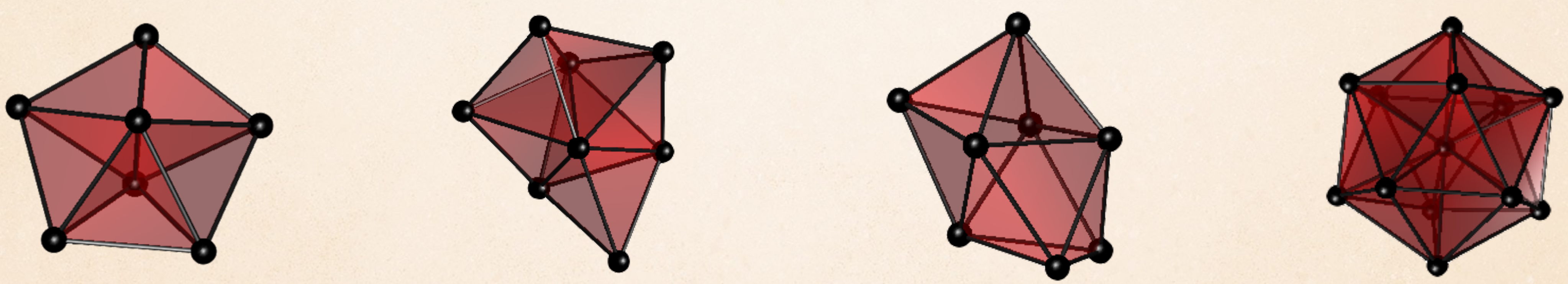
MAPS-REU 2016

MODELING AGGREGATION AND DYNAMICS OF INTERACTING PARTICLES VIA STOCHASTIC NETWORKS

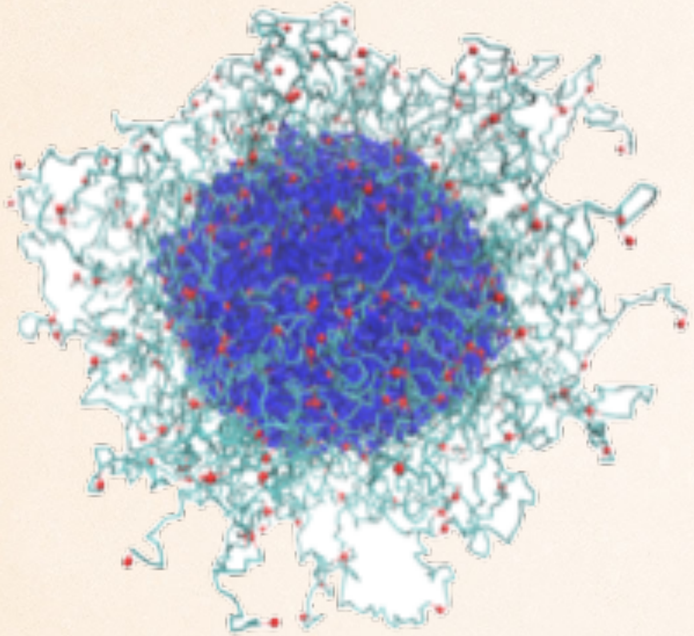
Maria Cameron

Joint work with Yakir Forman and S. Sousa Castellanos

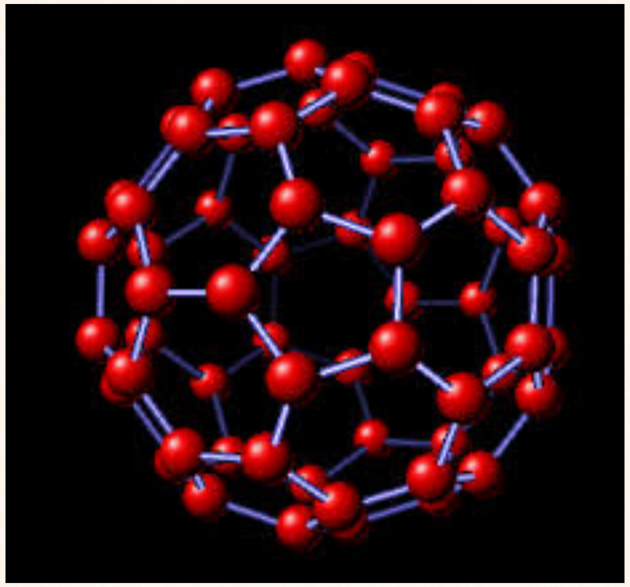


SIAM Dynamical Systems, Snowbird, UT, May 22, 2017

GOALS

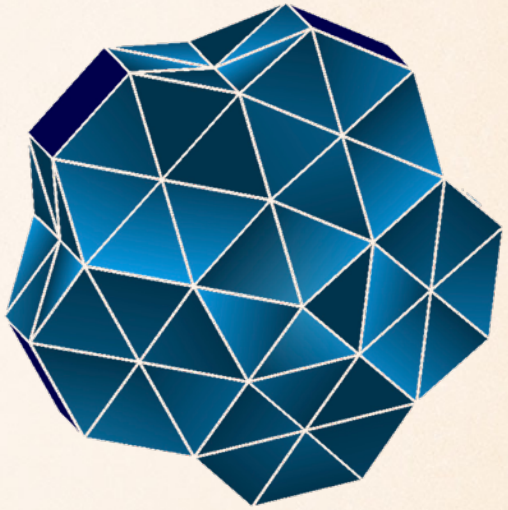


A core-shell microgel,
S. Maccarone et al,
Macromolecules 2016



A fullerene molecule

LJ_{55}
icosahedron



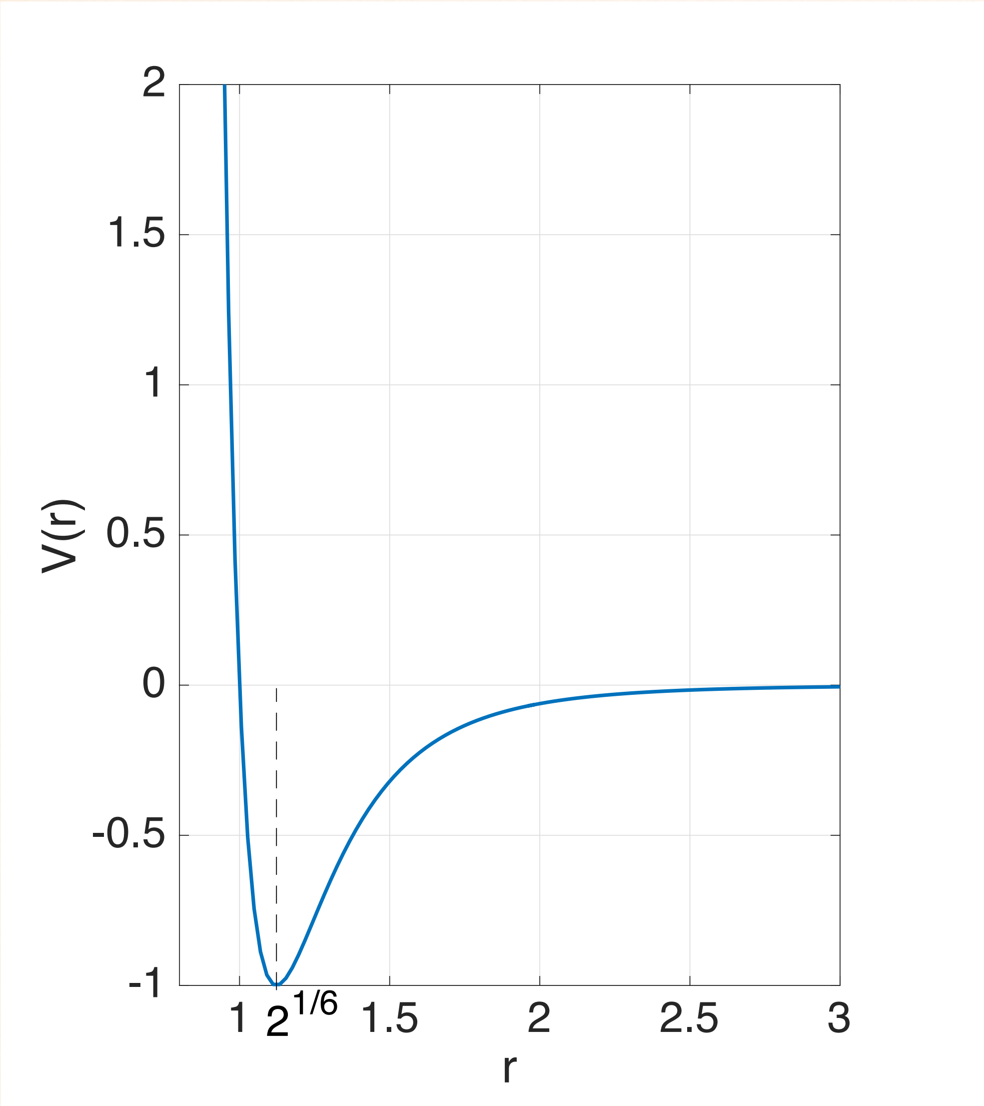
LJ_{75}
Marks decahedron

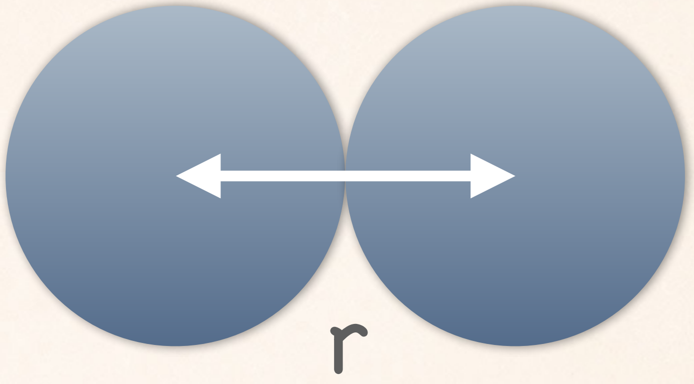
IMMEDIATE: Develop tools for the study of aggregation and dynamics of small clusters.

PERSPECTIVES: Extend to larger clusters. Understand crystal formation (check van de Waal's hypothesis). Design desired structures by self-assembly.

