Methods for simulating self-organising molecular systems

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Some general ideas behind dimensional reduction

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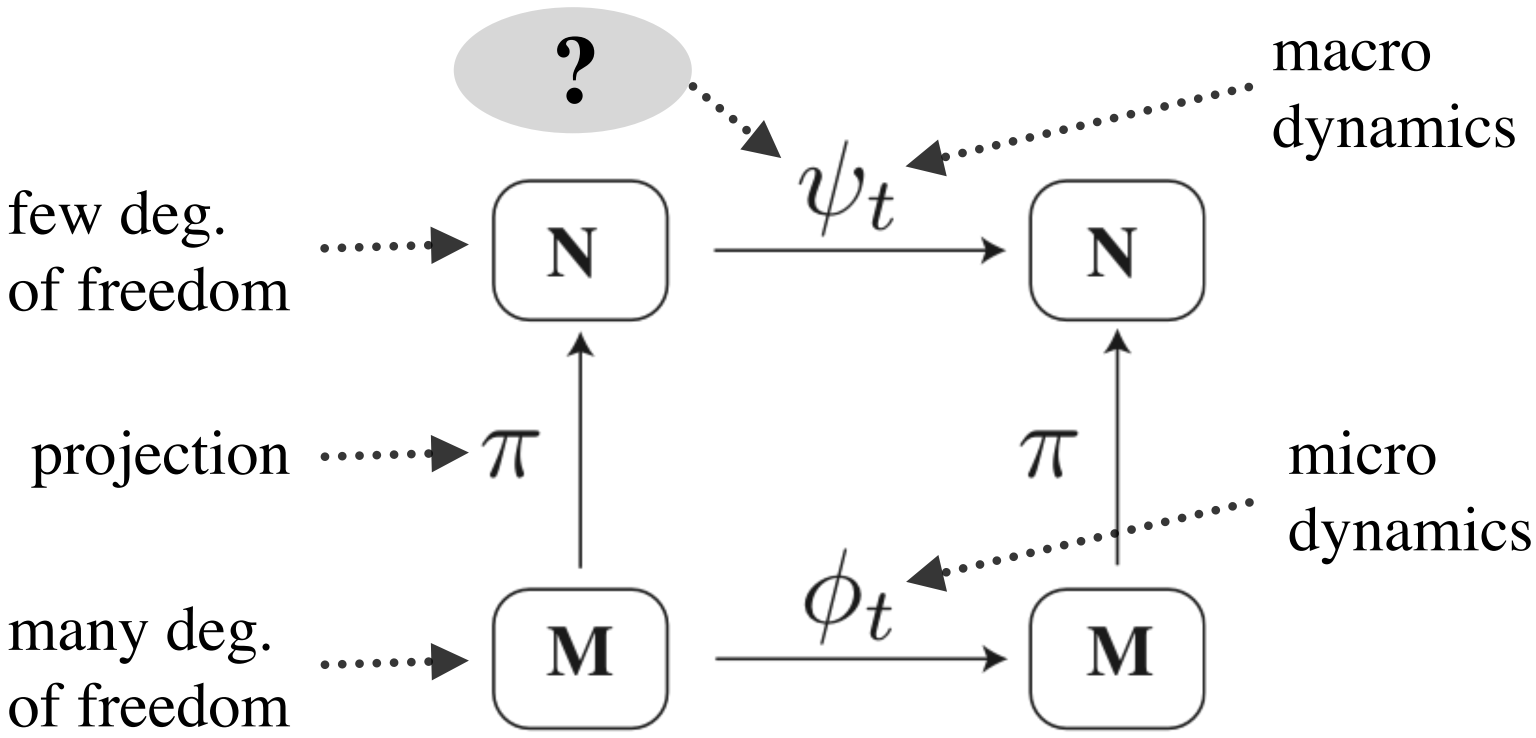
The generic setting

A large number of objects/particles which evolve according to a known (usually deterministic) dynamics:

$$\frac{d}{dt}\begin{pmatrix} m_1 x_1 \\ \vdots \\ m_n x_n \\ p_1 \\ \vdots \\ p_n \end{pmatrix} = \begin{pmatrix} p_1 \\ \vdots \\ p_n \\ F_1(x_1, \ldots, x_n, p_1, \ldots, p_n) \\ \vdots \\ F_n(x_1, \ldots, x_n, p_1, \ldots, p_n) \end{pmatrix}$$

Dimensional reduction



M and N are phase spaces

$$\pi \circ \phi_t = \psi_t \circ \pi$$

diagram commutes?

Generic mechanisms

- Global symmetries and conserved quantities (Noether's theorem).
- Local symmetries:
  - Trajectories confined to a volume of phase space where symmetries exist:
    - Trajectories are on an invariant manifold.
    - Trajectories converge quickly to a positively invariant (inertial) manifold.
- Separation on time scales: chaotic (mixing) fast degrees of freedom (DOF) can be treated as (Markovian) noise; or averaging removes the fast DOF.

Most important example for us

Particle bases Langevin dynamics derived from molecular dynamics (dissipative particle dynamics).

Principles: separation of time scales, adiabatic elimination, and decomposable symmetries (momentum conservation).

But also a complicated projection that lumps particles together into clusters, which are viewed as coarse grained particles. The clusters exchange (micro-) particles. This gives rise to an affective repulsion between the cluster centers, i.e. the coarse grained particles repel each other.

