MODELING THE DYNAMICS OF INTERACTING PARTICLES BY MEANS OF STOCHASTIC NETWORKS

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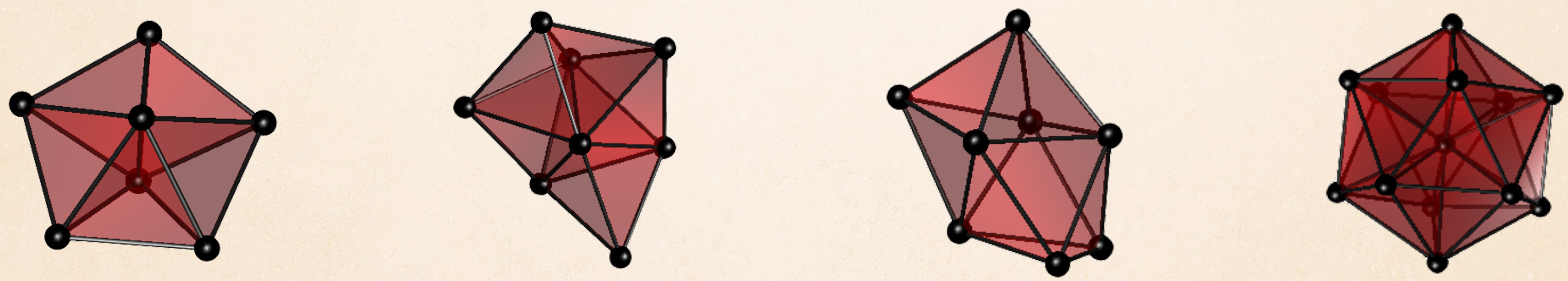
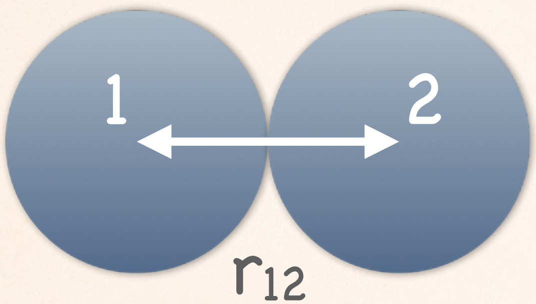


Data Seminar, John Hopkins University, Oct. 12, 2016

INTERACTION POTENTIAL

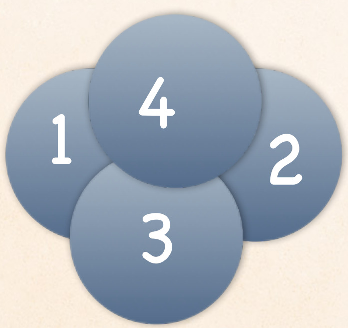
We assume the interaction under a pair potential, i.e.,



$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

Total potential energy:

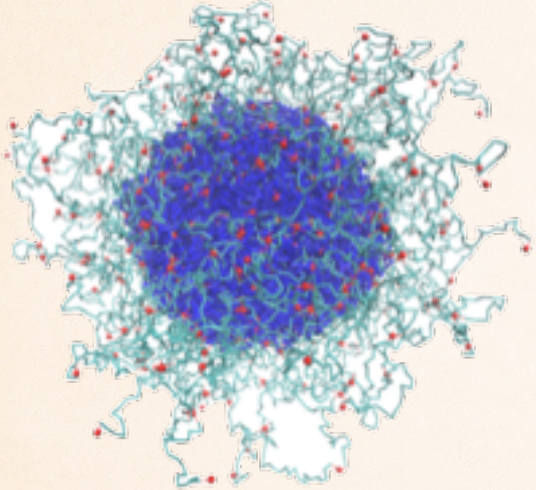
$$V = \sum_{i<j} V(r_{ij})$$



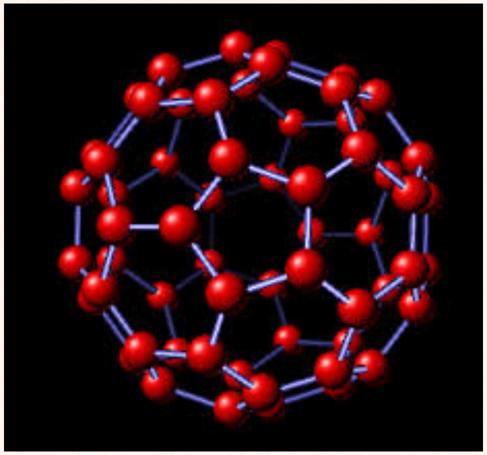
Force acting on particle i:

$$\begin{bmatrix} \frac{\partial V}{\partial x_i} \\ \frac{\partial V}{\partial y_i} \\ \frac{\partial V}{\partial z_i} \end{bmatrix} = \sum_{j=1}^{N} \frac{dV}{dr_{ij}} \frac{1}{r_{ij}} \begin{bmatrix} x_i - x_j \\ y_i - y_j \\ z_i - z_j \end{bmatrix}$$

GOAL

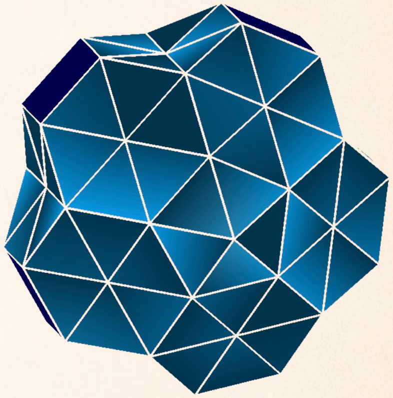


A core-shell microgel,
S. Maccarone et al,
Macromolecules 2016



A fullerene molecule

LJ_{55}
icosahedron



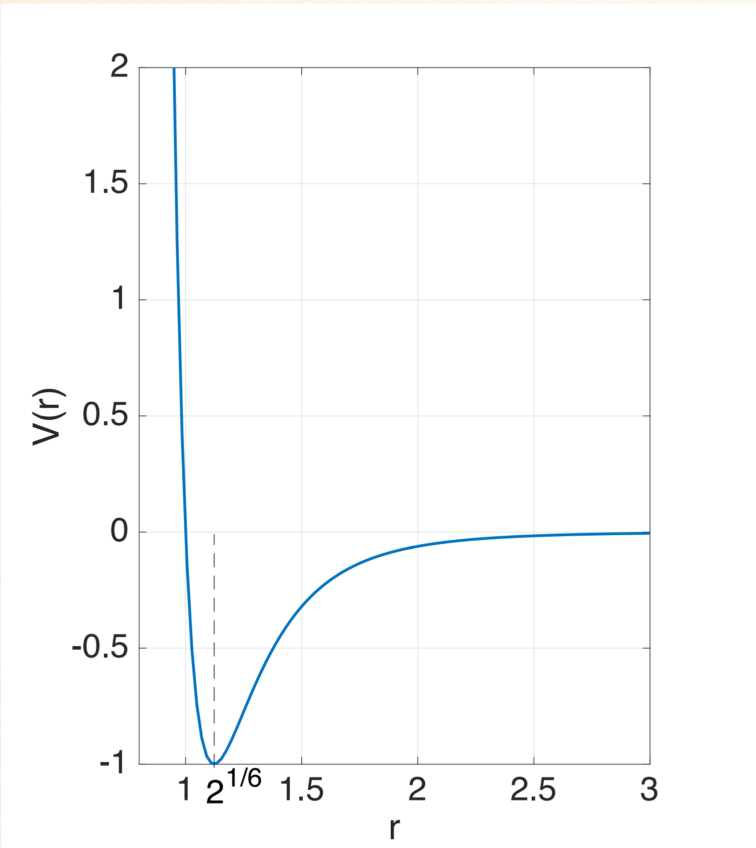
LJ_{75}
Marks decahedron

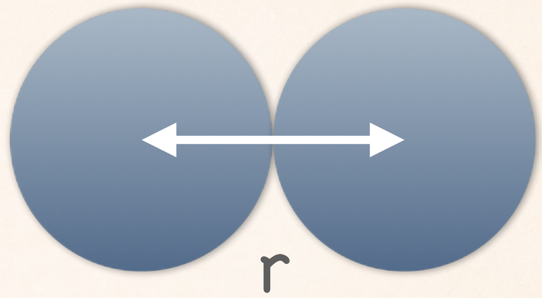
Develop tools for the study of the cluster dynamics

Design desired structures by self-assembly

LENNARD-JONES PAIR POTENTIAL

$$V(r) = 4(r^{-12} - r^{-6})$$





Adequate for rare gases:
Ar, Kr, Xe, Rn

Often used for modeling interaction of other spherical particles.

Large datasets are available thanks to Wales's group (Cambridge, UK).

EXPERIMENTAL WORKS: MASS SPECTRA

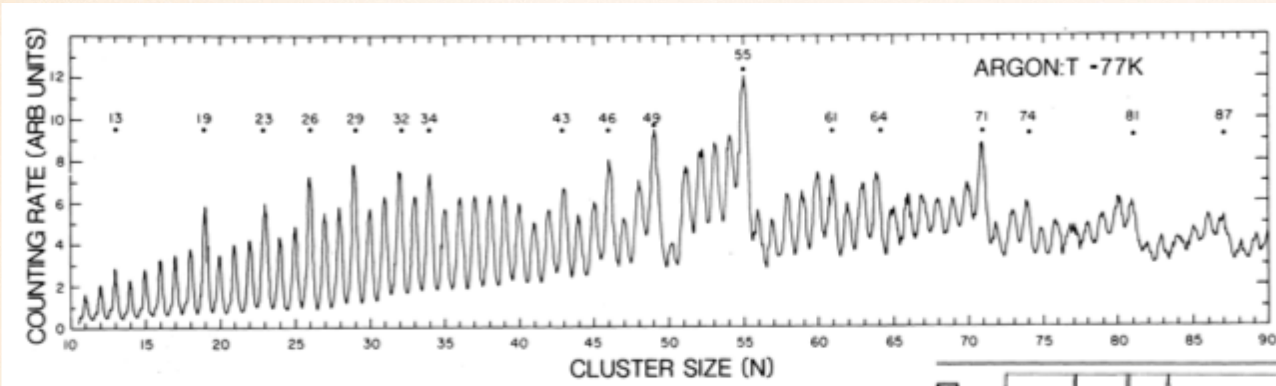
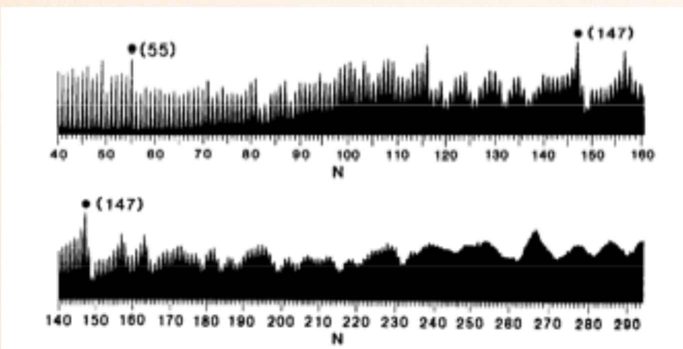
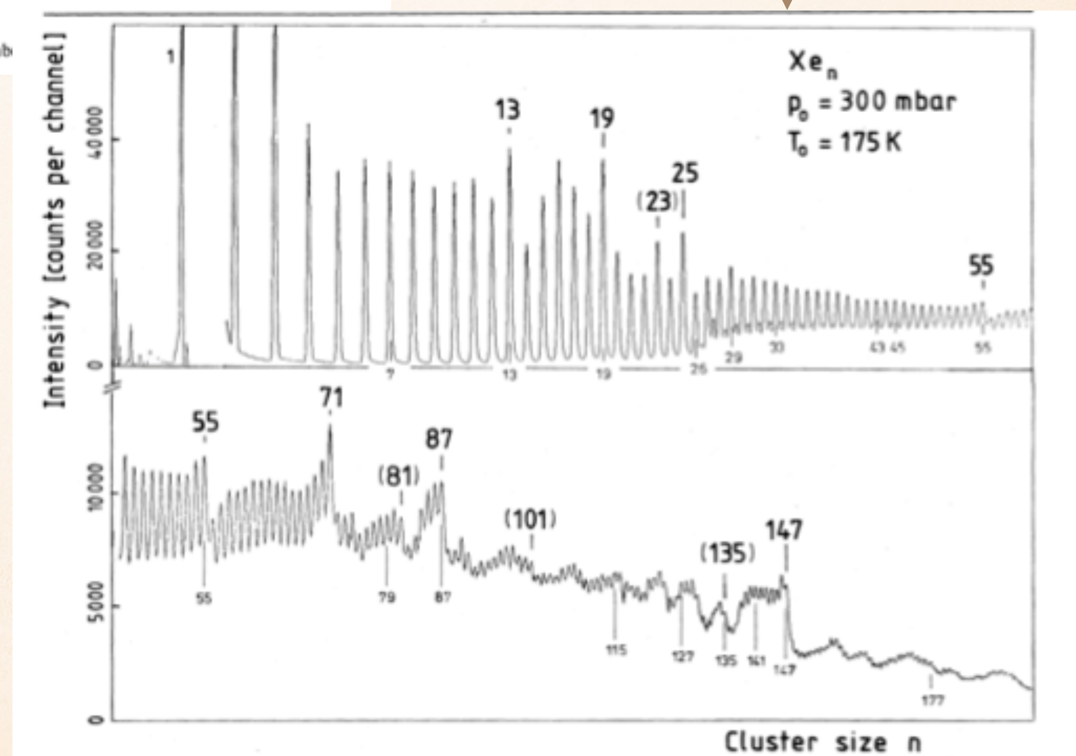


FIG. 1. Experimental mass spectrum for charged argon clusters. Intensity vs numb

Harris, Kidwell, Northby, PRL 1984

Echt, Sattler, Recknagel, PRL 1981



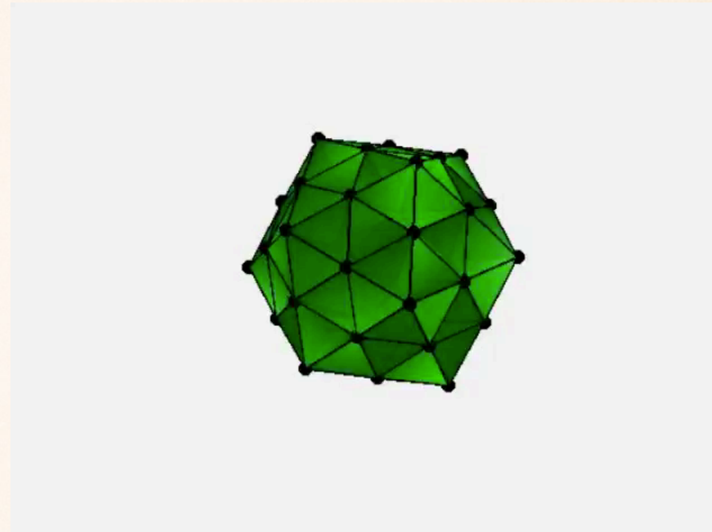


Harris, Norman, Mulkern, Northby, Chem Phys Lett 1986

MAGIC NUMBERS

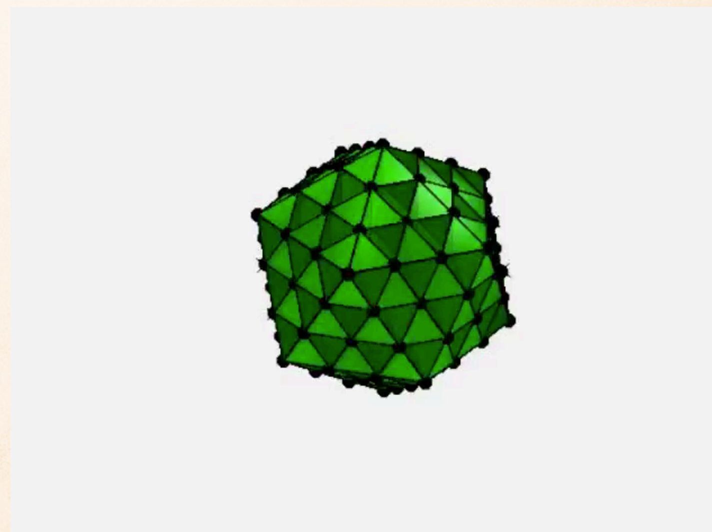
13, 55, 147, 309, ...
admit complete
icosahedrons
Point group I_h, $|I_h|=120$

LJ_{55}



LJ_{13}

LJ_{147}



OTHER HIGH SYMMETRY CONFIGURATIONS

LJ_{38}

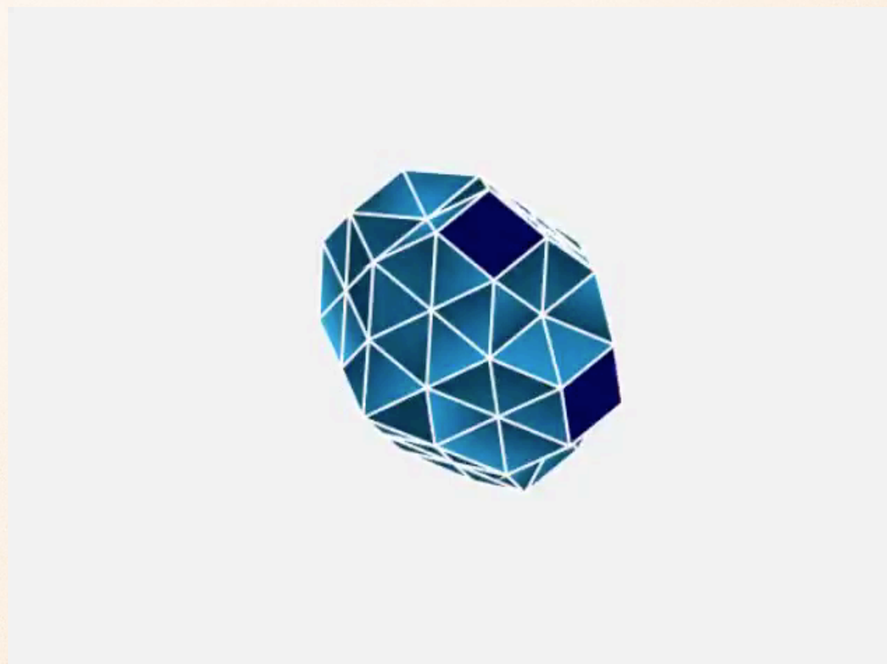
Truncated octahedron

Point group O_h, $|O_h|=48$

LJ_{75}

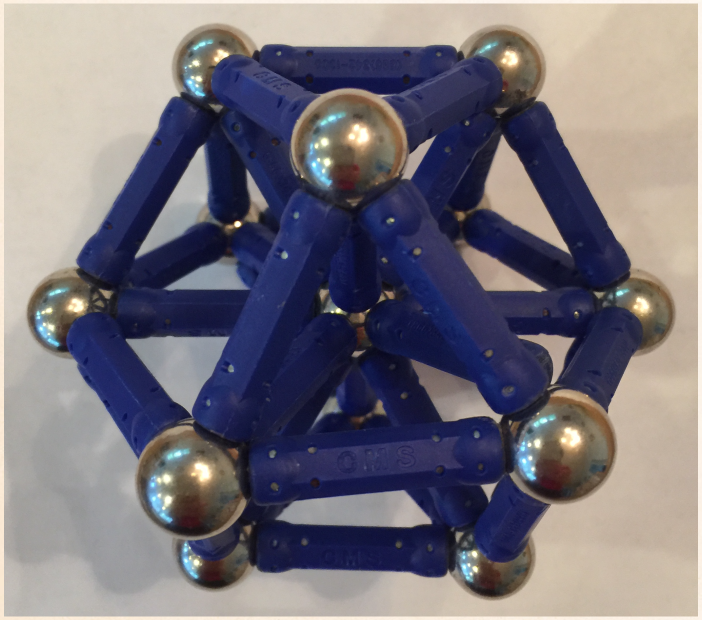
Marks decahedron

Point group D_{5h}, $|D_{5h}|=20$

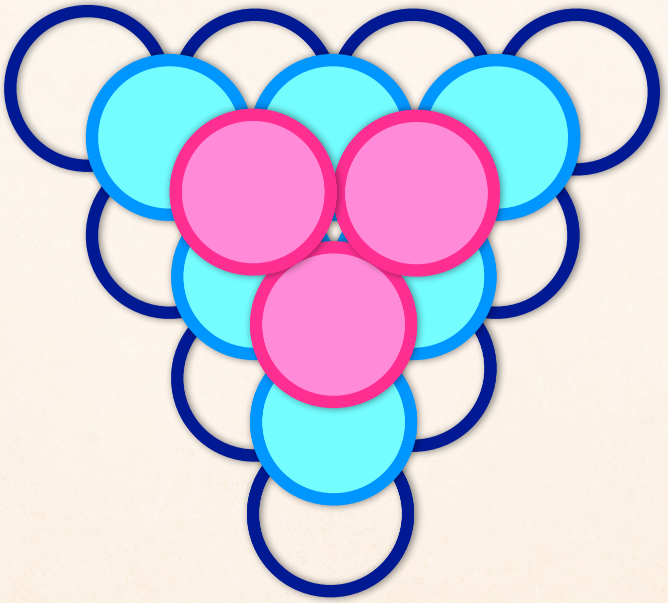


CRYSTAL STRUCTURE FOR RARE GASES: FCC (FACE CENTERED CUBIC)

