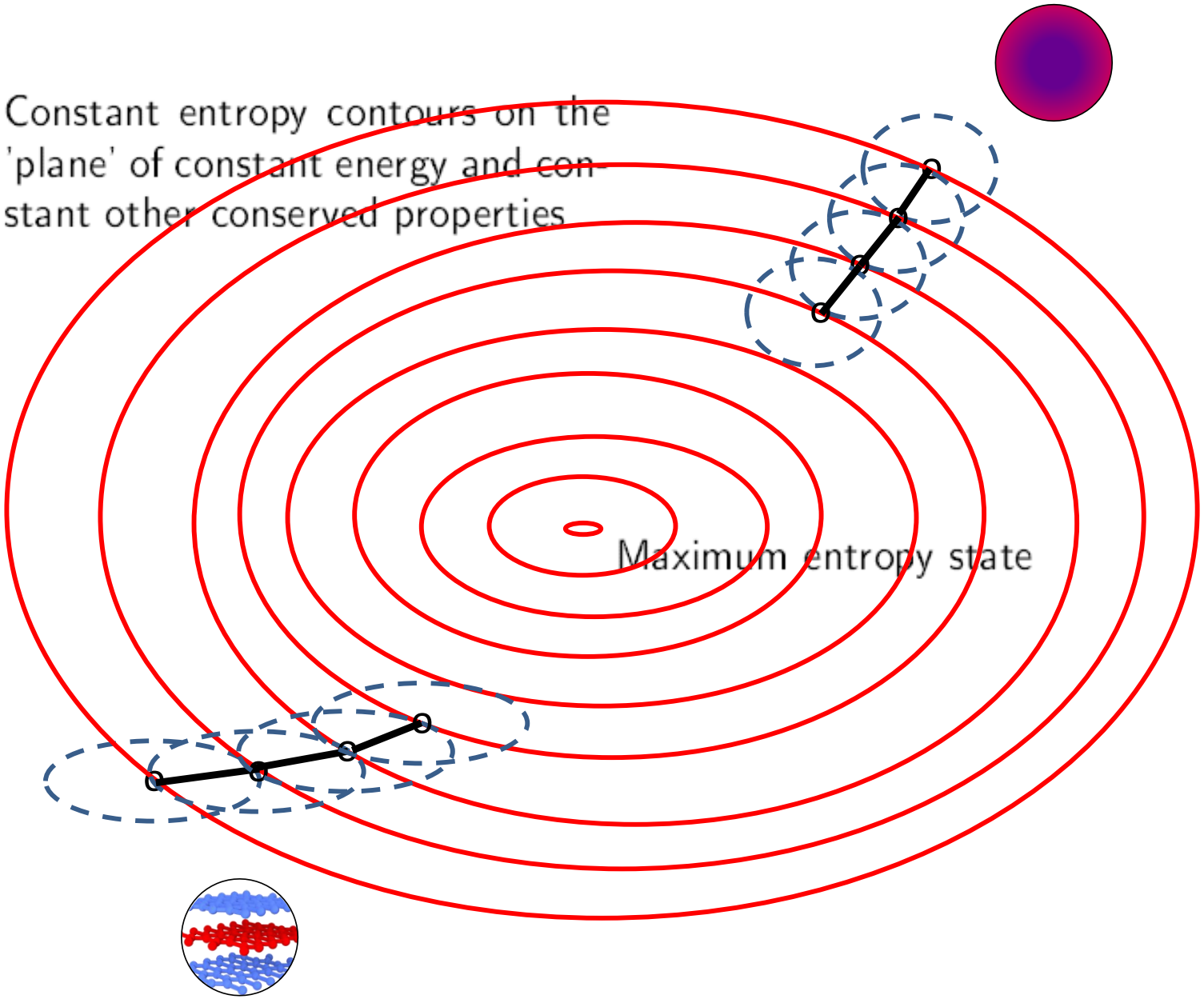

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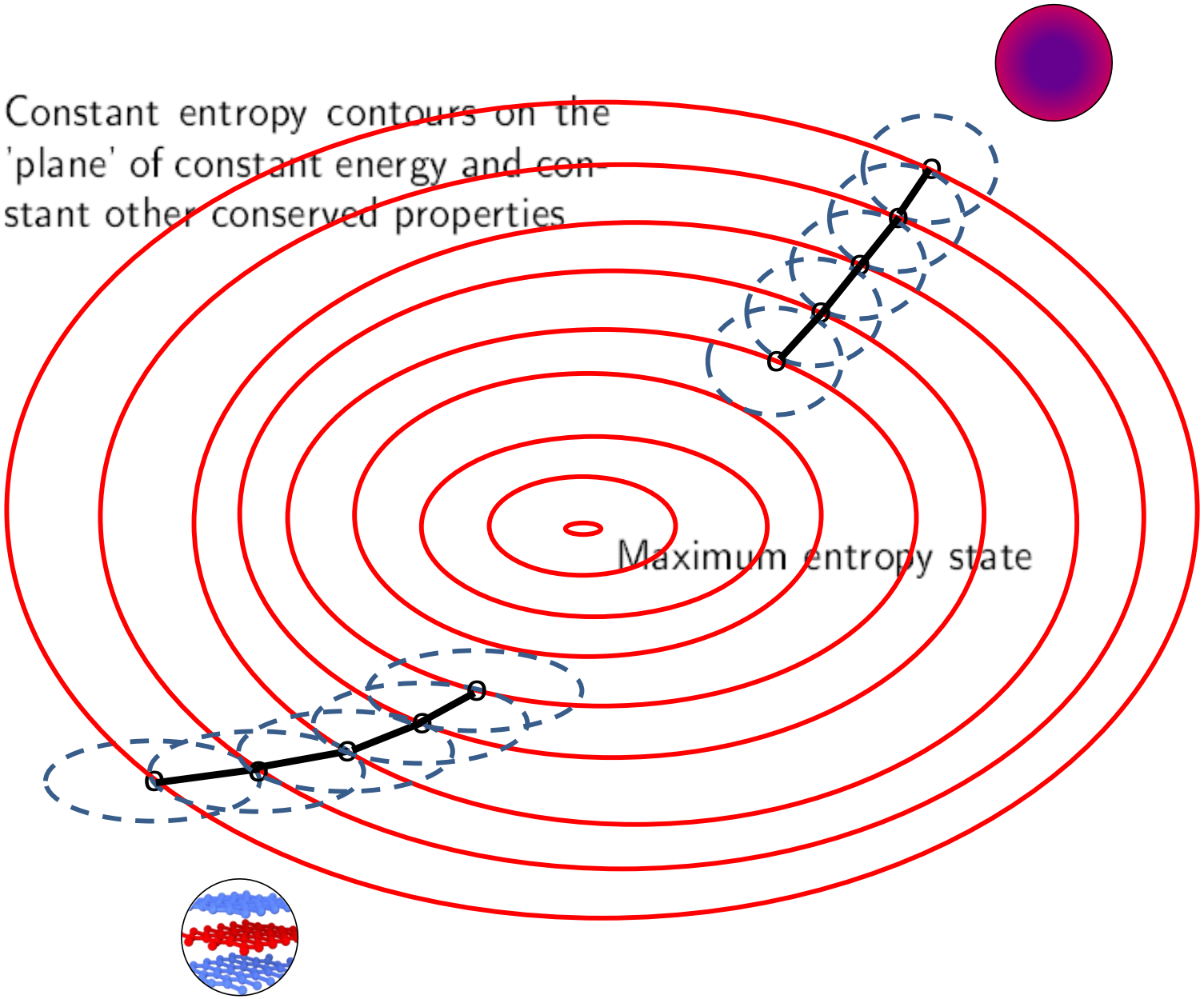

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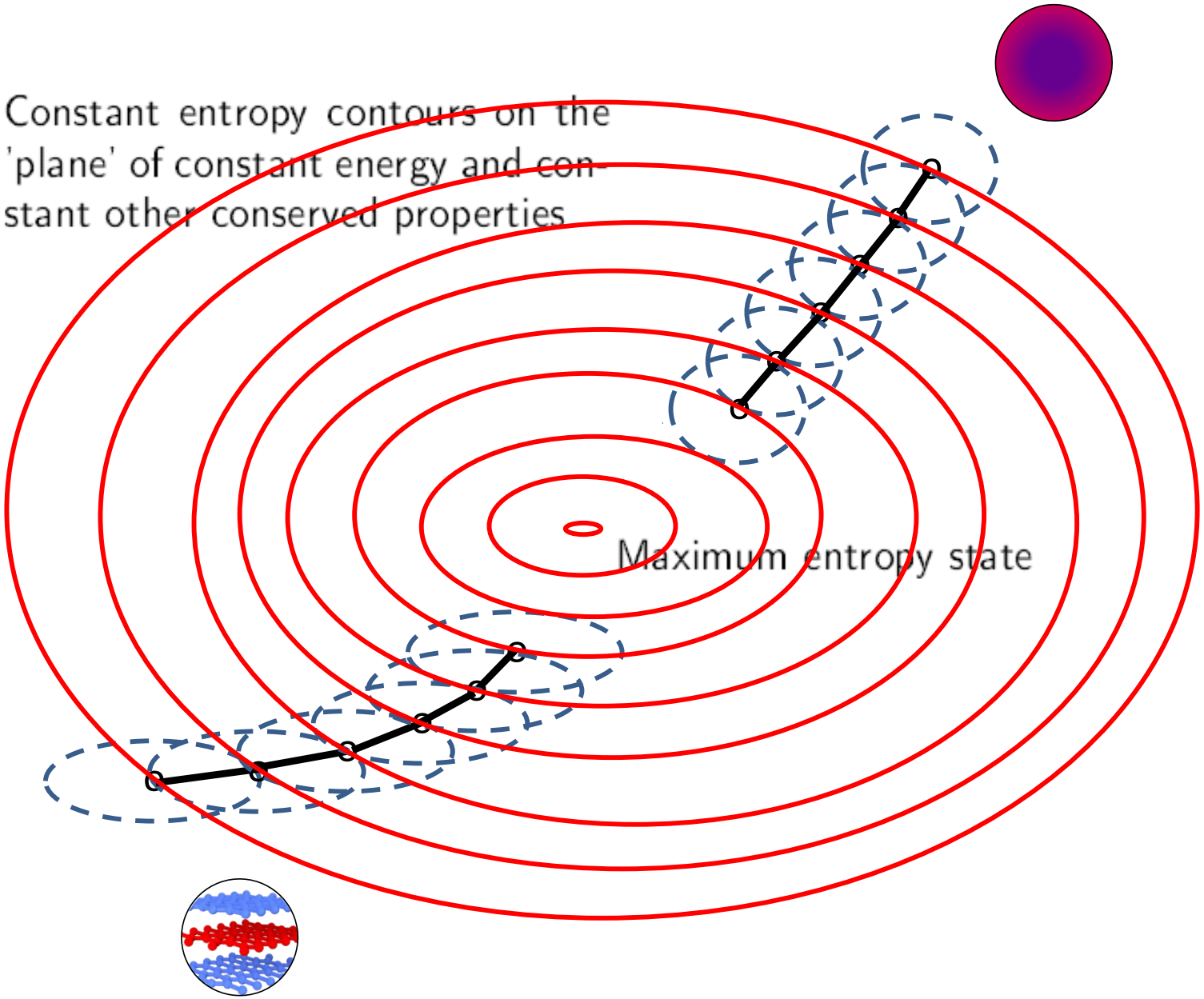

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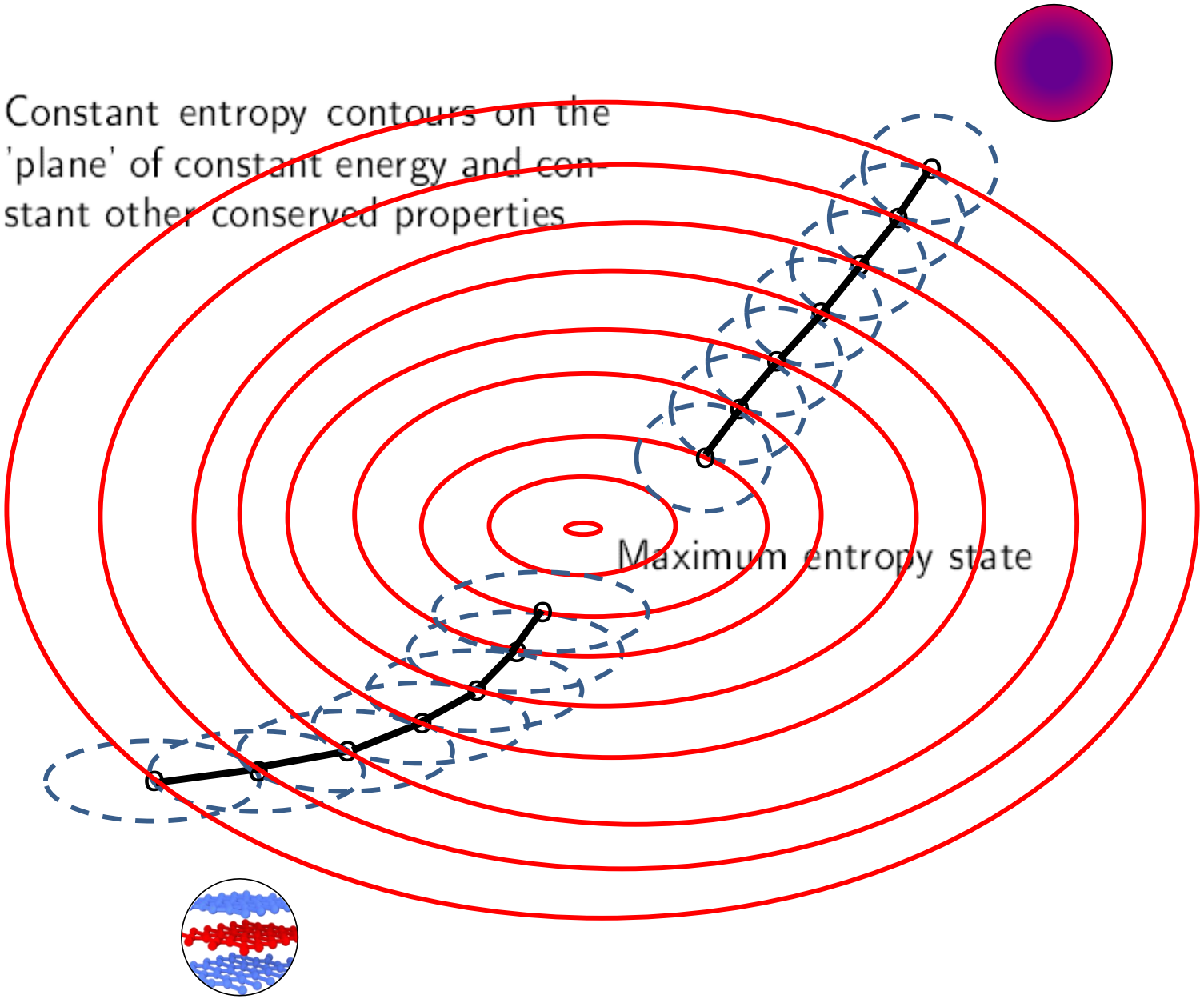

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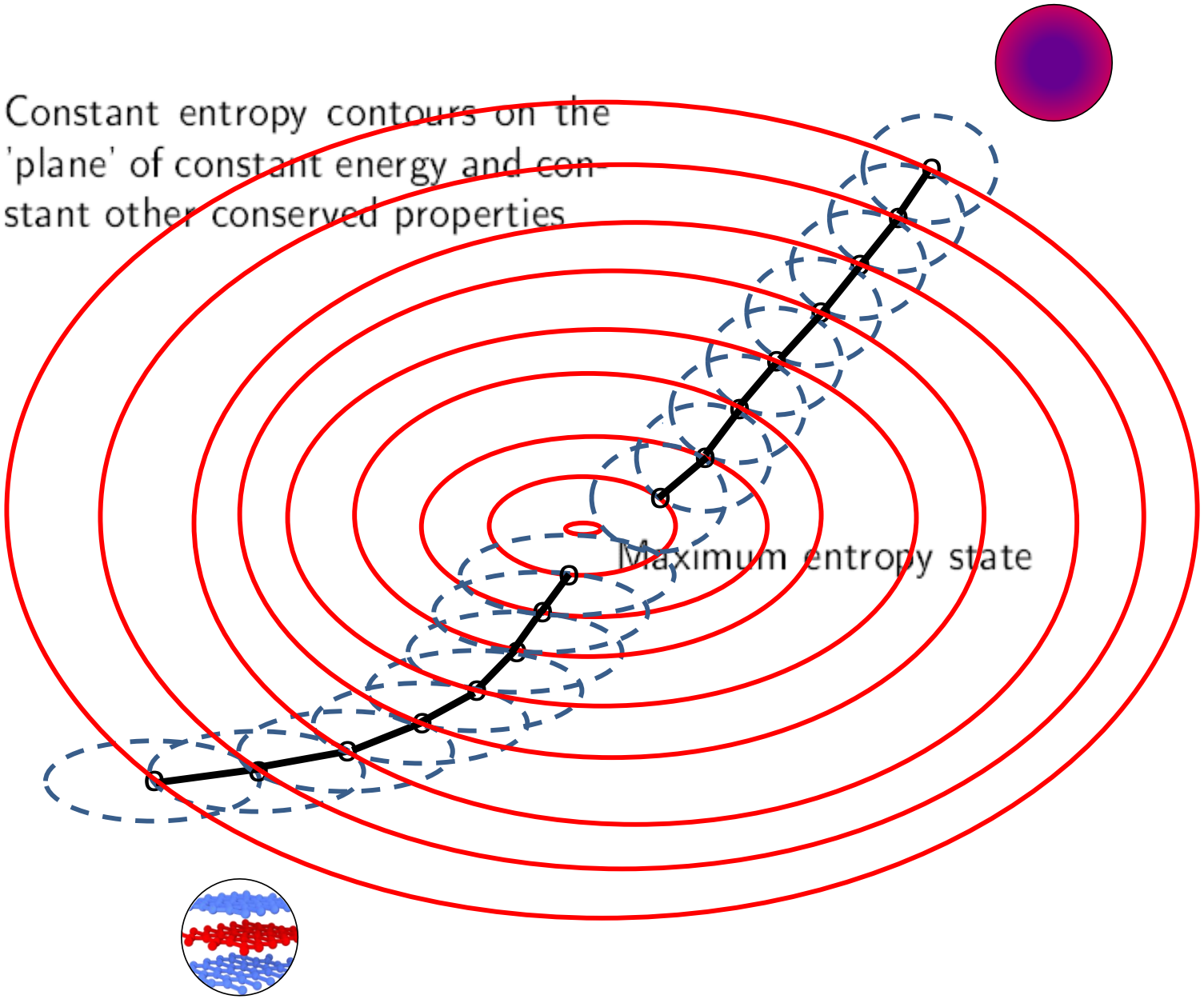