Self-assembly of amphiphiles using Dissipative Particle Dynamics

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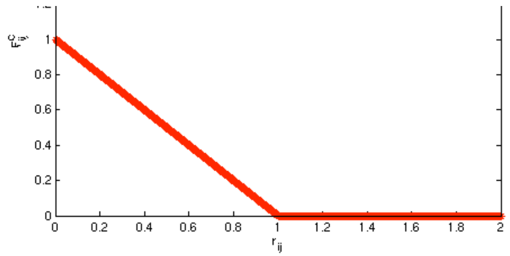
The Dissipative Particle Dynamics model

- Particles corresponds to N_m atoms or molecules.
- Pairwise interactions between particles within a finite range.
- Position and momentum of particles obey a Langevin equation:

$$\frac{dx_i}{dt} = v_i \qquad m_i \frac{dv_i}{dt} = f_i^C + f_i^D + f_i^R$$



$$f_i^C = \sum_j \psi_{ij}(r_{ij})\, \hat{r}_{ij}$$

$$\psi_{ij}(r) = a_{ij} \max(1 - r, 0)$$

$$f_i^D = -\sum_j \gamma\, \phi(r_{ij})^2\, \hat{r}_{ij} \cdot (v_i - v_j)\, \hat{r}_{ij}$$

$$\phi(r) = \max(1 - r, 0)$$

$$f_i^R = \sum_j \sqrt{2\gamma}\, \phi(r_{ij})\, \zeta_{ij}\, \hat{r}_{ij} \qquad \langle \zeta_{ij}(t) \zeta_{kl}(t') \rangle = \delta(t - t')(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$

Water in Dissipative Particle Dynamics

- Several water molecules are grouped together to form a DPD water particle
- The water-water potential is obtained from the Lennard-Jones potential of individual atoms, averaged over the atomic motion in short time intervals.
- Equation of state for a system of DPD water particles in equilibrium is approximately (for $\rho > 2$):

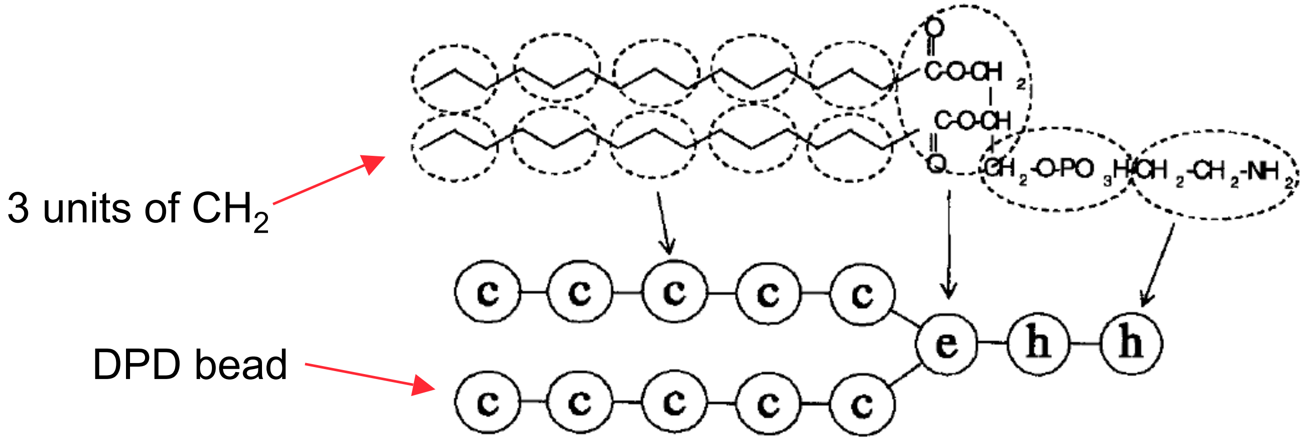
$$P = N_m \, \rho \, k_B T + a \, \alpha \, \rho^2, \text{ where } \alpha \approx 0.101$$

One may use this to determine *a* from the isothermal compressibility of water.

Coarse-grained models of amphiphiles

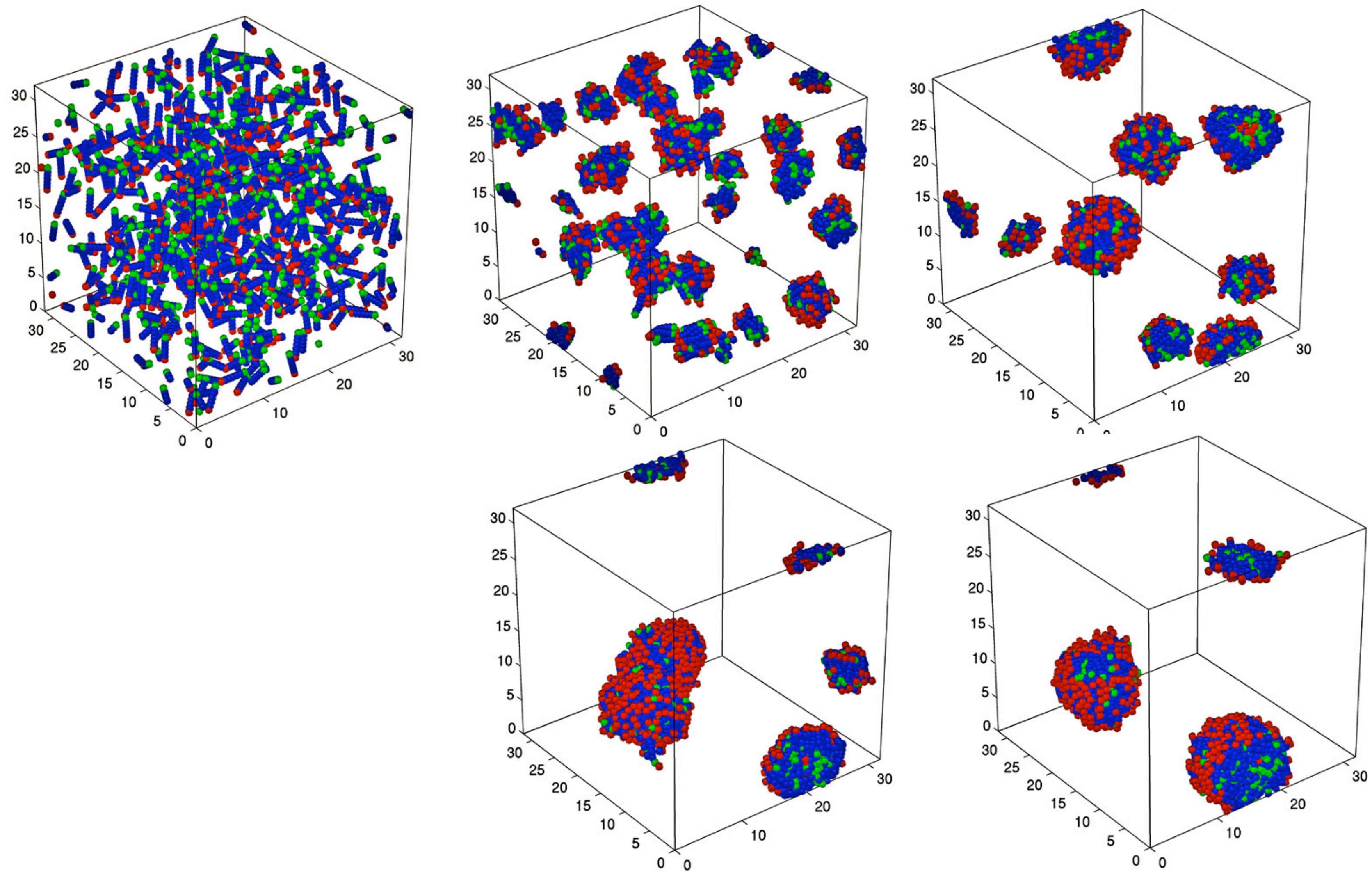
- Molecules with important internal structure, such as amphiphiles, needs to be represented by several beads.
  - Typically chosen so that the partial volumes agree as closely as possible