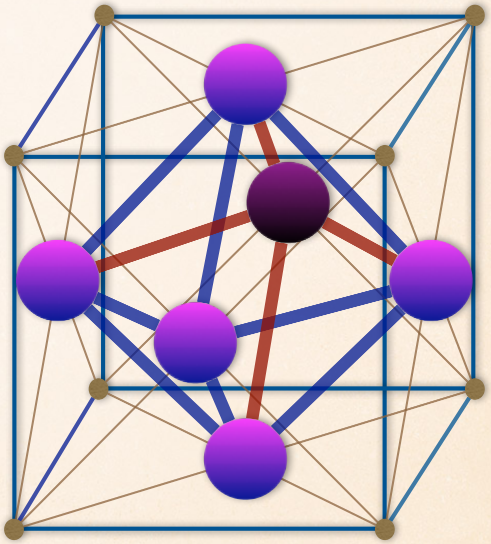
13 particle fragment of FCC crystal



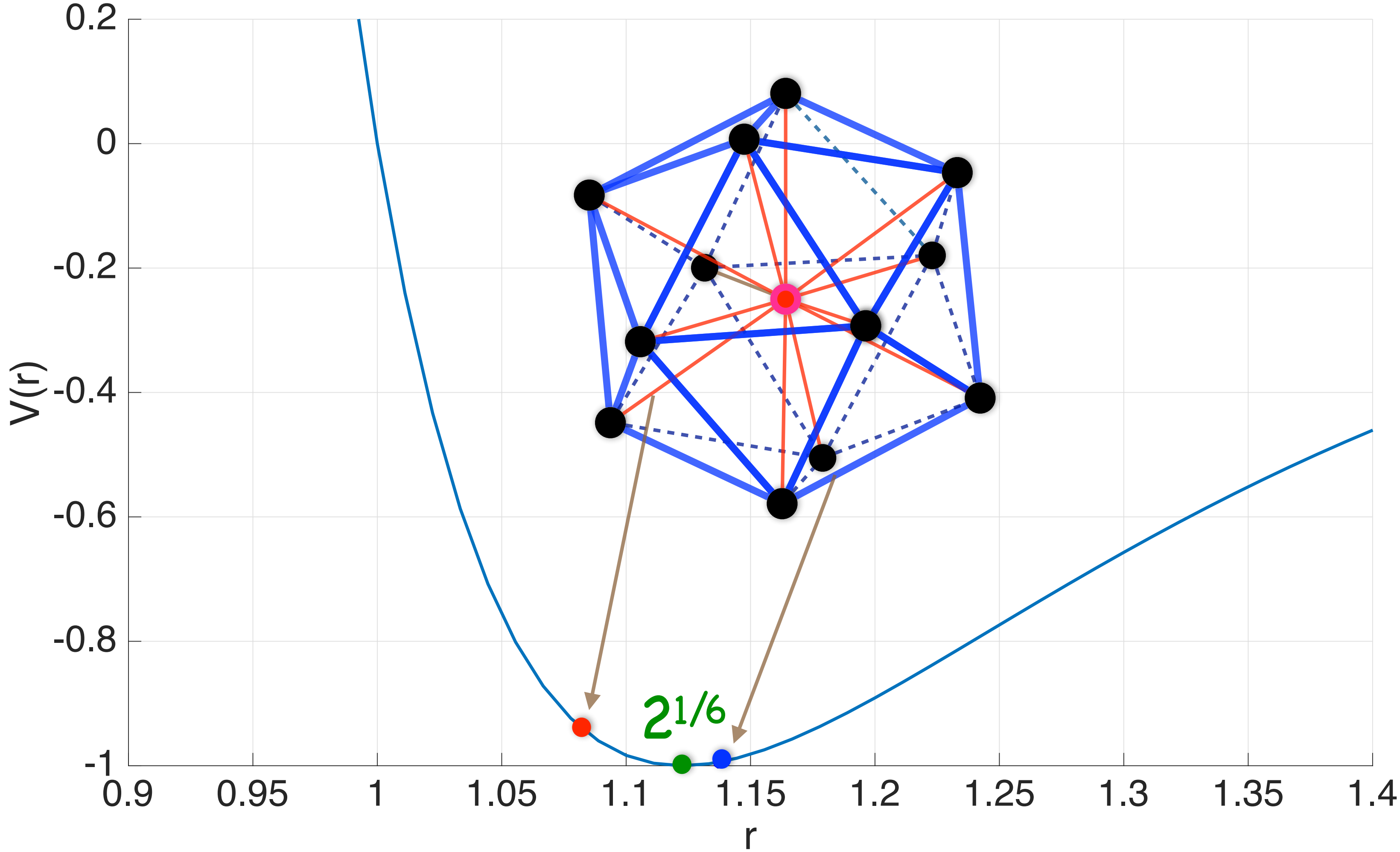
FCC packing



FCC elementary cell



FRUSTRATION

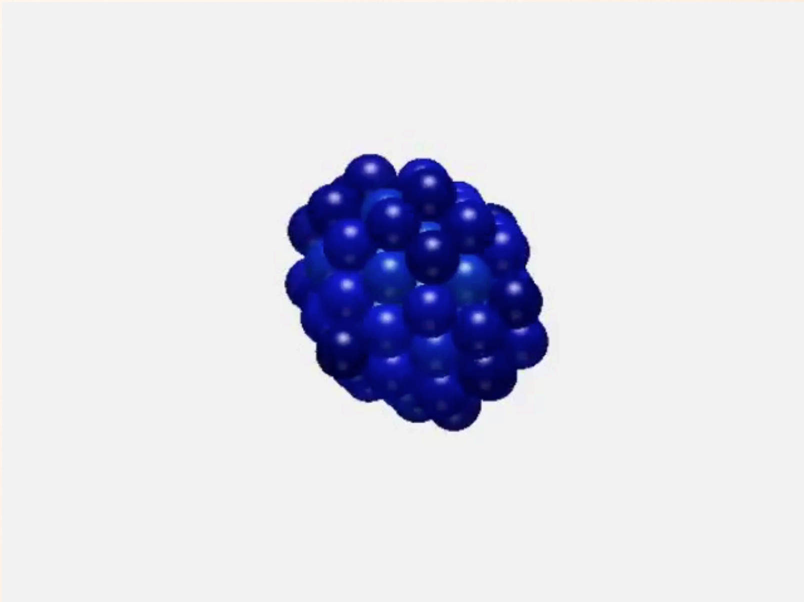


DIFFICULTIES IN MODELING THE DYNAMICS OF LJ CLUSTERS

- High dimensionality:
  3n coordinates, 3n momenta

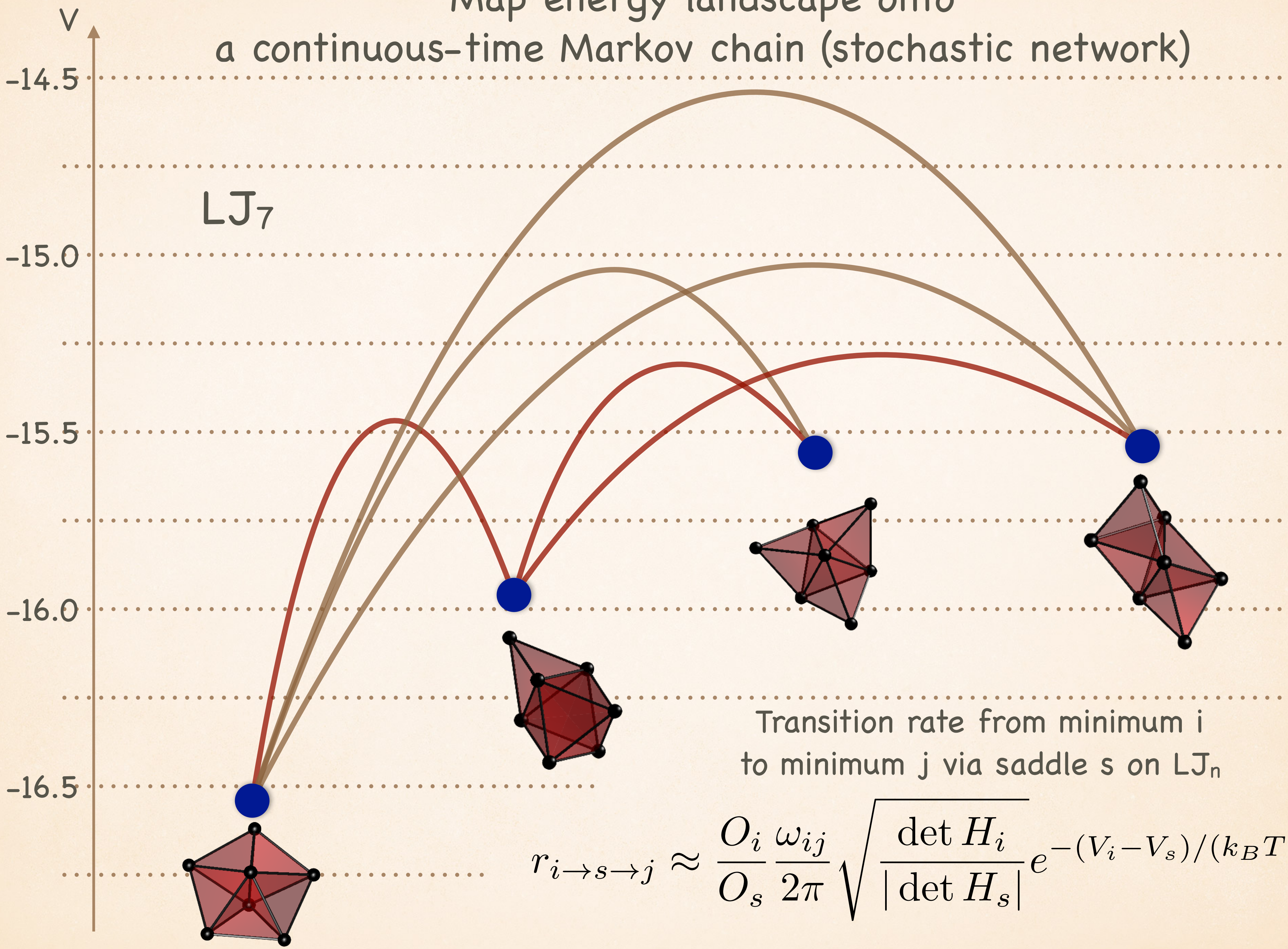
- Long waiting time in
  direct simulations:
  structural transitions occur rarely
  on the timescale of the system

- Large range of timescales
  for various transition processes



LJ_{75}

Map energy landscape onto a continuous-time Markov chain (stochastic network)



Transition rate from minimum i to minimum j via saddle s on LJ$_n$

$$r_{i\to s\to j} \approx \frac{O_i}{O_s}\frac{\omega_{ij}}{2\pi}\sqrt{\frac{\det H_i}{|\det H_s|}}e^{-(V_i-V_s)/(k_B T)}$$

BUILDING LENNARD-JONES NETWORKS

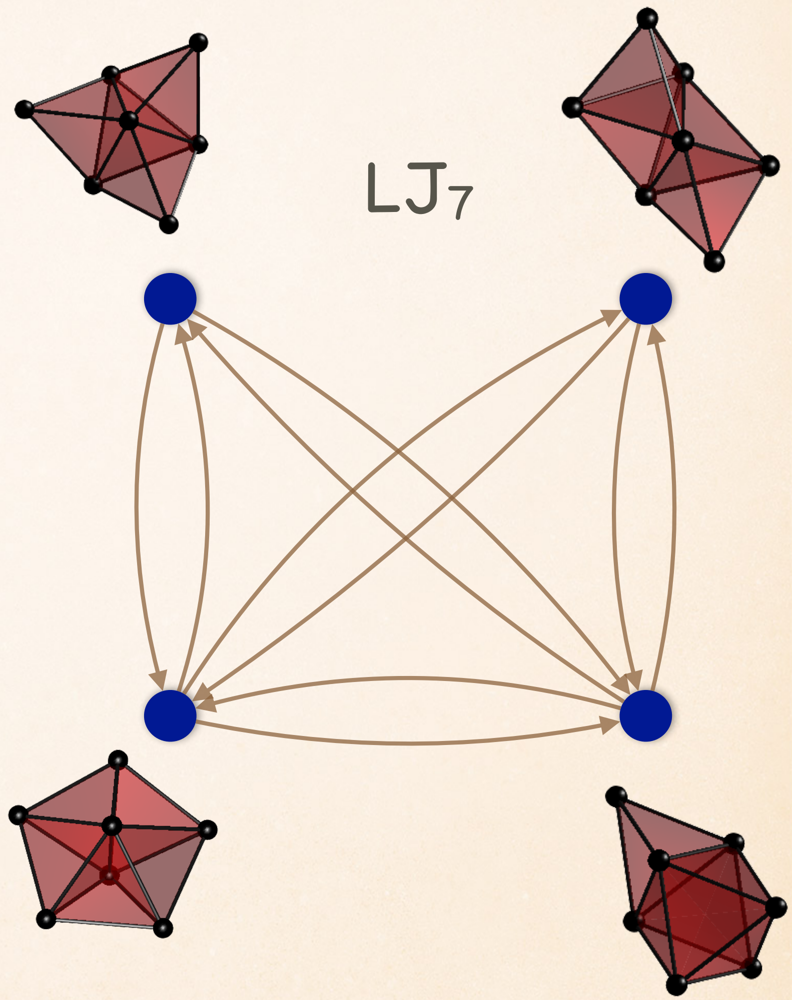
Vertices

- Find the set of local energy minima.

Edges & rates in LJ_n

- Find the set of Morse index one saddles
- Calculate transition rate along each arc

$$L_{i\to j} = \sum_s \frac{O_i}{O_s}\frac{\omega_{ij}}{2\pi}\sqrt{\frac{\det H_i}{|\det H_s|}}\, e^{-(V_i - V_s)/(k_B T)}$$



STATS FOR LJ NETWORKS

LJ6:
N vertices = 2
N arcs = 2

LJ7:
N states = 4
N arcs = 10

LJ8:
N states = 8
N arcs = 16

LJ9:
N states = 21
N arcs = 86

LJ10
N states = 63
N arcs = 742

LJ11
N states = 169
N arcs = 1028

LJ12
N states = 501
N arcs = 2278

LJ13 (by D. Wales)
N states = 1510
N arcs = 41168

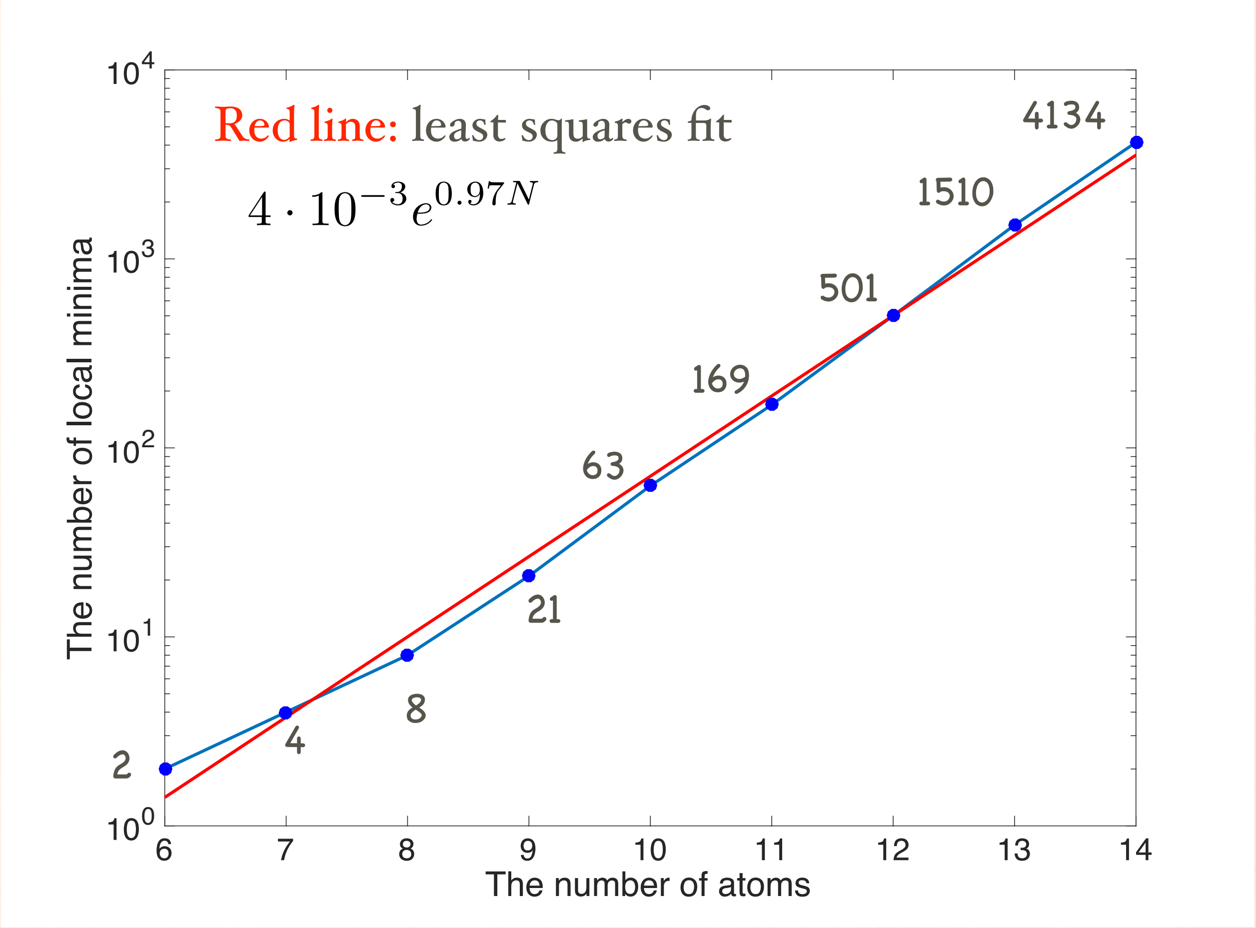
LJ14
N states = 4134
N arcs = 17116

LJ38 (by D. Wales)
N states = 71887
N arcs = 239706

N states ~10^{13}

LJ75 (by D. Wales)
N states = 169523
N arcs = 441016

N states ~10^{29}



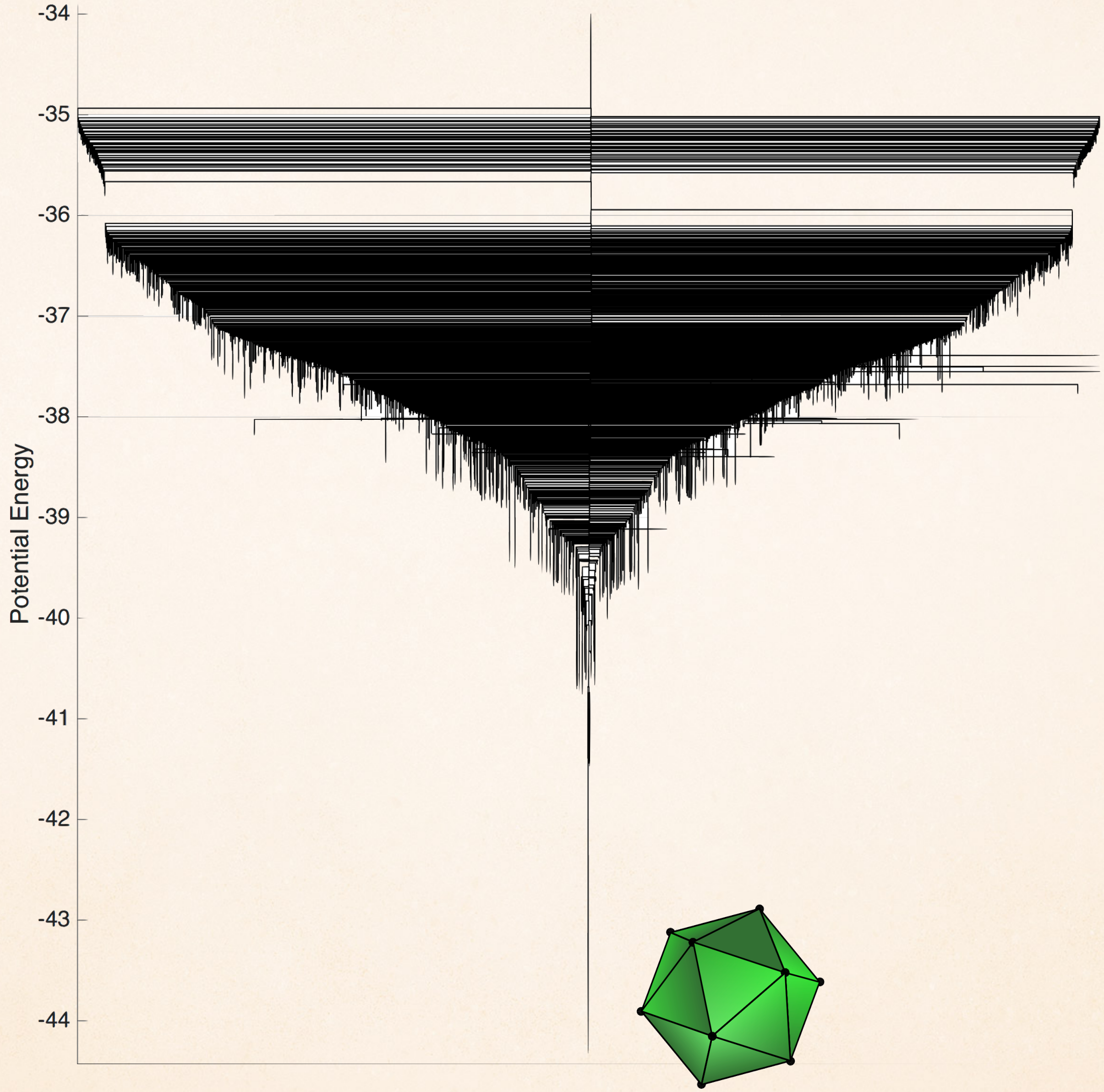
Wales's group, Cambridge University, UK
Basin Hopping Method (1997), Discrete Path Sampling (2002)