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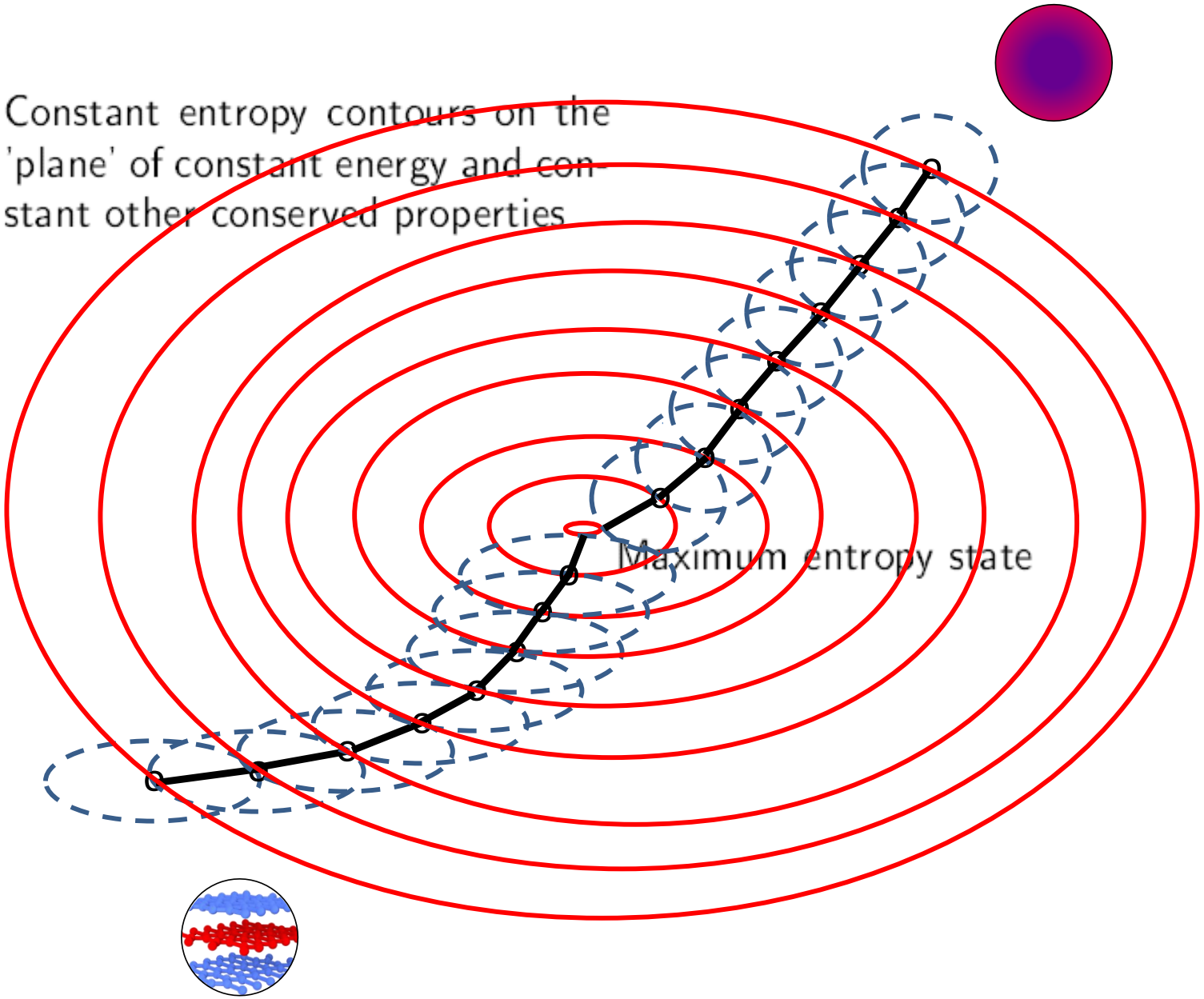

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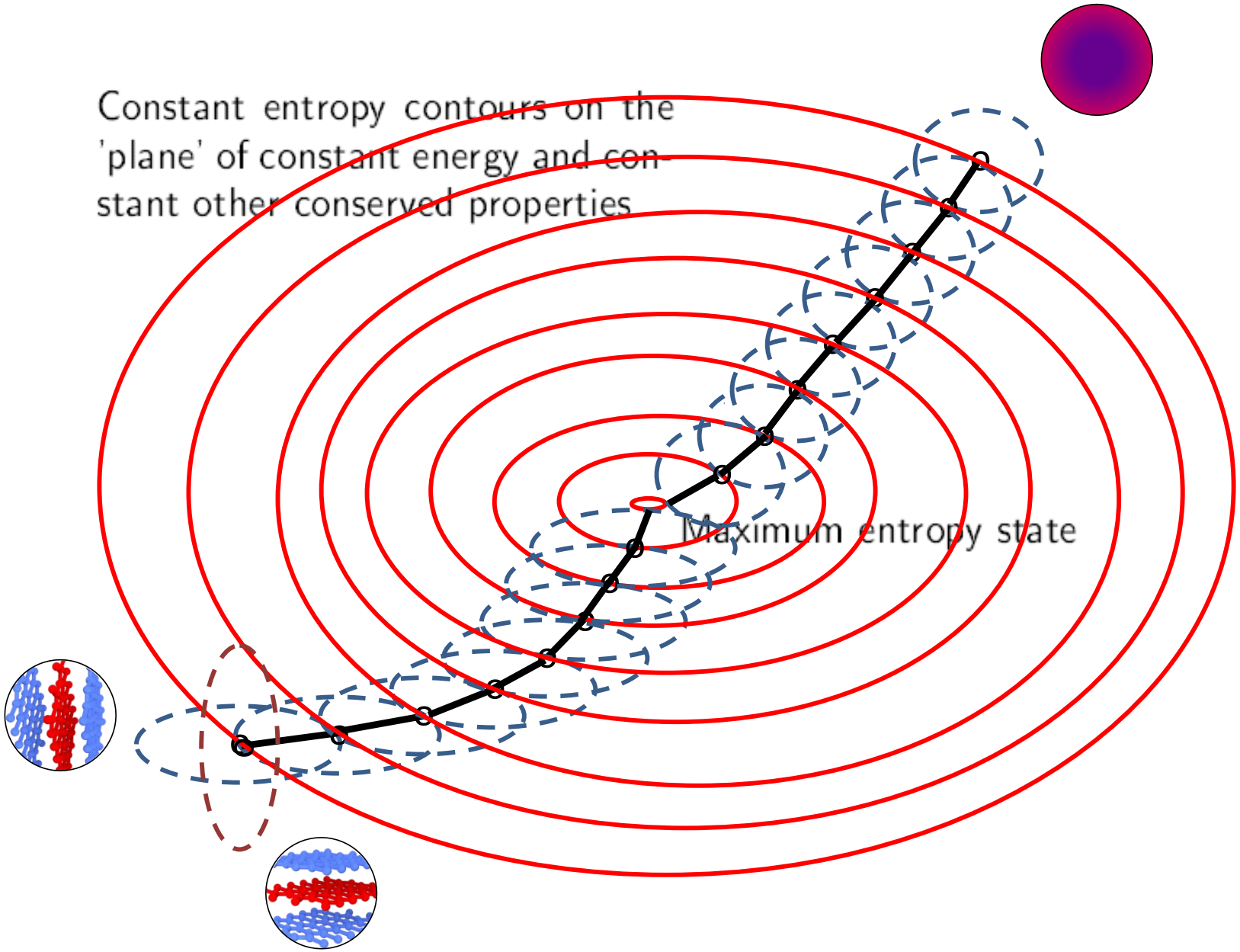

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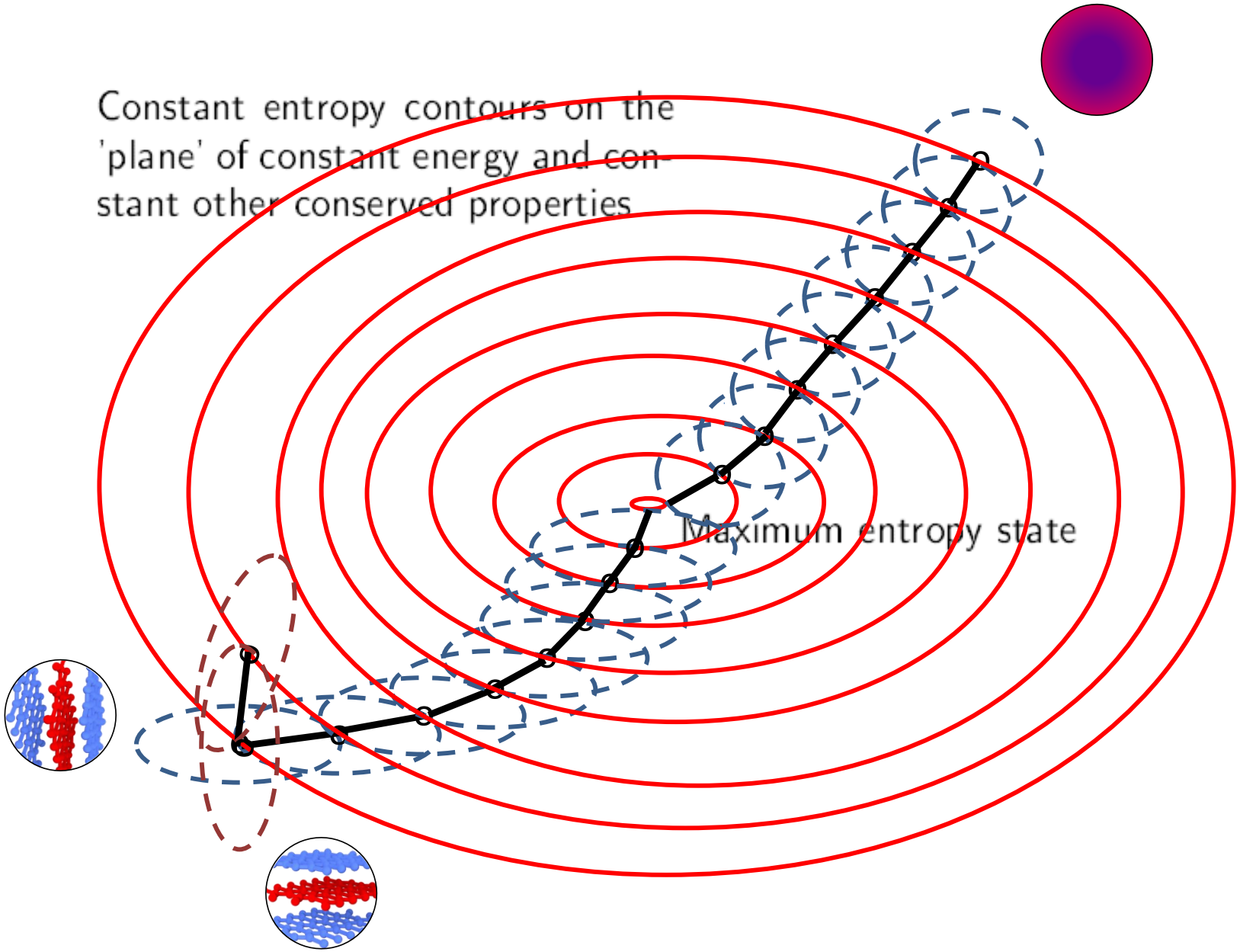

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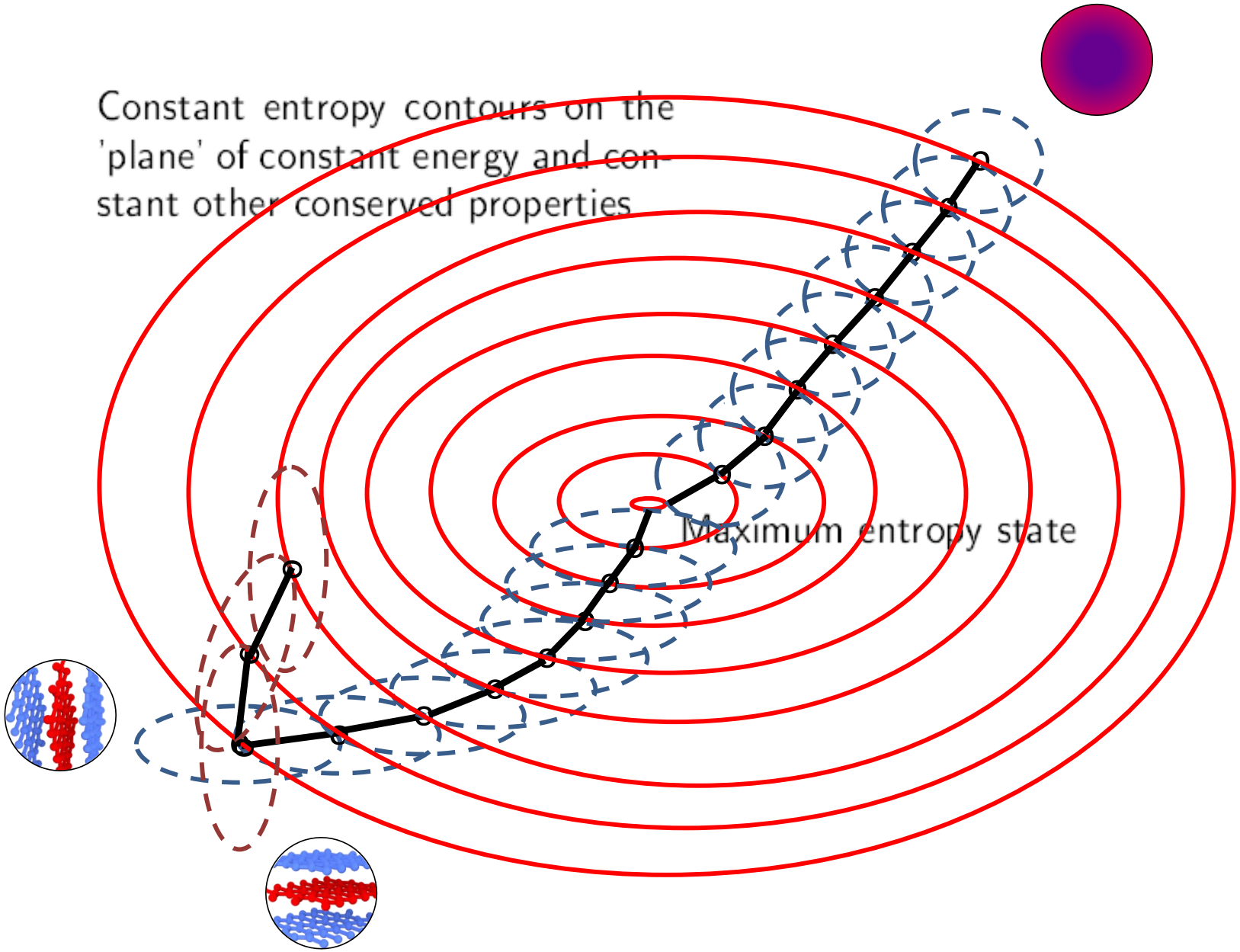

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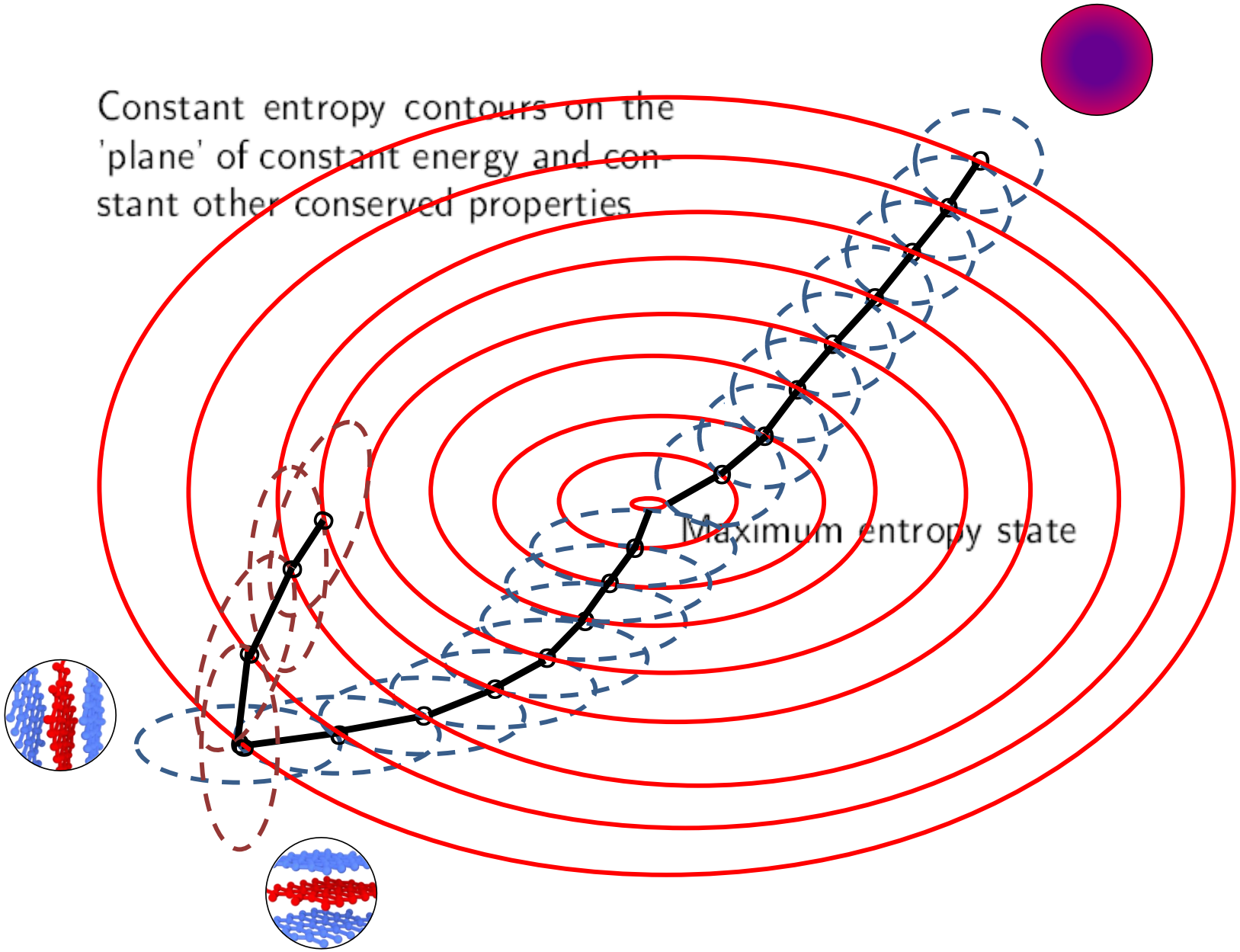

