MODELING THE DYNAMICS OF INTERACTING PARTICLES BY MEANS OF STOCHASTIC NETWORKS

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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

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: \( \text{Ar, Kr, Xe, Rn} \)

Often used for modeling interaction of other spherical particles.

Large datasets are available thanks to Wales’ group (Cambridge, UK).
EXPERIMENTAL WORKS: MASS SPECTRA

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 $I_h$, $|I_h|=120$

$LJ_{13}$

$LJ_{55}$

$LJ_{147}$
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
Map energy landscape onto a continuous-time Markov chain (stochastic network)

Transition rate from minimum $i$ to minimum $j$ via saddle $s$ on $\text{LJ}_7$

$$r_{i \rightarrow s \rightarrow j} \approx \frac{O_i \omega_{ij}}{O_s} \frac{\sqrt{\det H_i}}{2\pi \sqrt{\det H_s}} e^{-(V_i - V_j)/(k_B T)}$$
BUILDING LENNARD-JONES NETWORKS

- Find the set of local energy minima.
- Find the set of Morse index one saddles.
- Calculate transition rate along each arc.

\[ L_{i \rightarrow j} = \sum_s \frac{O_i \, \omega_{ij}}{O_s \, 2\pi} \sqrt{\frac{\det H_i}{\det H_s}} \, e^{-\frac{(V_i - V_s)}{(k_BT)}} \]
### STATS FOR LJ NETWORKS

<table>
<thead>
<tr>
<th>Network</th>
<th>Vertices</th>
<th>Arches</th>
<th>States</th>
<th>Arches</th>
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<tr>
<td>LJ6</td>
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<td>169</td>
<td>1028</td>
<td>169523</td>
<td>441016</td>
</tr>
</tbody>
</table>

**Red line:** least squares fit

\[ 4 \cdot 10^{-3} e^{0.97N} \]

Wales’s group, Cambridge University, UK
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 \( L \):

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

Right eigenvectors

Eigenvalues

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

Left eigenvectors

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 \( \pi \) decaying uniformly with rate \( \lambda_k \) across the network
**INTERPRETATION OF LEFT AND RIGHT EIGENVECTORS IN TIME-REVERSIBLE NETWORKS**

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

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

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 \( \lambda_k \)

and \( \phi_k \) 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 ($n \sim 100000$), entries of $L$ range by tens of orders of magnitude, $L$ has no special structure

**Advantage:** $L$ has entries of the form

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

$$\epsilon = k_B T = \text{small parameter}$$

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

Wentzell, 1972
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 \( \epsilon \)

\[ \lambda_k = A_k \exp(-\Delta_k/T) \]

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

\[ V^{(k)} = \sum_{(i \to j) \in g^*_k} U_{ij} \]

\[ A_k = \frac{\prod_{i \to j \in g^*_k} U_{ij}}{\prod_{i \to j \in g^*_{k+1}} U_{ij}} + o(1) \]
NESTED PROPERTIES OF OPTIMAL W-GRAPHS (GAN AND C. 2016)

- \{\text{The set of sinks of } g_k^* \} \subset \{\text{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 \( S \setminus S_k \) in \( g_k^* \) and \( g_{k+1}^* \) coincide.
- In \( g_k^* \), there is a single arc from \( S_k \) to \( S \setminus S_k \)
Approaches to the study of Markov processes with rates $L_{ij} = a_{ij} e^{-U_{ij}/\epsilon}$ at time scales from 0 to $\infty$

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

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 = functions $t(\epsilon)$

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

For brevity, we write

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

if

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

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

\[
\begin{align*}
c & \rightarrow a : \quad U = 1 \\
b & \rightarrow c : \quad U = 3 \\
a & \rightarrow b : \quad U = 4 \\
d & \rightarrow c : \quad U = 10
\end{align*}
\]

The numbers next to arcs \(i \rightarrow j\) are \(U_{ij}\)
On the time scale

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

each state of the Markov chain is absorbing

\[
\begin{align*}
  c \to a : & \quad U = 1 \\
  b \to c : & \quad U = 3 \\
  a \to b : & \quad U = 4 \\
  d \to c : & \quad U = 10 \\
\end{align*}
\]

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 $\gamma_i$

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

$\gamma_1 = 1$

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

$a_{ca}e^{-\gamma_1/\epsilon} = a_{ca}e^{-U_{ca}/\epsilon} = a_{ca}e^{-1/\epsilon}$
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
\[ a_{bc} e^{-\gamma_2/\epsilon} = a_{bc} e^{-U_{bc}/\epsilon} = a_{ca} e^{-3/\epsilon} \]
$d \rightarrow c: \quad U = 10$

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

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\}:

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

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

The exit rate from cycle \{a, b, c\} via arc \(c \rightarrow d\) :

\[
\tilde{L}_{cd} = \pi_{abc}(c)L_{cd} = \frac{\alpha_{cd}\alpha_{ab}}{\alpha_{ca}} e^{-5/\epsilon}
\]
In general, if a cycle is encountered:

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

The invariant distribution in the cycle

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

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:**

$$\alpha_{ij} \rightarrow \frac{\alpha_m(M) \alpha_{ij}}{\alpha_{12}}$$

$$U_{ij} \rightarrow U_{ij} + (U_m(M) - U_{12})$$

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

\[ d \to c : \ U = 10 \]

\[ \gamma_1 = 1 \]
\[ \gamma_2 = 3 \]
\[ \gamma_3 = 4 \]
\[ \gamma_4 = 5 \]

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.

\[ T_4 = g_1^* \]
Remove the last min-arc

The set of critical time scales

\[ \begin{align*}
\gamma_1 &= 1 \\
\gamma_2 &= 3 \\
\gamma_3 &= 4 \\
\gamma_4 &= 5 \\
\gamma_5 &= 10
\end{align*} \]

On the time scale

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

all states are recurrent
Output:

\[
\begin{align*}
T_0 & \quad \gamma_1 = 1 \\
T_1 & \quad e^{1/\epsilon} \leq t < e^{3/\epsilon} \\
T_2 & \quad e^{3/\epsilon} \leq t < e^{4/\epsilon} \\
T_3 & \quad \gamma_3 = 4 \\
T_4 & \quad \gamma_4 = 5 \\
T_5 & \quad \gamma_5 = 10
\end{align*}
\]
Asymptotics for eigenvectors for **time-reversible** networks (under assumption that all optimal W-graphs are unique)

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

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

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

\[ \lambda_k = \frac{O_{s^*_k+1} \tilde{\nu}^{219}}{O_{p^*_kq^*_k} \tilde{\nu}^{218}} e^{-\Delta_k/T} \]

\[ k = 4395 \]

\[ \lambda_{4395} \approx 147.2 e^{-7.897/T}. \]

\[ |S_{4395}| = 92883 \]

\[ (p_{4395}^* \rightarrow q_{4395}^*) = (25811 \rightarrow 73992) \]
Asymptotic zero-temperature path (the MinMax path)

The lowest possible highest barrier
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)

\[ F_{ij}^k = \text{the net average number of transitions along the edge } i \rightarrow j \]

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

\[ \frac{d \rho_i}{dt} = -\sum_{k=0}^{n-1} c_k \sum_{j \neq i} F_{ij}^k \]

\[ \sum_{j \neq i} F_{ij}^k = e^{-\lambda_k t} \lambda_k \pi_k \phi_i^k \]
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 \( s_k^* \) and largely absorbed at the sink \( t_k^* \)
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: \(\lambda_{4395}:\)

\[ 0.05 \leq T \leq 0.25 \]

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

For \( T \geq 0.17, \) convergence to a wrong eigenpair takes place
Remedy 1: lumping

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

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

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

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

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

The lumped network

\[
\begin{bmatrix}
\tilde{L}_{N \times N} & = & A_{N \times n} & L_{n \times n} & B_{n \times N}
\end{bmatrix}
\]
Remedy 2: truncation

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

The resulting network is smaller, the components that used to be nearly transient or make it nearly reducible are removed.
Eigenvalue $\lambda_{4395}$ of $\text{LJ}_{75}$

- Truncation: $V_{\text{max}} = 10.0$; lumping: $\Delta_{\text{min}} = 6.0$
- Truncation: $V_{\text{max}} = 12.0$; lumping: $\Delta_{\text{min}} = 4.0$
- Lumping: $\Delta_{\text{min}} = 4.0$
- Full network

Best linear fit:
Theoretical prediction for the rate $\text{ICO} \rightarrow \text{MARKS}$

$$r_{\text{ICO} \rightarrow \text{MARKS}}(T) = 1.55 \cdot 10^2 \cdot e^{-7.96/T}$$

Best linear fit:
Theoretical prediction for the rate $\text{MARKS} \rightarrow \text{ICO}$

$$r_{\text{MARKS} \rightarrow \text{ICO}}(T) = 4.3 \cdot 10^8 \cdot e^{-9.18/T}$$
The emission-absorption cut: location

0.17 \leq T \leq 0.235

0.245 \leq T \leq 0.25

T = 0.24

The highest barrier

Potential Energy

α
Eigencurrent distribution in the emission-absorption cut
The distribution functions

Emission, $T=0.17$
Absorption, $T=0.17$
Emission, $T=0.19$
Absorption, $T=0.19$
Emission, $T=0.21$
Absorption, $T=0.21$
Emission, $T=0.23$
Absorption, $T=0.23$
Emission, $T=0.25$
Absorption, $T=0.25$
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
In $LJ_n$, probability distribution evolves according to: \[ \frac{dp}{dt} = pL \]

Eigendecomposition of $L$: \[ L = \Phi \Lambda \Psi \]

Initial distribution: \[ p_{init} = \pi + \sum_{k=1}^{N-1} c_k \psi_k, \text{ where } c_k = p(0) \phi_k \]

Attachment time has pdf: \[ f_T(t) = \mu e^{-\mu t} \]

Preacttachment distribution:

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