ANALYSIS OF LJ NETWORKS

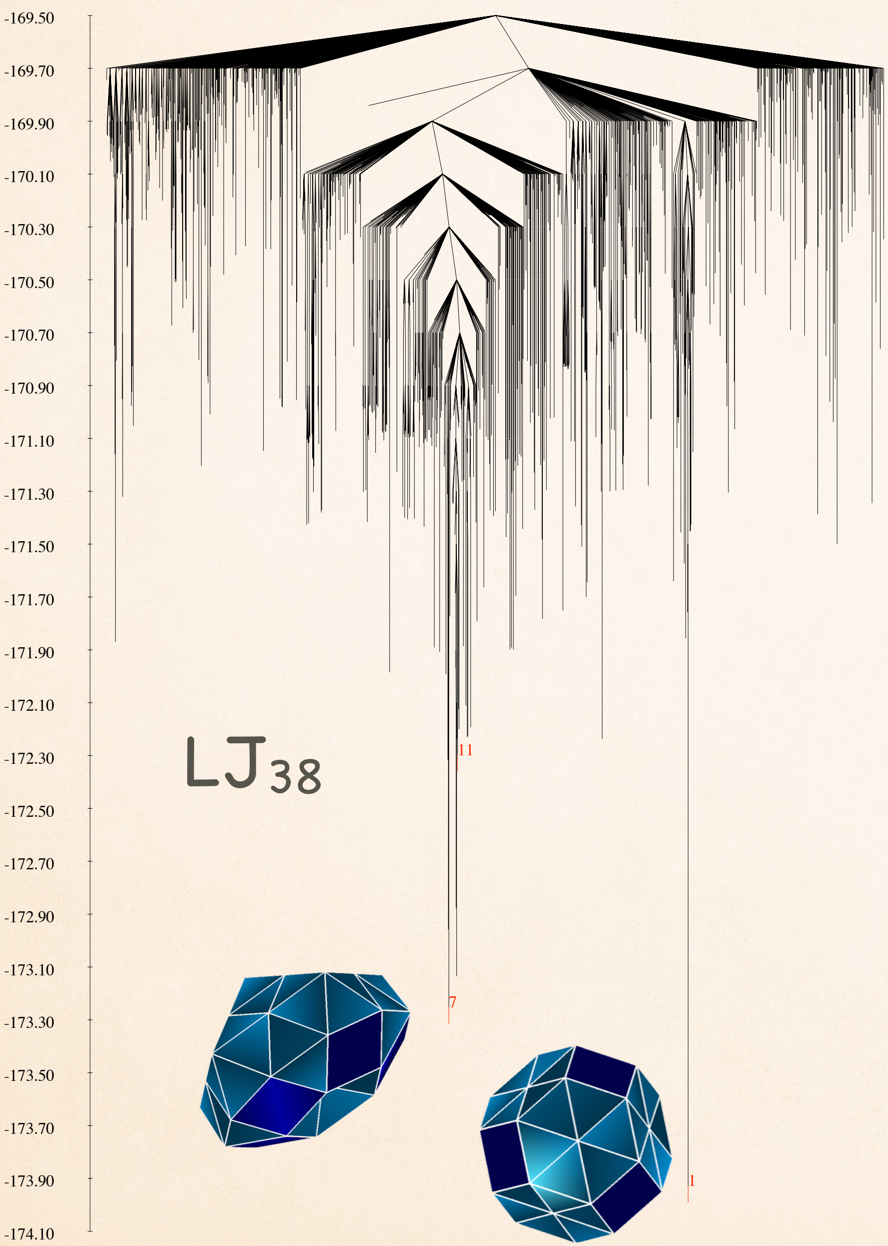
- Disconnectivity graphs, Discrete path sampling (Wales et al, starting from late 1990s)
- Transition path theory (E & Vanden-Eijnden 2006, Metzner et al 2009, Cameron & Vanden-Eijnden, 2014)
- Spectral analysis (Cameron 2014, Cameron & Gan 2016)

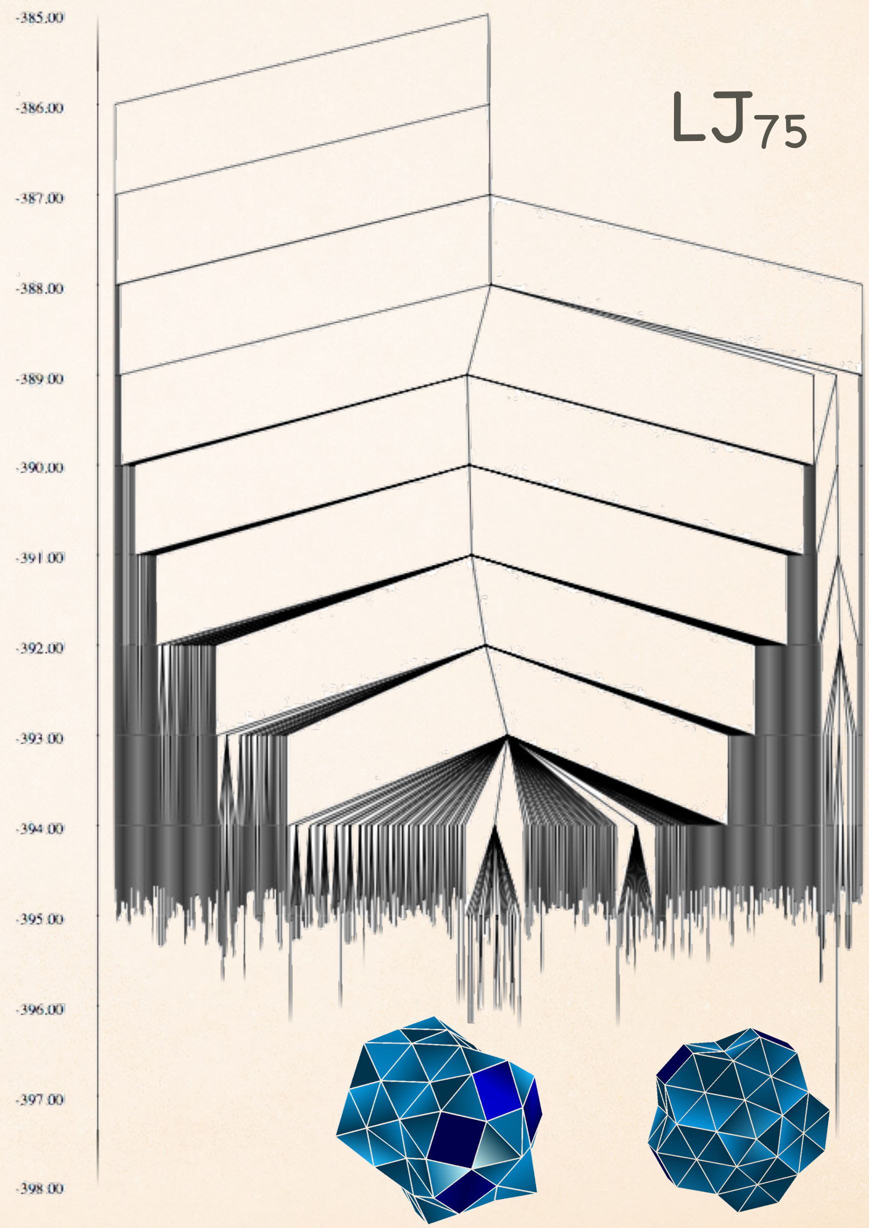
DISCONNECTIVITY GRAPHS: SINGLE FUNNEL

LJ_{13}



DISCONNECTIVITY GRAPHS: DOUBLE FUNNEL
(COURTESY OF D. WALES)





SIGNIFICANCE OF SPECTRAL DECOMPOSITION

(For any irreducible continuous-time Markov chain)

The Fokker-Planck equation
or the Master equation

$$\frac{dp(t)}{dt} = p(t)L$$

L = the generator matrix
p(0) = the initial distribution

Spectral decomposition of L:

$$L = \Phi\Lambda\Psi = \begin{bmatrix} 1 & \phi_1 & \cdots & \phi_{n-1} \\ \downarrow & \downarrow & & \downarrow \end{bmatrix} \begin{bmatrix} 0 & & & \\ & z_1 & & \\ & & \ddots & \\ & & & z_{n-1} \end{bmatrix} \begin{bmatrix} \pi & \rightarrow \\ \psi_1 & \rightarrow \\ \vdots & \\ \psi_{n-1} & \rightarrow \end{bmatrix}$$

Right eigenvectors

Eigenvalues

Left eigenvectors

$$z_k = -\lambda_k + i\mu_k, \quad 0 < \lambda_1 \leq \ldots \leq \lambda_{n-1}$$

The time evolution of the probability distribution

$$p(t) = p(0)\Phi e^{t\Lambda}\Psi = \pi + \sum_{k=1}^{n-1} (p(0)\phi_k) e^{-\lambda_k t} e^{i\mu_k t} \psi_k$$

Projection of p(0)
onto right e-vector

Left e-vector:
perturbation to π
decaying **uniformly** with rate λ_k
across the network

INTERPRETATION OF LEFT AND RIGHT EIGENVECTORS IN TIME-REVERSIBLE NETWORKS

$L = P^{-1}Q$, where $P = diag\{\pi_1, \ldots, \pi_n\}$, Q is symmetric

$$\boxed{p(t) = p(0)\Phi e^{t\Lambda}\Psi = \pi + \sum_{k=1}^{n-1}(p(0)\phi_k)e^{-\lambda_k t}\psi_k}$$

Right eigenvectors: $\Phi = [\phi_0, \ldots \phi_{n-1}]$

Left eigenvectors: $\Psi = P\phi = [P\phi_0, \ldots P\phi_{n-1}]$

If $p(0) = \pi + \psi_k = \pi + P\phi_k = \begin{bmatrix} \pi_1(1+\phi_{k,1}) \\ \pi_2(1+\phi_{k,2}) \\ \vdots \\ \pi_n(1+\phi_{k,n}) \end{bmatrix}$

then it decays **uniformly** across the network with rate λ_k and ϕ_k shows the proportions by which the states are under/overpopulated in p(0).

STRATEGY

Goal: compute eigenvalues and eigenvectors of L corresponding to transition processes of physical interest

Difficulties: L is large (n ~ 100000),
entries of L range by tens of orders of magnitude,
L has no special structure

Advantage: L has entries of the form $L_{ij} = \alpha_{ij} e^{-U_{ij}/\epsilon}$

$\epsilon = k_B T$ = small parameter

Idea:
- compute asymptotic estimates for eigenvalues/eigenvectors of L
- use continuation techniques to find eigenvalues/eigenvectors at desired temperatures

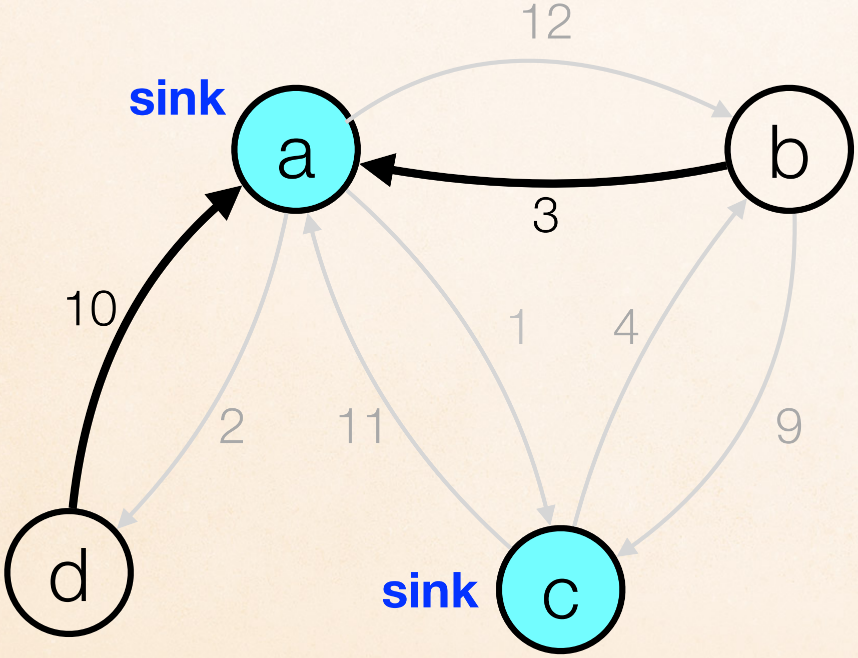
W-GRAPHS

Wentzell, 1972

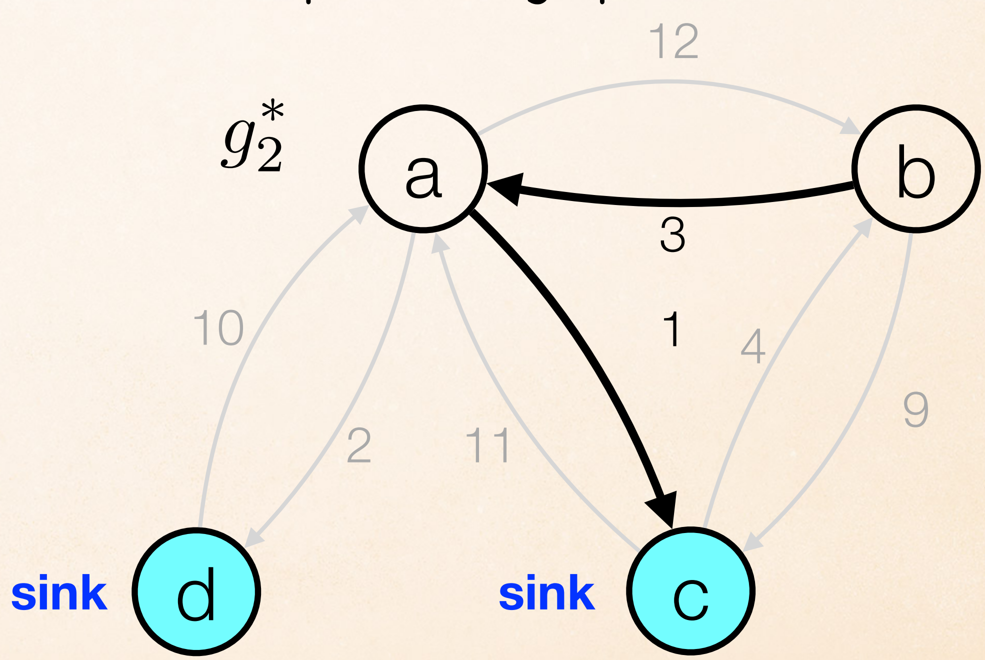
Definition. Let G(S,A,U) be a weighted directed graph.
A W-graph with k sinks is its subgraph satisfying:
(1) any sink has no outgoing arcs; any non-sink has exactly one outgoing arc;
(2) the graph has no cycles.