DPD representation of phosphatidylethanolamine



From Groot and Rabone 2001, Biophys. J. 81, p. 728

Self-assembly of lipids into micelles



Clustering as a mechanism for repulsion between particles in DPD simulations

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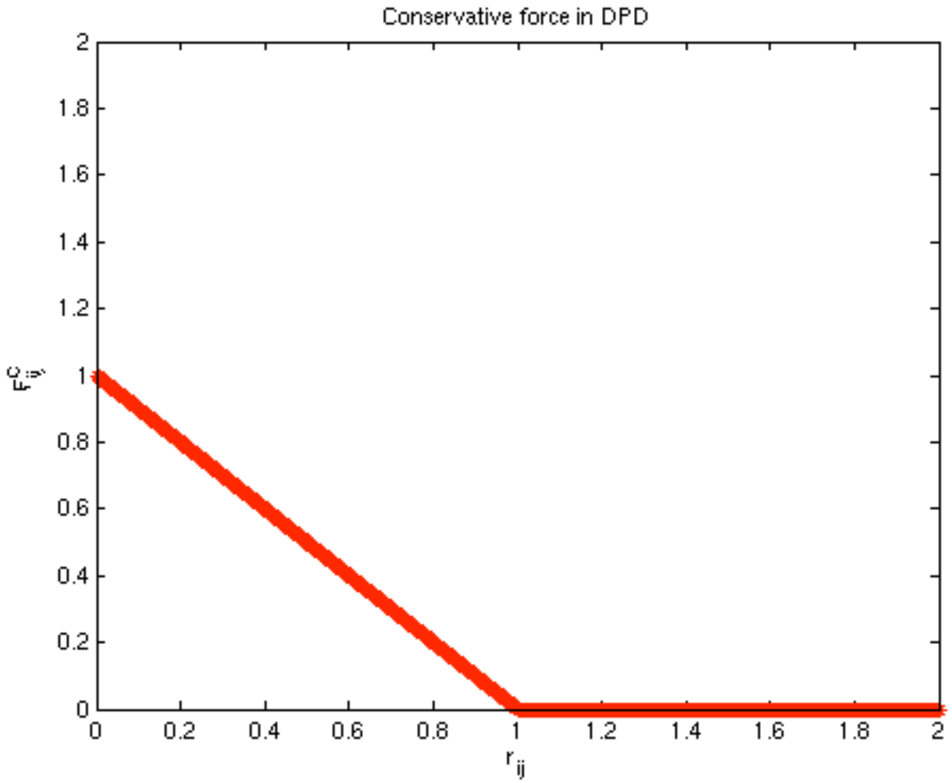
Objectives

- To connect the Dissipative Particle Dynamics (DPD) simulation technique with an underlying microscopic description.
- To show that clustering can explain repulsion between DPD particles.

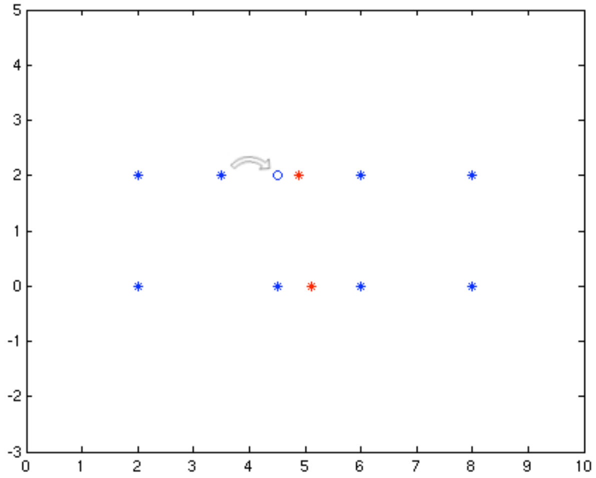
Standard DPD

$$\frac{d\mathbf{r_i}}{dt} = \mathbf{v}_i, \quad \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i \qquad \mathbf{f}_i = \sum_{j \neq i} \left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right)$$