LENNARD-JONES PAIR POTENTIAL

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





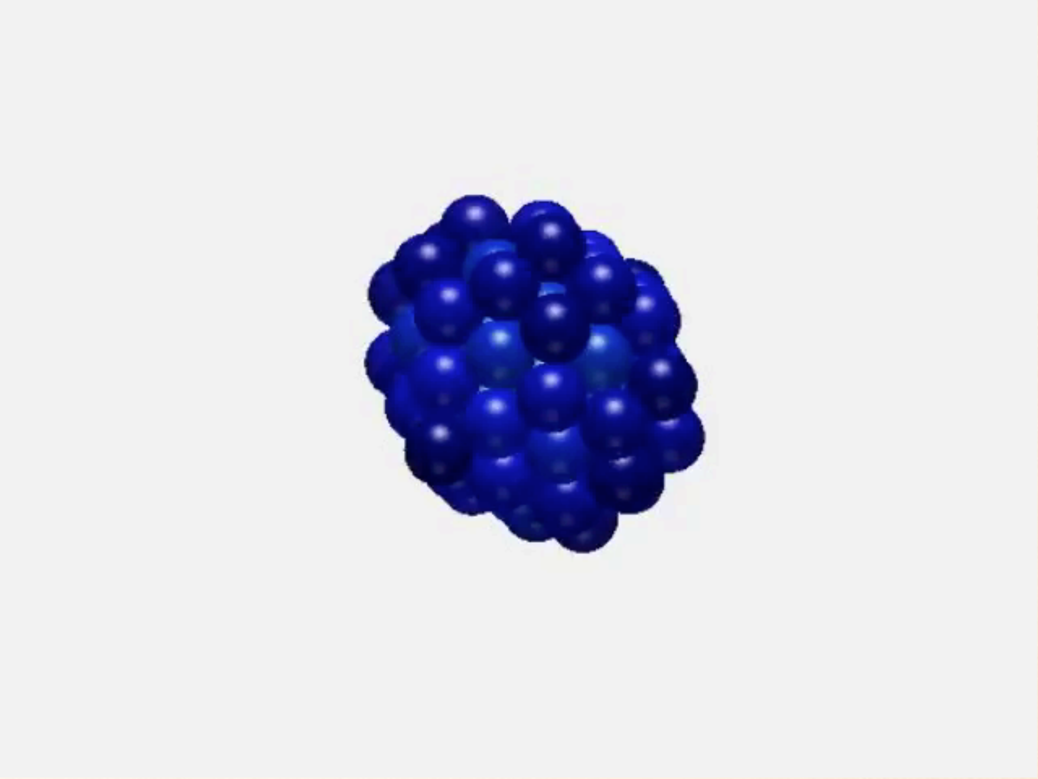
Adequate for rare gases:
Ar, Kr, Xe, Rn

Often used for modeling interaction of other spherical particles.

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

DIFFICULTIES IN MODELING THE DYNAMICS OF LENNARD-JONES 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

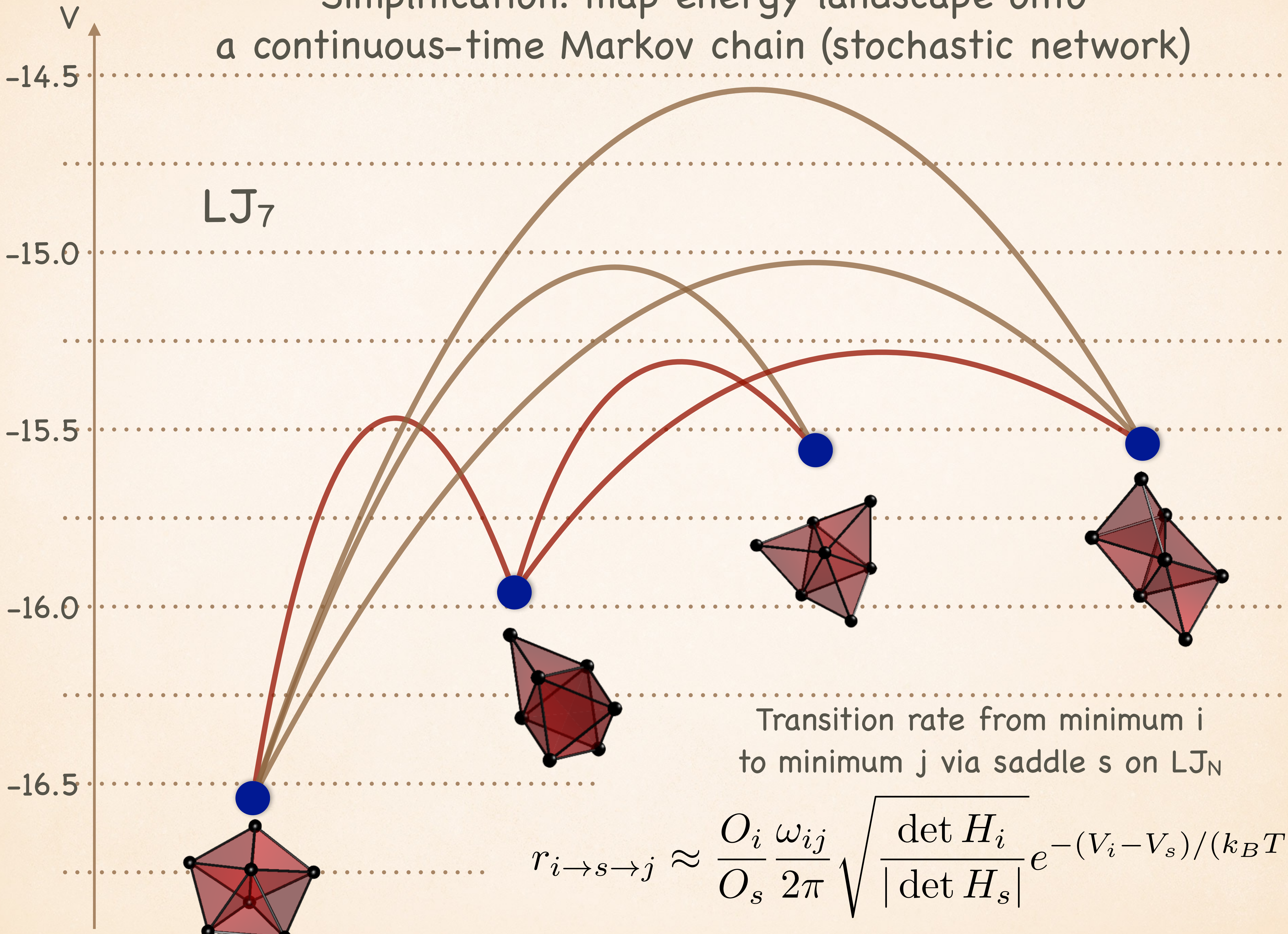


LJ_{75}

Success of full-space Monte Carlo approach

- Multiple structural transformations in LJ clusters, generic vs size-specific behavior, Mandelshtam and Frantsuzov, 2006
- Direct transition current sampling in LJ_{38}, Picciani, Athenes, Kurchan, Taileur, 2011