Optimal W-graph with k sinks: sum of weights of its arcs is minimal possible

A W-graph with two sinks



An optimal W-graph with two sinks



ASYMPTOTIC ESTIMATES FOR EIGENVALUES

(TIME REVERSIBILITY IS NOT ASSUMED)

A. Wentzell, 1972

For a continuous-time Markov chain with pairwise rates of the form

$$L_{ij} \sim e^{-U_{ij}/T}$$

Let $z_k = -\lambda_k + i\mu_k$ be eigenvalues of the generator matrix, and

$$0 < \lambda_1 \leq \ldots \leq \lambda_{n-1}$$

$$\lambda_k \asymp \exp(-\Delta_k/T)$$

$$\Delta_k = V^{(k)} - V^{(k+1)}$$

$$V^{(k)} = \sum_{(i \to j) \in g_k^*} U_{ij}$$

where g_k^* is the optimal W-graph with k sinks

T. Gan, C., 2016

For a continuous-time Markov chain with pairwise rates of the form

$$L_{ij} = a_{ij} e^{-U_{ij}/T}$$

if all **optimal W-graphs are unique,** eigenvalues of the generator matrix are real and distinct for small enough ϵ

$$\lambda_k = A_k \exp(-\Delta_k/T)$$

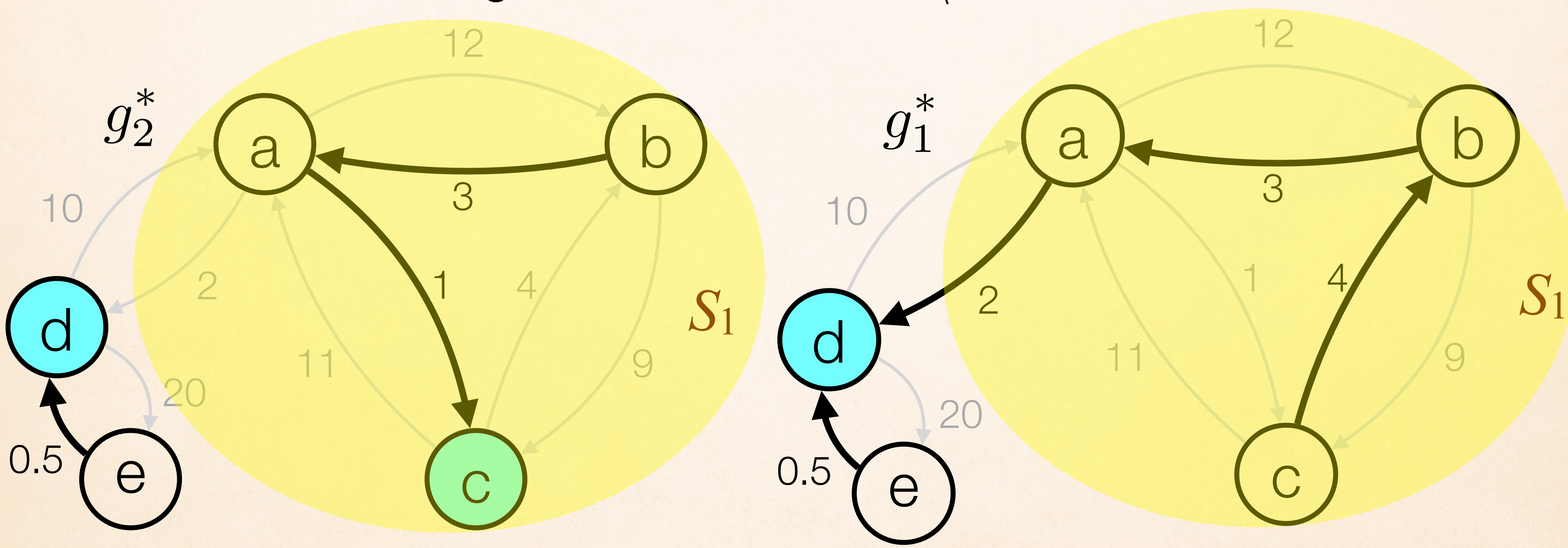
$$\Delta_k = V^{(k)} - V^{(k+1)}$$

$$V^{(k)} = \sum_{(i \to j) \in g_k^*} U_{ij}$$

$$A_k = \frac{\prod_{i \to j \in g_k^*} U_{ij}}{\prod_{i \to j \in g_{k+1}^*} U_{ij}} + o(1)$$

NESTED PROPERTIES OF OPTIMAL W-GRAPHS (GAN AND C. 2016)

- {The set of sinks of g_k^* } $\subset$ {The set of sinks of g_{k+1}^* }
- There exists a connected component S_k of g_{k+1}^* whose set of vertices contains no sink of g_k^*.
- The sets of arcs connecting vertices $S \backslash S_k$ in g_k^* and g_{k+1}^* coincide.
- In g_k^*, there is a single arc from S_k to $S \backslash S_k$



Approaches to the study of Markov processes with rates $L_{ij} = a_{ij}e^{-U_{ij}/\epsilon}$ at time scales from 0 to ∞

M. Freidlin, early 1970s:

* **The hierarchy of Freidlin's cycles**
  Idea: for each vertex, find the vertex where the system most likely jumps and detect cycles
  Tool: ***i*-graphs** for finding exit rates from cycles
  Feature: the exit time scales from cycles are only **partially ordered**.
  Extension: Freidlin, 2014: case with symmetry: hierarchy of Markov chains

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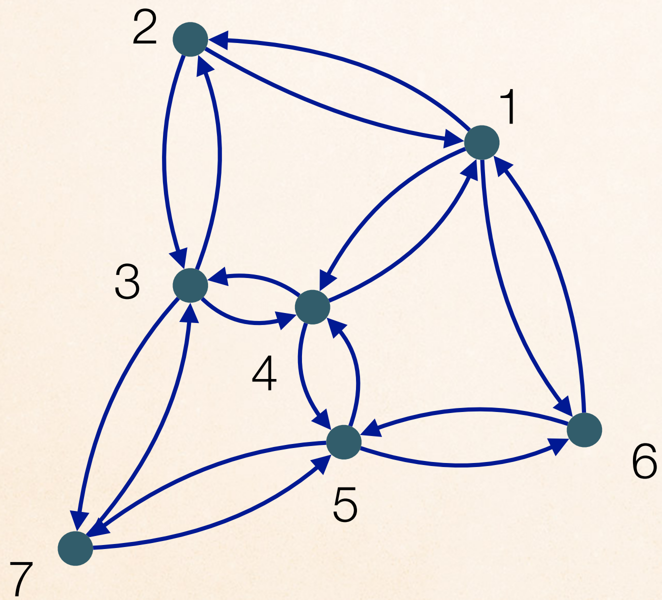
A. Wentzell, early 1970s:

* **Asymptotic estimates for eigenvalues**
  Tool: W-graphs
  Idea: reduce the problem of finding eigenvalues to an optimization problem on graphs.
  Motivation for me: No algorithm was proposed to solve this optimization problem
  Extension: Berglund & Dutercq, 2015, time-reversible case with symmetry

TIMESCALES

Timescales = functions $t(\epsilon)$



$$L_{ij} = a_{ij} e^{-U_{ij}/\epsilon}$$

$$t(\epsilon) \asymp e^{\Delta/\epsilon} \quad \text{if} \quad \lim_{\epsilon \to 0} \epsilon \log t(\epsilon) = \Delta$$

For brevity, we write

$$e^{\Delta_1/\epsilon} < t(\epsilon) < e^{\Delta_1/\epsilon}$$

if

$$\Delta_1 < \lim_{\epsilon \to 0} \epsilon \log t(\epsilon) < \Delta_2$$

THE GRAPH-ALGORITHMIC APPROACH FOR THE STUDY OF METASTABILITY IN MARKOV CHAINS

(T. Gan and M. C., 2016)

An algorithm for:

- finding the sequence of critical timescales at which the dynamics of the system undergoes a qualitative change
- finding the hierarchy of graphs effectively describing the dynamics of the system

The algorithm simultaneously finds

- the hierarchy of optimal W-graphs giving asymptotic estimates for eigenvalues
- the hierarchy of Freidlin's cycles
- critical timescales are ordered in the increasing order

Initialization

Find **min-arc** for each vertex

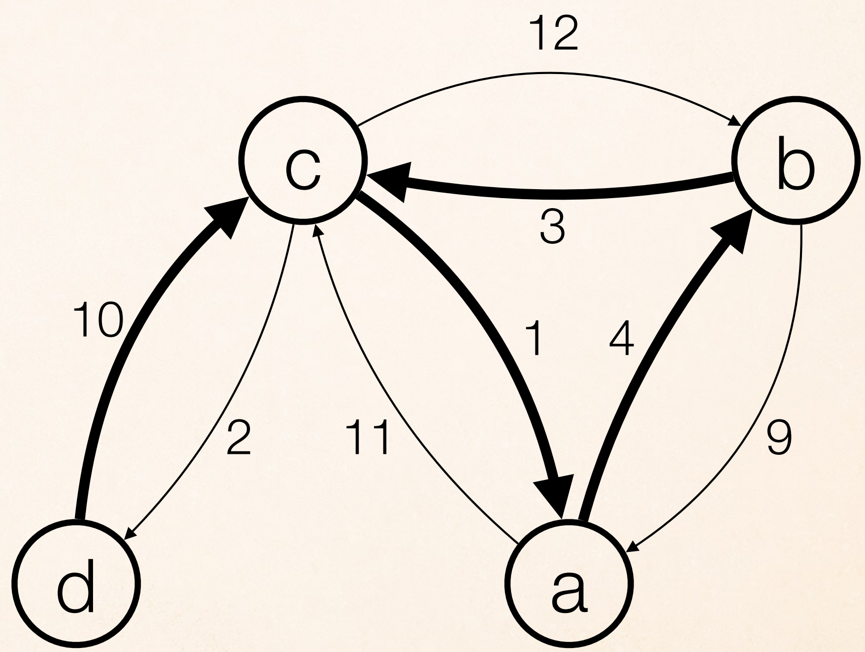
Sort the set of min-arcs in increasing order

$c \to a: \quad U = 1$

$b \to c: \quad U = 3$

$a \to b: \quad U = 4$

$d \to c: \quad U = 10$



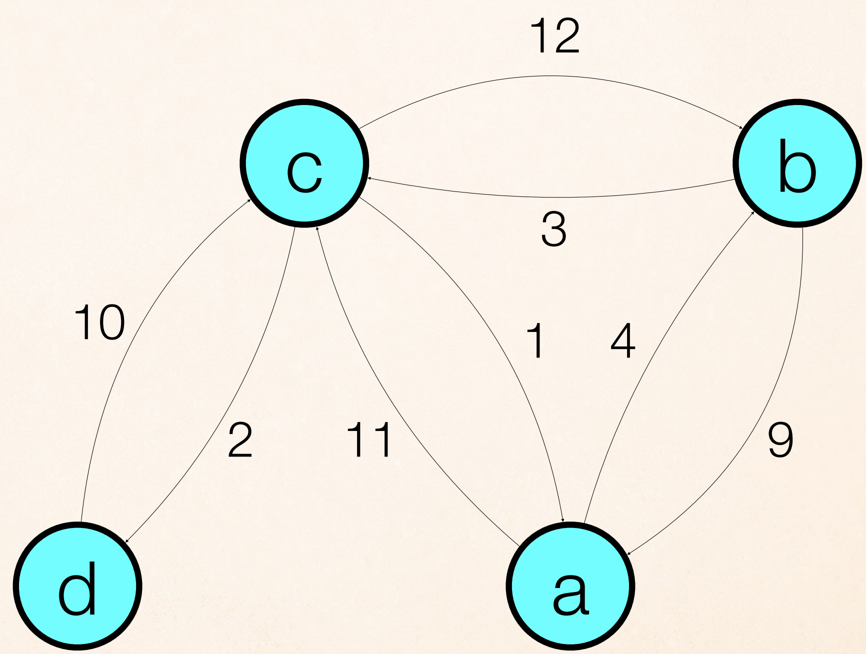
The numbers next to arcs $i \to j$ are U_{ij}

On the time scale

$$t(\epsilon) < e^{\gamma_1/\epsilon}, \quad \text{where} \quad \gamma_1 = \min_{i,j} U_{ij}$$

each state of the Markov chain is absorbing

$$c \to a: \quad U = 1$$
$$b \to c: \quad U = 3$$
$$a \to b: \quad U = 4$$
$$d \to c: \quad U = 10$$



In this example, $\gamma_1 = 1$

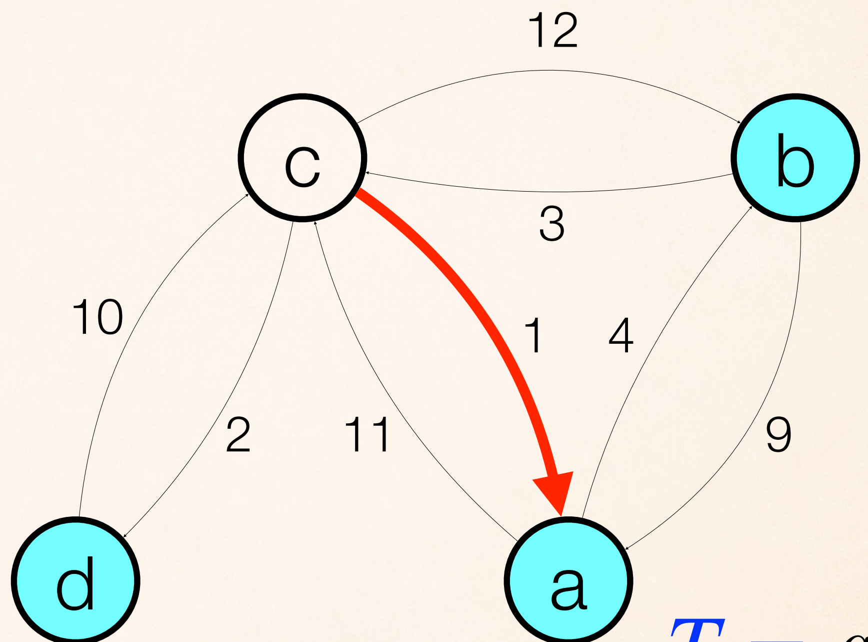
The main cycle

Remove arcs from the set of min-arcs one in a time

The corresponding U's are the characteristic time scales γ_i

$$b \to c : \quad U = 3$$
$$a \to b : \quad U = 4$$
$$d \to c : \quad U = 10$$

$$\gamma_1 = 1$$



$T_1 = g_3^*$

On the time scale

$$e^{\gamma_1/\epsilon} < t(\epsilon) < e^{\gamma_2/\epsilon}$$

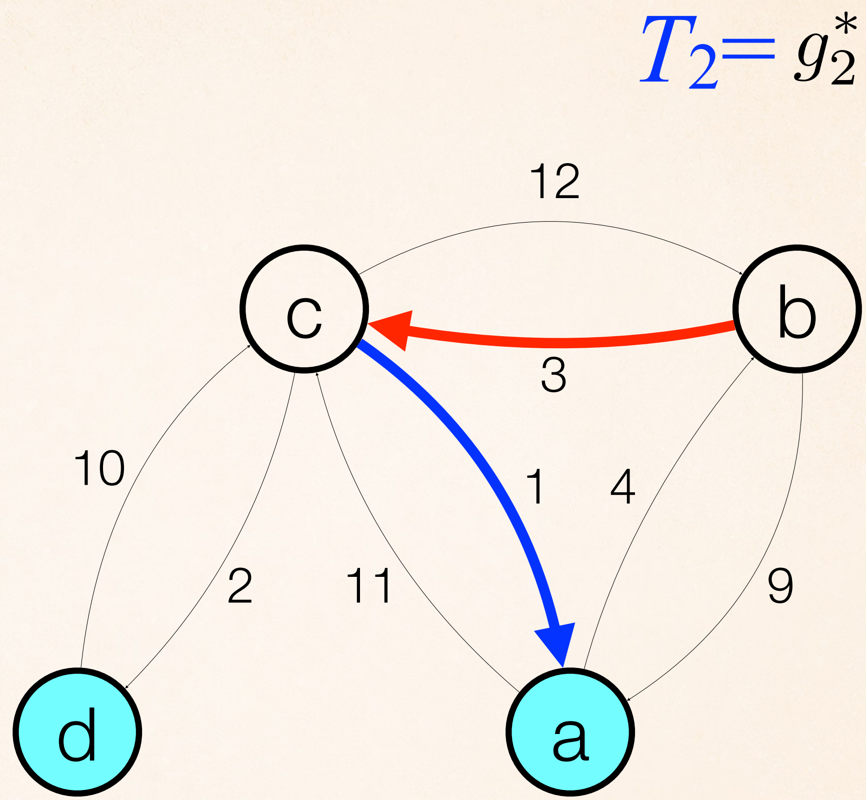
states a, b, and d are absorbing,

state c is transient, the exit rate from c is

$$a_{ca} e^{-\gamma_1/\epsilon} = a_{ca} e^{-U_{ca}/\epsilon} = a_{ca} e^{-1/\epsilon}$$

$$\boxed{\begin{array}{ll} a \to b: & U = 4 \\ d \to c: & U = 10 \end{array}}$$

$$\gamma_1 = 1$$
$$\gamma_2 = 3$$



On the time scale

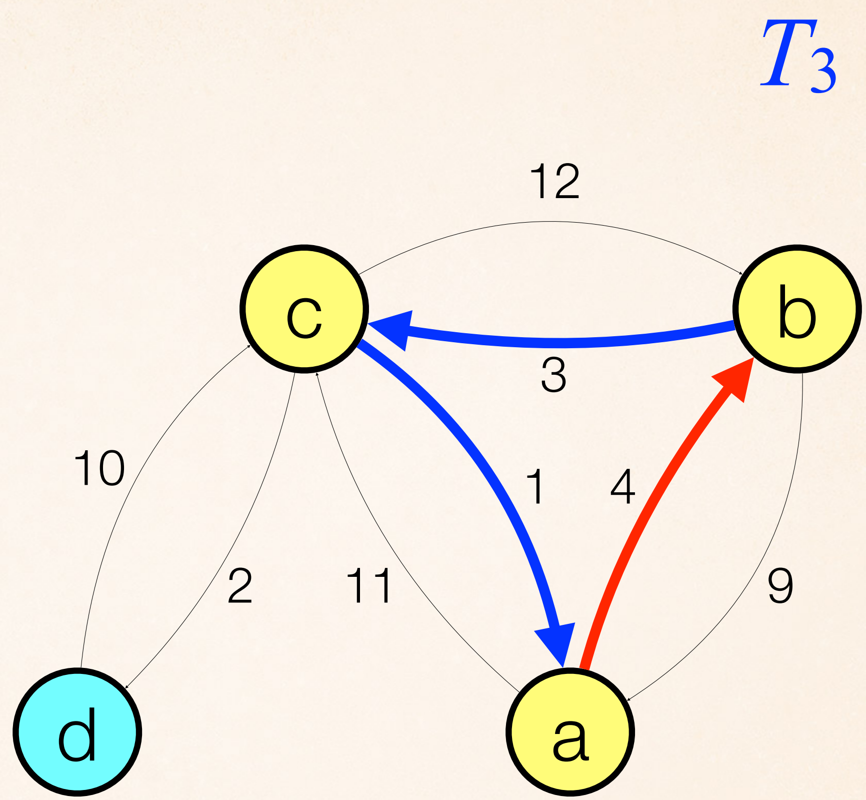
$$e^{\gamma_2/\epsilon} < t(\epsilon) < e^{\gamma_3/\epsilon}$$

states a and d are absorbing,
states c and b are transient, the exit rate from b is

$$a_{bc} e^{-\gamma_2/\epsilon} = a_{bc} e^{-U_{bc}/\epsilon} = a_{ca} e^{-3/\epsilon}$$

$$\boxed{d \to c: \quad U = 10}$$

$$\gamma_1 = 1$$
$$\gamma_2 = 3$$
$$\gamma_3 = 4$$



On the time scale

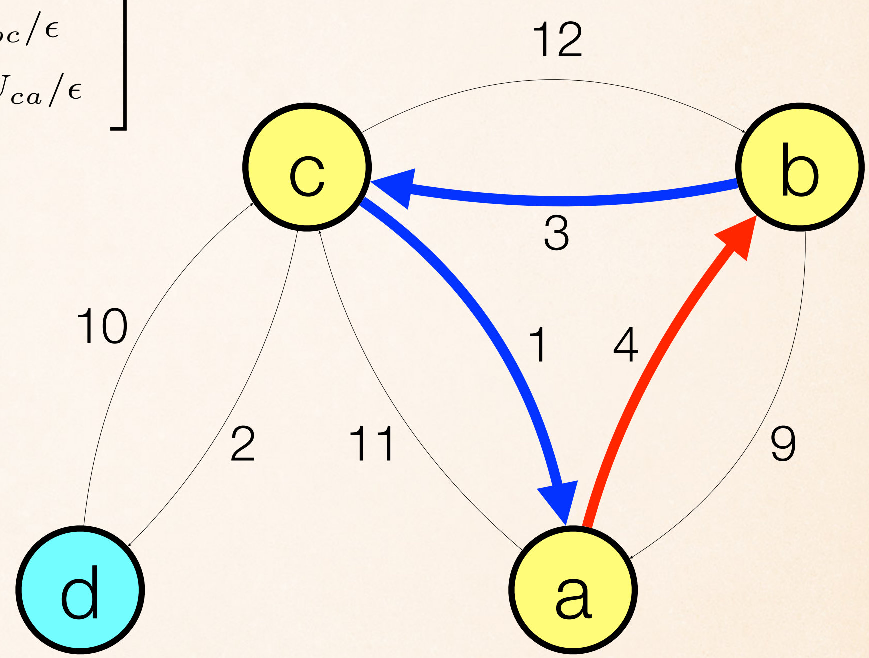
$$e^{\gamma_3/\epsilon} < t(\epsilon) < e^{\gamma_4/\epsilon}$$

state d is absorbing,
states a, b, and c are recurrent,
the rotation rate in the cycle {a, b, c} is

$$a_{ab}e^{-\gamma_3/\epsilon} = a_{ab}e^{-U_{ab}/\epsilon} = a_{ab}e^{-4/\epsilon}$$

If a **cycle** is encountered, find **the most likely exit** from it

$$L_{abc} = \begin{bmatrix} -\alpha_{ab}e^{-U_{ab}/\epsilon} & \alpha_{ab}e^{-U_{ab}/\epsilon} & 0 \\ 0 & -\alpha_{bc}e^{-U_{bc}/\epsilon} & \alpha_{bc}e^{-U_{bc}/\epsilon} \\ \alpha_{ca}e^{-U_{ca}/\epsilon} & 0 & -\alpha_{ca}e^{-U_{ca}/\epsilon} \end{bmatrix}$$



The invariant distribution in the cycle {a, b, c}:

$$\pi_{abc} = \frac{\left[\frac{e^{U_{ab}/\epsilon}}{\alpha_{ab}}, \frac{e^{U_{bc}/\epsilon}}{\alpha_{bc}}, \frac{e^{U_{ca}/\epsilon}}{\alpha_{ca}}\right]}{\frac{e^{U_{ab}/\epsilon}}{\alpha_{ab}} + \frac{e^{U_{bc}/\epsilon}}{\alpha_{bc}} + \frac{e^{U_{ca}/\epsilon}}{\alpha_{ca}}}$$

$$\pi_{abc} \approx \left[1, \frac{\alpha_{ab}}{\alpha_{bc}}e^{-1/\epsilon}, \frac{\alpha_{ab}}{\alpha_{ca}}e^{-3/\epsilon}\right]$$

The exit rate from cycle {a, b, c} via arc c $\to$ d :

$$\tilde{L}_{cd} = \pi_{abc}(c)L_{cd} = \frac{\alpha_{cd}\alpha_{ab}}{\alpha_{ca}}e^{-5/\epsilon}$$

In general, if a cycle is encountered:

$$L_C = \begin{bmatrix} -\alpha_{12}e^{-U_{12}/\epsilon} & \alpha_{12}e^{-U_{12}/\epsilon} & & \\ & -\alpha_{12}e^{-U_{12}/\epsilon} & \alpha_{12}e^{-U_{12}/\epsilon} & \\ & & \dots & \dots \\ \alpha_{n1}e^{-U_{n1}/\epsilon} & & & -\alpha_{n1}e^{-U_{n1}/\epsilon} \end{bmatrix}$$

M = the main state in the cycle.