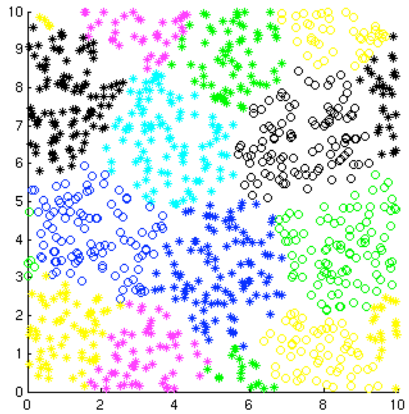


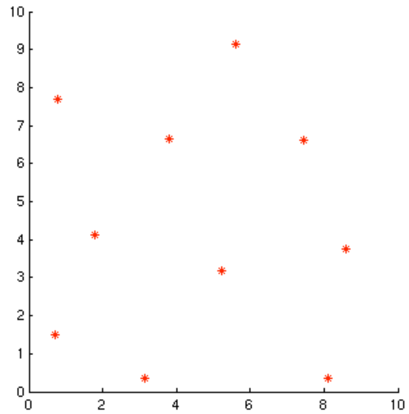
Model

- Step 1: Move underlying particles

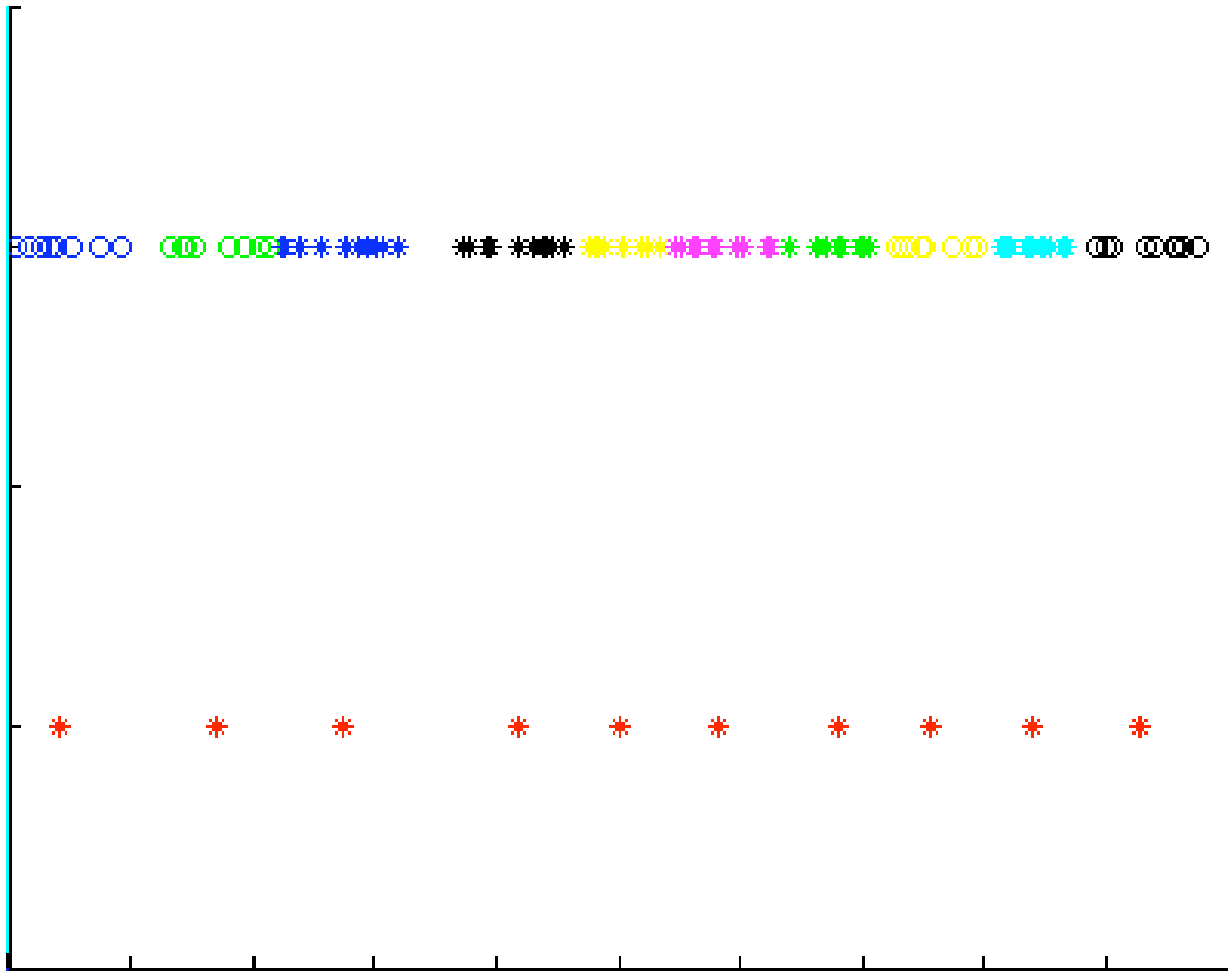


- Step 2: Group particles into clusters

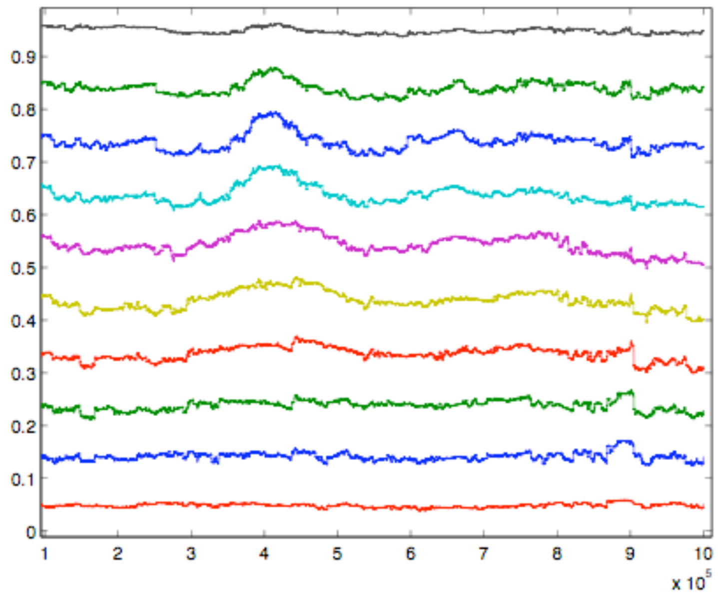




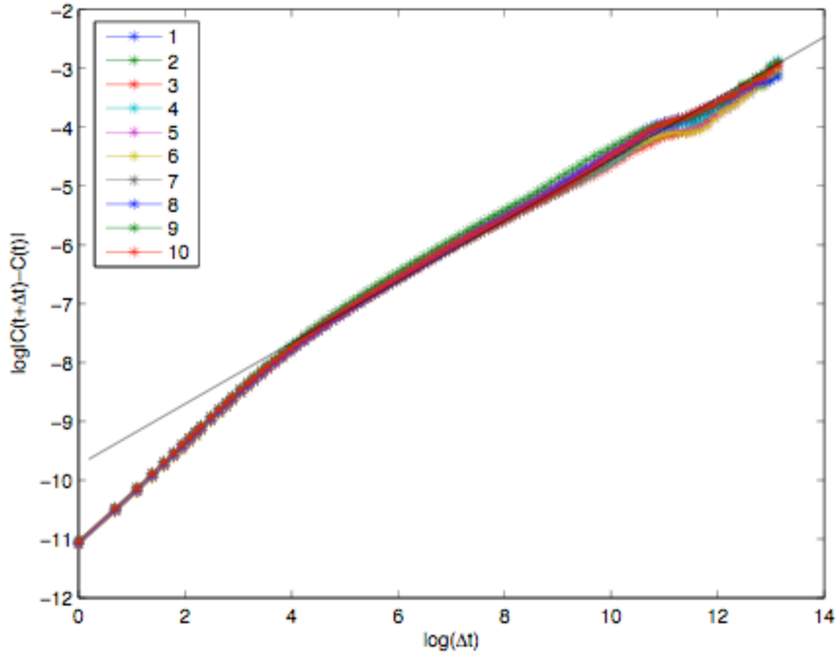
Results



Results



$$|\Delta c| = a(\Delta t)^d$$



Work in progress

- Derive an SDE, describing the cluster motion in the 1-D case.
- Use data from e.g. an MD simulation to move the underlying particles.
- Look for hydrodynamic modes.

Phase space partitioning in the context of simple dynamical systems

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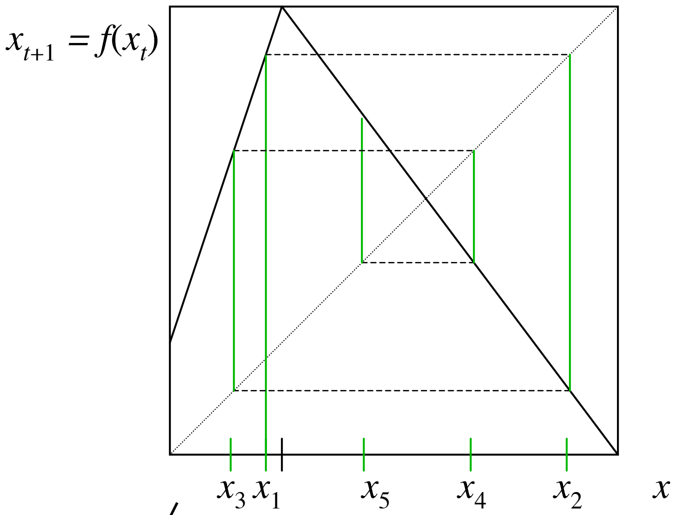
System - Encoding - Reconstruction

- Simple time-discrete dynamical systems are considered