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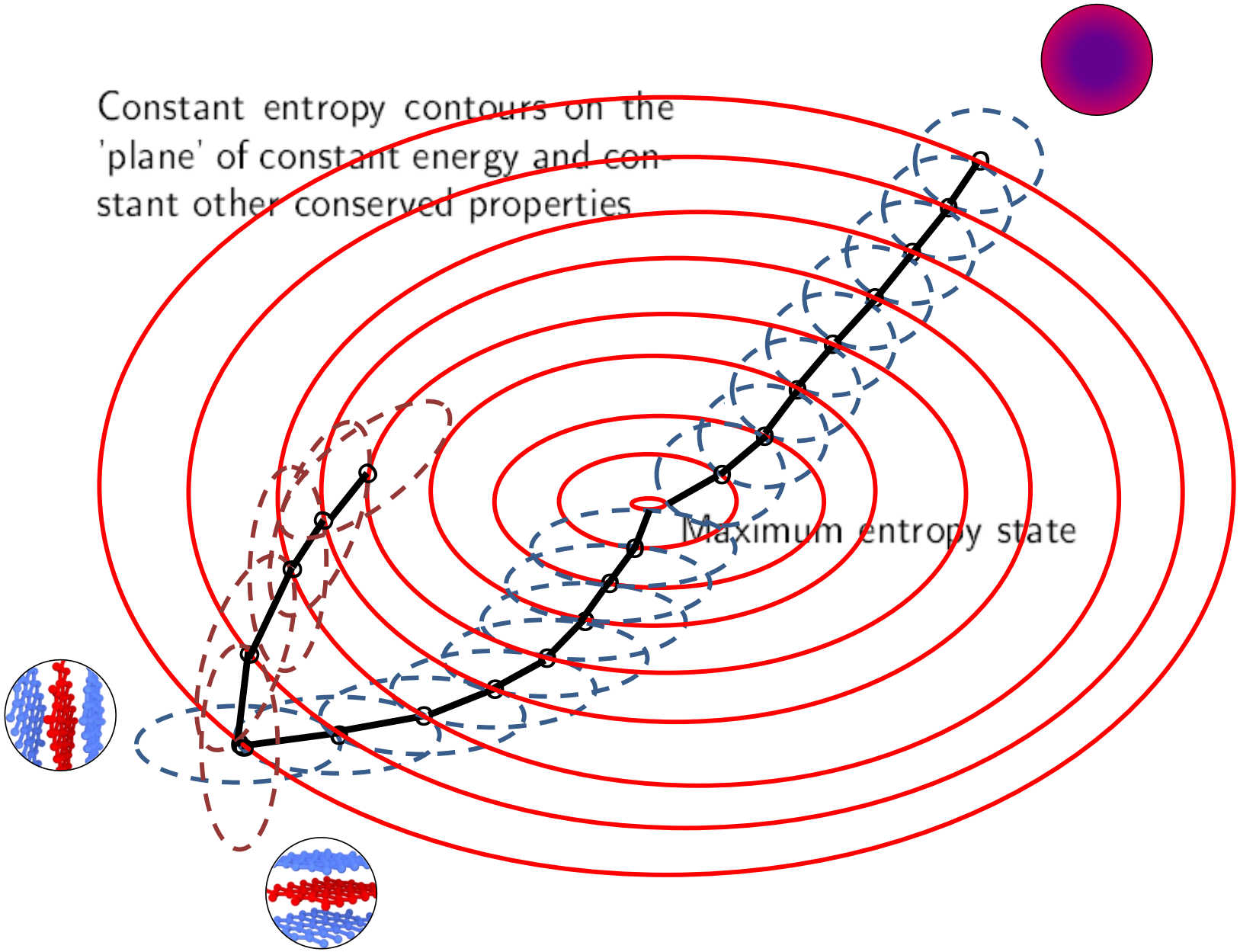

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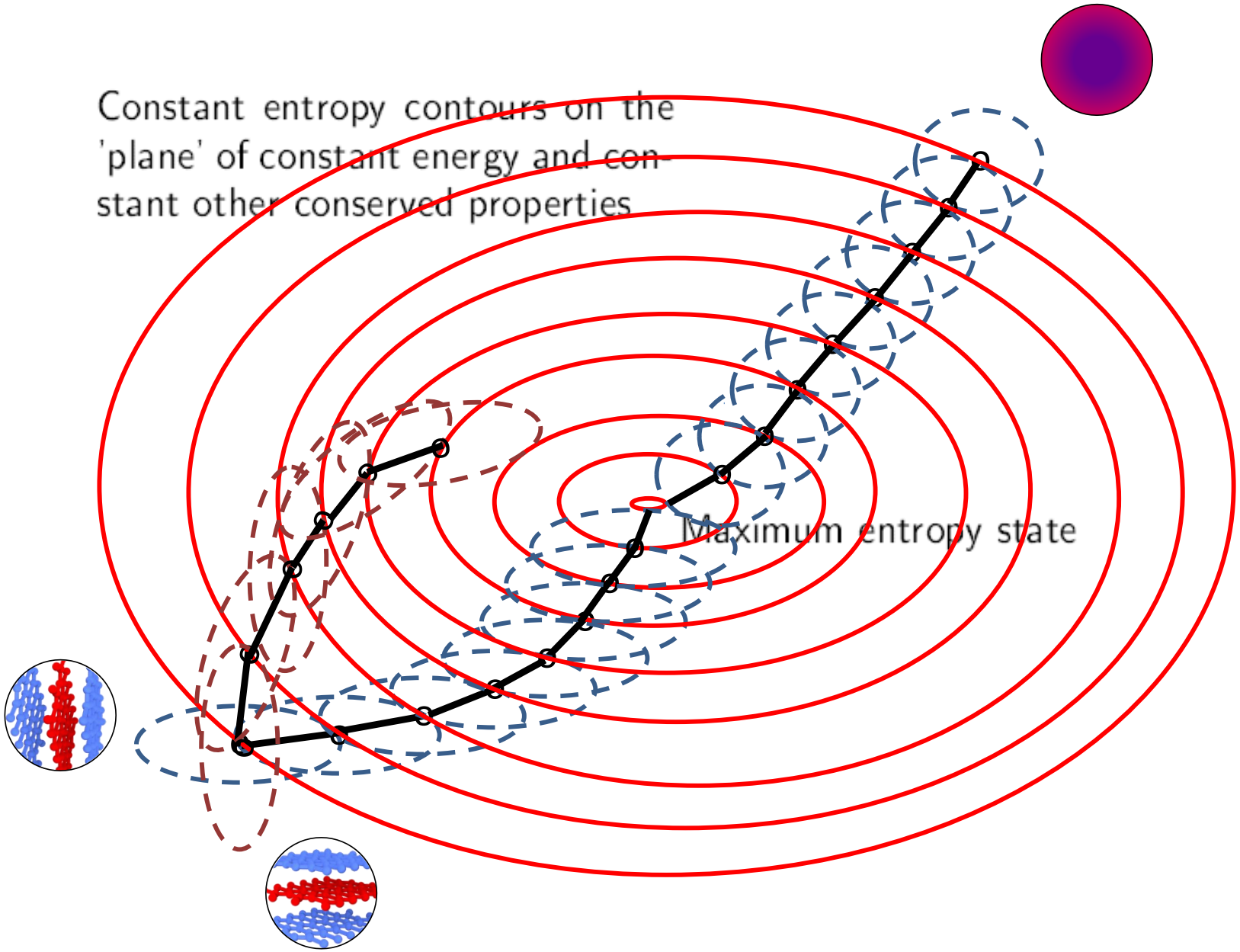

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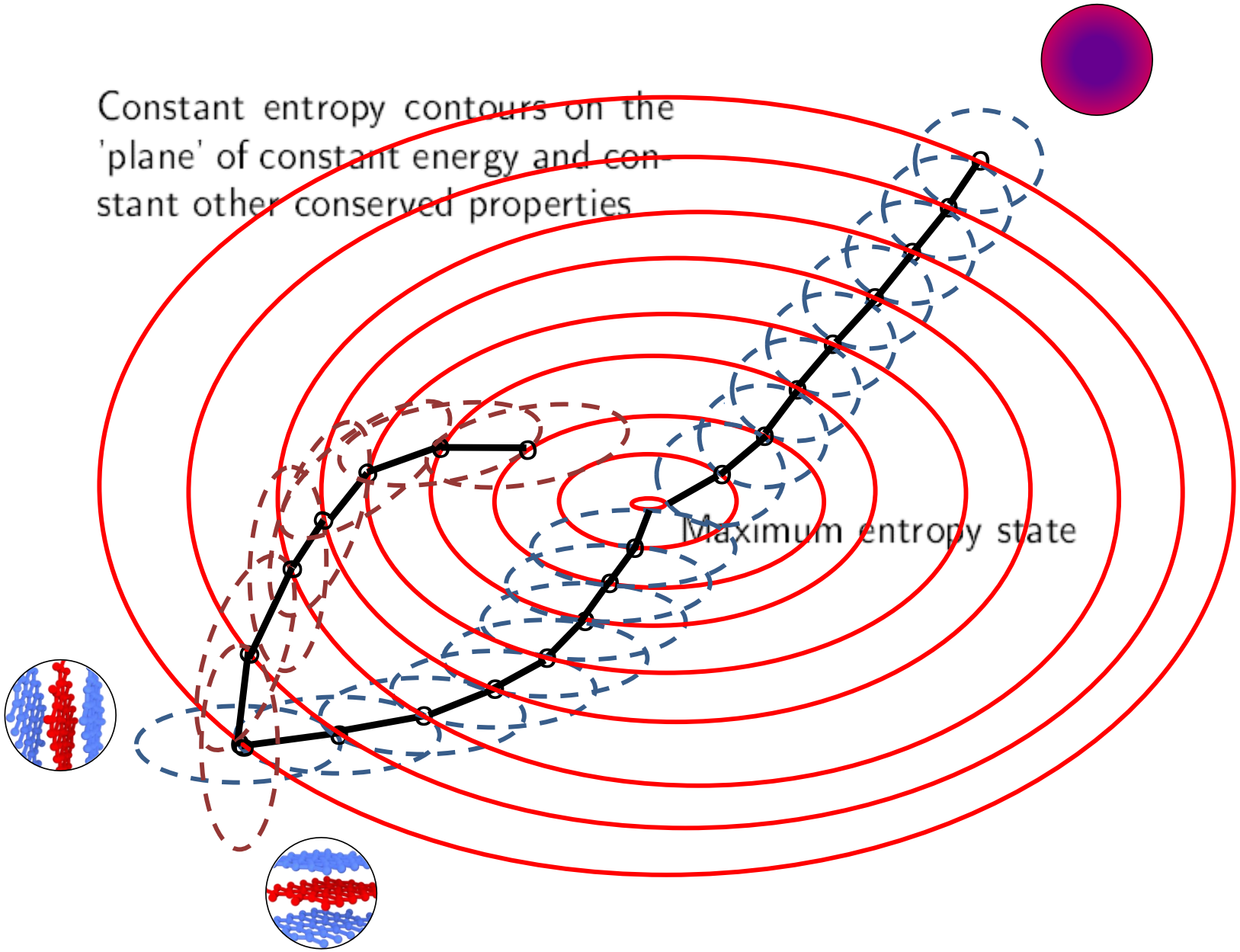

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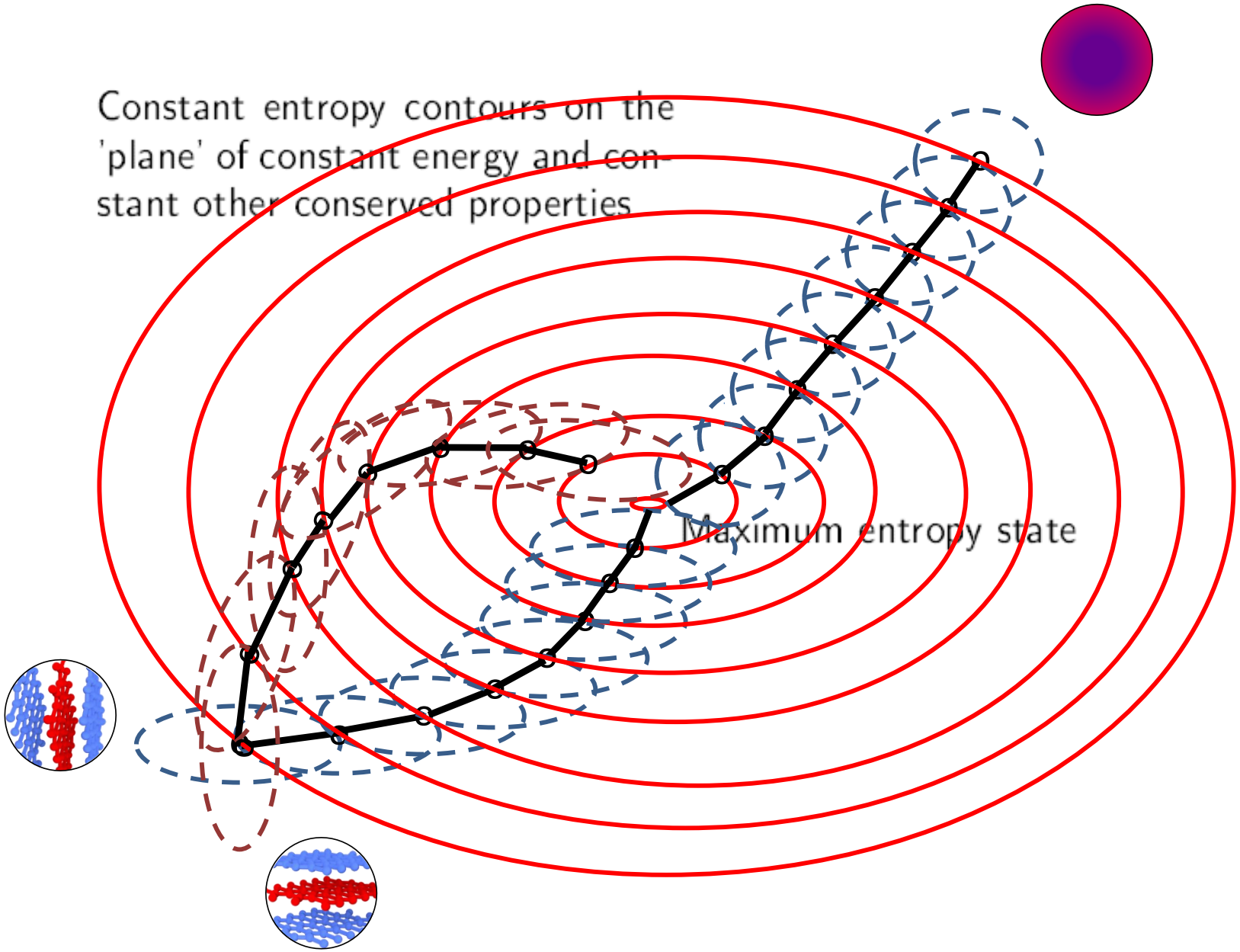

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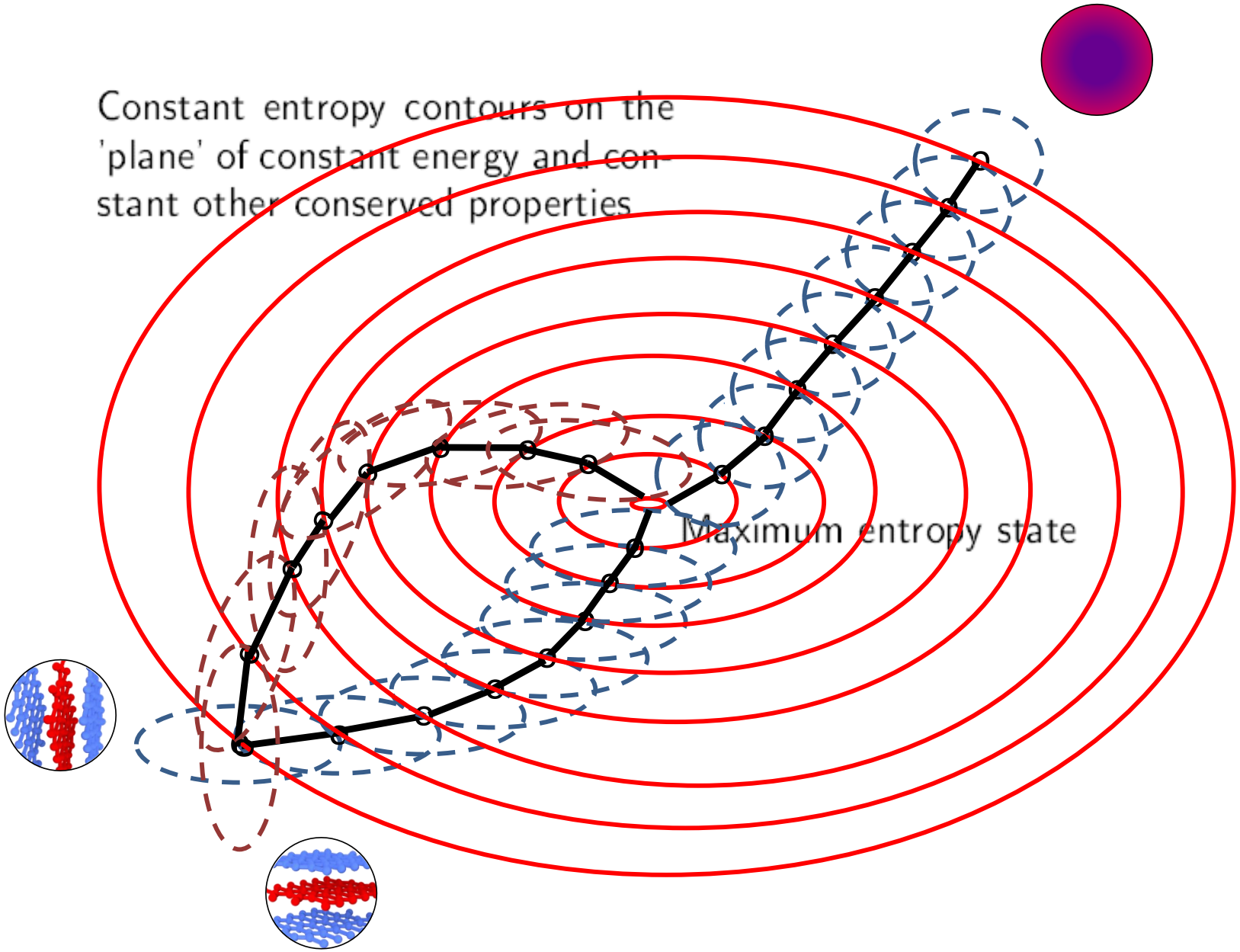
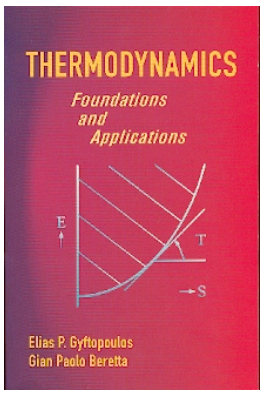


Entropy defined for non-equilibrium states

Hatsopoulos, Gyftopoulos, Found.Phys. **6**, 15, 127, 439, 561 (1976).

Beretta, J.Math.Phys. **25**, 1507 (1984).

Gyftopoulos, Beretta, Thermodynamics. Foundations and Applications, Macmillan 1991, reprint Dover 2005.



See also (>1998):
Lieb, Yngvason, Proc.R.Soc.A **470**, 192 (2014) and refs. therein.

Zanchini, Beretta, Entropy **16**, 1547 (2014) and refs. therein.