The invariant distribution in the cycle C:

$$\pi_C = \left[\frac{\alpha_{m(M)}}{\alpha_{12}}e^{-(U_{m(M)}-U_{12})/\epsilon}, \dots, 1, \dots, \frac{\alpha_{m(M)}}{\alpha_{n1}}e^{-(U_{m(M)}-U_{n1})/\epsilon}\right]$$

M

Note: m(M) is the last added arc in the cycle

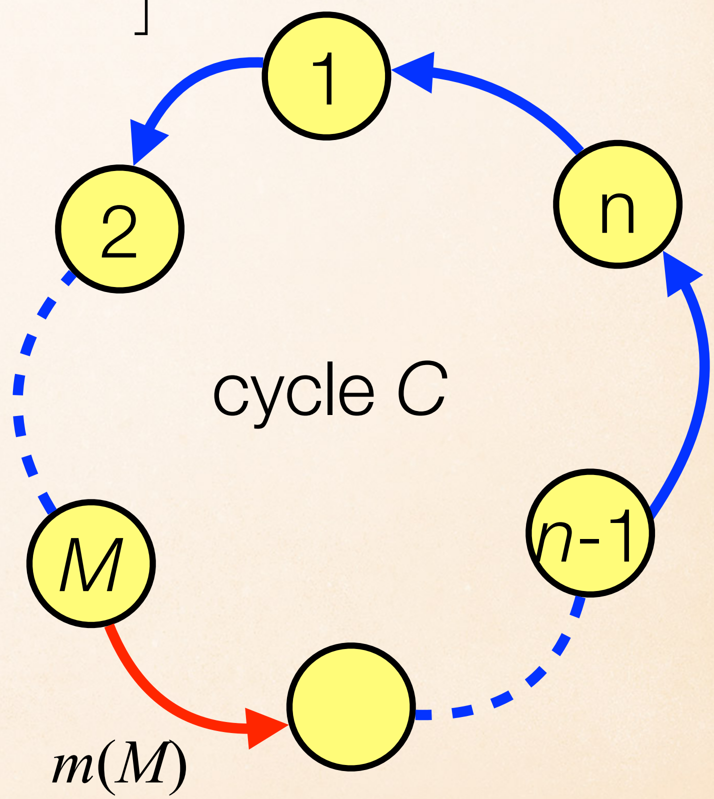
Exit rate from C via arc $i \to j$

$$\tilde{L}_{ij} = \frac{\alpha_{m(M)}\alpha_{ij}}{\alpha_{m(i)}}e^{-(U_{ij}+(U_{m(M)}-U_{m(i)})/\epsilon}$$

Update rules:

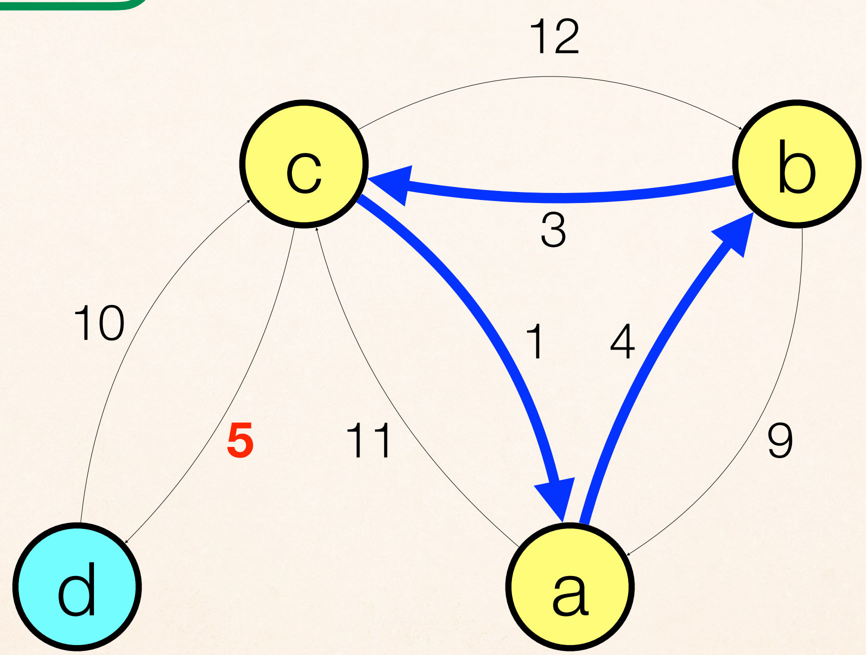
$$\alpha_{ij} \to \frac{\alpha_{m(M)}\alpha_{ij}}{\alpha_{12}}$$

$$U_{ij} \to U_{ij} + (U_{m(M)} - U_{12})$$



Add the min-exit-arc from the cycle to the set of min-arcs

$$c \to d: \quad U = 5$$
$$d \to c: \quad U = 10$$



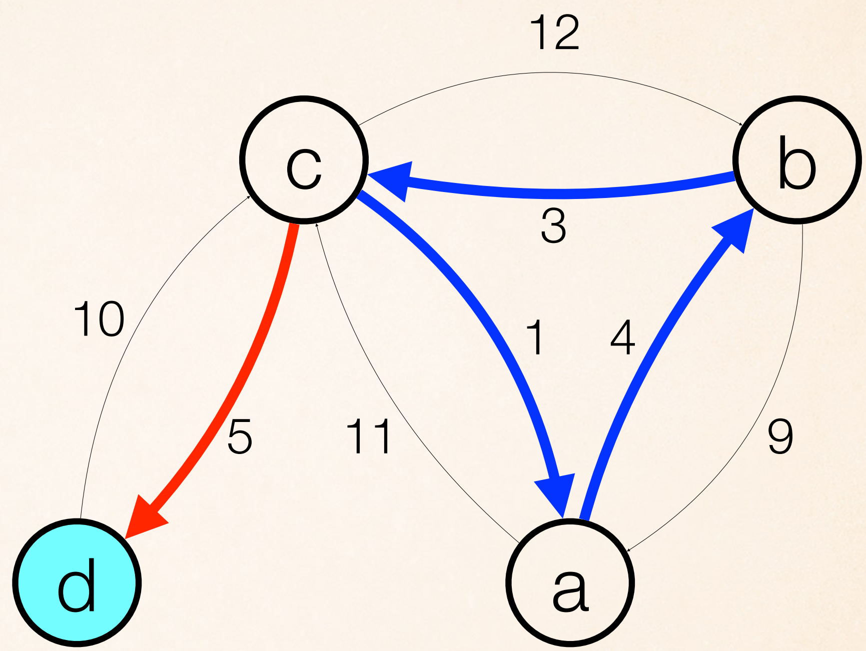
5 = 2 + 4 - 1

Remove the next min-arc

$$\boxed{d \to c: \quad U = 10}$$

$$T_4 = g_1^*$$

$$\gamma_1 = 1$$
$$\gamma_2 = 3$$
$$\gamma_3 = 4$$
$$\gamma_4 = 5$$



On the time scale

$$e^{\gamma_4/\epsilon} < t(\epsilon) < e^{\gamma_5/\epsilon}$$

states a, b, and c are transient,
state d is absorbing.

Remove the last min-arc

The set of critical time scales

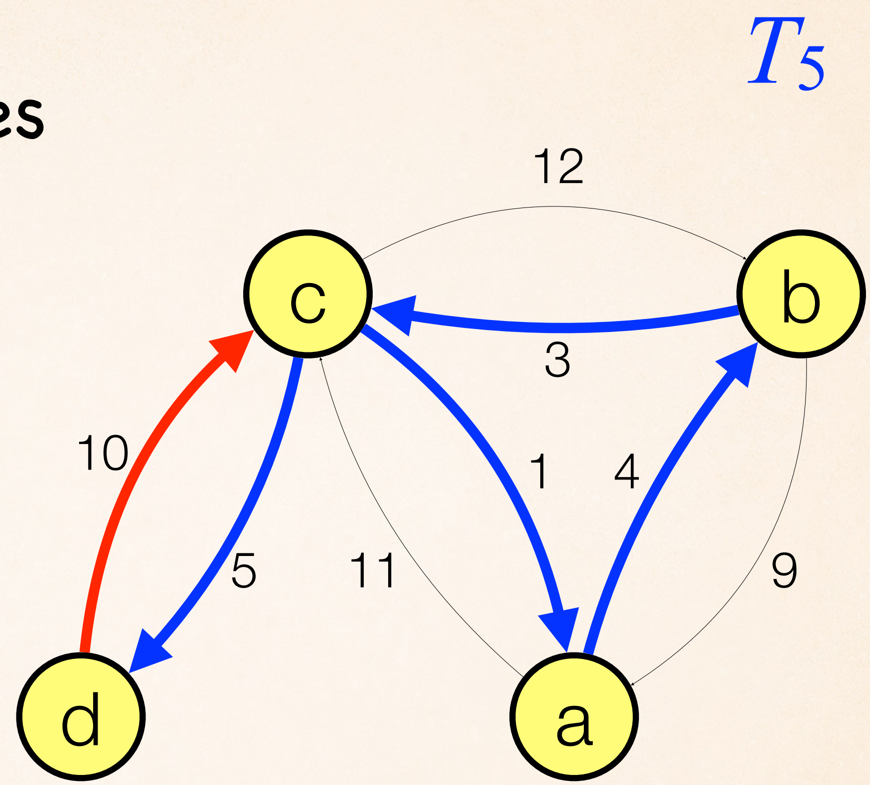
$$\gamma_1 = 1$$

$$\gamma_2 = 3$$

$$\gamma_3 = 4$$

$$\gamma_4 = 5$$

$$\gamma_5 = 10$$



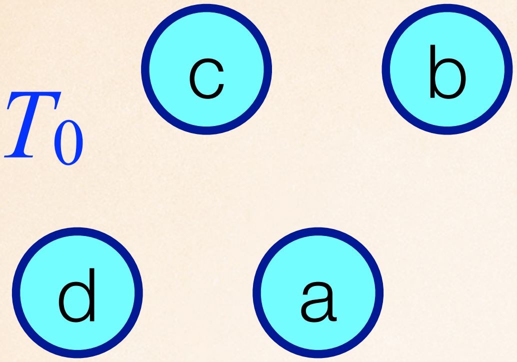
On the time scale

$$e^{\gamma_5/\epsilon} < t(\epsilon) < \infty$$

all states are recurrent

Output:

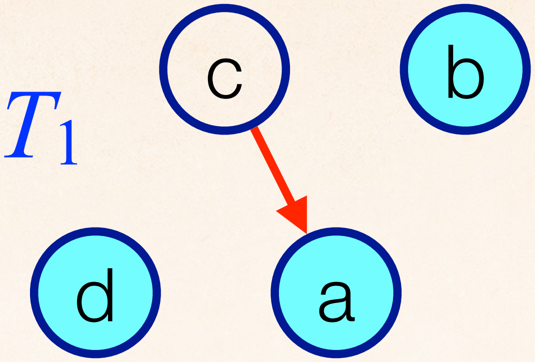
T_0



$0 \le t < e^{1/\epsilon}$

$\gamma_1 = 1$

T_1

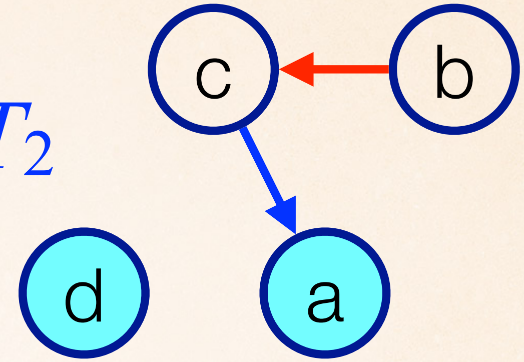


$e^{1/\epsilon} \le t < e^{3/\epsilon}$

$\lambda_1 \approx \alpha_{ca} e^{-1/\epsilon}$

$\gamma_2 = 3$

T_2

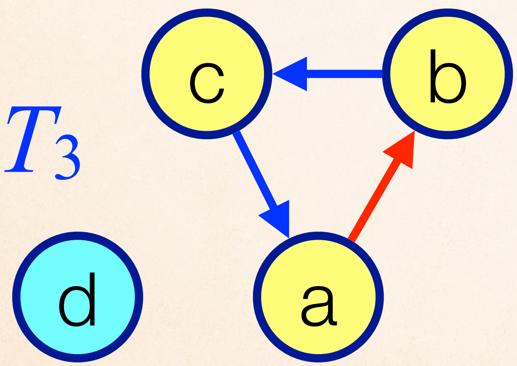


$e^{3/\epsilon} \le t < e^{4/\epsilon}$

$\lambda_2 \approx \alpha_{ab} e^{-3/\epsilon}$

$\gamma_3 = 4$

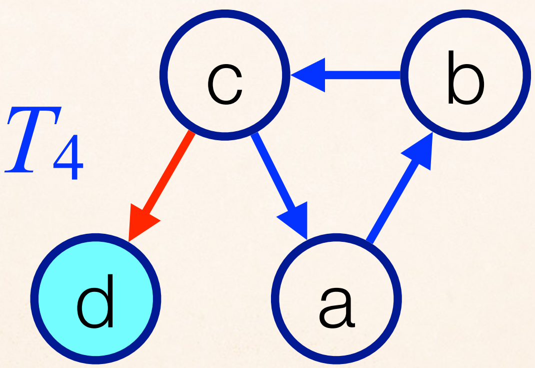
T_3



$e^{4/\epsilon} \le t < e^{5/\epsilon}$

$\gamma_4 = 5$

T_4

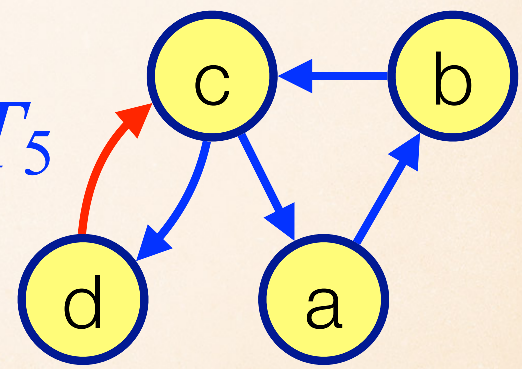


$e^{5/\epsilon} \le t < e^{10/\epsilon}$

$$\lambda_3 \approx \frac{\alpha_{cd}\alpha_{ab}}{\alpha_{ca}} e^{-5/\epsilon}$$

$\gamma_5 = 10$

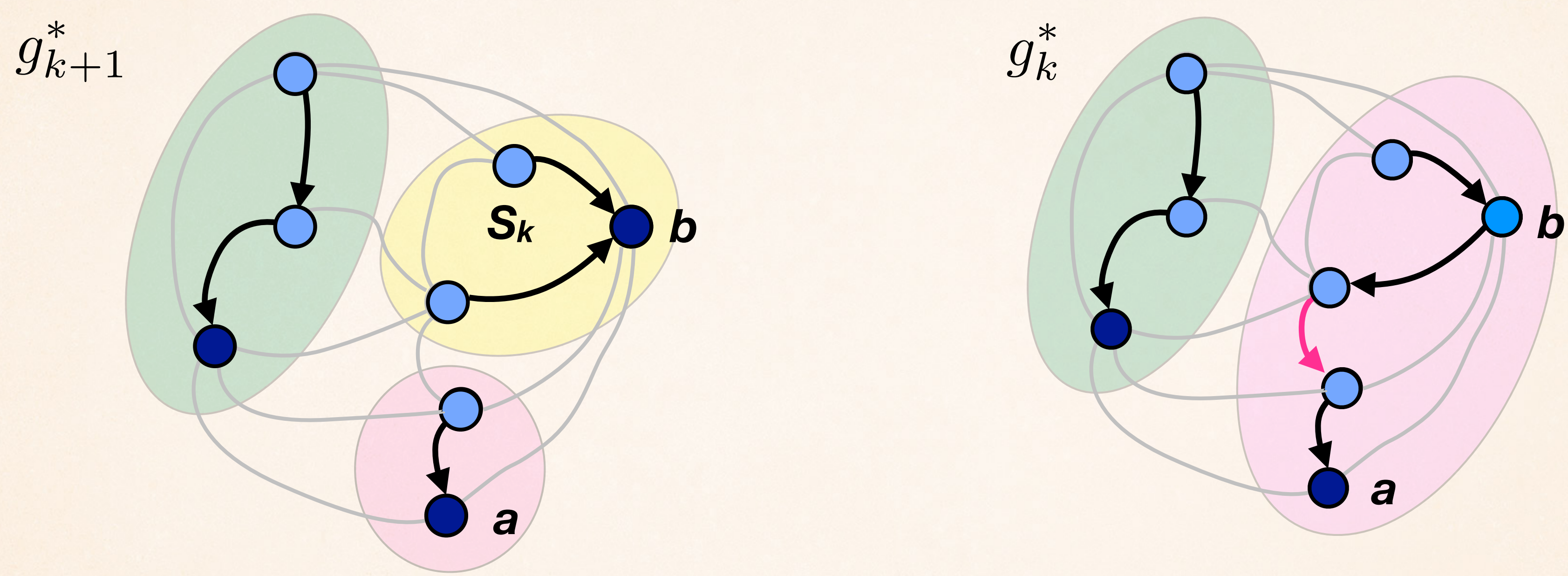
T_5



$e^{10/\epsilon} \le t < \infty$

Asymptotics for eigenvectors for time-reversible networks

(under assumption that all optimal W-graphs are unique)



Right eigenvectors: $$\phi_i^k = \begin{cases} 1, & i \in S_k \\ 0, & i \notin S_k \end{cases}$$

Time- reversible case:
Justification: Bovier, Eckort, Gayrard, Klein, early 2000's

Left eigenvectors: $$\psi_i^k = \begin{cases} 1, & i = b \\ -1, & i = a, \\ 0, & i \notin \{a, b\} \end{cases}$$

GENERALIZATION

- Case with symmetry: any coincidence in the set of exponential orders of eigenvalues and rotation rates in Freidlin's cycles (Gan & C, 2016, arXiv 1607.00078)

COMPUTATIONAL COST

N vertices, index of each vertex $\leq k$

Best case scenario:

Initialization: $O(Nk \log k)$

Routine: $O(N \log N)$

Worst case scenario:

Routine: $O((Nk)^2 \log(Nk))$ due to merging trees of reserve arcs when a cycle is created

PERFORMANCE

- **Lennard-Jones-38 network:** **71887** vertices, **239706** arcs
  - CPU time: **30** seconds,
  - the number of cycles encountered: **50266**
  - the number of arcs having appeared on the top of the main tree: **122152**
- **Lennard-Jones-75 network:** **169523** vertices, **441016** arcs
  - CPU time: **632** seconds (10.5 minutes)
  - the number of cycles encountered: **153164**
  - the number of arcs having appeared on the top of the main tree: **322686**