  - Exemplified by iterated maps
  - Piecewise linear approximations of underlying systems

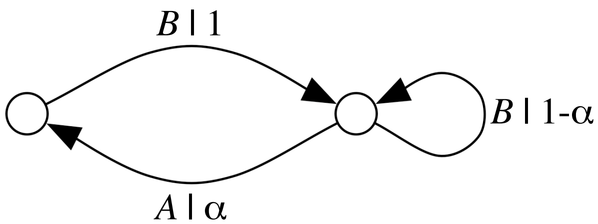


- The continuous phase space is discretized
  - Observations yield a symbol sequence

- Symbol sequence used to construct ε-machine

Time series: → Symbolic dynamics: →

$x_1, x_2, x_3, x_4, x_5, \ldots$ A, B, A, B, B, …



Partitioning

- One wants a partition such that no relevant feature of the original dynamics is lost

- Map F with phase space X
- Partition $\mathcal{B} = \{B_1, B_2, \ldots, B_n\}$
- Alphabet $\mathcal{A} = \{a_1, a_2, \ldots, a_n\}$

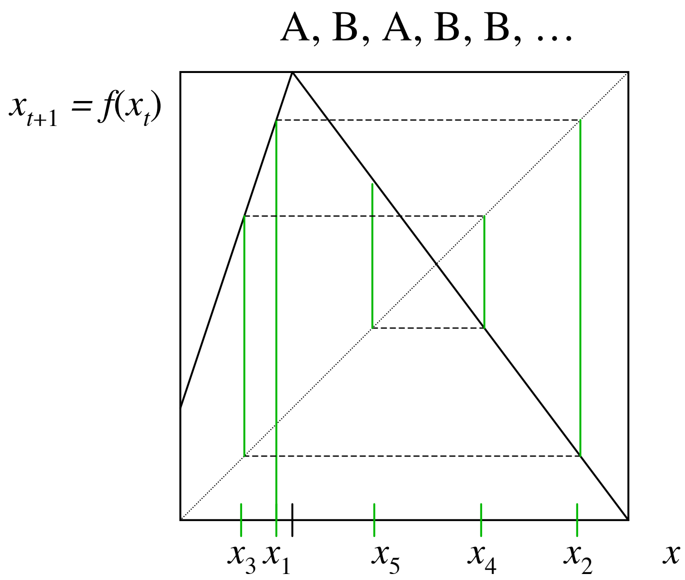
Elements of 1st refinement under F:

$$B_{a_i} \cap F^{-1}(B_{a_j}) \ \forall a_i, a_j \in \mathcal{A}$$

Elements of 2nd refinement under F:

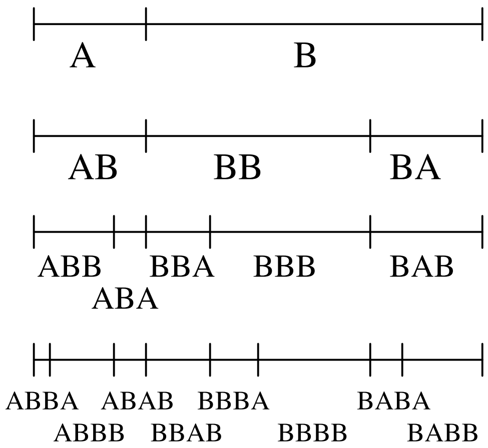
$$B_{a_i} \cap F^{-1}(B_{a_j}) \cap F^{-2}(B_{a_k}) \ \forall a_i, a_j, a_k \in \mathcal{A}$$

$\mathcal{B}$ can be refined indefinitely under F:
Generating partition



Partition:

Refinements:

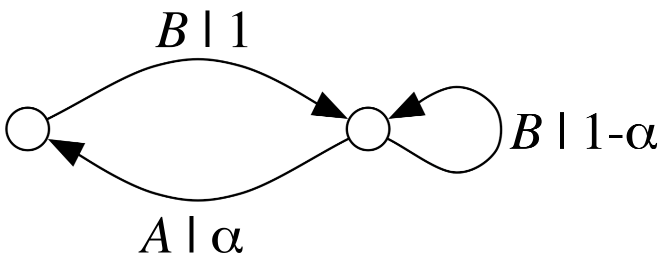


Markov partition

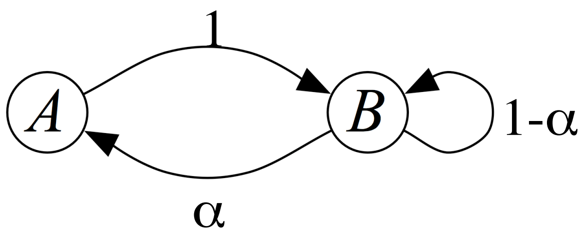
- Generating partition $\mathcal{B} = \{B_1, B_2, ..., B_n\}$ where each $\mathbf{F}(\bar{B}_i)$ is the union of some $\bar{B}_j$'s for all *i*
- Borders map to borders
- Enables a graph representation of the dynamics
- Conditional probability distribution of future symbols depends only on the current state

Roof map - Simple Markov

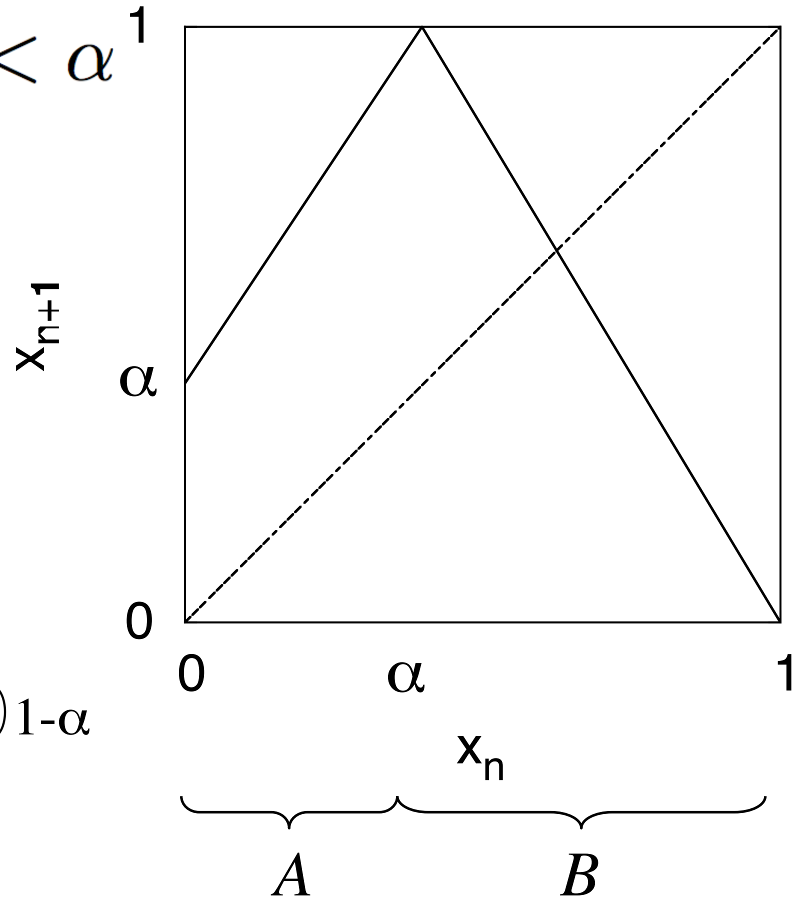
$$x_{n+1} = \begin{cases} \frac{1-\alpha}{\alpha} x_n + \alpha, \text{ if } x_n < \alpha \\ \frac{x_n - 1}{\alpha - 1} \text{ otherwise} \end{cases}$$