Simplification: 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

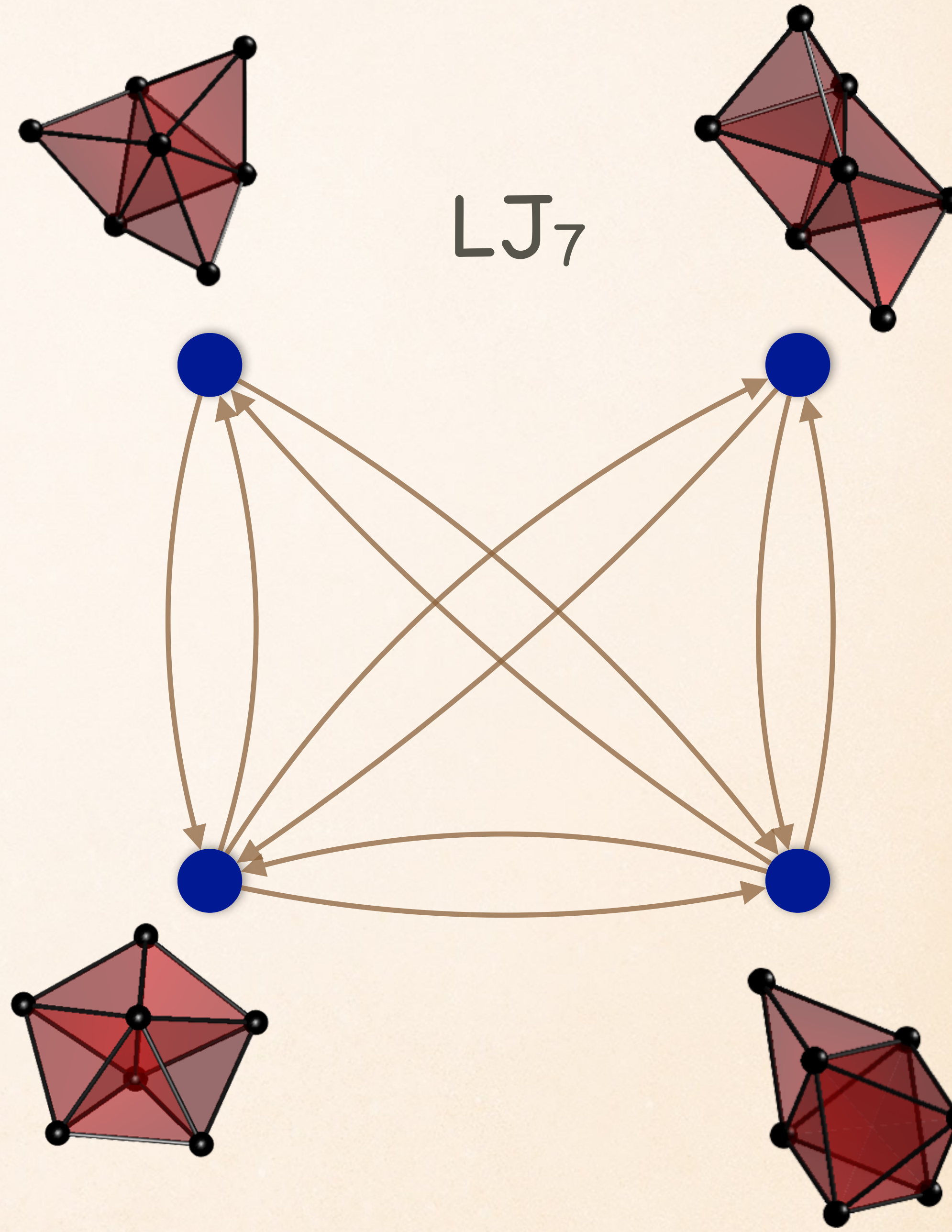
Vertices

- 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

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

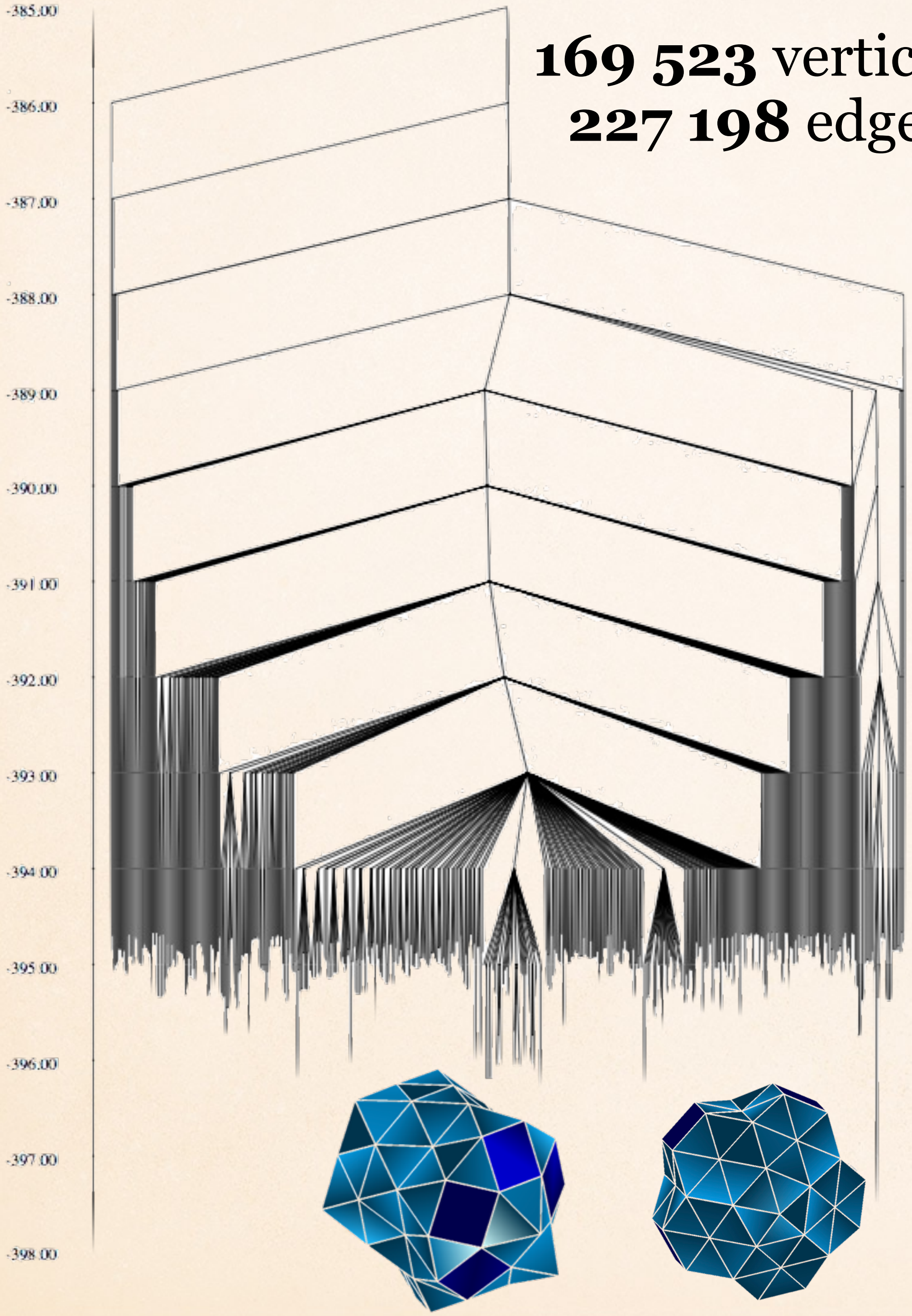


PREVIOUS WORK: ANALYSIS OF TRANSITIONS PROCESSES IN CLUSTERS WITH FIXED NUMBERS OF ATOMS MODELED VIA STOCHASTIC NETWORKS

- 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)