Application to Lennard-Jones-75 network

Data: courtesy of David Wales

Stats

593320 vertices, **452315** edges

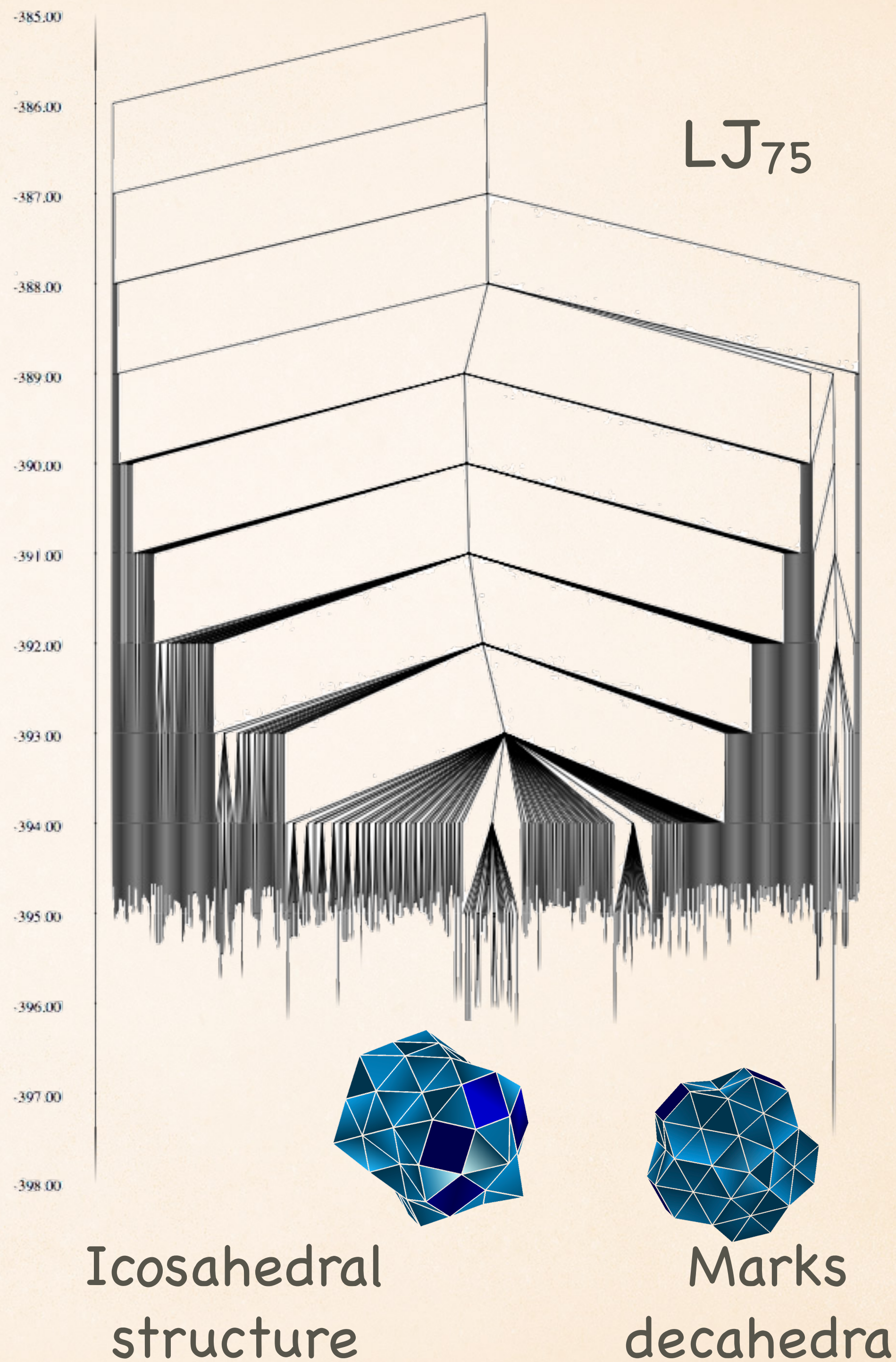
the maximal vertex index: **740**

The maximal connected component:

169523 vertices, **227198** edges

the maximal vertex degree: **740**

the number of edges
that are not loops and
connecting different pairs of vertices:
220508



Asymptotic estimates for eigenvalues

$$\lambda_k = \frac{O_{s^*_{k+1}} \bar{\nu}^{219}_{s^*_{k+1}}}{O_{p^*_k q^*_k} \bar{\nu}^{218}_{p^*_k q^*_k}} e^{-\Delta_k / T}$$

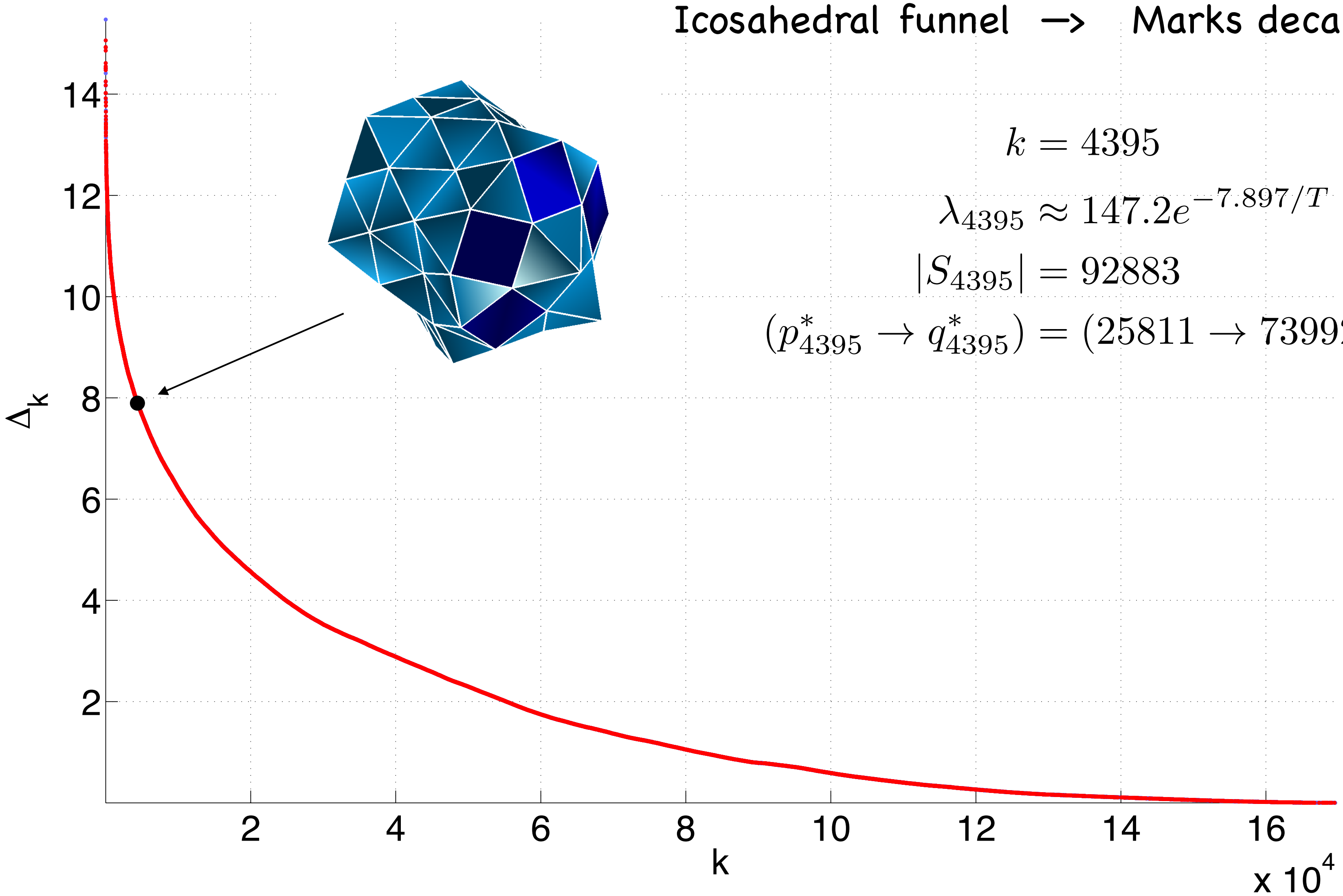
Icosahedral funnel —> Marks decahedron

$$k = 4395$$

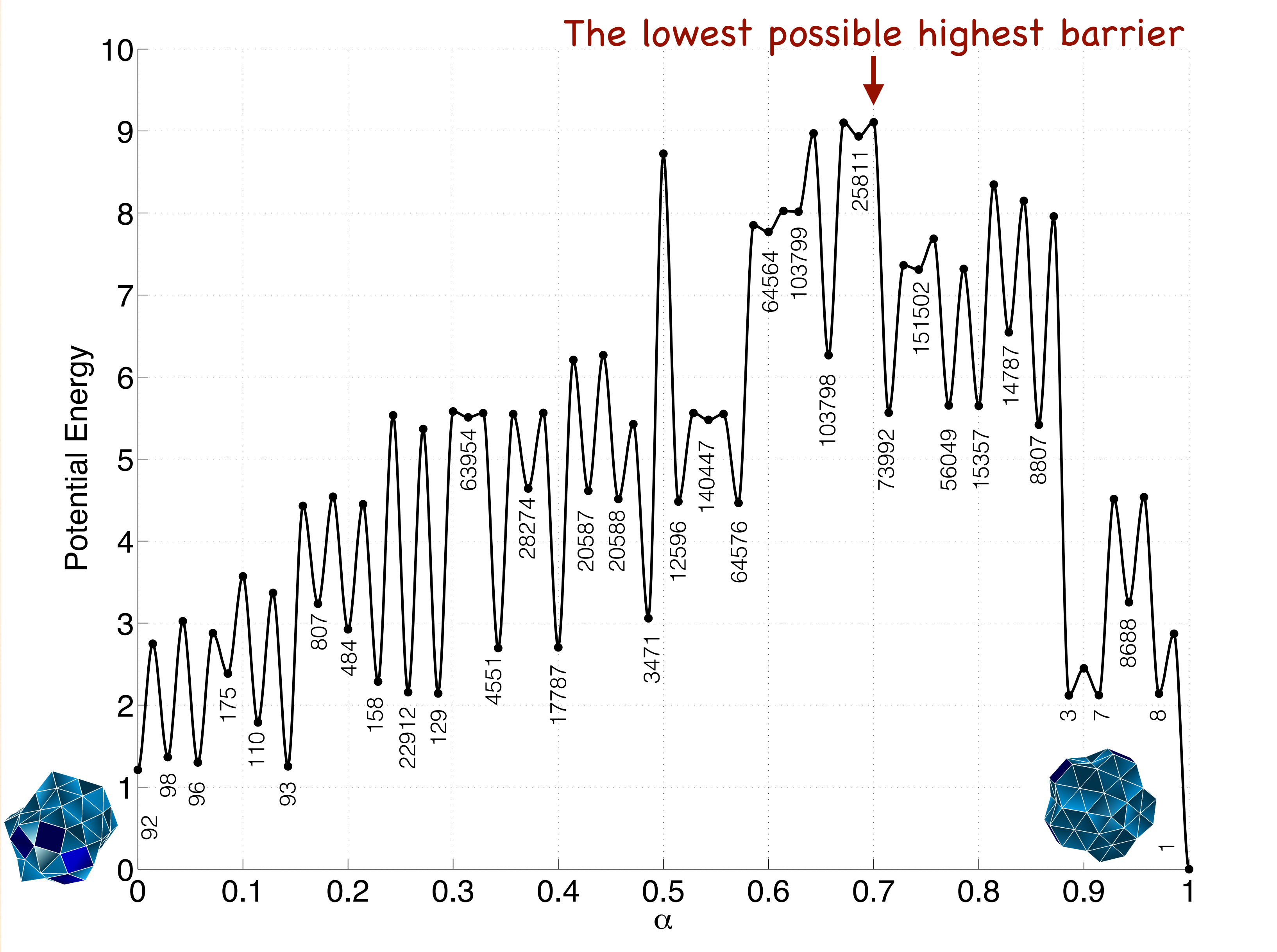
$$\lambda_{4395} \approx 147.2 e^{-7.897/T}$$

$$|S_{4395}| = 92883$$

$$(p^*_{4395} \to q^*_{4395}) = (25811 \to 73992)$$



Asymptotic zero-temperature path
(the MinMax path)



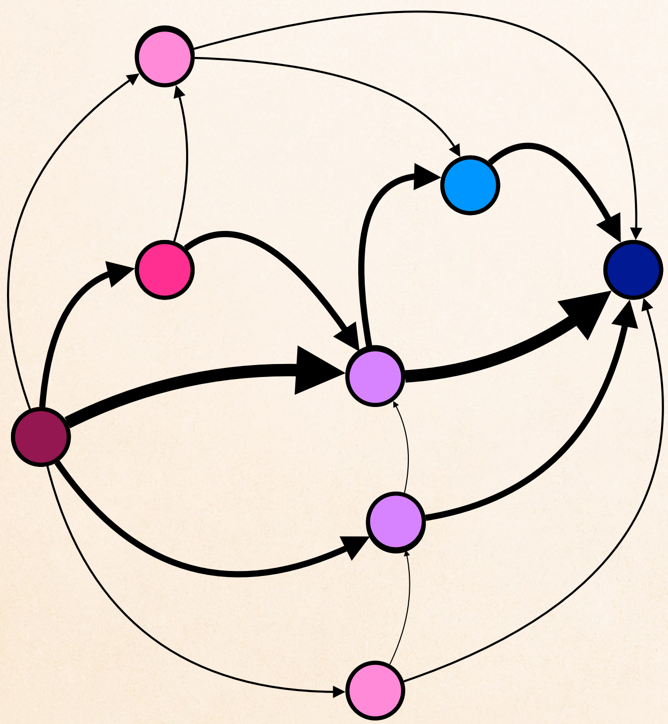
Continuation to finite temperature

of the eigenvalue
responsible for the relaxation process
from the icosahedral funnel
to Marks decahedron funnel

EIGENCURRENT $F_{ij}^k := \pi_i L_{ij} e^{-\lambda_k t}[(\phi_k)_i - (\phi_k)_j]$

(for time-reversible continuous-time Markov chains)

F_{ij}^k = the net average number of transitions along the edge i → j per unit time at time t in the relaxation process from the initial distribution $\pi + \psi_k = \pi + P\phi_k$

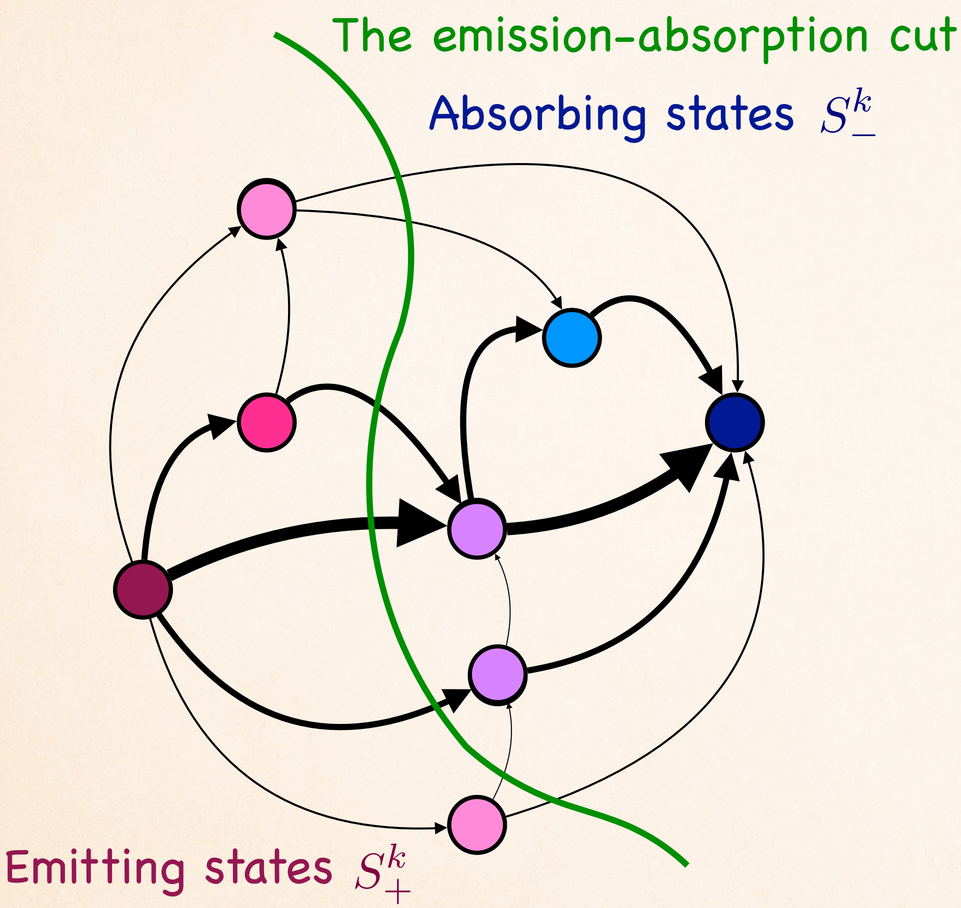


The Fokker-Planck equation in terms of eigencurrents

$$\frac{dp_i}{dt} = -\sum_{k=0}^{n-1} c_k \sum_{j\neq i} F_{ij}^k$$

$$\sum_{j\neq i} F_{ij}^k = e^{-\lambda_k t}\lambda_k \pi_k \phi_i^k$$

The emission-absorption cut



Consider the total eigencurrent **F**^{k} through the vertex i

$$\sum_{j \neq i} F_{ij}^k = \boxed{e^{-\lambda_k t} \lambda_k \pi_k} \boxed{\phi_i^k}$$

always > 0 any sign

$$S = S_+^k \cup S_-^k$$

$$S_+^k := \{ i \in S \ : \ (\phi_k)_i \geq 0 \}$$

$$S_-^k := \{ i \in S \ : \ (\phi_k)_i < 0 \}$$

Among all possible cuts, the eigencurrent F^k is maximal through the emission-absorption cut

CONTINUATION OF EIGENPAIRS TO FINITE TEMPERATURE

- **Difficulties:** (1) eigenvalues are close to 0 and may cross; (2) the matrix is large with widely varying entries

- **Useful fact:** the eigenvectors of the symmetrized generator matrix are orthonormal

$$L_{sym} := P^{1/2} L P^{-1/2} \equiv P^{-1/2} Q P^{-1/2}$$

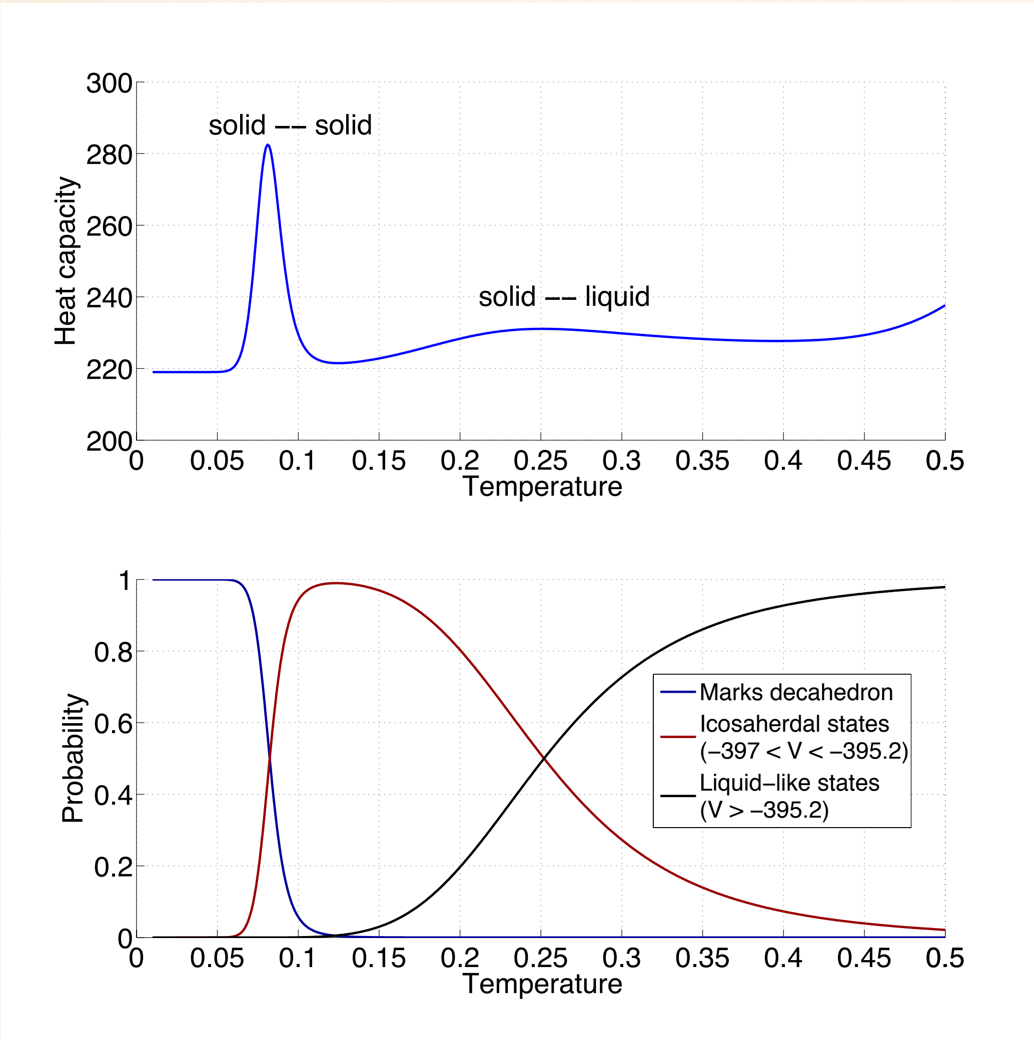
- **Rayleigh Quotient iteration** with initial approximation

$$(\psi_k^0)_i = \begin{cases} \sqrt{\pi_i}, & i \in S_k \\ 0, & i \notin S_k \end{cases}$$