ε-Machine



Symbol dynamics



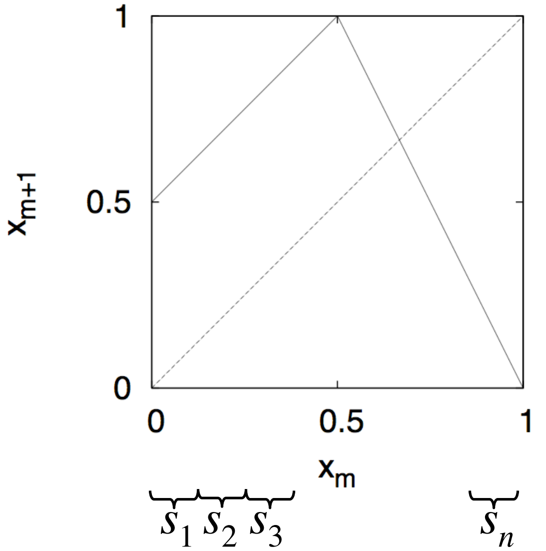
Markov partition

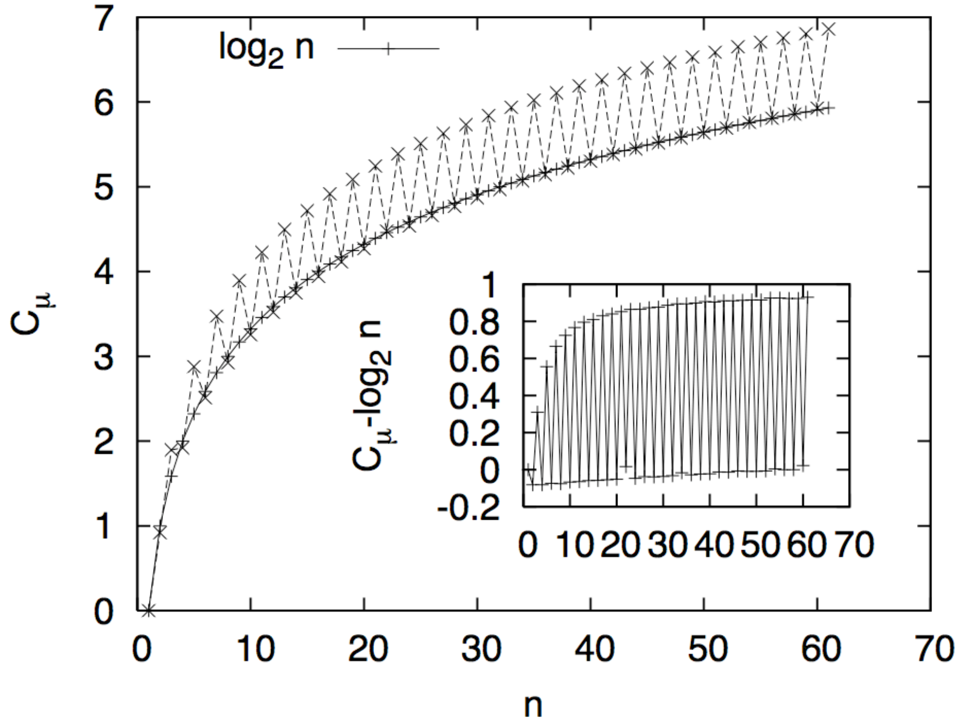
Roof map - Alphabet size dependence

- For α=1/2
- Partition evenly
- *n* symbols
- Reconstruction of ε-machine with CSSR algorithm*