SPECTRAL ANALYSIS: SHARP ASYMPTOTIC ESTIMATES FOR EIGENVALUES AND EIGENVECTORS

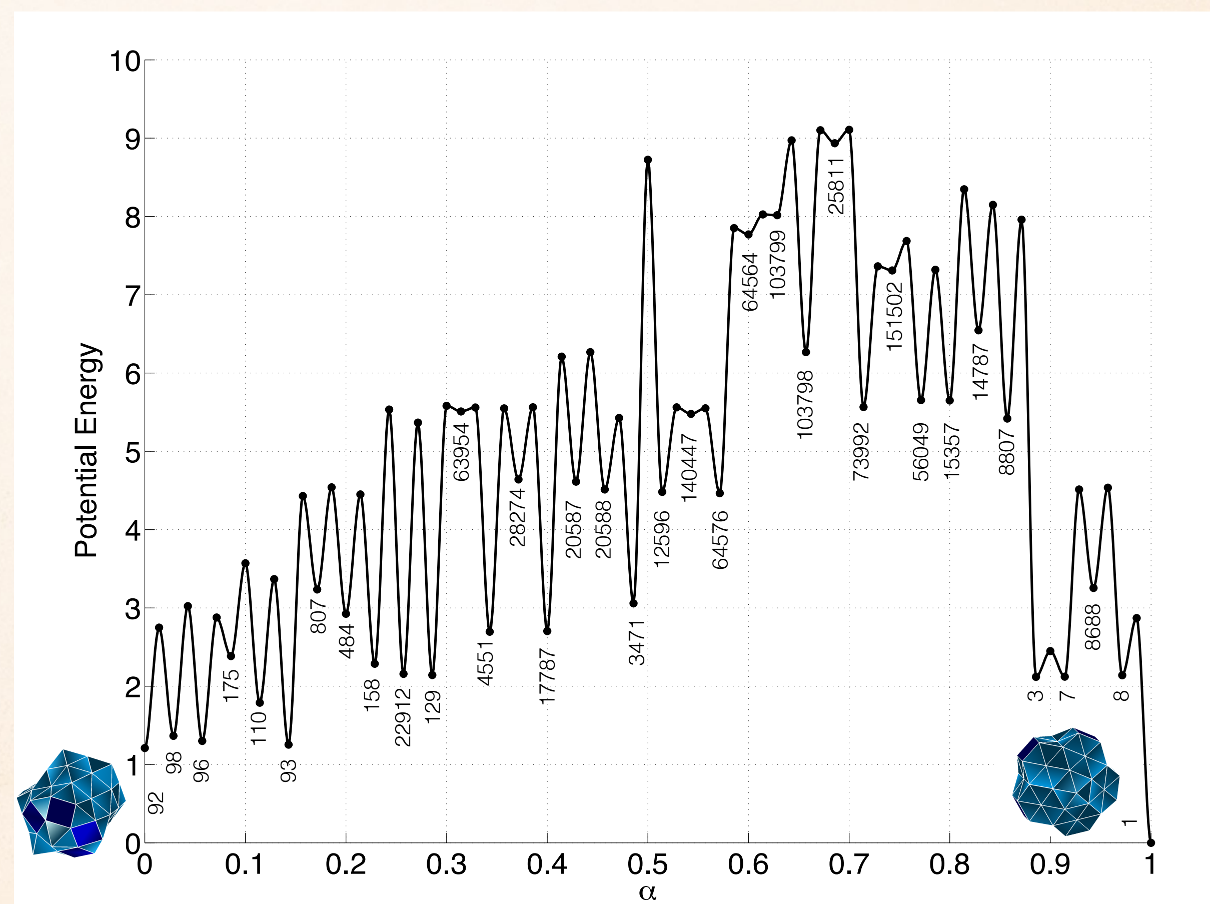
LJ_{75}



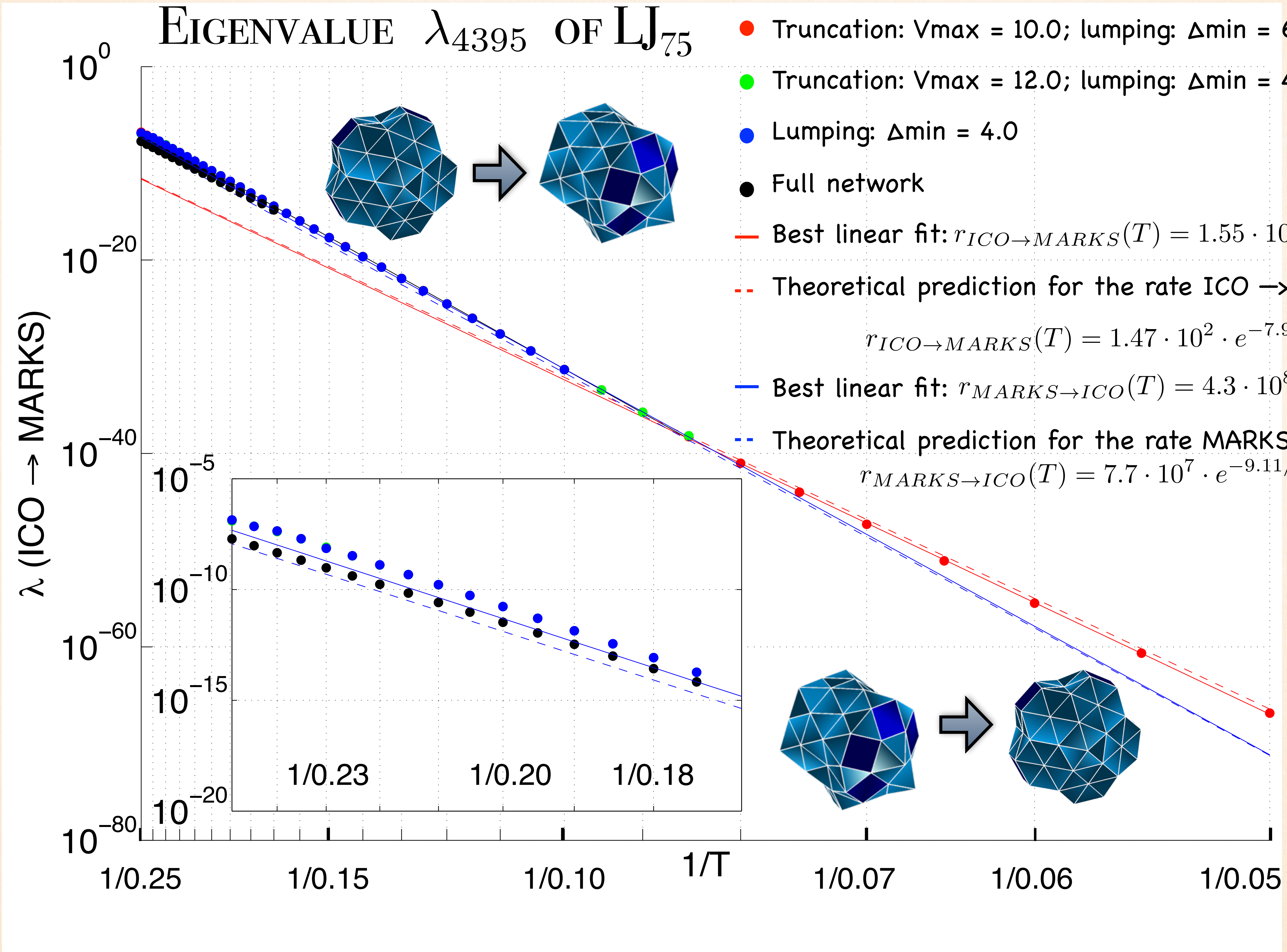
169 523 vertices,
227 198 edges

Tingyue Gan, AMSC, PhD 2017

A greedy/dynamical programing algorithm for asymptotic analysis of Markov chains with pairwise rates ~ $\exp(-U_{ij}/T)$