Energy vs Entropy diagram

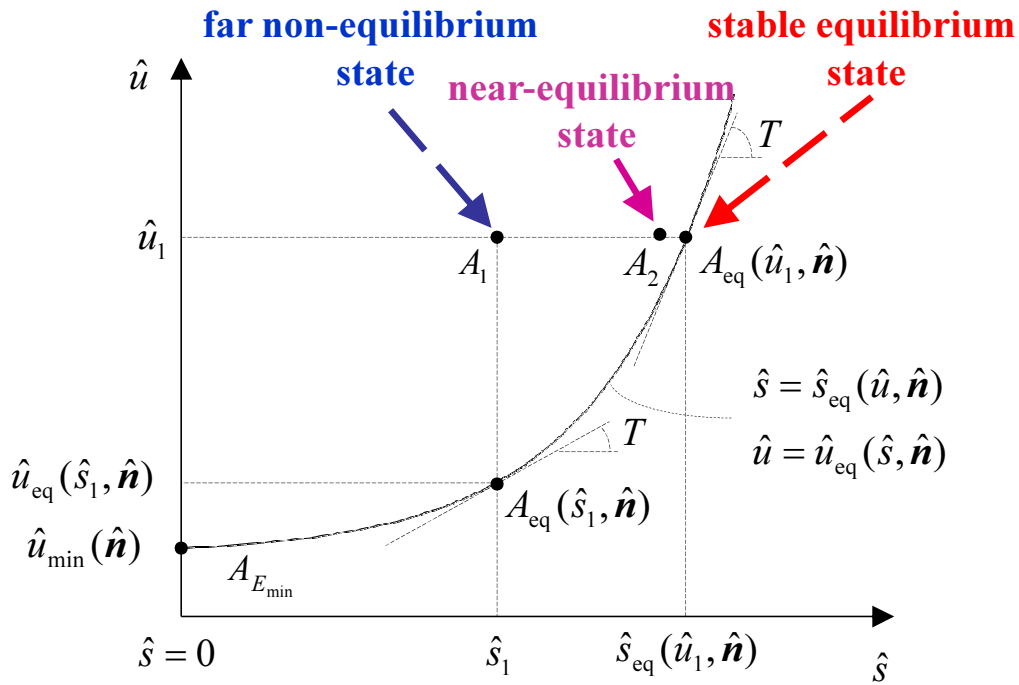
for a fluid or solid element of a continuum:

$\hat{u} = \rho u$, energy density

$\hat{s} = \rho s$, entropy density

$\hat{\boldsymbol{n}} = \hat{n}_1, \ldots, \hat{n}_n$, concentrations

Project all states with given $\hat{\boldsymbol{n}}$ onto the $\hat{u}$ vs $\hat{s}$ plane:



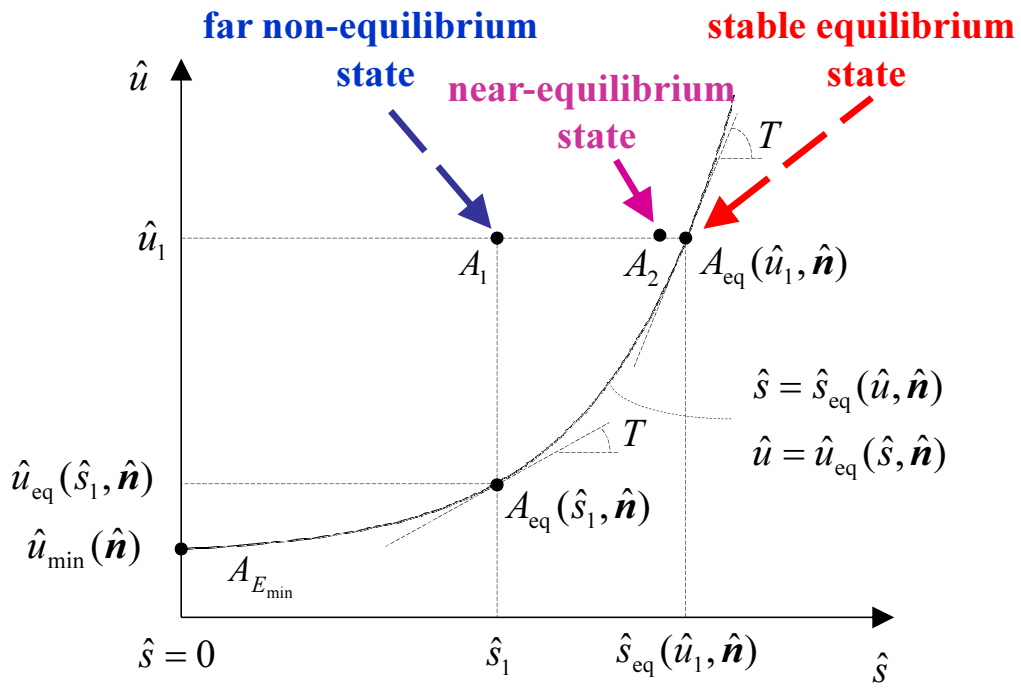
Non-equilibrium states require more independent variables

From the **second law** follows:
→ **maximum entropy principle:**
among all the states with given values of the energy density, $\hat{u}$, and the concentrations, $\underline{\hat{n}}$, the stable equilibrium states has maximal entropy density

$$\hat{s}_{\rm ne} < \hat{s}_{\rm eq}$$

→ **fundamental relation for the stable equilibrium states:**

$$\hat{s}_{\rm eq} = \hat{s}_{\rm eq}(\hat{u}, \underline{\hat{n}})$$



→ **a non-equilibrium fundamental relation** requires **more independent variables**:

$$\hat{s} = \hat{s}_{\rm ne}(\gamma) \quad \hat{u} = \hat{u}_{\rm ne}(\gamma) \quad \underline{\hat{n}} = \underline{\hat{n}}_{\rm ne}(\gamma) \qquad \text{with} \qquad \hat{s}_{\rm ne}(\gamma_{\rm eq}) = \hat{s}_{\rm eq}(\hat{u}_{\rm ne}(\gamma_{\rm eq}), \underline{\hat{n}}_{\rm ne}(\gamma_{\rm eq}))$$

the values $\gamma_{\rm eq} = \gamma_{\rm eq}(\hat{u}, \underline{\hat{n}})$ at stable equilibrium are fixed by the values of $\hat{u}$ and $\underline{\hat{n}}$.
The variables γ characterize the different approaches/models/levels of description/theories.

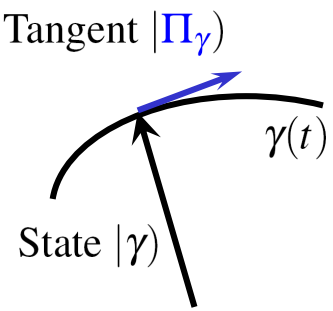
Far non-eq: states depend on many variables

		Framework	State	Entropy
A	IT SM	Information Theory Statistical Mechanics	$\{p_j(\mathbf{x},t)\}$	$\hat{s}=-k_{\rm B}\sum_j p_j \ln p_j$
B	RGD SSH	Rarefied Gases Dynamics Small-Scale Hydrodynamics	$f(\mathbf{c},\mathbf{x},t)$	$\hat{s}=-k_{\rm B}\iiint f \ln f \, d\mathbf{c}$
C	RET NET CK	Rational Extended Thermodynamics Non-Equilibrium Thermodynamics Chemical Kinetics	$\{y_j(\mathbf{x},t)\}$	$\hat{s}=\hat{s}(\{y_j\})$
D	MNET	Mesoscopic NE Thermodynamics	$P(\{y_j\},\mathbf{x},t)$	$\hat{s}=\hat{s}(P(\{y_j\}))$
E	QSM QT MNEQT	Quantum Statistical Mechanics Quantum Thermodynamics Mesoscopic NE QT	$\rho(\mathbf{x},t)$ $\hat{a}=\mathrm{Tr}\rho\, A$	$\hat{s}=-k_{\rm B}\mathrm{Tr}\rho\ln\rho$
F	QSM QT MNEQT	Cahn-Hilliard models Diffuse Interface methods Non-local NE models	$\{y_j(\mathbf{x},t)\}$	$\hat{s}=\hat{s}(\{y_i\},\{\nabla y_j\cdot\nabla y_k\})$

Reformulate in terms of square-root-probabilities

Framework		State	Redefine	Dynamics
A	IT SM	$\{p_j\}$	$\gamma = \mathrm{diag}\{\sqrt{p_j}\}$	$\frac{d\gamma}{dt} = \Pi_\gamma$
B	RGD SSH	$f(\mathbf{c},\mathbf{x},t)$	$\gamma = \sqrt{f}$	$\frac{\partial\gamma}{\partial t} + \mathbf{c}\cdot\nabla_{\mathbf{x}}\gamma + \mathbf{a}\cdot\nabla_{\mathbf{c}}\gamma = \Pi_\gamma$
C	RET NET CK	$\{y_j(\mathbf{x},t)\}$	$\gamma = \mathrm{diag}\{y_j\}$ dimensionless	$\frac{\partial\gamma}{\partial t} + \nabla_{\mathbf{x}}\cdot\mathbf{J}_\gamma = \Pi_\gamma$
D	MNET	$P(\{y_j\},\mathbf{x},t)$	$\gamma = \sqrt{P(\{y_j\},\mathbf{x},t)}$	$\frac{\partial\gamma}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{x}}\gamma = \Pi_\gamma$
E	QSM QT MNEQT	ρ	$\rho = \gamma\gamma^\dagger$	$\frac{d\gamma}{dt} + \frac{i}{\hbar}H\gamma = \Pi_\gamma$

In each framework, Π_γ may be viewed as the TANGENT VECTOR to the time-dependent trajectory of γ in state space as viewed from an appropriate local material frame, streaming frame, or Heisenberg picture.



Beretta, Phys. Rev. E **90**, 042113 (2014).

Quantum description of a QuDit (when $[H, \rho] = 0$)

For a D level system, we take

- $\gamma = \sum_{n=1}^{D} \sqrt{p_n} P_n$

The density operator is

- $\rho = \sum_{n=1}^{D} p_n P_n$

and for the special class of states with $[H, \rho] = 0$, the Hamiltonian operator is

- $H = \sum_{n=1}^{D} e_n P_n$

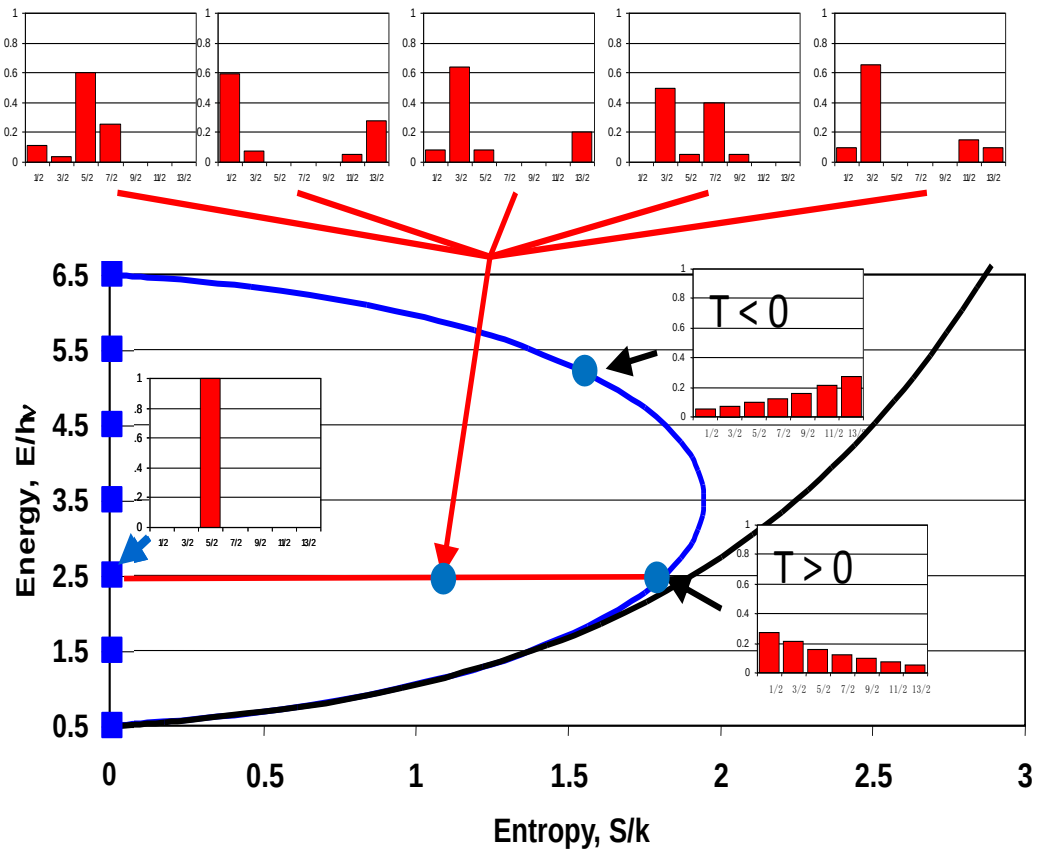
the energy

- $E = \sum_{n=1}^{D} p_n g_n e_n$

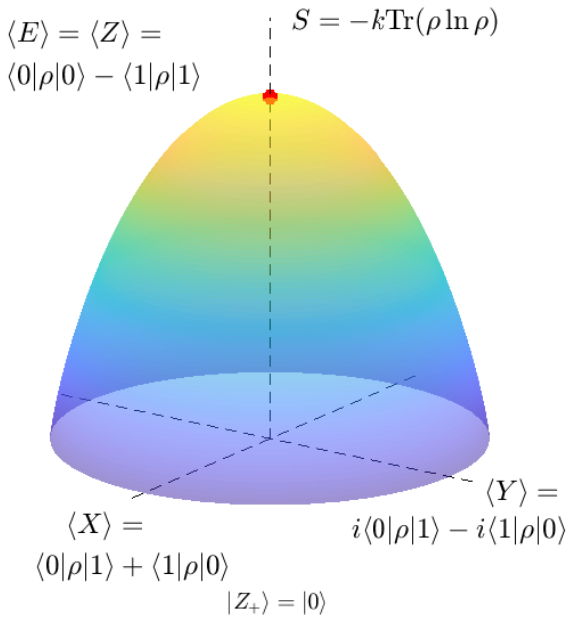
the entropy,

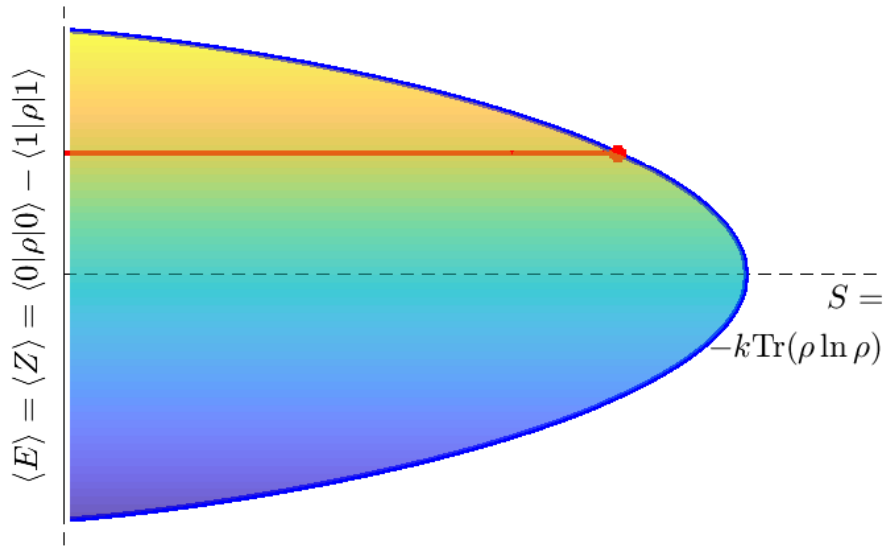
- $S = -k_{\mathrm{B}} \sum_{n=1}^{D} p_n g_n \ln p_n$

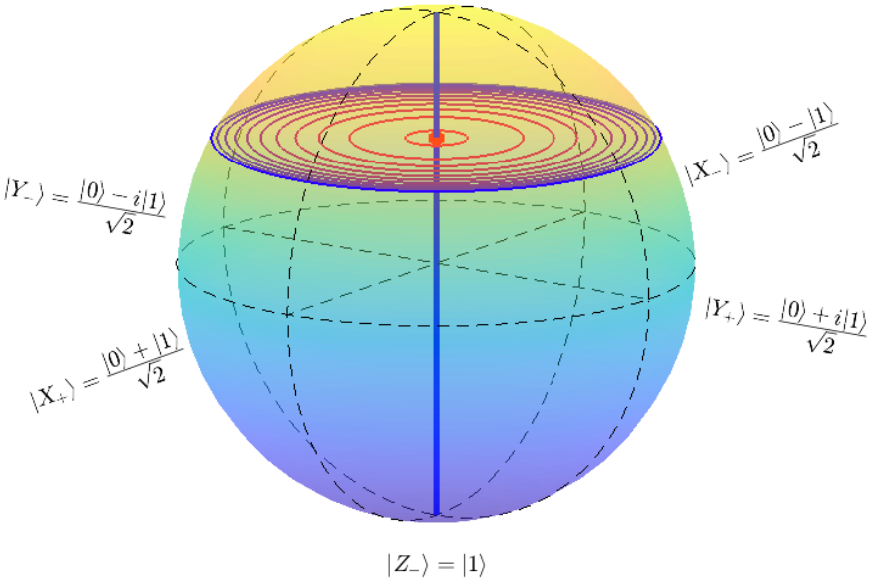
- p_n represents the degree of involvement of energy level e_n in sharing the energy load of the system
- $p_n e_n / E$ fraction of energy carried by level e_n
- S measures the overall degree of sharing

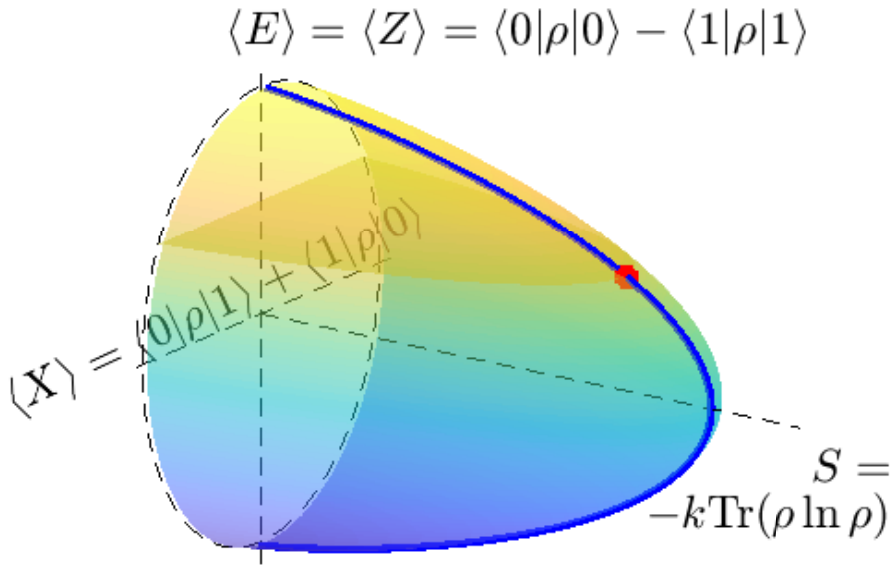


Quantum description (pictorial) of a single Qubit









Different laws of evolution, but same structure

They can all be written in the same **general form**:

$$\frac{d\gamma}{dt} = \mathcal{R}_\gamma + \mathbf{\Pi_\gamma}$$

as a result we have the BALANCE EQUATIONS:

- the term $\mathcal{R}_\gamma$ accounts for reversible dynamics, inertia, convective and diffusive transport between adjacent elements of the continuum
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Moreover, there exists a **metric** G with which the system "perceives" the distance between neighbouring states, $d(\gamma, \gamma + {\rm d}\gamma)^2 = ({\rm d}\gamma|G|{\rm d}\gamma)$

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Moreover, there exists a **metric** G with which the system "perceives" the distance between neighbouring states, $d(\gamma, \gamma + {\rm d}\gamma)^2 = ({\rm d}\gamma|G|{\rm d}\gamma)$

with respect to which the term $\boldsymbol{\Pi_\gamma}$ has the **direction of steepest entropy ascent** compatible with the conservation laws:

$$|\boldsymbol{\Pi_\gamma}) = G^{-1}|\frac{\delta \hat{s}_{\rm ne}}{\delta\gamma} - \beta_u \frac{\delta \hat{u}_{\rm ne}}{\delta\gamma} - \boldsymbol{\beta}_n \cdot \frac{\delta \hat{\boldsymbol{n}}_{\rm ne}}{\delta\gamma})$$

SEA Quantum Thermodynamics version 1984 assumed $\hat{G}_\gamma = \hat{I}$

$$\rho = \gamma^\dagger \gamma \;\Rightarrow\; \dot{\rho} = \dot{\gamma}^\dagger \gamma + \gamma^\dagger \dot{\gamma}$$

$$\frac{d\gamma}{dt} - \frac{i}{\hbar}\gamma H = \boldsymbol{\Pi_\gamma} \;\Rightarrow$$