$$C_0 = p_V \log \frac{1}{p_V} + p_H \log \frac{1}{p_H}$$

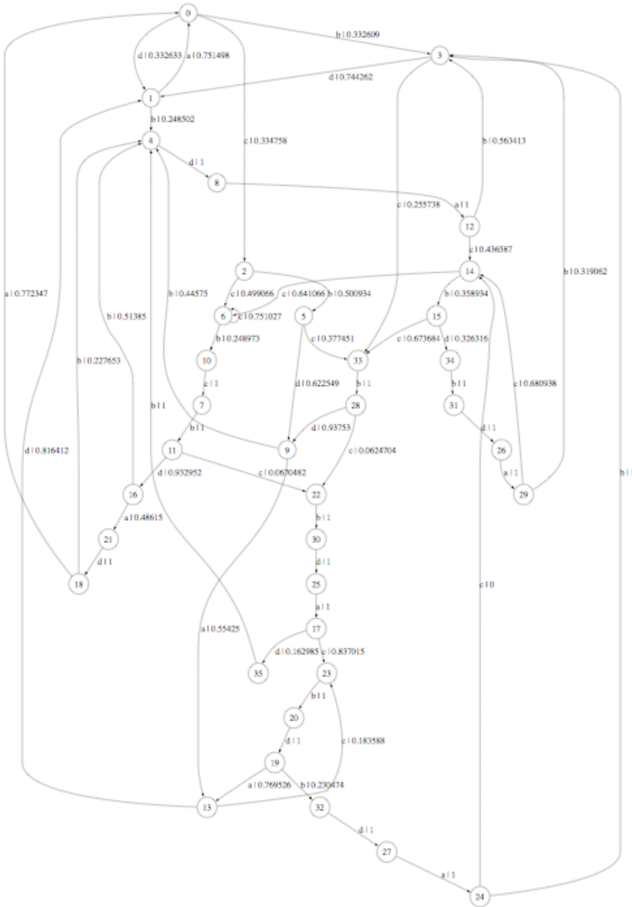
$$C_{2m} = C_0 - \log 2 + \log(2m)$$

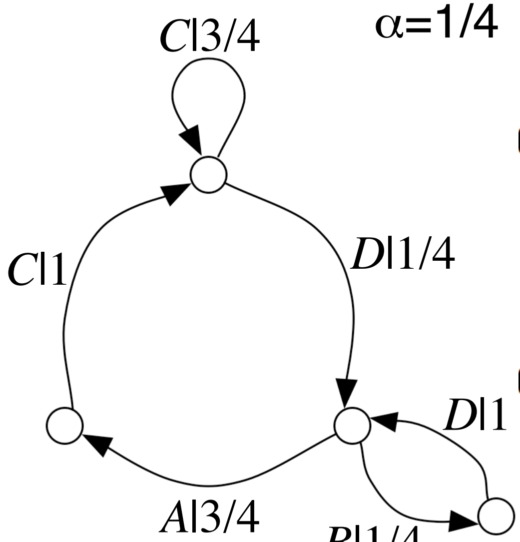


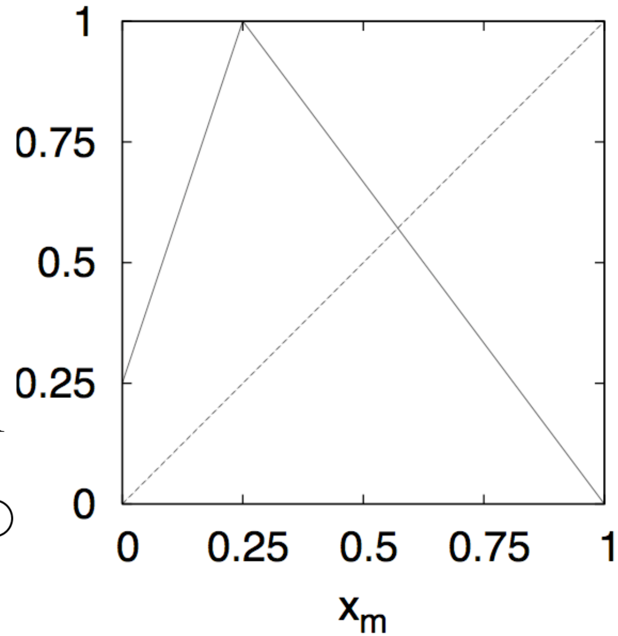


**Causal-State Splitting Reconstruction* by Shalizi, Shalizi and Crutchfield

Roof map - Generating versus Markov

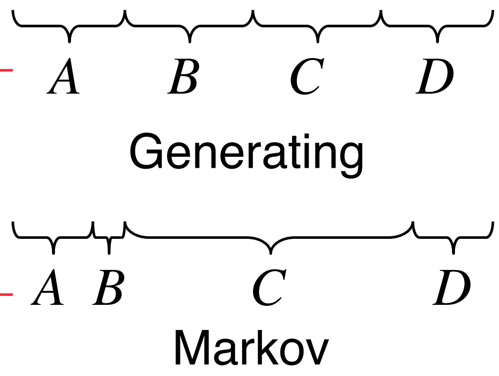






$C\mu \approx 4.40$ bits
#states = 36

$C\mu \approx 1.53$ bits
#states = 4

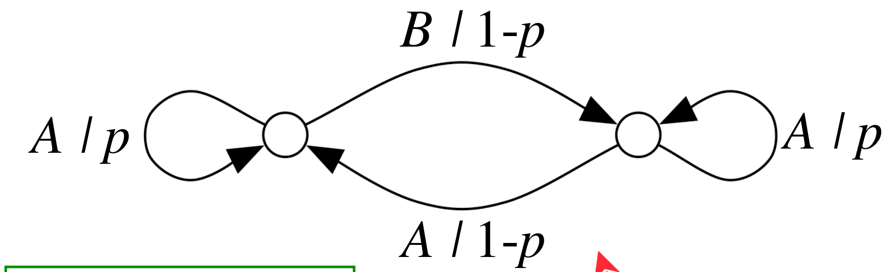


(500 000 data points, max history: 10)

$A \to C,\ B \to D,\ C \to C \cup D,\ D \to A \cup B$

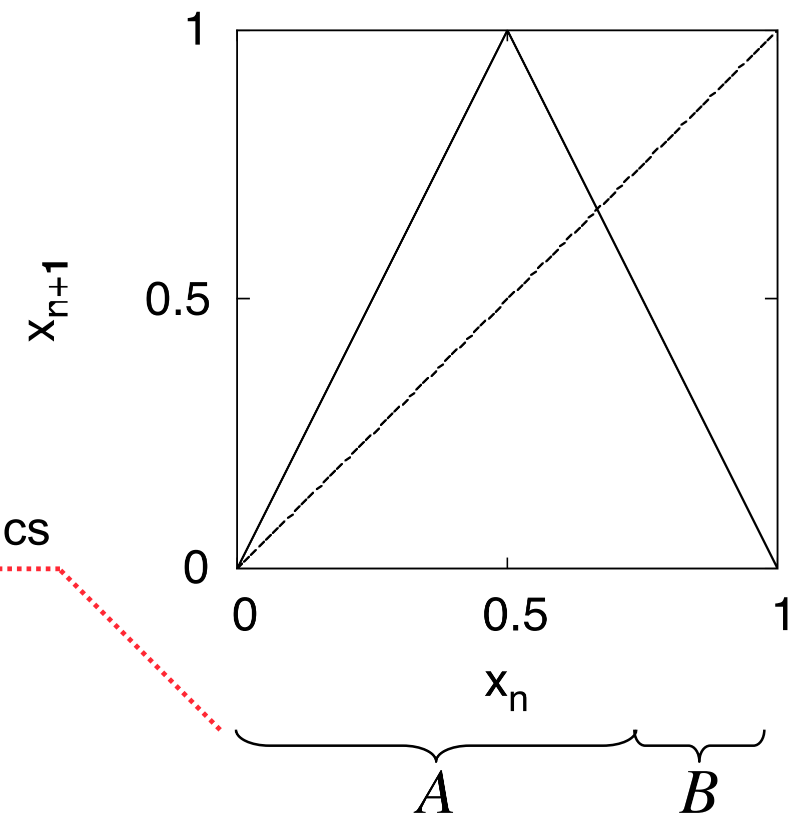
Tent map - Non-determinism

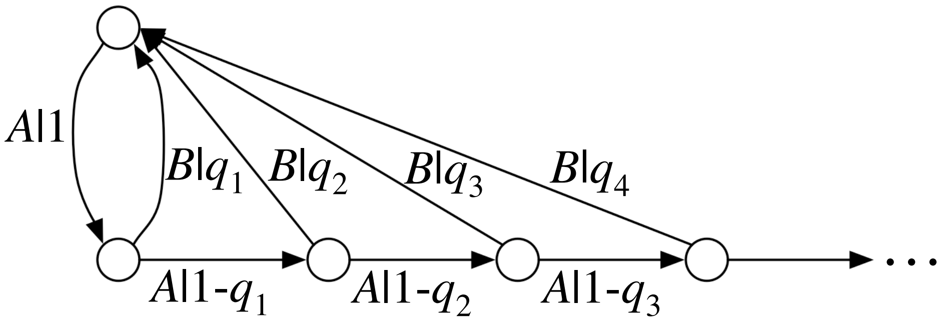
$$x_{n+1} = 1 - 2|x_n - \frac{1}{2}|$$



Not ε-machine

Symbol dynamics





Corresponding ε-machine

$$q_n = \frac{n(1-p)^2}{n - np + p}$$

- Infinite number of states
- Finite C_μ

Recapitulation and conclusions

- Choice of partition crucial
  - Generating - Good
  - Markov - Better
  - Neither - Bad
- General issue: Difficult to know if good partition is used
  - Dynamics F typically not know explicitly
- Compact exact non-deterministic representation may not be found