Finite Temperature Continuation



SHOCKING DISCOVERY: MASS SPECTRA

Harris, Kidwell, Northby, PRL 1984

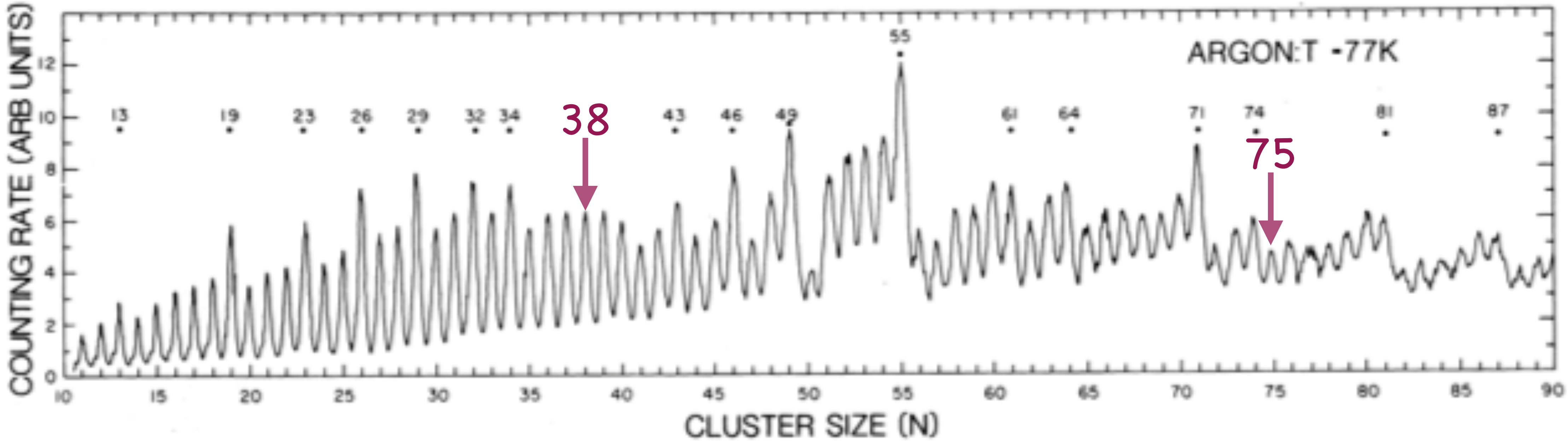
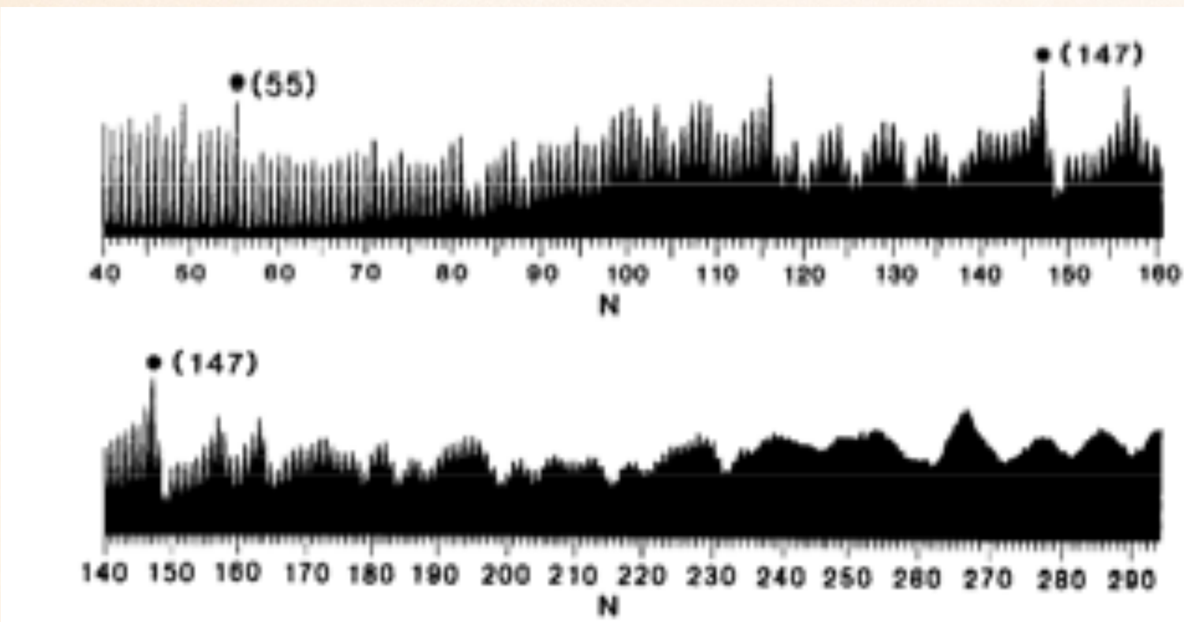
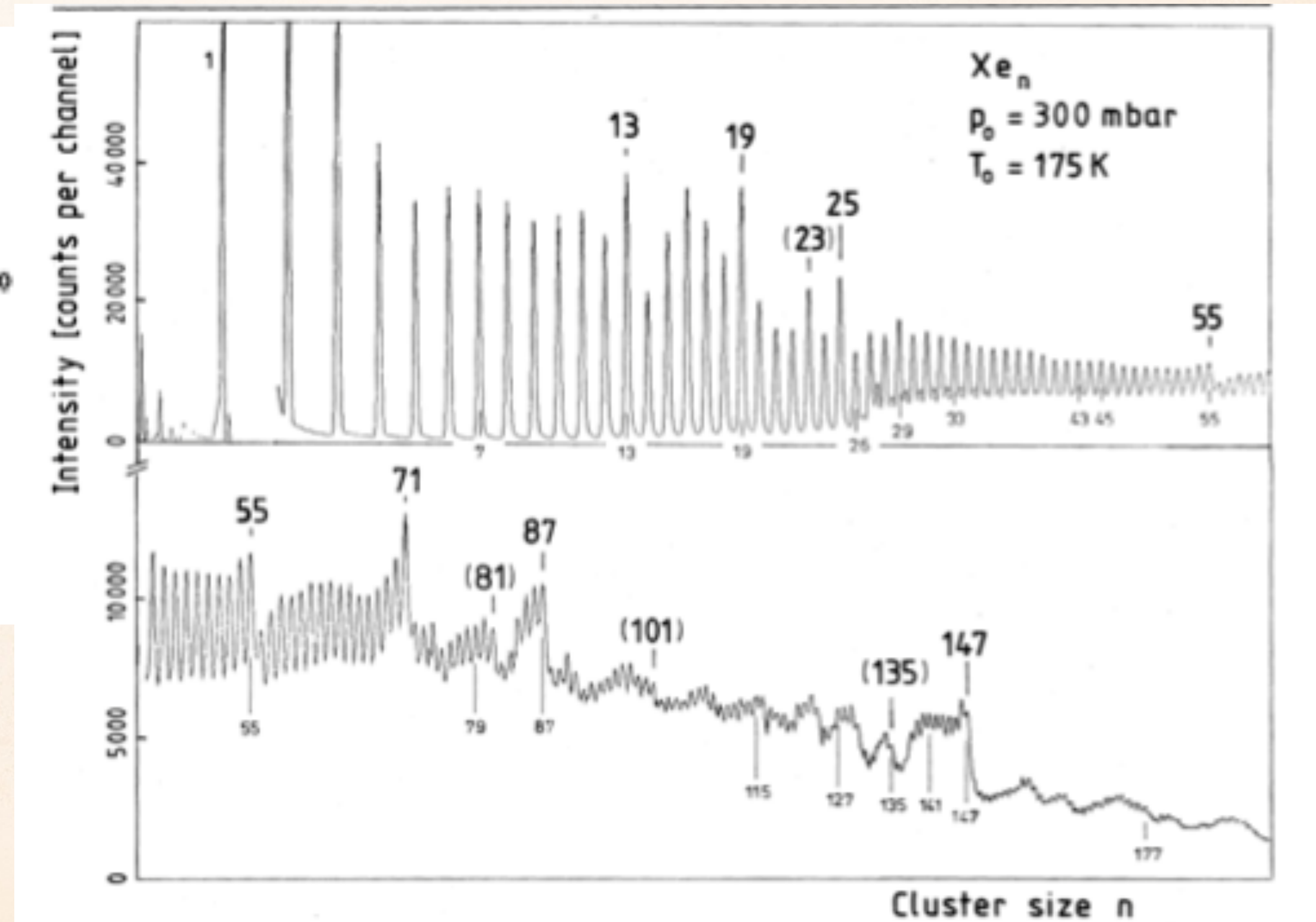


FIG. 1. Experimental mass spectrum for charged argon clusters. Intensity vs number of atoms in cluster.