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = \boldsymbol{\Pi}_\gamma^\dagger \gamma + \gamma^\dagger \boldsymbol{\Pi_\gamma}$$

$$S = -k\mathrm{Tr}\rho\ln\rho, \quad E = \mathrm{Tr}\rho H$$

$$\Delta H = H - E\, I$$

$$\Delta S = -k\ln\rho - S\, I$$

$$\langle \Delta H \Delta H \rangle = \mathrm{Tr}\rho(\Delta H)^2 = \mathrm{Tr}\rho H^2 - E^2$$

$$\langle \Delta S \Delta H \rangle = \mathrm{Tr}\rho \Delta S \Delta H = -k\mathrm{Tr}\rho H \ln\rho - E\, S$$

$$\dot{S} = (2\gamma\Delta M_\rho | \hat{G}_\gamma^{-1} | 2\gamma\Delta M_\rho)$$

As stable equilibrium is approached

$$\rho_{\mathrm{eq}}(E) \Rightarrow \frac{\exp(-H/kT(E))}{\mathrm{Tr}\exp(-H/kT(E))} \quad :$$

SEA dynamics with respect to metric $\hat{G}_\gamma$:

$$|\boldsymbol{\Pi_\gamma}) = \hat{G}_\gamma^{-1} \left| \frac{\delta \hat{s}_{\mathrm{ne}}}{\delta\gamma} \right|_c)$$

$$\frac{\delta \hat{s}_{\mathrm{ne}}}{\delta\gamma}\Big|_c = -2k \frac{\begin{vmatrix} \gamma\ln\rho & \gamma & \gamma H \\ \mathrm{Tr}\rho\ln\rho & \mathbf{1} & \mathrm{Tr}\rho H \\ \mathrm{Tr}\rho H\ln\rho & \mathrm{Tr}\rho H & \mathrm{Tr}\rho H^2 \end{vmatrix}}{\begin{vmatrix} \mathbf{1} & \mathrm{Tr}\rho H \\ \mathrm{Tr}\rho H & \mathrm{Tr}\rho H^2 \end{vmatrix}}$$

$$= 2\gamma\Delta S - \frac{1}{\theta_H(\rho)}\gamma\Delta H = 2\gamma\Delta M_\rho$$

where $\theta_H(\rho) = \dfrac{\langle \Delta H \Delta H \rangle}{\langle \Delta S \Delta H \rangle}$ **nonequilibrium dynamical temperature**

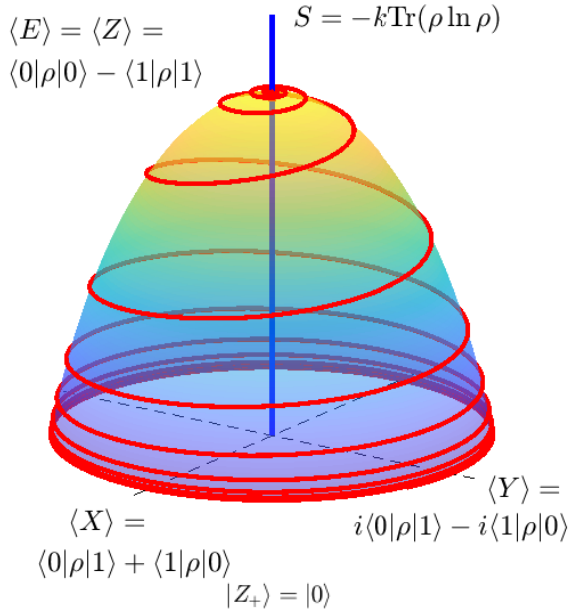
and $M_\rho = -k\ln\rho - \dfrac{H}{\theta_H(\rho)}$ **nonequilibrium Massieu operator**

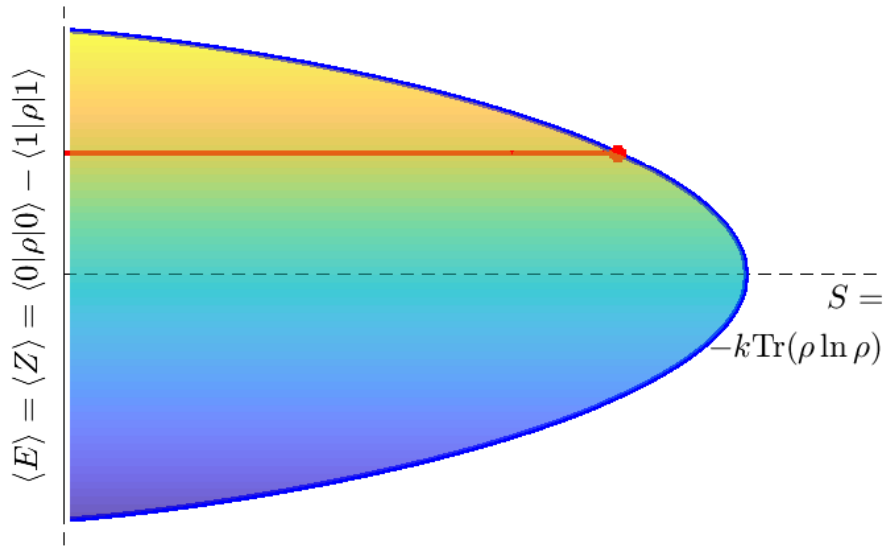
$$\mathrm{Tr}\rho M_\rho \Rightarrow S_{\mathrm{eq}}(E) - \frac{E}{T(E)}$$

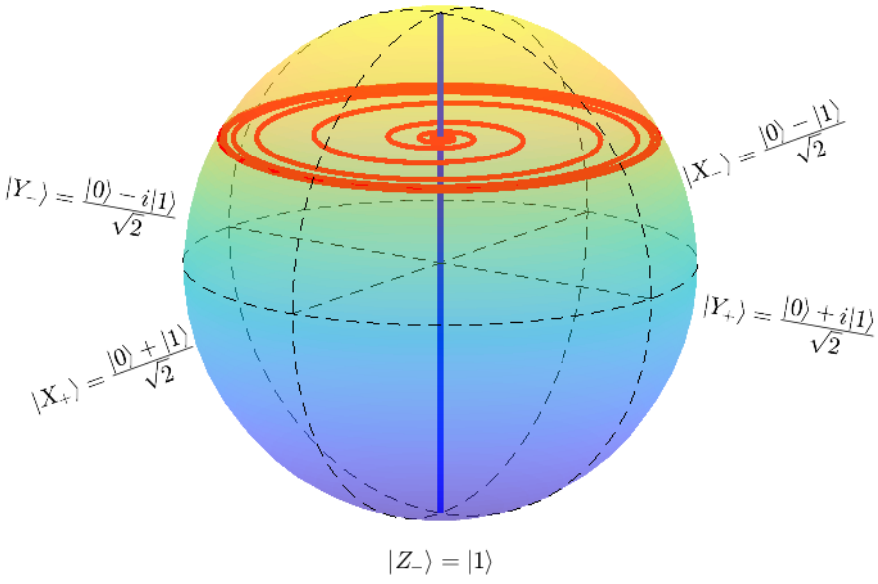
$$\theta_H(\rho) \Rightarrow T(E) \qquad 2\gamma\Delta M_\rho \Rightarrow 0$$

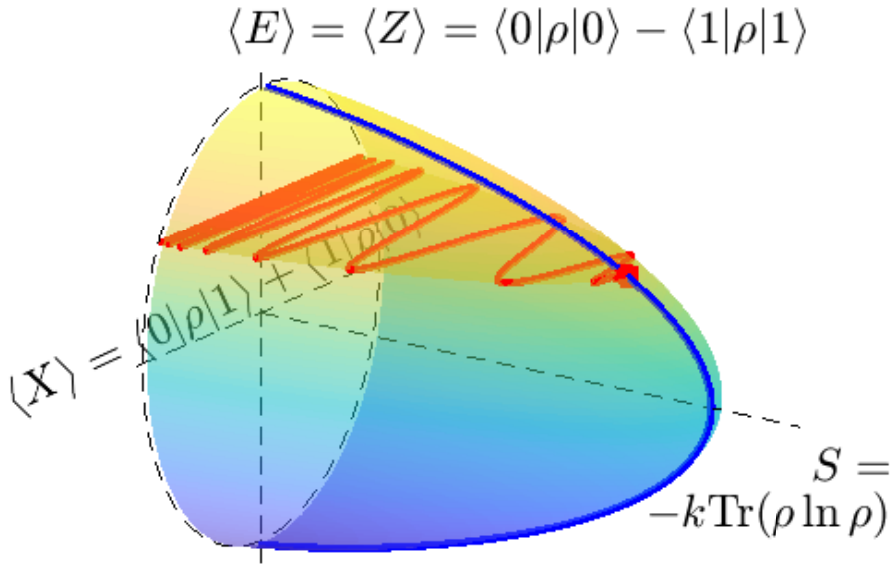
See Refs. [12–23] and [27–32] in Montefusco et al, Phys.Rev.E, 91, 042138 (2015) and Beretta, Rep.Math.Phys., 64, 139 (2009)

Steepest Entropy Ascent for a single Qubit



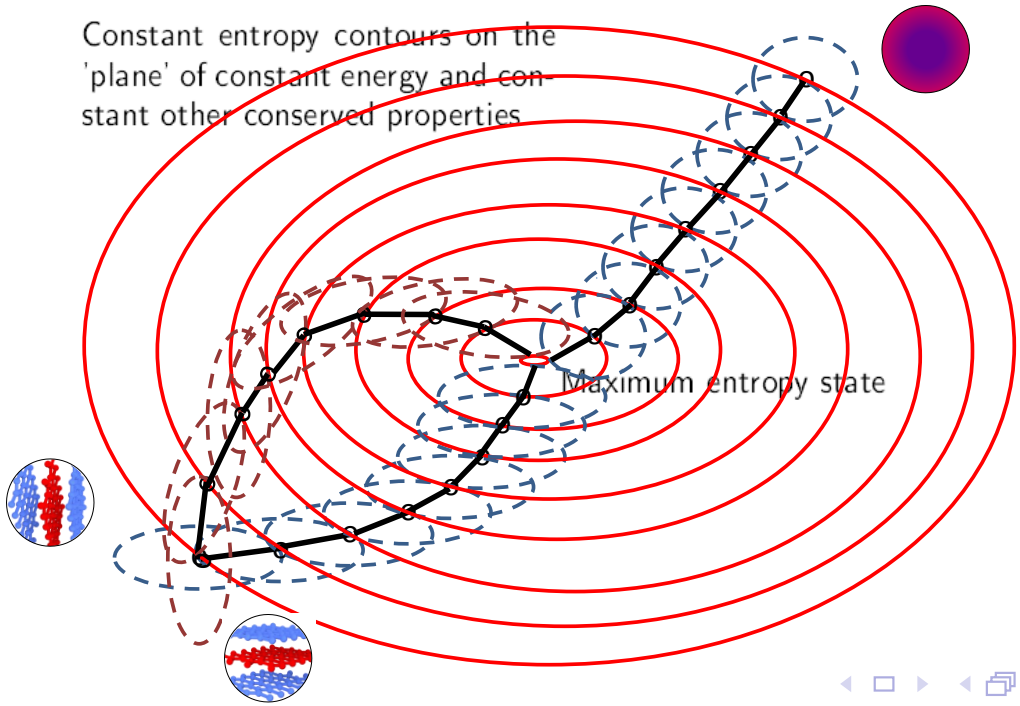






Four rules of thermodynamic modeling reveal four general Laws of Nature

1. ENERGY must be defined for all states of the SYSTEM.
2. ENTROPY must be defined for all states of the SYSTEM.
3. maximum entropy states must be STABLE EQUILIBRIA of the dynamical model, and those of lowest energy must have zero temperature.
4. each NONEQUILIBRIUM state of each LOCAL subsystem must equipped with a METRIC IN STATE SPACE with respect to which the irreversible component of its time evolution is STEEPEST ENTROPY ASCENT.



The principle of local steepest entropy ascent is a 1984 precursor of several modern theories of non-equilibrium dynamics

- Ziegler's attempts to generalize Onsager's principle (1958)
- metriplectic formalism (1984: Morrison, Kaufman, Grmela)
- least action in chemical kinetics (1987: Sieniutycz)
- GENERIC (>1997: Grmela, Öttinger)
- gradient flows (>1998: Jordan, Kinderlehrer, Otto, Mielke)
- maximum entropy production principle MEPP (2003: Dewar, Martyushev)
- large deviation theory (>2004: Evans, Touchette, Peletier)
- SEAQT (>2014: von Spakovsky)

If: steady state, no convection, no reactions, linear regime, constant conductivities

Then: local MEP (SEA) implies min global EP

Glansdorff-Prigogine (1954) noted that assuming

- stationary boundary conditions, $d\underline{\Gamma}/dt|_{\Omega} = 0$
- no convection and no reactions, so that $\underline{\underline{X}} = \nabla\underline{\Gamma}$
- linear regime, $\underline{\underline{J}} = \underline{\underline{L}} \odot \underline{\underline{X}}$, $\sigma = \underline{\underline{X}} \odot \underline{\underline{L}} \odot \underline{\underline{X}}$
- constant Onsager conductivities, $d\underline{\underline{L}}/dt = 0$
- $\hat{s} = \hat{s}(\hat{u})$ with all $\hat{u}$ conserved
- $\dfrac{d\underline{\hat{u}}}{dt} = -\boldsymbol{\nabla} \cdot \underline{\underline{J}}$ with $\underline{\underline{J}} = \boldsymbol{J}_{\underline{\hat{u}}}$
- $\underline{\Gamma} = \dfrac{\partial \hat{s}}{\partial \underline{\hat{u}}}$ and $\dfrac{\partial \underline{\Gamma}}{\partial \underline{\hat{u}}} = \dfrac{\partial^2 \hat{s}}{\partial \underline{\hat{u}} \partial \underline{\hat{u}}} \leq 0$

Then:

$$\frac{d\dot{S}_{\rm gen}}{dt} = \iiint \frac{d\sigma}{dt}\, dV = 2 \iiint \underline{\underline{J}} \odot \frac{d\underline{\underline{X}}}{dt}\, dV = 2 \iiint \frac{d\underline{\hat{u}}}{dt} \odot \frac{\partial^2 \hat{s}}{\partial \underline{\hat{u}} \partial \underline{\hat{u}}} \odot \frac{d\underline{\hat{u}}}{dt}\, dV \leq 0$$

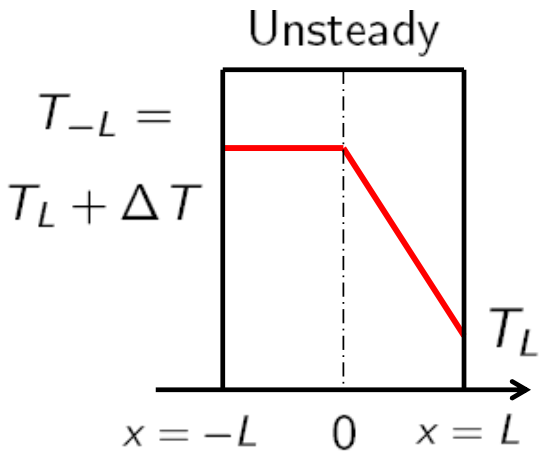
i.e., the free fluxes and forces adjust until the system reaches a stable **stationary state with minimum** $\dot{S}_{\rm gen}$. For variable conductivities, $d\underline{\underline{L}}/dt \neq 0$, the theorem loses validity.

$$\frac{d\dot{S}_{\rm gen}}{dt} = \iiint \frac{d\sigma}{dt}\, dV = \iiint \frac{d}{dt} \underline{\underline{X}} \odot \underline{\underline{L}} \odot \underline{\underline{X}}\, dV = 2 \iiint \underline{\underline{J}} \odot \frac{d\underline{\underline{X}}}{dt}\, dV + \cancel{\iiint \underline{\underline{X}} \odot \frac{d\underline{\underline{L}}}{dt} \odot \underline{\underline{X}}\, dV}$$

$$\iiint_V \underline{\underline{J}} \odot \frac{d\underline{\underline{X}}}{dt}\, dV = \iiint_V \underline{\underline{J}} \odot \frac{d\nabla\underline{\Gamma}}{dt}\, dV = \cancel{\iint_{\partial V} \underline{\underline{J}} \odot \frac{d\underline{\Gamma}}{dt} \cdot \boldsymbol{n}\, dA} - \iiint_V \frac{d\underline{\Gamma}}{dt} \odot \nabla \cdot \underline{\underline{J}}\, dV$$

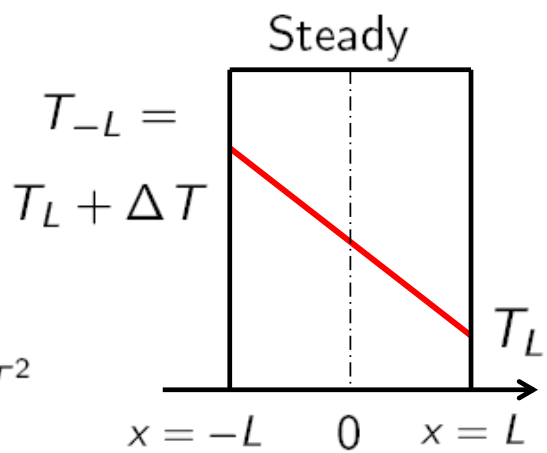
$$- \iiint \frac{d\underline{\Gamma}}{dt} \odot \nabla \cdot \underline{\underline{J}}\, dV = \iiint \frac{d\underline{\Gamma}}{dt} \odot \frac{d\underline{\hat{u}}}{dt}\, dV = \iiint \frac{d\underline{\hat{u}}}{dt} \odot \frac{\partial \underline{\Gamma}}{\partial \underline{\hat{u}}} \odot \frac{d\underline{\hat{u}}}{dt}\, dV = \iiint \frac{d\underline{\hat{u}}}{dt} \odot \frac{\partial^2 \hat{s}}{\partial \underline{\hat{u}} \partial \underline{\hat{u}}} \odot \frac{d\underline{\hat{u}}}{dt}\, dV \leq 0$$

Local MEP (SEA) implies min global EP



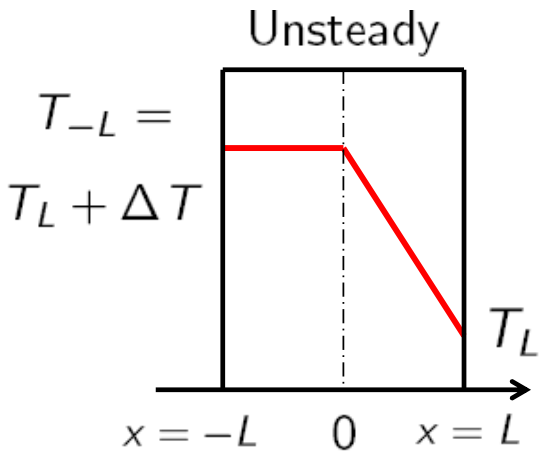
$$q''_x = -k\, dT/dx$$

$$\sigma = (dT/dx)^2 k/T^2$$



$$\dot{S}_{\rm gen} = A \int_{-L}^{L} \sigma\, dx = (\Delta T)^2 kA/L \quad \Rightarrow \quad \dot{S}_{\rm gen} = (\Delta T)^2 kA/2L \ \ \text{(minimum)}$$