- **Precaution:** check whether the corresponding eigencurrent is largely emitted at the sink $\mathbf{s_k^*}$ and largely absorbed at the sink $\mathbf{t_k^*}$

Difficulties with Lennard-Jones-75

$$c_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T}\left(\frac{\sum E_i e^{-E_i/T}/k_i}{\sum e^{-E_i/T}/k_i} \right)$$



Marks decahedron - icosahedral states solid - solid transition: T = 0.08

Icosahedral - liquid-like states transition: T = 0.25

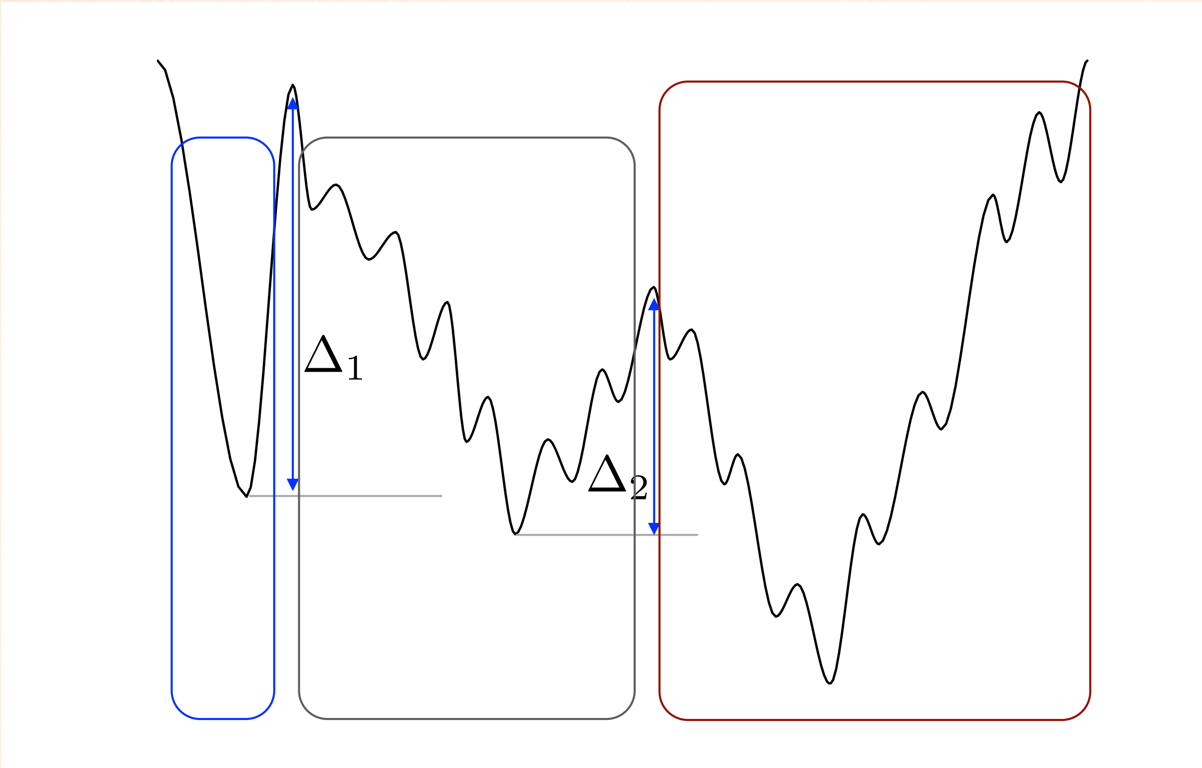
The range of temperatures to which we would like to continue λ_{4395} :

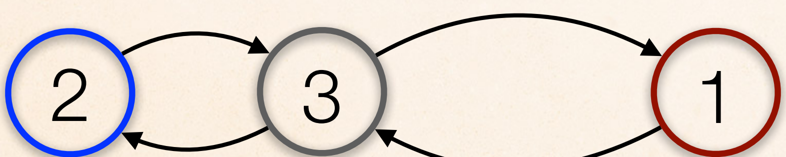
$$0.05 \leq T \leq 0.25$$

For T < 0.17, the matrix is badly scaled, and the results are inaccurate or NaN

For T ≥ 0.17, convergence to a wrong eigenpair takes place

Remedy 1: lumping





The lumped network

Pick $\Delta_{\min}$. Here $\Delta_{\min} = \Delta_2$

Lump the quasi-invariant sets with $\Delta_k < \Delta_{\min}$

Re-calculate pairwise rates

$$\tilde{L}_{kl} = \sum_{i \in S_k, j \in S_l} L_{ij} \frac{\pi_i}{\sum_{i' \in S_k} \pi_{i'}}$$

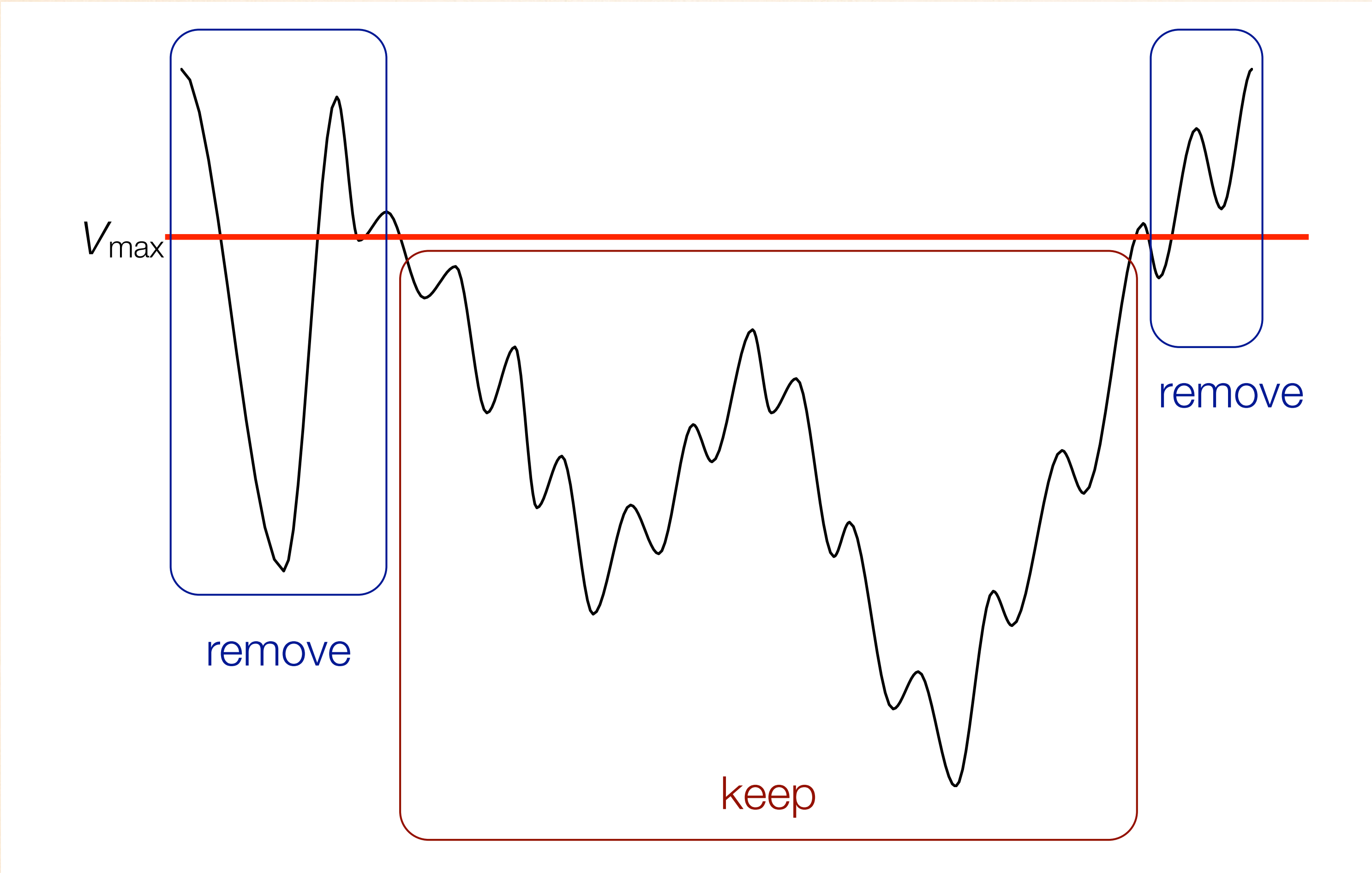
The resulting generator matrix $\tilde{L}$ is smaller,
the largest entries of L are gone

$$A_{ki} = \begin{cases} \frac{\pi_i}{\sum_{i' \in S_k} \pi_{i'}}, & i \in S_k \\ 0, & \text{otherwise} \end{cases}$$

$$B_{jl} = \begin{cases} 1, & j \in S_l \\ 0, & \text{otherwise} \end{cases}$$

$$\boxed{\tilde{L}_{N\times N}} = \boxed{A_{N\times n}} \boxed{L_{n\times n}} \boxed{B_{n\times N}}$$

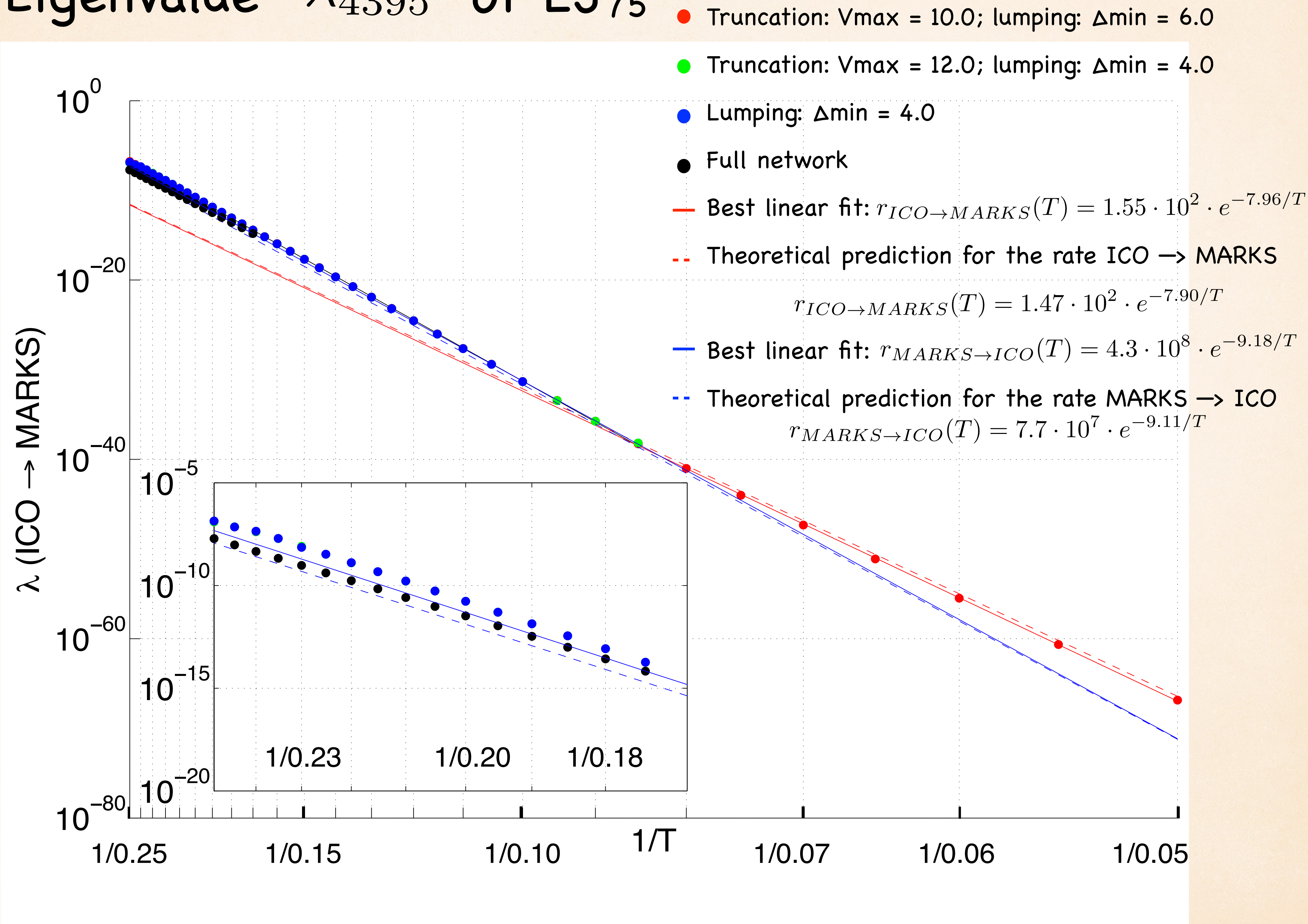
Remedy 2: truncation



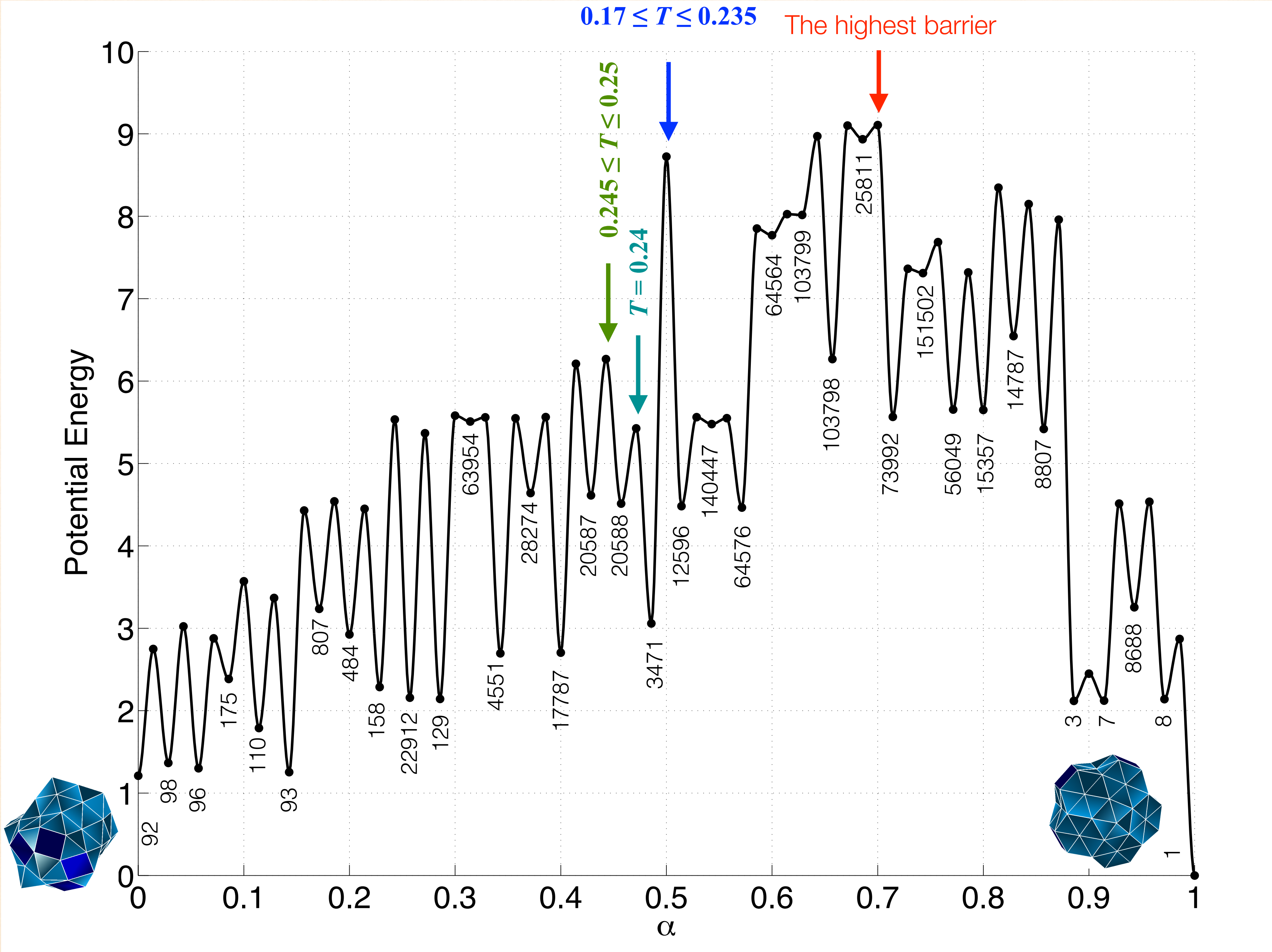
Pick V_{max}, remove all states separated from the global minimum by a barrier exceeding V_{max}

The resulting network is smaller, the components that used to be nearly transient or make it nearly reducible are removed