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

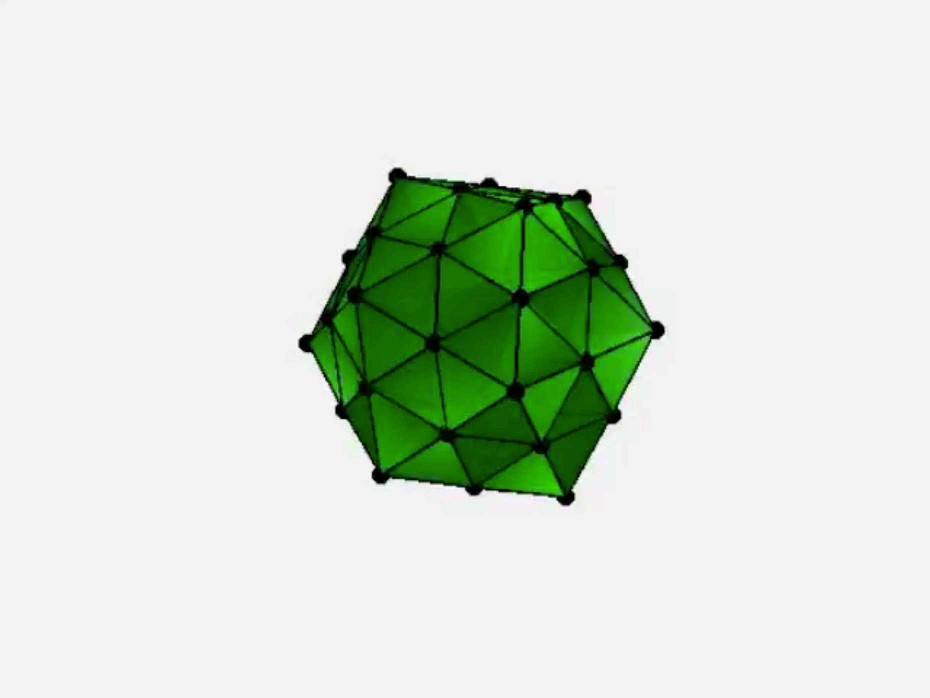
Echt, Sattler, Recknagel, PRL 1981



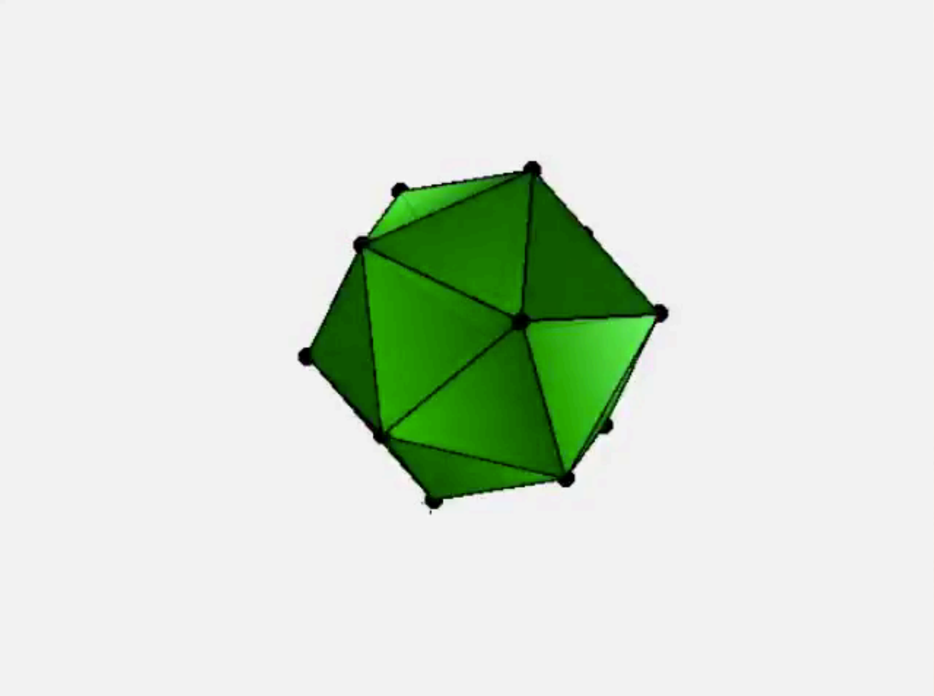
CONSISTENT SUBSEQUENCE OF PEAKS IN MASS SPECTRA: MAGIC NUMBERS

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

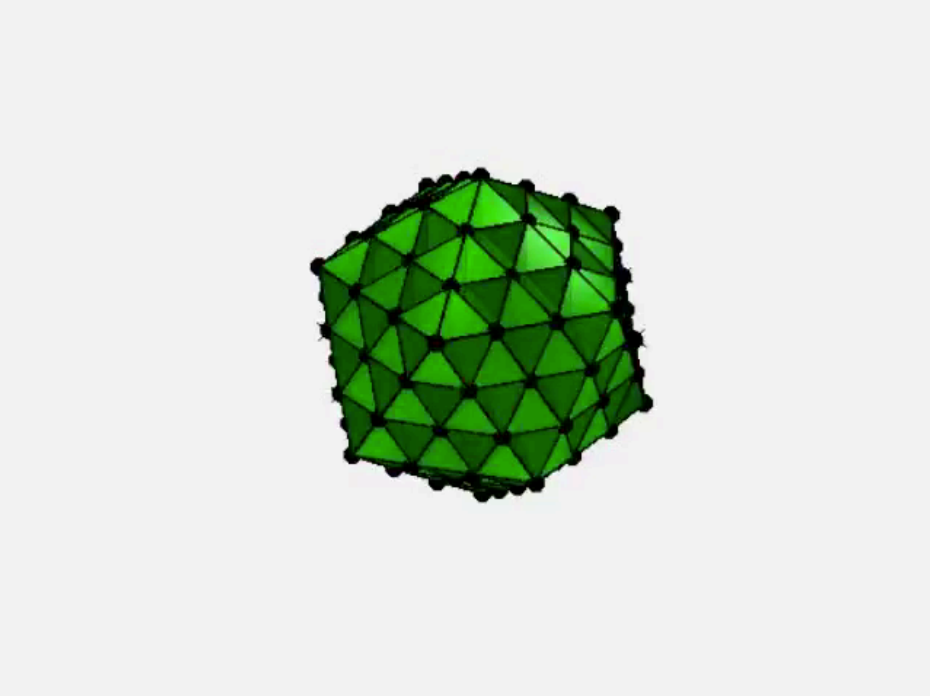
LJ_{55}



LJ_{13}



LJ_{147}



WHAT HAPPENED TO THESE HIGH SYMMETRY CONFIGURATIONS?