Local MEP (SEA) implies min global EP



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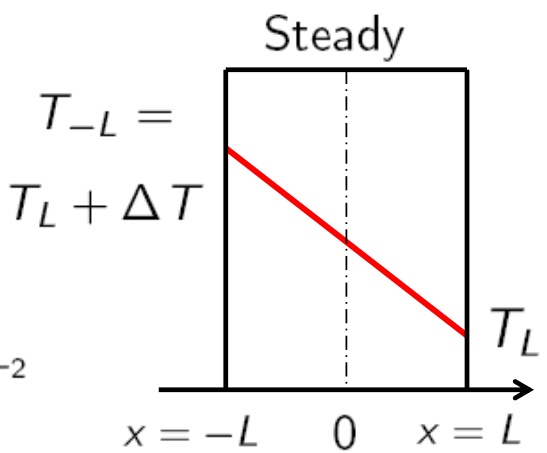

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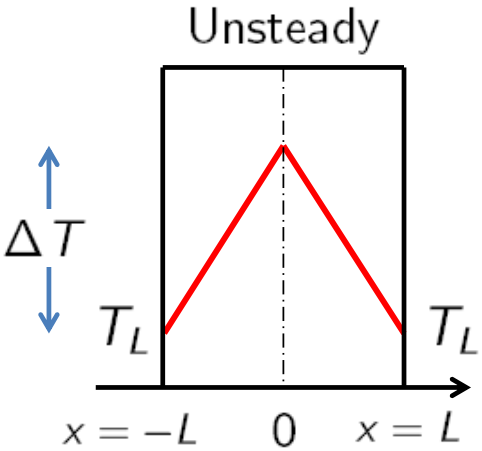

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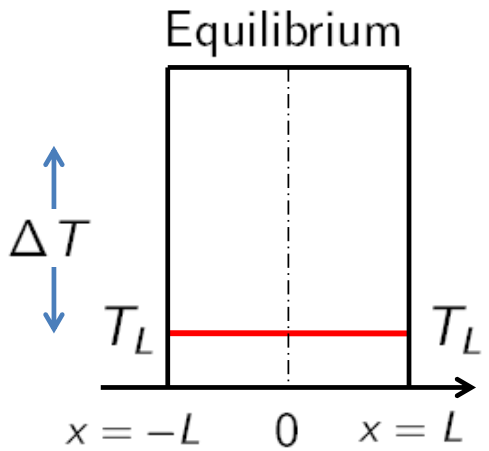


$$\dot{S}_{\rm gen} = 2\,(\Delta T)^2 kA/L \quad \Rightarrow \quad \dot{S}_{\rm gen} = 0 \ \ \text{(minimum)}$$

GENERIC merges SEA with symplectic machinery

The **entropy of non-equilibrium states depends on many more macroscopic properties**

$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \underline{\hat{a}}_{\rm slow}, \underline{\hat{a}}_{\rm fast})$$

Neglecting the fast variables, i.e., assuming

$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \underline{\hat{a}}_{\rm slow})$$

Öttinger and Grmela (1997) introduce the GENERIC evolution equation, which in effect **adds the idea of steepest entropy ascent** (irreversible dynamics) to the powerful **Hamiltonian and symplectic machinery** of reversible dynamics. The reversible/irreversible evolutions of the slow variables are generated by the gradients of an energy functional $E(\underline{\hat{a}}_{\rm slow})$ and an entropy function $S(\underline{\hat{a}}_{\rm slow})$:

$$\frac{d\hat{a}_f^{\rm slow}}{dt} = \hat{L}_{fg}^{\rm rev}\frac{\delta E(\underline{\hat{a}}_{\rm slow})}{\delta a_g^{\rm slow}} + \hat{M}_{fg}^{\rm irr}\frac{\delta S(\underline{\hat{a}}_{\rm slow})}{\delta a_g^{\rm slow}}$$

Although GENERIC functionals are typically global while SEA functionals are local, we have shown their essential equivalence.
In our notation, the dissipative part and degeneracy condition of GENERIC are

$$|\Pi_\gamma) = \hat{M}\,|\Phi) \quad \text{with} \quad \hat{M}\,|\Psi_i) = 0 \;\forall i$$

Thus, in terms of the SEA projection operator

$$\hat{P}_{\perp\boldsymbol{\Psi}}|\Phi) = |\Phi_C) = |\Phi - \sum_i \beta_i\,\Psi_i)$$

we have the essential equivalence

$$\hat{M} = \frac{1}{\tau}\hat{G}^{-1}\hat{P}_{\perp\boldsymbol{\Psi}}$$

provided of course that the chosen state variable and conserved properties are the same.

Grmela, Öttinger, Phys. Rev. E **56**, 6620 (1997).
Montefusco, Consonni, Beretta, Phys. Rev. E **91**, 042138 (2015).

Gradient flows are SEA-like dynamical systems

Let the states γ be points of a Riemannian manifold $(\mathcal{M},\hat{G})$ and assume S a (dimensionless) functional on $\mathcal{M}$. The gradient flow of S on $(\mathcal{M},\hat{G})$ is a dynamical system in $\mathcal{M}$ given by the differential equation (in dimensionless time)

$$\left|\tau\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right) = |\mathrm{grad}S_{|\gamma})$$

The metric tensor $\hat{G}$ is an essential element of the notion. It converts the differential DS of S, which is a cotangent vector field, into the gradient of S, which is a tangent vector field: for all vector fields v on $\mathcal{M}$

$$(\mathrm{diff}S|v) = \hat{G}(\mathrm{grad}S, v)$$

Therefore, for all vector fields v along γ

$$(\mathrm{diff}S_{|\gamma}|v) = \hat{G}_{|\gamma}(\mathrm{grad}S_{|\gamma}, v) = \hat{G}\left(\tau\frac{\mathrm{d}\gamma}{\mathrm{d}t}, v\right)$$

The rate of change of the entropy is

$$k_{\mathrm{B}}\frac{\mathrm{d}S(\gamma)}{\mathrm{d}t} = (\mathrm{diff}S_{|\gamma}\left|\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right)k_{\mathrm{B}} = \hat{G}_{\gamma}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}t}, \frac{\mathrm{d}\gamma}{\mathrm{d}t}\right)k_{\mathrm{B}}\tau$$

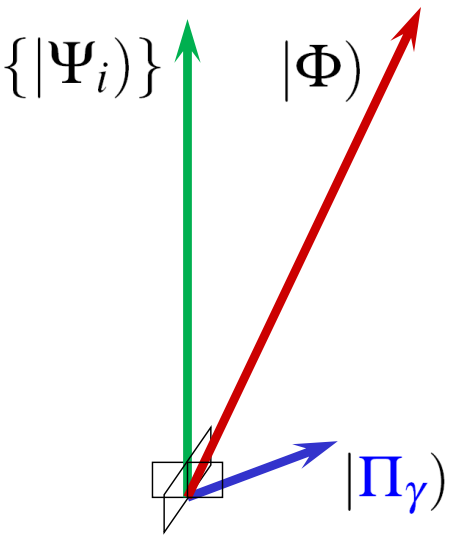
to be compared with the SEA

$$\sigma = \left(\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right|\hat{G}_{\gamma}\left|\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right)k_{\mathrm{B}}\tau$$

The main differences between SEA, the dissipative part of GENERIC, and gradient flow formulations stem from the technical nature of the bilinear forms adopted to define gradients.

Jordan, Kinderlehrer, Otto, SIAM J. Math. Analysis **29**, 1 (1998). Otto, Comm. Par. Diff. Eqs. **26**, 101 (2001). Mielke, Nonlinearity **24**, 1329 (2011). Sieniutycz, Chem. Eng. Sci. **42**, 2697 (1987).

A	$\dfrac{d(\gamma^2\|C_i)}{dt} = \Pi_{C_i}$	$-k_{\rm B}\dfrac{d(\gamma^2\|\ln\gamma^2)}{dt} = \sigma$
B	$\dfrac{\partial(\gamma^2\|C_i)}{\partial t} + \nabla_{\mathbf{x}}\cdot(\gamma^2\|\mathbf{c}\,C_i) = \Pi_{C_i}$	$-k_{\rm B}\dfrac{\partial(\gamma^2\|\ln\gamma^2)}{\partial t} + k_{\rm B}\nabla_{\mathbf{x}}\cdot(\gamma^2\|\mathbf{c}\,\ln\gamma^2) = \sigma$
C,D	$\dfrac{\partial C_i}{\partial t} + \nabla_{\mathbf{x}}\cdot\mathbf{J}_{C_i} = \Pi_{C_i}$	$\dfrac{\partial S}{\partial t} + \nabla_{\mathbf{x}}\cdot\mathbf{J}_S = \sigma$
E	$\dfrac{d(\gamma\|C_i\,\gamma)}{dt} - \dfrac{i}{\hbar}(\gamma\|[H, C_i]\gamma) = \Pi_{C_i}$	$-k_{\rm B}\dfrac{d(\gamma\|(\ln\gamma\gamma^\dagger)\,\gamma)}{dt} = \sigma$



In each framework, the **production terms** can be written as **scalar products** of $|\Pi_\gamma)$ with other vectors in the same space

$$\Pi_{A_k} = (\alpha_k|\Pi_\gamma) \qquad \Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0 \qquad \sigma = (\Phi|\Pi_\gamma)\,k_{\rm B}$$

Framework	α_k	Ψ_i	Φ
A, B, D	$2A_k\,\gamma$	$2C_i\,\gamma$	$-2(\ln\gamma^2)\,\gamma$
C	$\mathrm{vect}\{\alpha_{ky_j}\}$	$\mathrm{vect}\{\Psi_{iy_j}\}$	$\mathrm{vect}\{\Phi_{y_j}\}$
E	$2A_k\,\gamma$	$2C_i\,\gamma$	$-2(\ln\gamma\gamma^\dagger)\,\gamma$

Adding SEA dissipation to the dynamics to make it 'thermo'

Hamiltonian dynamics: von Neumann equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho]$$

i.e., for density matrix elements $\rho_{nm} = \langle \epsilon_n | \rho | \epsilon_m \rangle$ with respect to an eigenbasis $\{|\epsilon_n\rangle\}$ of H

$$\frac{\mathrm{d}\rho_{nm}}{\mathrm{d}t} = -\frac{i}{\hbar}(e_n - e_m)\,\rho_{nm}$$

My original objective (1981), was to add a dissipative term

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \hat{D}(\rho)$$

'designed' (postulated) so that the canonical equilibrium states $\rho_{\mathrm{eq}}(E)$ would be the only stable equilibrium states of the dynamics and, therefore, the Hatsopoulos-Keenan statement of the second law would emerge as a general theorem of the dynamics.

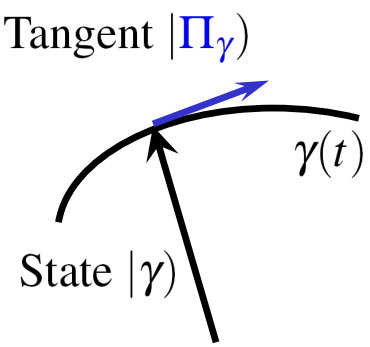
To preserve positivity and hermiticity we reformulate in terms of the square-root of ρ

$$\gamma = U\sqrt{\rho} \qquad \rho = \gamma\gamma^\dagger$$

U is irrelevant (we can take $U = I$)

$$\frac{d\gamma}{dt} + \frac{i}{\hbar} H\,\gamma = \Pi_\gamma$$

Operator Π_γ may be viewed as the dissipative component of the TANGENT VECTOR to the time-dependent trajectory of the state vector γ.



Π_γ should conserve the state functionals

$$C_i(\gamma) = \mathrm{Tr}\, C_i \gamma\gamma^\dagger$$

with $C_1 = I$, $C_2 = H$, and possibly additional conservations.

SEA nonlinear master equation

w.r.to the uniform Fisher-Rao metric $\hat{G} = \hat{I}$ on the unit octant $\mathrm{Tr}(\gamma\gamma^\dagger) = 1$

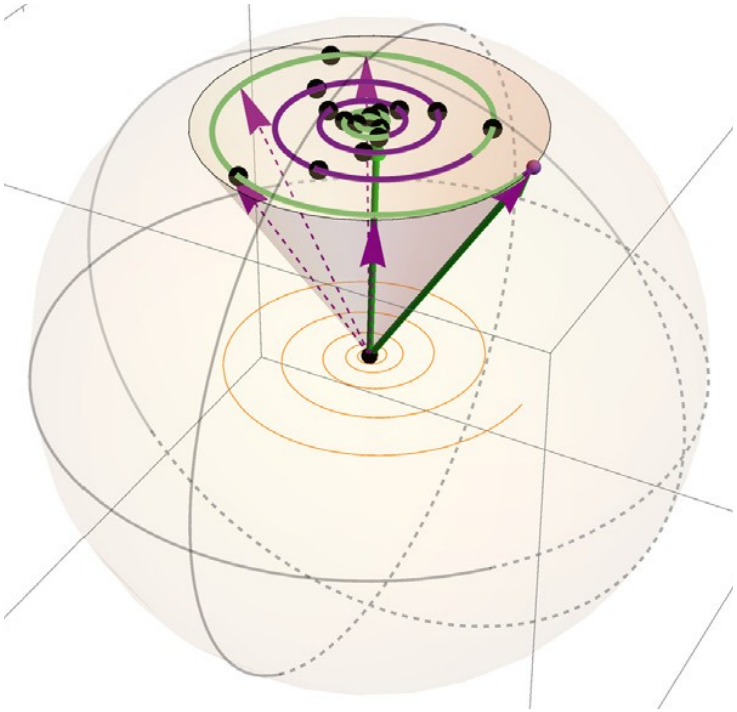
When written for density matrix elements with respect to an eigenbasis $\{|\epsilon_j\rangle\}$ of H

$$\frac{\mathrm{d}\rho_{nm}}{\mathrm{d}t} = -\frac{i}{\hbar}\rho_{nm}(e_n - e_m) + \frac{1}{k_\mathrm{B}\tau}\sum_r u_{nr}u^*_{mr}p_r\left(\Delta s_r - \frac{\Delta e_n + \Delta e_m}{2\theta_H}\right)$$

where $u_{jk} = \langle\epsilon_j|\eta_k\rangle$, $\{|\eta_k\rangle\}$ is an eigenbasis of ρ, p_k's its eigenvalues, $\Delta s_k = s_k - \langle S\rangle$, $s_k = -k_\mathrm{B}\ln p_k$ if $p_k \neq 0$, $s_k = 0$ if $p_k = 0$, e_j the eigenvalues of H, $\Delta e_j = e_j - \langle H\rangle$, and

$$\theta_H = \frac{\langle\Delta H\Delta H\rangle}{\langle\Delta S\Delta H\rangle}$$

$$= \frac{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i\right)^2}{\sum_i e_i p_i \ln p_i - \sum_i p_i \ln p_i \sum_j e_j p_j}$$



Beretta, Reps.Math.Phys. **64**, 139 (2009). Beretta, Int.J.Theor.Phys. **24**, 119, 1233 (1985). Tabakin, Ann.Phys. **383**, 33 (2017). Militello, Phys.Rev.E **97**, 052113 (2018).

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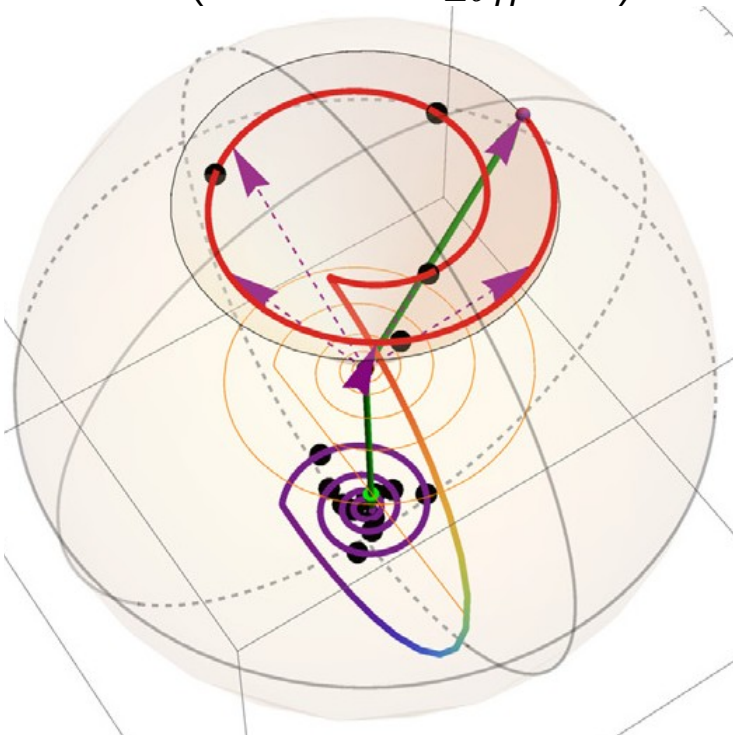

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SEAQT master equation

w.r.to a nonuniform metric based on the spectral decomposition $|H) = \sum_n e_n |P_n)$

Li&vonSpakovsky effectively adopt the metric

$$\frac{1}{\tau}\hat{G}^{-1} = \sum_n \frac{1}{\tau_n}|P_n)(P_n| \quad \tau\hat{G} = \sum_n \frac{\tau_n}{\tau}|P_n)(P_n|$$

and consider only states with $[H,\rho] = 0$. Then, $u_{jk} = \langle \epsilon_j | \eta_k \rangle = \delta_{jk}$, the eigenvalues p_n of ρ are the "energy level occupation probabilities," and they get redistributed according to

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = \frac{p_n}{\tau_n}\left[-\ln p_n - \alpha + \beta\, e_n\right]$$

with the nonlinear functionals α and β given by

$$\alpha = \frac{\sum_i \lambda_i e_i \sum_j \lambda_j e_j \ln p_j - \sum_i \lambda_i \ln p_i \sum_j \lambda_j e_j^2}{\sum_i \lambda_i e_i^2 - \left(\sum_i \lambda_i e_i\right)^2}$$

$$\beta = \frac{\sum_i \lambda_i e_i \ln p_i - \sum_i \lambda_i \ln p_i \sum_j \lambda_j e_j}{\sum_i \lambda_i e_i^2 - \left(\sum_i \lambda_i e_i\right)^2} \qquad \lambda_i = \frac{g_i p_i}{\tau_i}$$

Beretta, Phys.Rev.E **73**, 026113 (2006). Beretta, Reps.Math.Phys. **64**, 139 (2009).
Li, von Spakovsky, Phys.Rev.E **93**, 012137 (2016); E **94**, 032117 (2016); B **97**, 024308 (2018).

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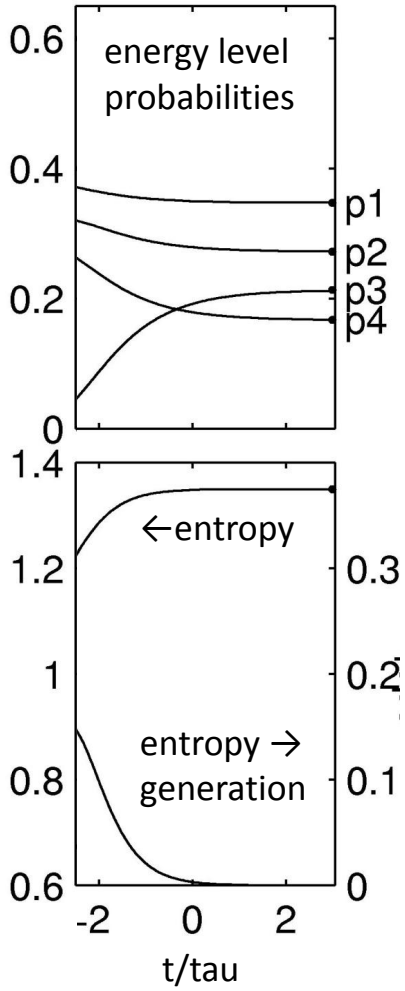
$$\beta = \frac{\sum_i \lambda_i e_i \ln p_i - \sum_i \lambda_i \ln p_i \sum_j \lambda_j e_j}{\sum_i \lambda_i e_i^2 - \left(\sum_i \lambda_i e_i\right)^2} \qquad \lambda_i = \frac{g_i p_i}{\tau_i}$$



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Li, von Spakovsky, Phys.Rev.E **93**, 012137 (2016); E **94**, 032117 (2016); B **97**, 024308 (2018).