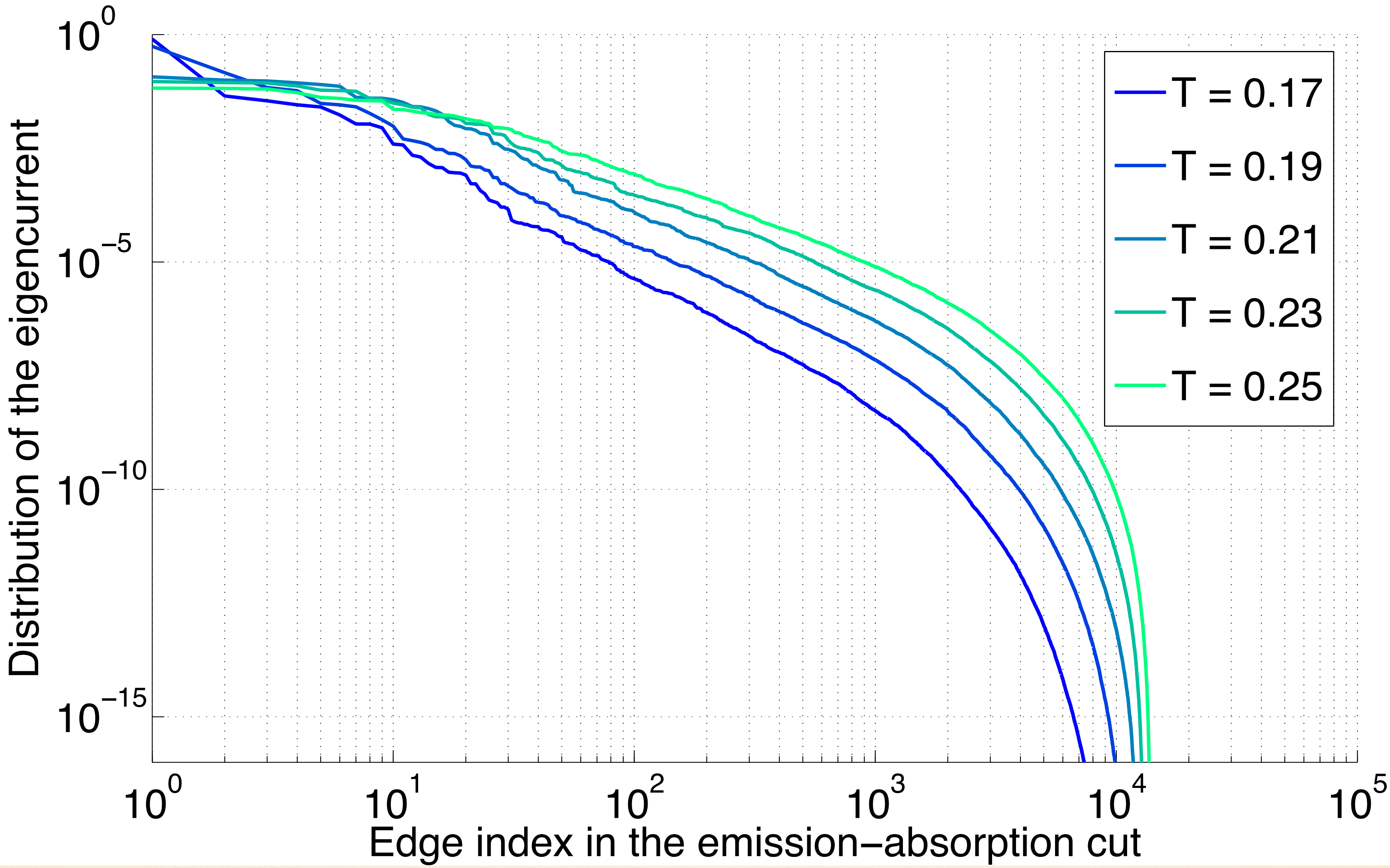
Eigenvalue λ_{4395} of LJ_{75}



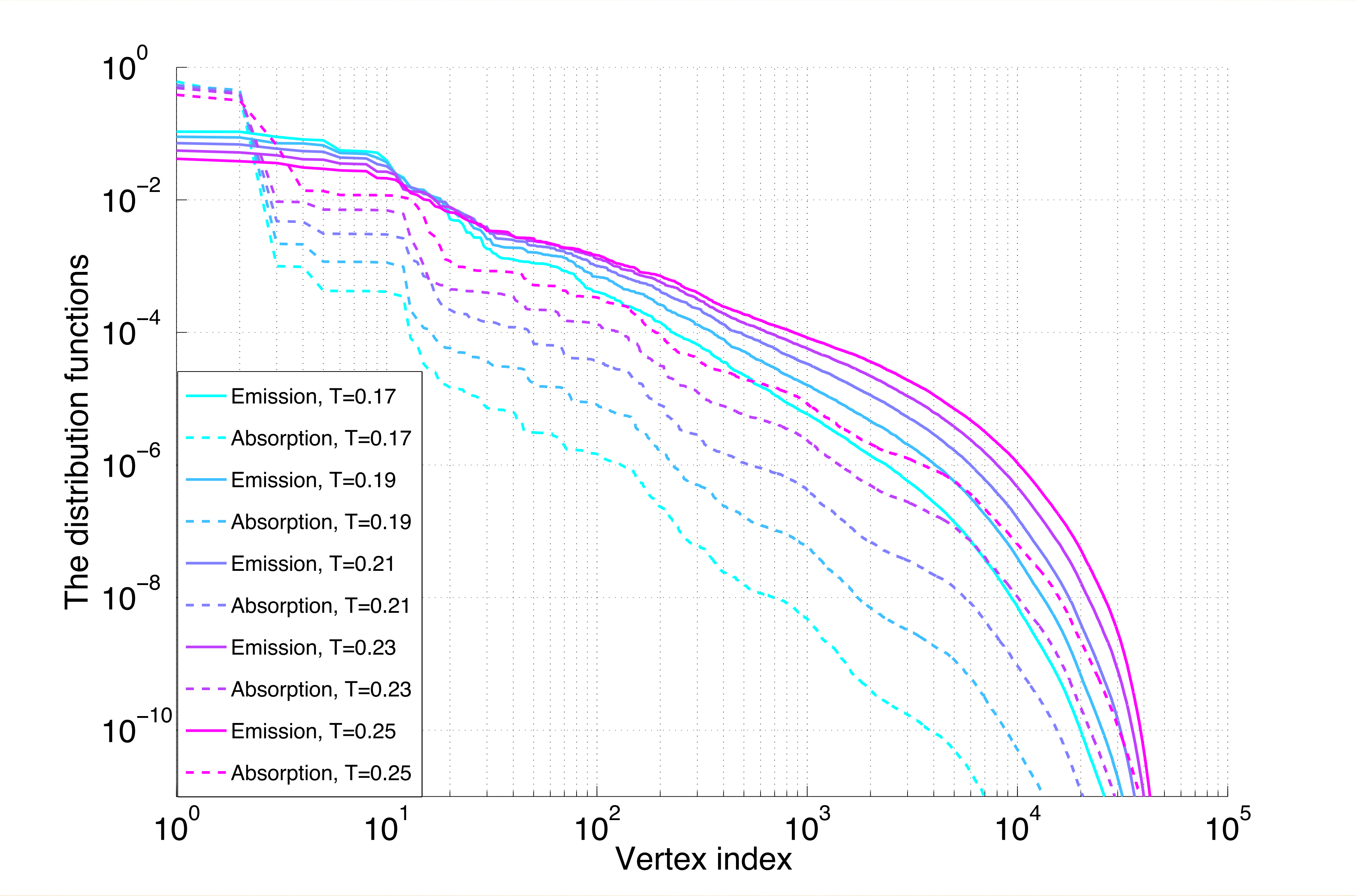
The emission-absorption cut: location



Eigencurrent distribution in the emission-absorption cut



Emission-absorption distribution



VAN DE WAAL'S HYPOTHESIS

Mass spectrography by electron or X-ray diffraction (since 1980s)

Results: clusters with < ~1500 atoms have icosahedral packing;
larger clusters have FCC packing

Van de Waal, PRL, 1996

No Evidence for Size-Dependent Icosahedral —> FCC Structural Transition in Rare-Gas Clusters

Faulty face-centered cubic layers grow on icosahedral core

Experimental confirmation:

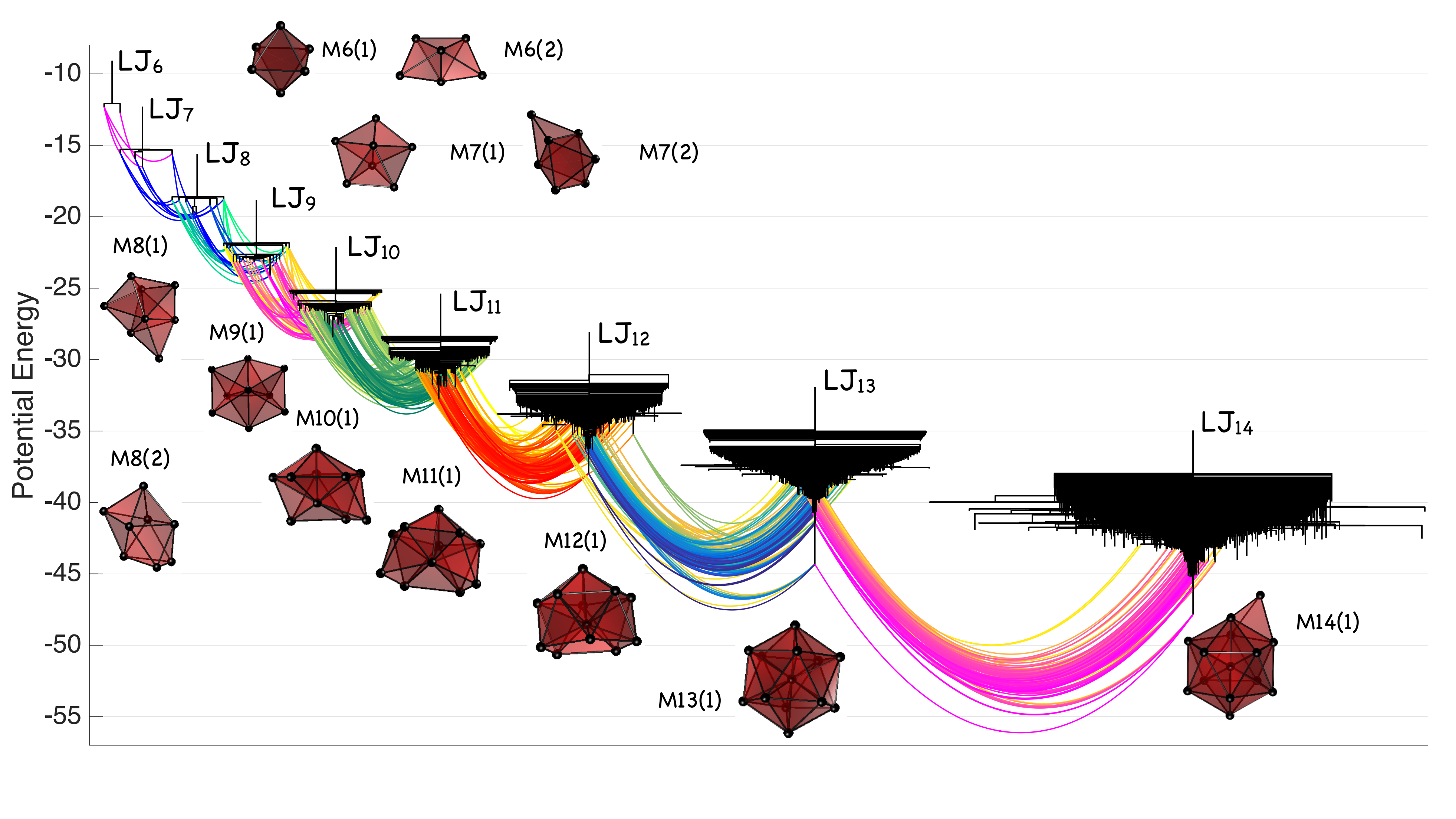
Kovalenko, Solnyshkin, Verkhovtseva, Low Temp Phys, 2000

On the mechanism of transformation of icosahedral rare-gas clusters into FCC aggregations

The experimental results correlate with the calculation if it is assumed that the clusters have a face-centered cubic structure with a constant number of intersecting stacking faults.

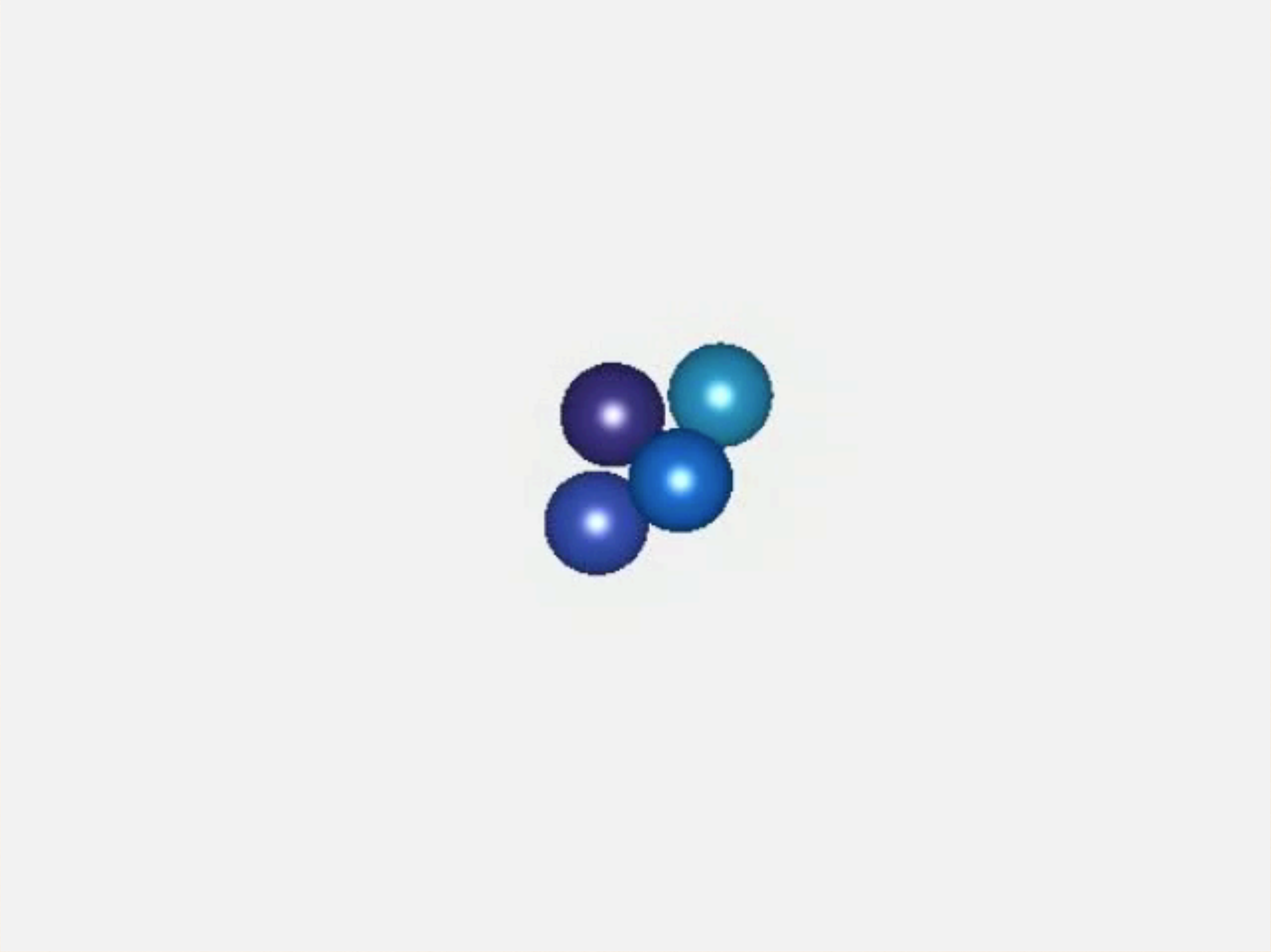
LJ6-14 AGGREGATION/DEFORMATION NETWORK

Y. Forman, S. Sousa and M. Cameron (REU 2016)



AGGREGATION OF LENNARD-JONES PARTICLES

Movie
by
Y. Forman

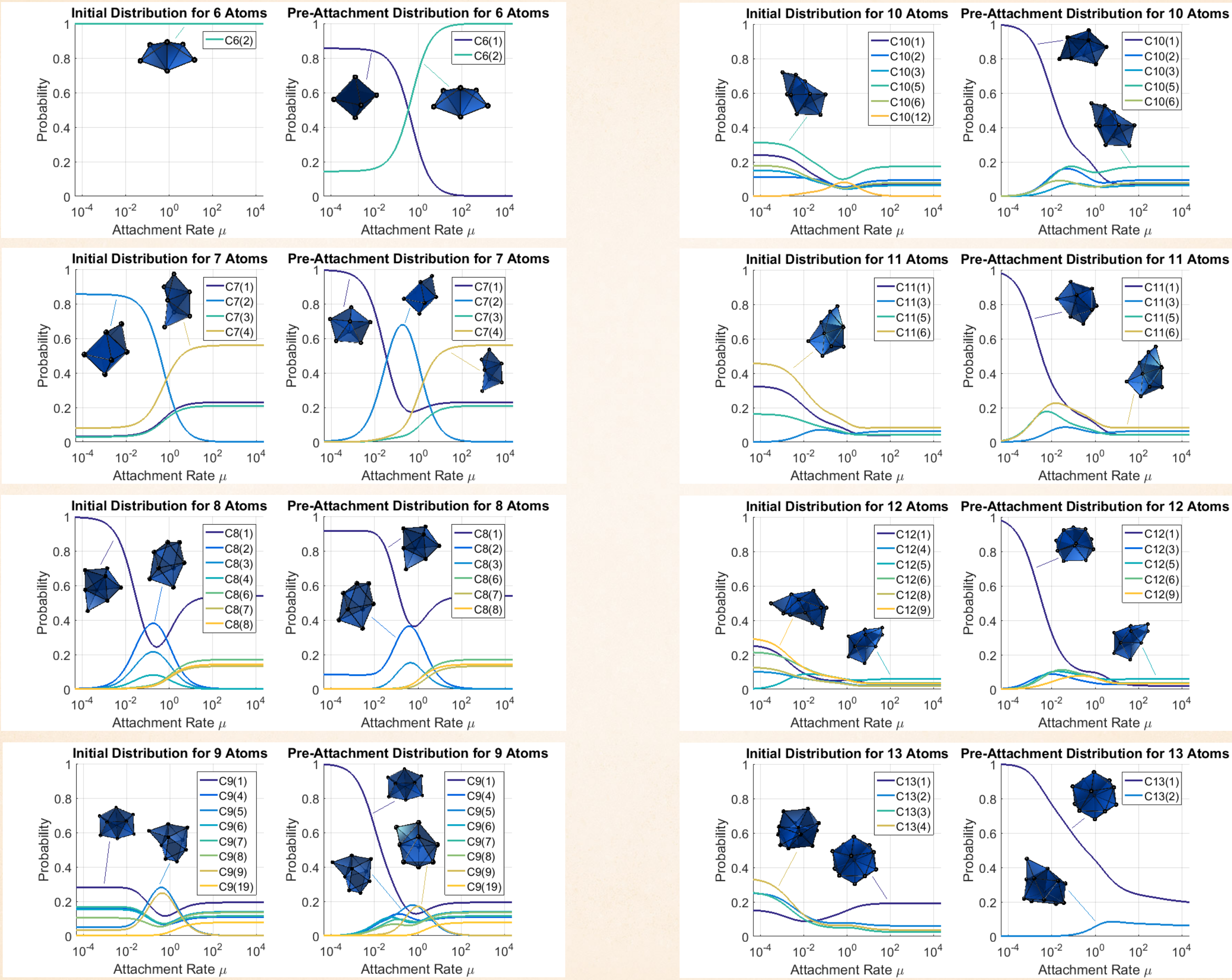


ANALYSIS OF AGGREGATION/DEFORMATION LJ NETWORK

Y. Forman

- In LJ_n, probability distribution evolves according to: $\frac{dp}{dt} = pL$
- Eigendecomposition of L: $L = \Phi\Lambda\Psi$
- Initial distribution: $p_{init} = \pi + \sum_{k=1}^{N-1} c_k \psi_k$, where $c_k = p(0)\phi_k$
- Attachment time has pdf: $f_T(t) = \mu e^{-\mu t}$
- Preattachment distribution:

$$p_{preatt} = \int_0^\infty p(t) f_T(t) dt = \pi + \sum_{k=1}^{N-1} c_k \frac{\mu}{\mu + \lambda_k} \psi_k$$


Initial Distribution for 6 Atoms
C6(2)
Pre-Attachment Distribution for 6 Atoms
C6(1)
C6(2)
Initial Distribution for 10 Atoms
C10(1)
C10(2)
C10(3)
C10(5)
C10(6)
C10(12)
Pre-Attachment Distribution for 10 Atoms
C10(1)
C10(2)
C10(3)
C10(5)
C10(6)
Initial Distribution for 7 Atoms
C7(1)
C7(2)
C7(3)
C7(4)
Pre-Attachment Distribution for 7 Atoms
C7(1)
C7(2)
C7(3)
C7(4)
Initial Distribution for 11 Atoms
C11(1)
C11(3)
C11(5)
C11(6)
Pre-Attachment Distribution for 11 Atoms
C11(1)
C11(3)
C11(5)
C11(6)
Initial Distribution for 8 Atoms
C8(1)
C8(2)
C8(3)
C8(4)
C8(6)
C8(7)
C8(8)
Pre-Attachment Distribution for 8 Atoms
C8(1)
C8(2)
C8(3)
C8(6)
C8(7)
C8(8)
Initial Distribution for 12 Atoms
C12(1)
C12(4)
C12(5)
C12(6)
C12(8)
C12(9)
Pre-Attachment Distribution for 12 Atoms
C12(1)
C12(3)
C12(5)
C12(6)
C12(9)
Initial Distribution for 9 Atoms
C9(1)
C9(4)
C9(5)
C9(6)
C9(7)
C9(8)
C9(9)
C9(19)
Pre-Attachment Distribution for 9 Atoms
C9(1)
C9(4)
C9(5)
C9(6)
C9(7)
C9(8)
C9(9)
C9(19)
Initial Distribution for 13 Atoms
C13(1)
C13(2)
C13(3)
C13(4)
Pre-Attachment Distribution for 13 Atoms
C13(1)
C13(2)
Probability
Attachment Rate μ

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LJ75

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Theory

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Tingyue Gan and Maria Cameron, J. Nonlinear Science, Vol. 27, 3, (June 2017), pp. 927-972 ArXiv: 1607.00078