LJ_{38}

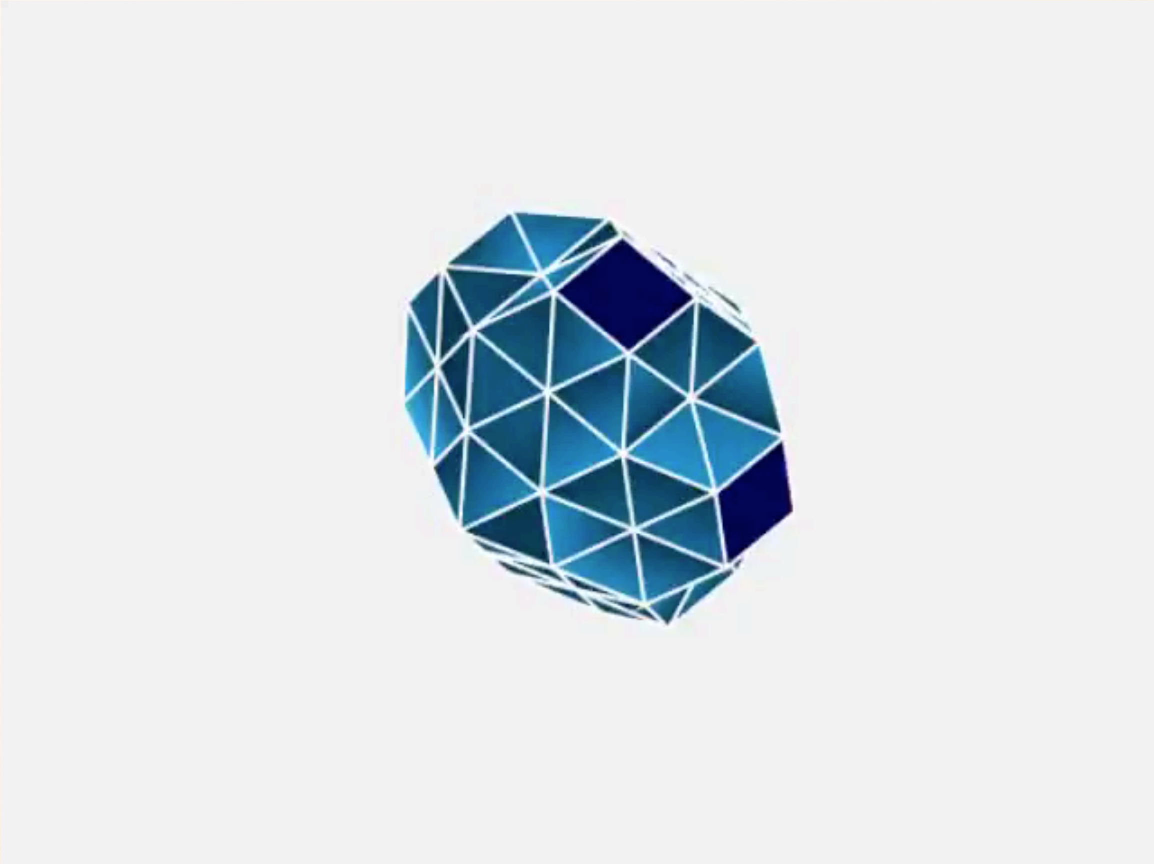
Truncated octahedron

Point group O_h, $|O_h|=48$

LJ_{75}

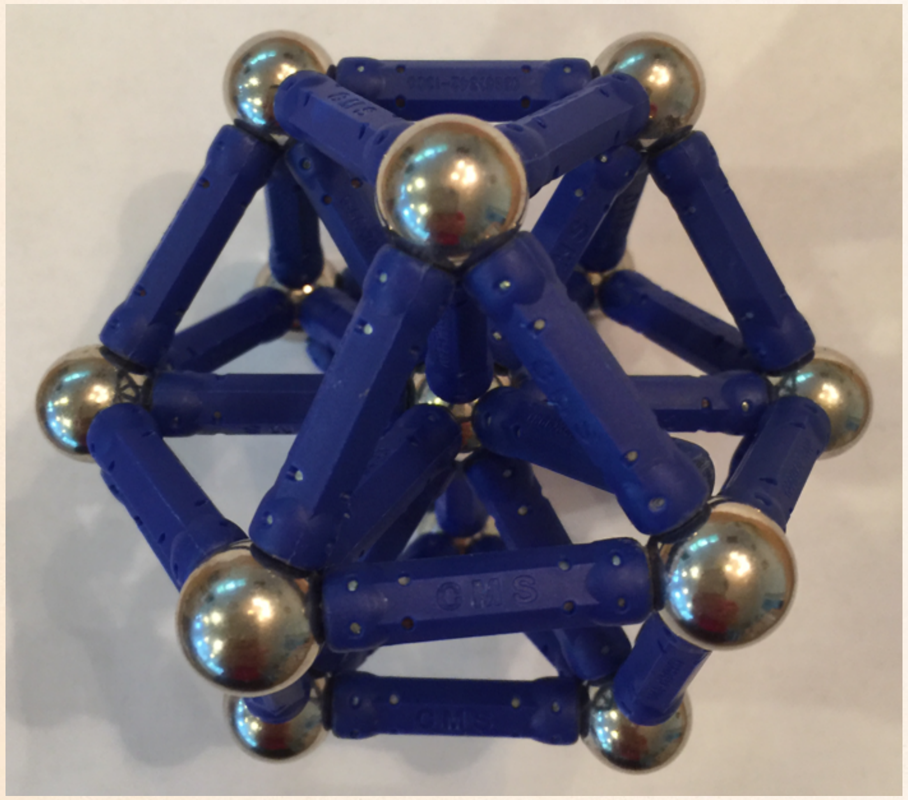
Marks decahedron

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

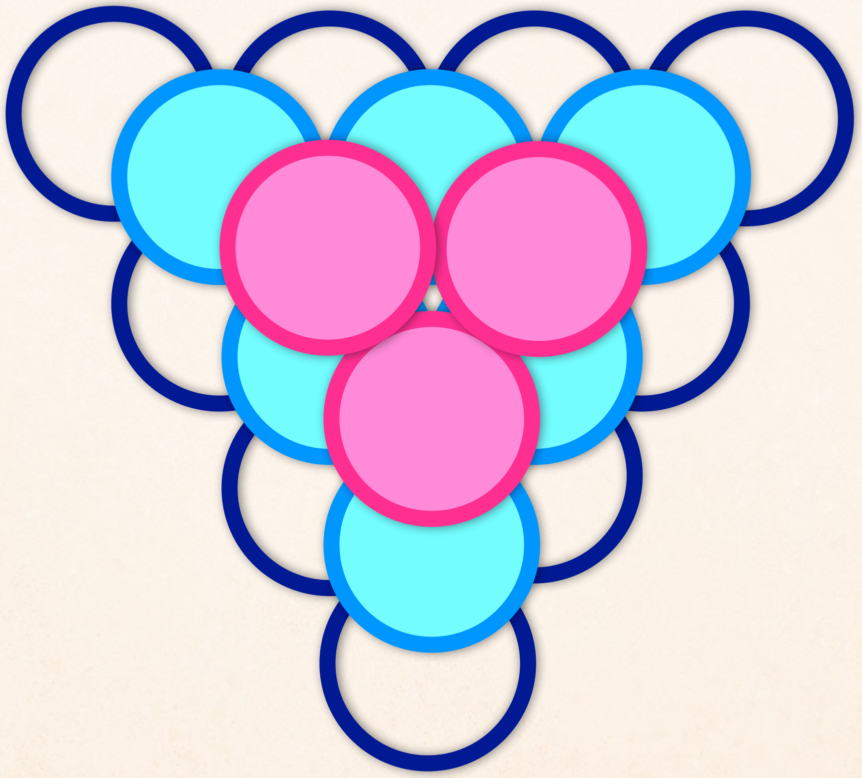


CRYSTAL STRUCTURE FOR RARE GASES: FCC (FACE CENTERED CUBIC)