SEAQT master equation

w.r.to a nonuniform metric based on the spectral decomposition $|H) = \sum_n e_n |P_n)$

Li&vonSpakovsky effectively adopt the metric

$$\frac{1}{\tau}\hat{G}^{-1} = \sum_n \frac{1}{\tau_n}|P_n)(P_n| \quad \tau\hat{G} = \sum_n \frac{\tau_n}{\tau}|P_n)(P_n|$$

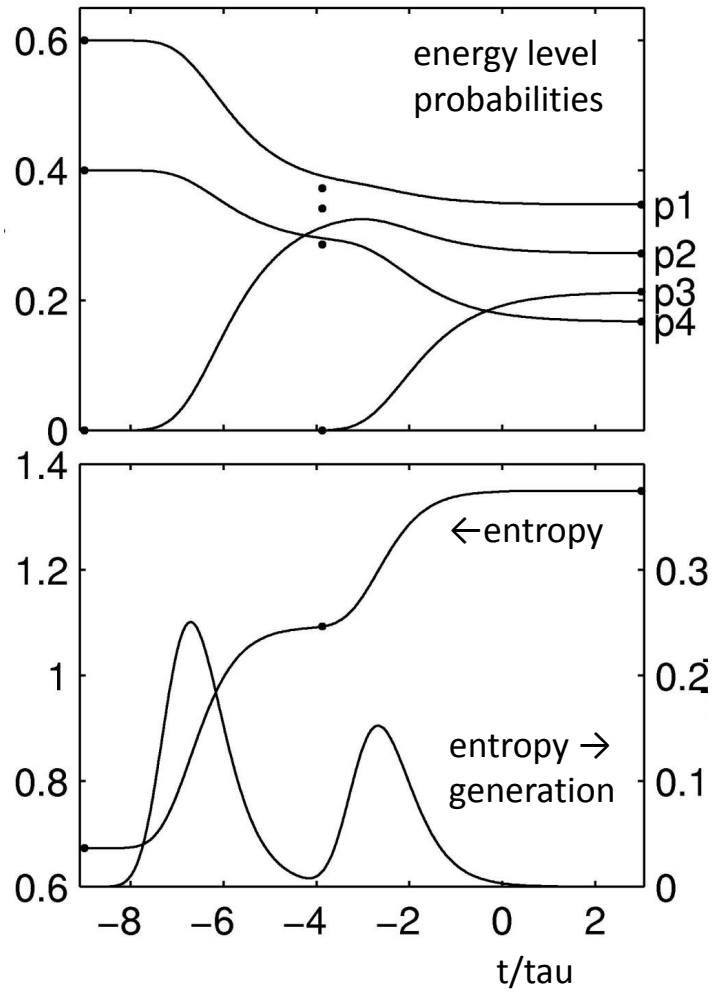
and consider only states with $[H,\rho] = 0$. Then, $u_{jk} = \langle \epsilon_j | \eta_k \rangle = \delta_{jk}$, the eigenvalues p_n of ρ are the "energy level occupation probabilities," and they get redistributed according to

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = \frac{p_n}{\tau_n}\left[-\ln p_n - \alpha + \beta\, e_n\right]$$

with the nonlinear functionals α and β given by

$$\alpha = \frac{\sum_i \lambda_i e_i \sum_j \lambda_j e_j \ln p_j - \sum_i \lambda_i \ln p_i \sum_j \lambda_j e_j^2}{\sum_i \lambda_i e_i^2 - \left(\sum_i \lambda_i e_i\right)^2}$$

$$\beta = \frac{\sum_i \lambda_i e_i \ln p_i - \sum_i \lambda_i \ln p_i \sum_j \lambda_j e_j}{\sum_i \lambda_i e_i^2 - \left(\sum_i \lambda_i e_i\right)^2} \qquad \lambda_i = \frac{g_i p_i}{\tau_i}$$



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Li, von Spakovsky, Phys.Rev.E **93**, 012137 (2016); E **94**, 032117 (2016); B **97**, 024308 (2018).

SEAQT nonlinear master equation

w.r.to uniform Fisher-Rao or simplest nonuniform metric

If $[H,\rho] = 0$, then $u_{jk} = \langle \epsilon_j | \eta_k \rangle = \delta_{jk}$ and the eigenvalues of ρ are interpreted as "occupation probabilities". The SEAQT nonlinear master equation with nonuniform metric $\hat{G} = mboxdiag\{\tau_n/\tau\}$ redistributes them according to

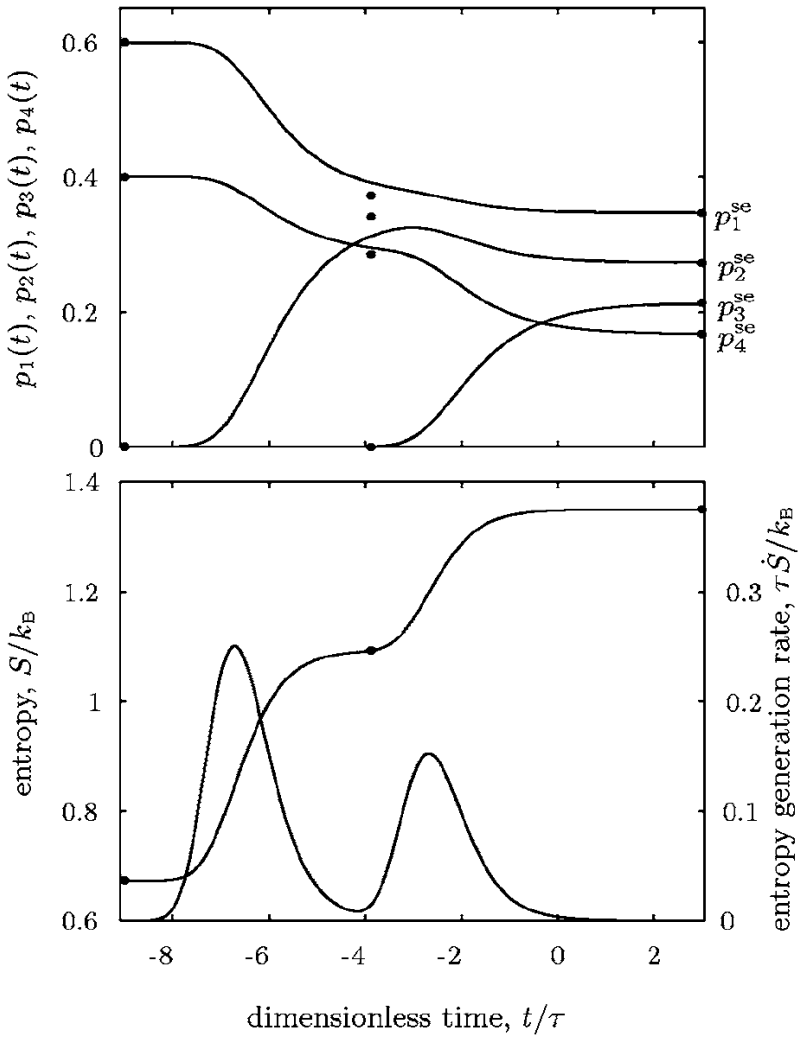
$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = \frac{1}{k_B \tau_n} p_n \left(\Delta s_n - \frac{\Delta e_n}{\theta_H} \right)$$

$$= \frac{p_n}{\tau_n} \left[-\ln p_n - \alpha + \beta\, e_n \right]$$

with the nonlinear functionals α and β given by

$$\alpha = \frac{\sum_i e_i p_i \sum_j e_j p_j \ln p_j - \sum_i p_i \ln p_i \sum_j e_j^2 p_j}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i \right)^2}$$

$$\beta = \frac{\sum_i e_i p_i \ln p_i - \sum_i p_i \ln p_i \sum_j e_j p_j}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i \right)^2}$$



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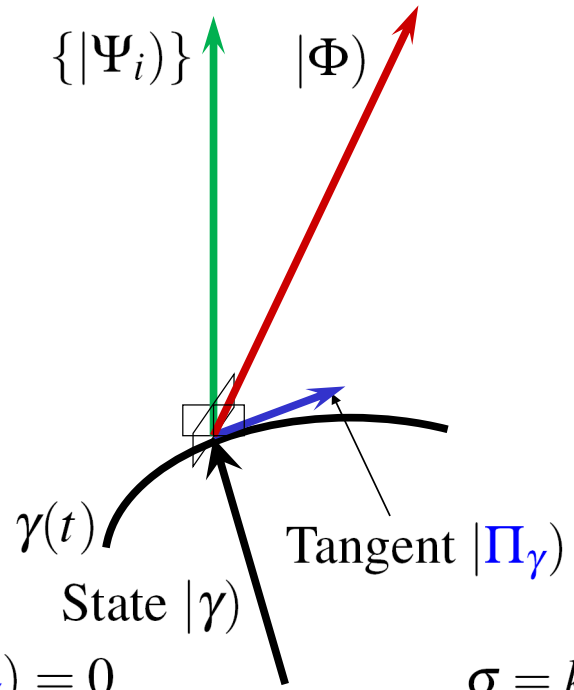
Steepest Entropy Ascent

with respect to the systems' metric tensor field $\hat{G}(\gamma)$



$$\Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0 \qquad \sigma = k_{\rm B}(\Phi|\Pi_\gamma)$$

Beretta, Lecture Notes in Physics **278**, 441 (1986). See also: Beretta, Reps. Math. Phys. **64**, 139 (2009) presented in Torun, Poland for Kossakowski's 70th birthday.

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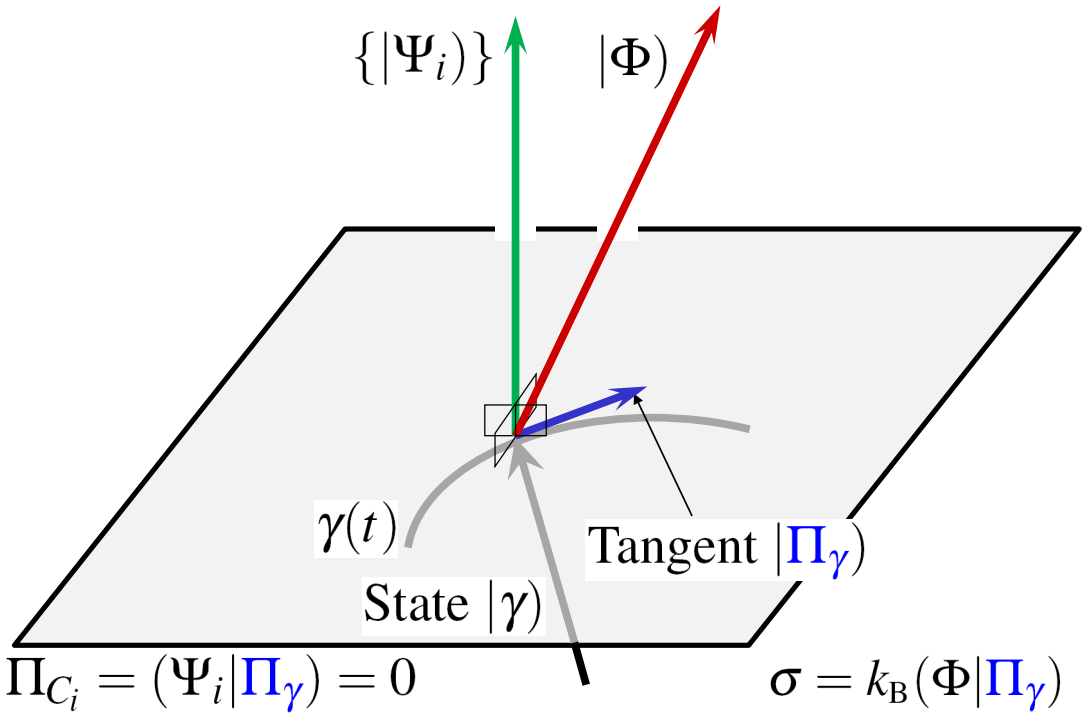

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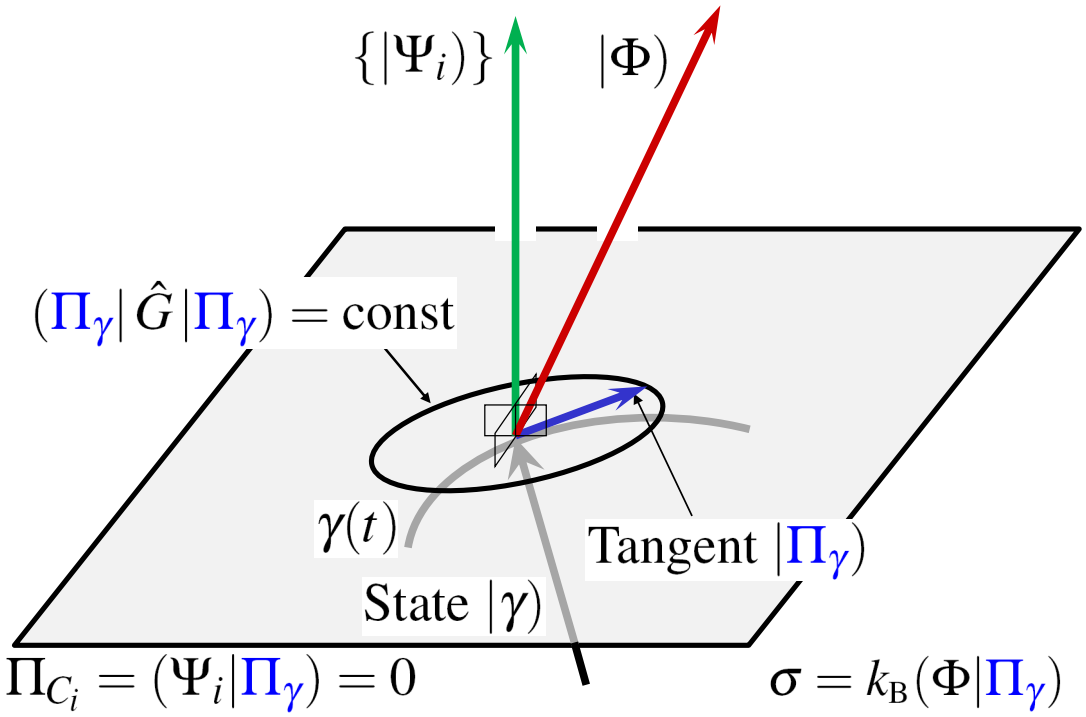

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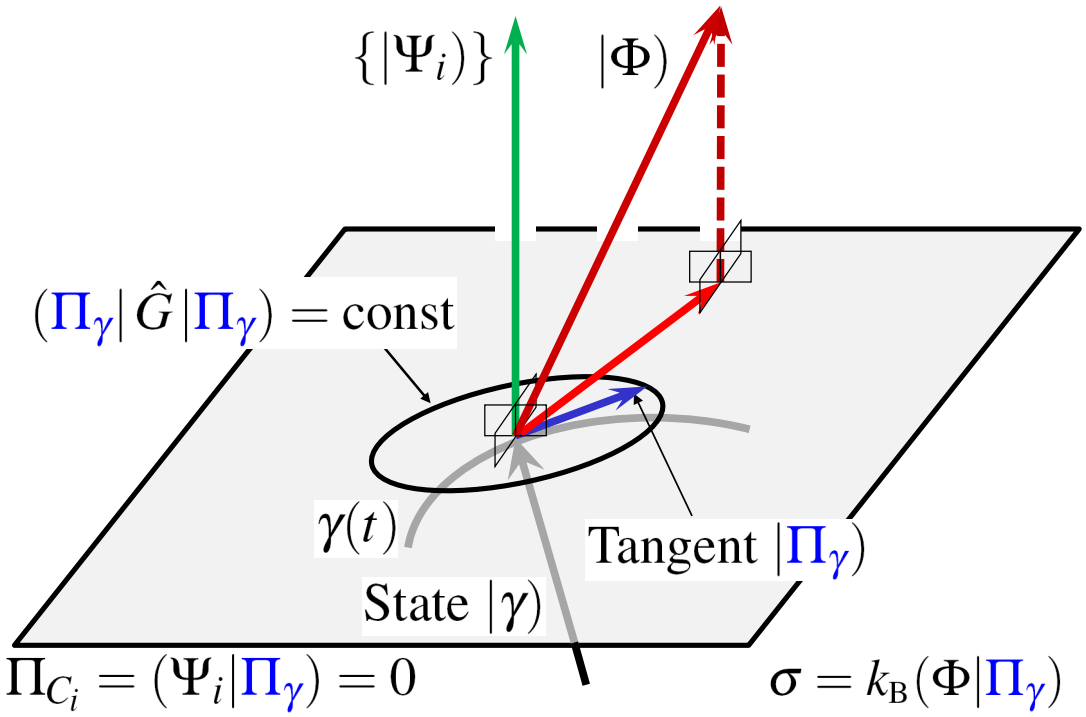

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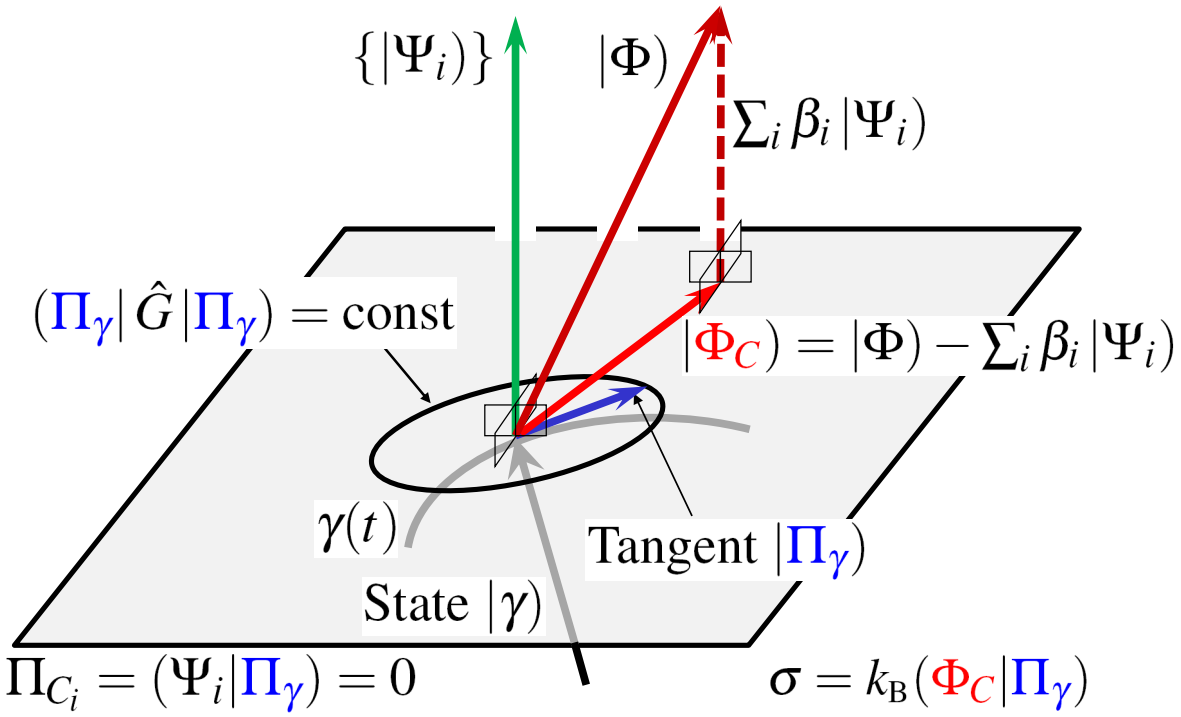

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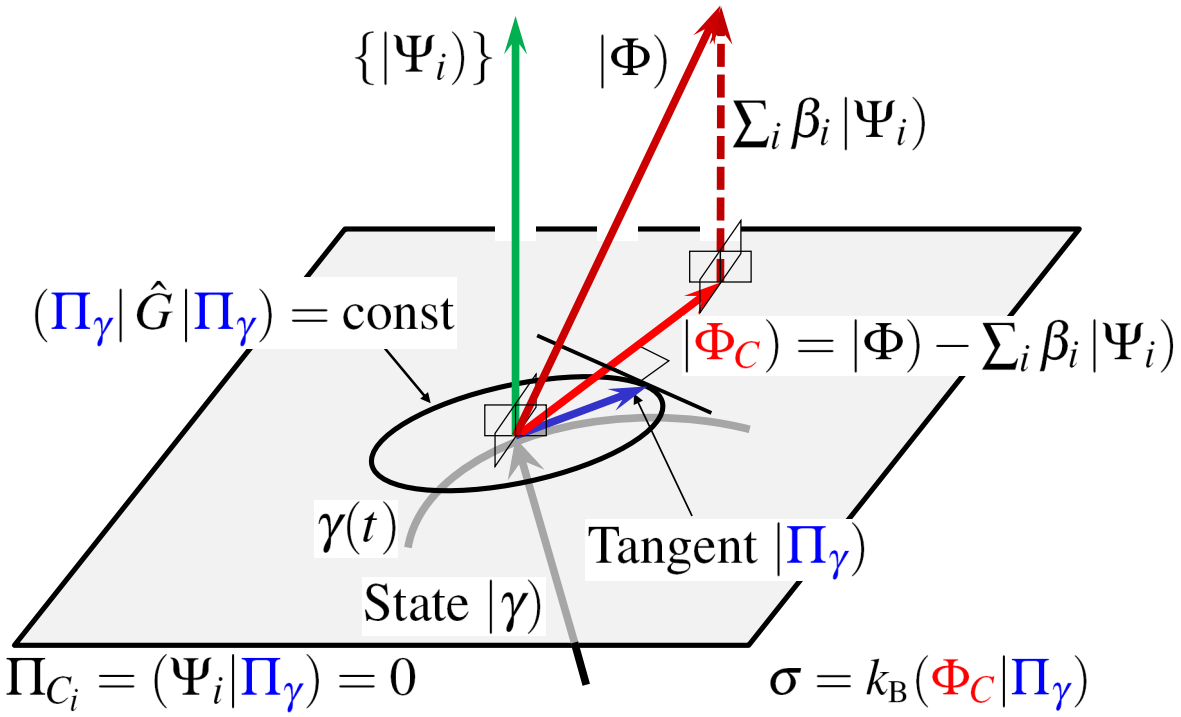

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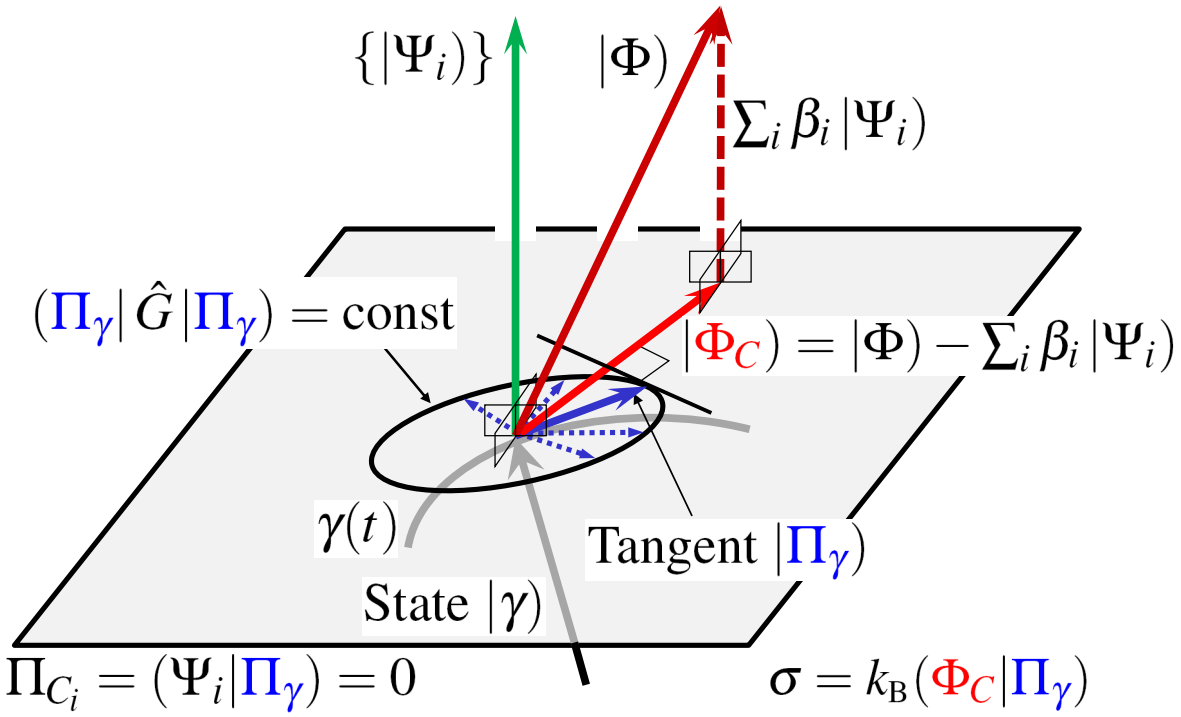

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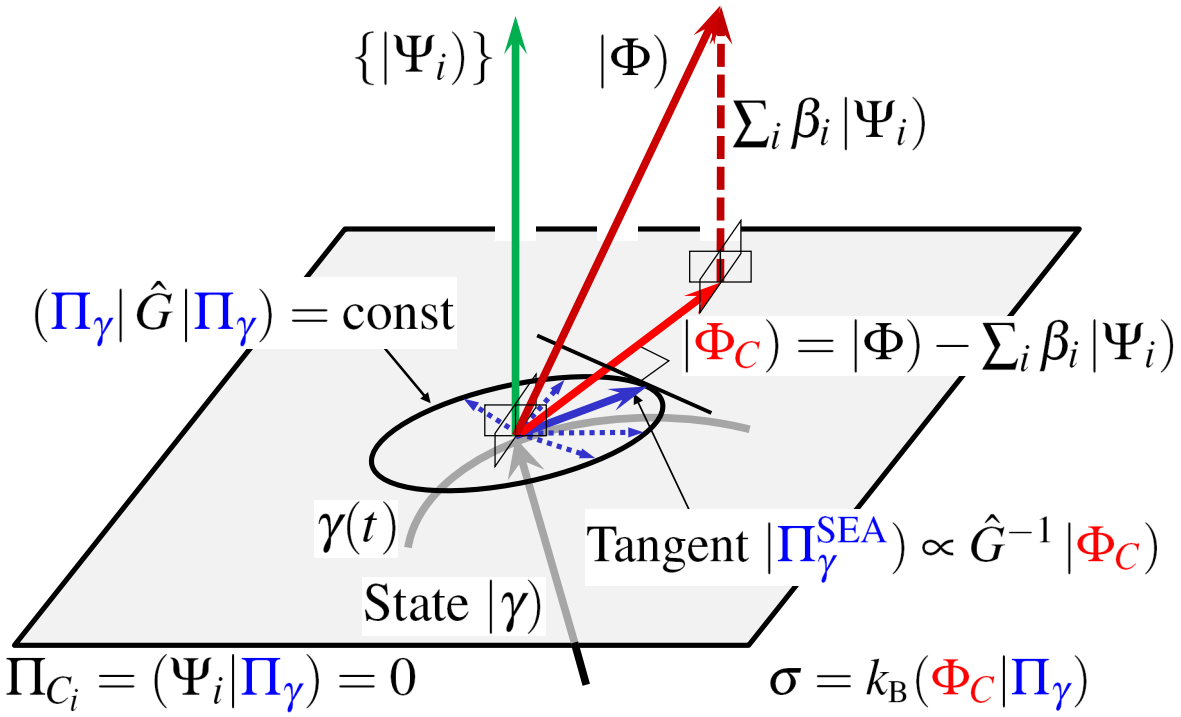

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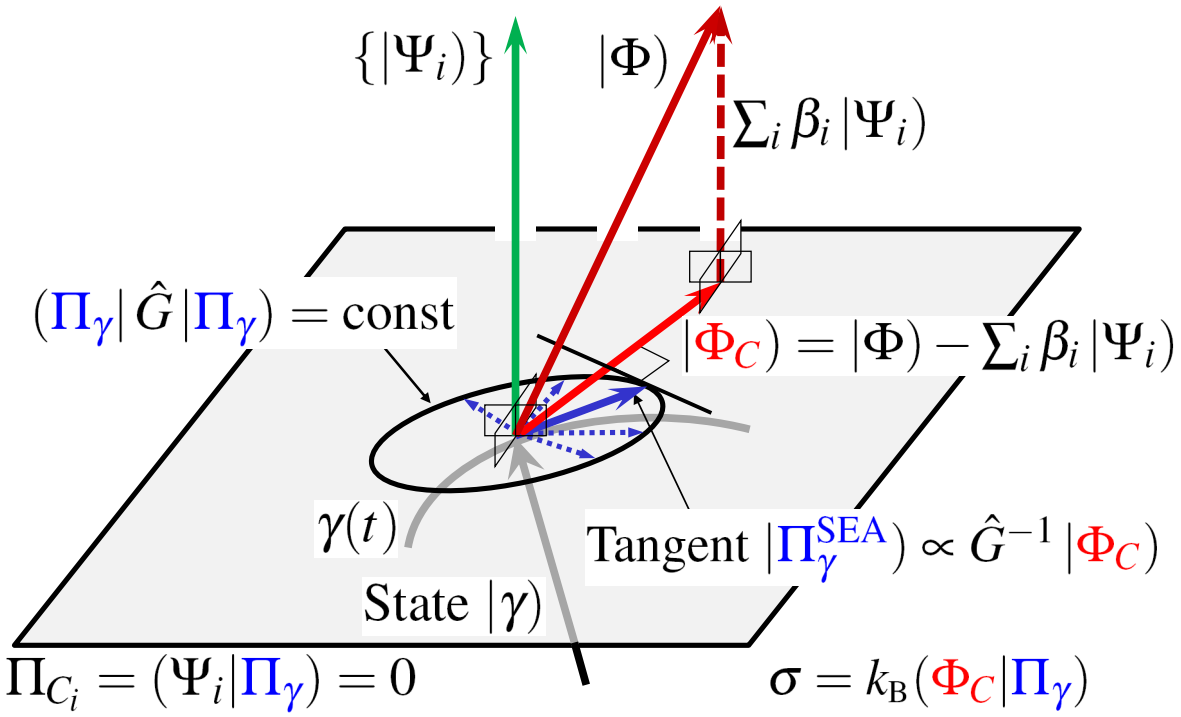
Steepest Entropy Ascent with respect to the systems' metric tensor field $\hat{G}(\gamma)$



The corresponding SEA **evolution equation** is

$$|\Pi_\gamma^{\text{SEA}}) = \frac{1}{\tau}\,\hat{G}^{-1}\,|\Phi_C) = \frac{1}{\tau}\,\hat{G}^{-1}\,|\Phi - \sum_i \beta_i\,\Psi_i)$$

The geometric construction is simply summarized by defining the **SEA projection operator**

$$\hat{P}_{\perp\boldsymbol{\Psi}}|\Phi) = |\Phi_C) = |\Phi - \sum_i \beta_i\,\Psi_i)$$

where the **nonequilibrium potentials** β_i **of the conserved generators of the motion** are nonlinearly related to γ by the orthogonality conditions

$$(\Psi_j|\hat{G}^{-1}|\Phi_C) = 0$$

where $|\Phi_C)$ is the dimensionless **constrained variational derivative** of the entropy.

Beretta, Lecture Notes in Physics **278**, 441 (1986). See also: Beretta, Reps. Math. Phys. **64**, 139 (2009) presented in Torun, Poland for Kossakowski's 70th birthday.

Multipliers β_i are not preset! They emerge from the SEA construction

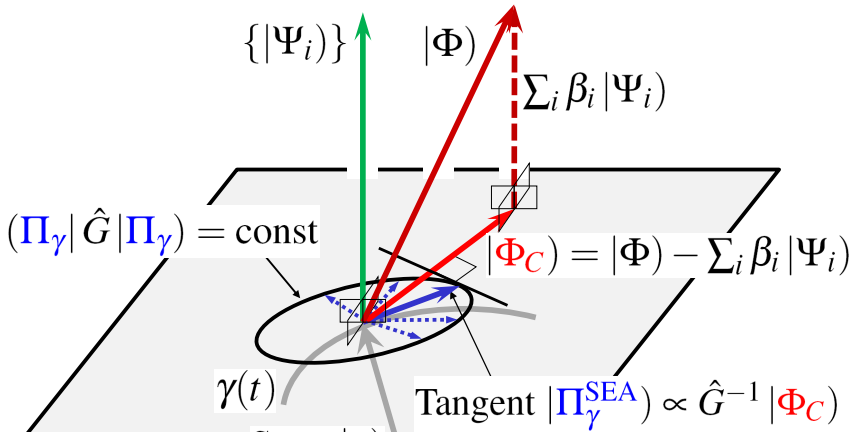
The β_i's are defined by SEA orthogonality condition $(\Psi_j|\hat{G}^{-1}|\Phi_C) = 0$, i.e., by the system of equations $\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$, which solved with Cramer's rule, yields the constrained variational derivative as a ratio of determinants

$$|\Phi_C) = |\Phi - \sum_i \beta_i|\Psi_i) = \frac{\begin{vmatrix} |\Phi) & |\Psi_1) & \cdots & |\Psi_n) \\ (\Phi|\hat{G}^{-1}|\Psi_1) & (\Psi_1|\hat{G}^{-1}|\Psi_1) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_1) \\ \vdots & \vdots & \ddots & \vdots \\ (\Phi|\hat{G}^{-1}|\Psi_n) & (\Psi_1|\hat{G}^{-1}|\Psi_n) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_n) \end{vmatrix}}{\begin{vmatrix} (\Psi_1|\hat{G}^{-1}|\Psi_1) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_1) \\ \vdots & \ddots & \vdots \\ (\Psi_1|\hat{G}^{-1}|\Psi_n) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_n) \end{vmatrix}}$$

where $\hat{c}_1, \ldots, \hat{c}_n$ is a subset of the conserved properties $\hat{c}_i$'s such that the variational derivatives $\Psi_1, \ldots, \Psi_n$ are linearly independent. By virtue of this choice, the determinant at the denominator is always a positive definite Gram determinant.

see, e.g., Beretta, Phys.Rev.E, 73, 026113 (2006) and Beretta, Rep.Math.Phys., 64, 139 (2009)

Steepest Entropy Ascent with respect to the systems' metric tensor field $\hat{G}(\gamma)$



The SEA **evolution equation** takes various equivalent forms

$$|\Pi_\gamma^{\rm SEA}) = \frac{1}{\tau}\,\hat{G}^{-1}\left|\Phi - \sum_i \beta_i(\gamma)\,\Psi_i\right)$$

$$= \frac{1}{\tau}\,\hat{G}^{-1}\,|\Phi_C) = \frac{1}{k_{\rm B}\tau}\,\hat{G}^{-1}\left|\frac{\delta M}{\delta\gamma}\right)$$

where M is our **nonequilibrium Massieu operator** $|\delta M/\delta\gamma) = k_{\rm B}|\Phi_C)$

$$M(\gamma) = S(\gamma) - k_{\rm B}\sum_i \beta_i\, C_i(\gamma)$$

The **nonequilibrium potentials** $\beta_i(\gamma)$'s are the solution of the system of equations

$$\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$$

Defining the **overall nonequilibrium affinity** or **overall degree of disequilibrium**

$$|\Lambda) = \hat{G}^{-1/2}\,|\Phi - \sum_i \beta_i\,\Psi_i)$$

the **entropy production rate** takes the forms

$$\sigma = \Pi_S = (\Phi|\Pi_\gamma)\,k_{\rm B} = (\Phi_C|\Pi_\gamma)\,k_{\rm B} = \Pi_M$$

$$= \frac{k_{\rm B}}{\tau}(\Phi_C|\hat{G}^{-1}|\Phi_C) = (\Pi_\gamma|\hat{G}|\Pi_\gamma)\,k_{\rm B}\tau$$

$$= \frac{k_{\rm B}}{\tau}(\Lambda|\Lambda) = \frac{k_{\rm B}}{\tau}\left[\frac{d\ell}{d(t/\tau)}\right]^2$$

Where the speed of evolution along the SEA trajectory in state space is

$$\frac{d\ell}{dt} = \sqrt{(\Pi_\gamma|\,\hat{G}\,|\Pi_\gamma)}$$

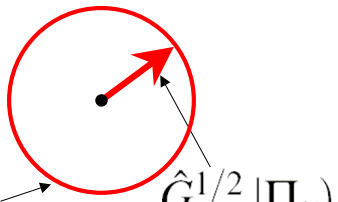
Beretta, Phys.Rev. E **90**, 042113 (2014).

SEA Variational Statement

Let $\hat{G}(\gamma)$ be the **tensor field** defining the internal **metric** used by the system to sense distances between states and length of trajectories in state space. Then,

$$||\Pi_\gamma||\, dt = \sqrt{(\Pi_\gamma|\, \hat{G}\, |\Pi_\gamma)}\, dt = d\ell = \dot{\varepsilon}\, dt$$

is the **distance traveled** during dt.



Variational Statement: For a given distance traveled, **the tangent vector** $|\Pi_\gamma)$ **maximizes the (local) entropy production rate**

$$\sigma = \Pi_S = (\Phi|\Pi_\gamma)$$

subject to the conservation constraints

$$\Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0$$

Introducing **Lagrange multipliers** (independent of Π_γ but will be functions of γ), we need to find the unconstrained maximum of

$$\Upsilon = (\Phi|\Pi_\gamma) - \sum_i \beta_i\, (\Psi_i|\Pi_\gamma) - \frac{\tau}{2}(\Pi_\gamma|\, \hat{G}\, |\Pi_\gamma)$$

Setting

$$\frac{\delta \Upsilon}{\delta \Pi_\gamma} = |\Phi) - \sum_i \beta_i\, |\Psi_i) - \tau \hat{G}|\Pi_\gamma) = 0$$

yields the SEA **general evolution equation**

$$|\Pi_\gamma) = \frac{1}{\tau}\, \hat{G}^{-1/2}\, |\Lambda)$$

where

$$|\Lambda) = \hat{G}^{-1/2}\, |\Phi - \sum_i \beta_i\, \Psi_i)$$

and substitution back into the constraints yields the Lagrange multipliers through the system of equations

$$\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\, \beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$$