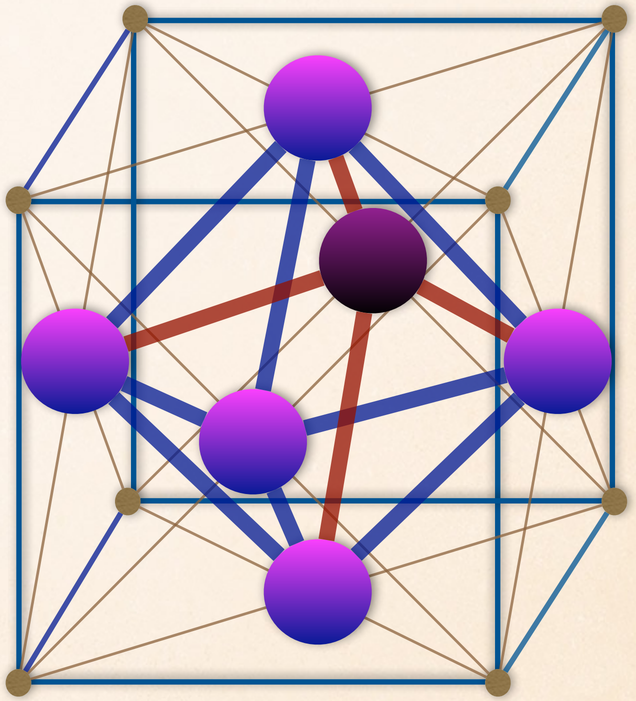
13 particle fragment of FCC crystal



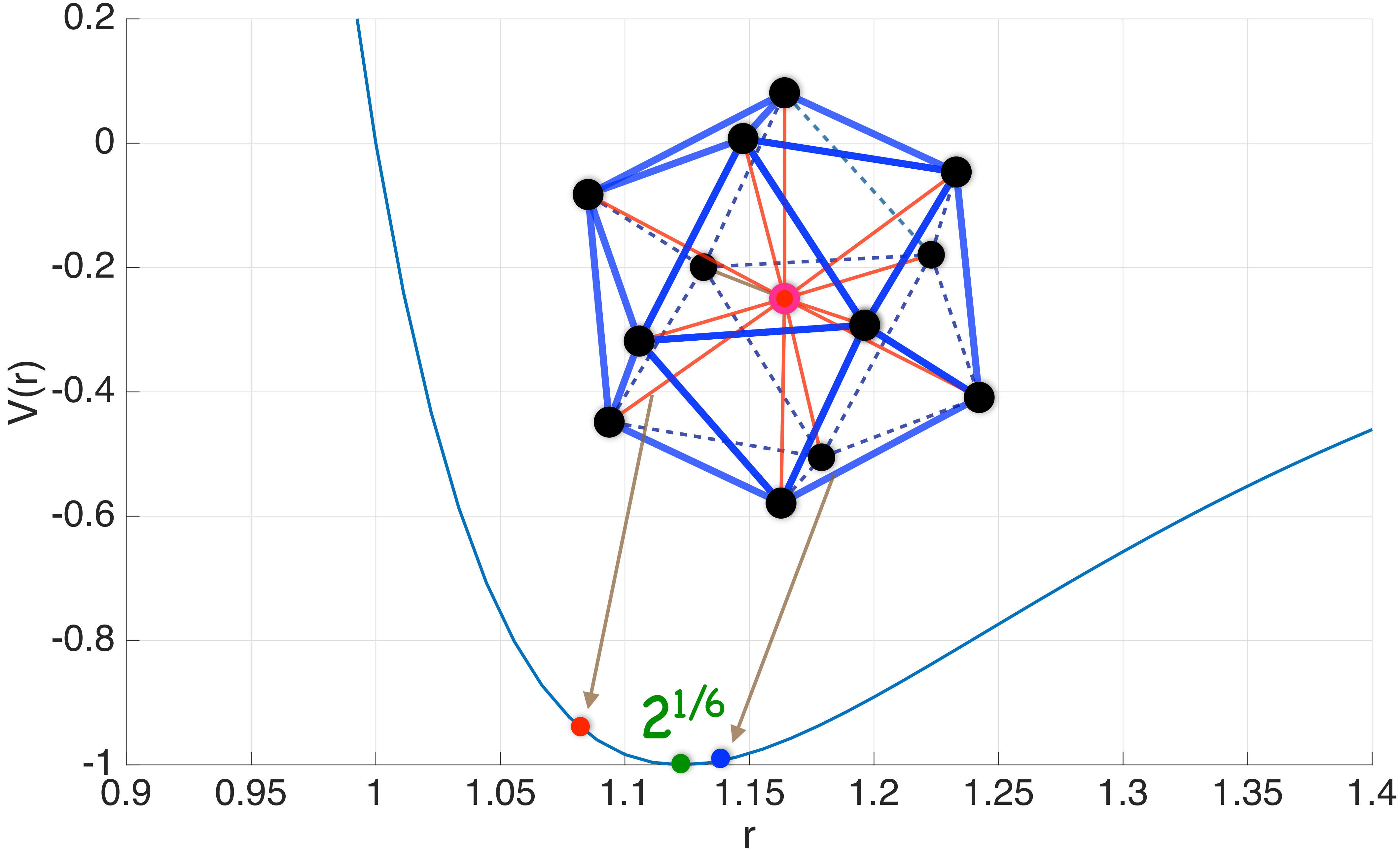
FCC packing



FCC elementary cell



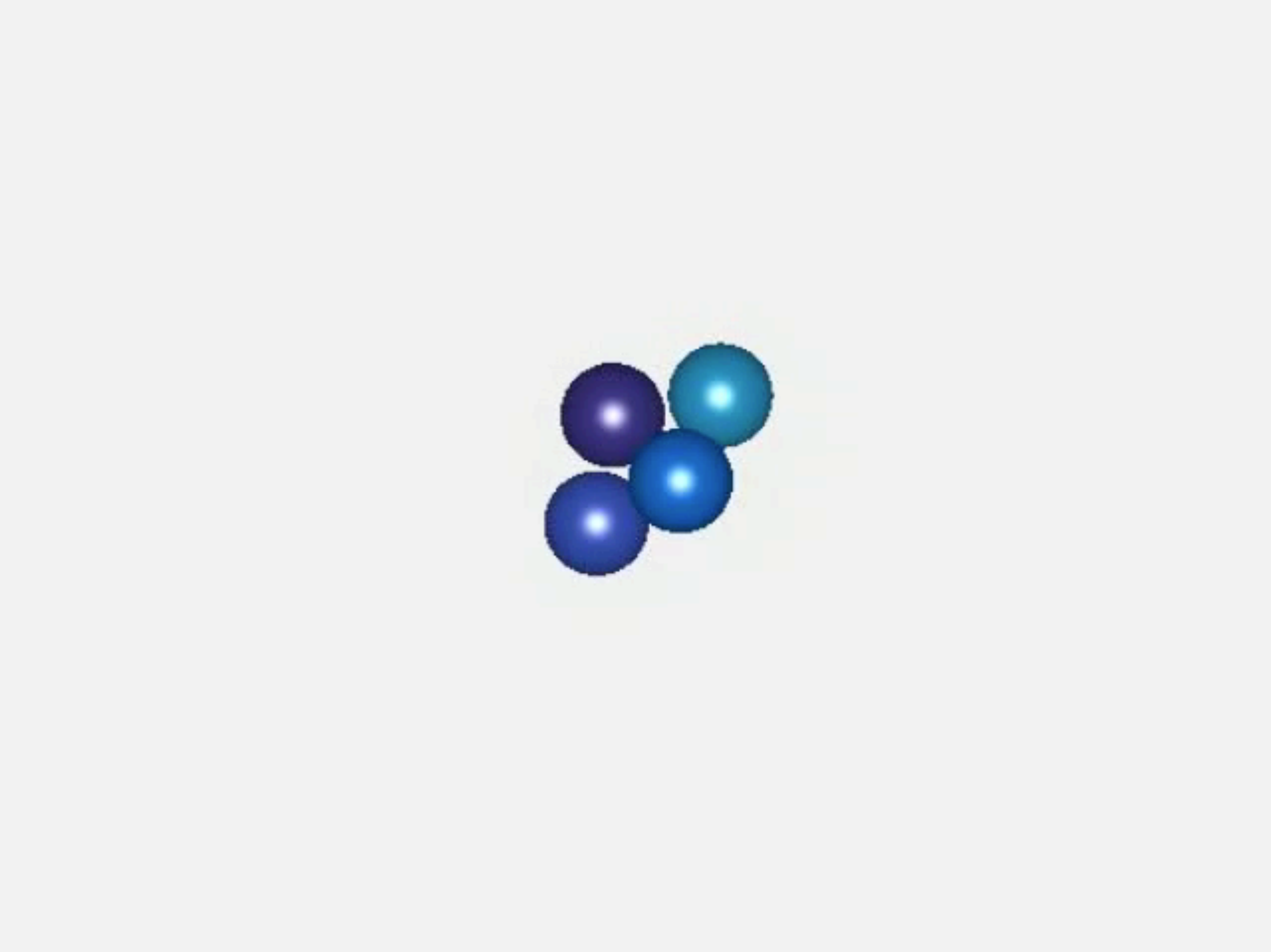
FRUSTRATION

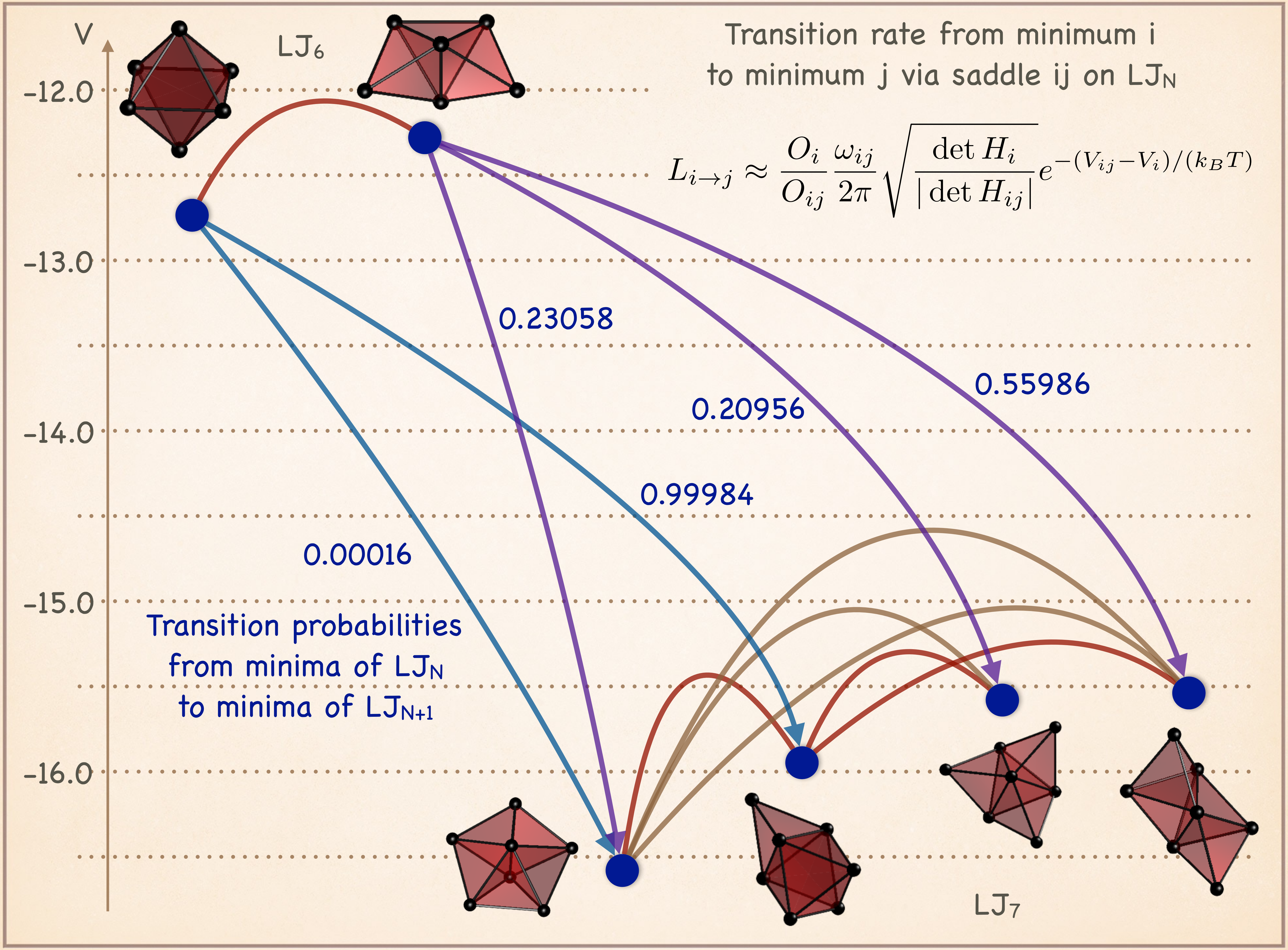


NEW CHALLENGE: MODELING AGGREGATION

MAPS-REU 2016:
Yakir Forman (Yeshiva U), Sebastian Sousa Castellanos (UEC)

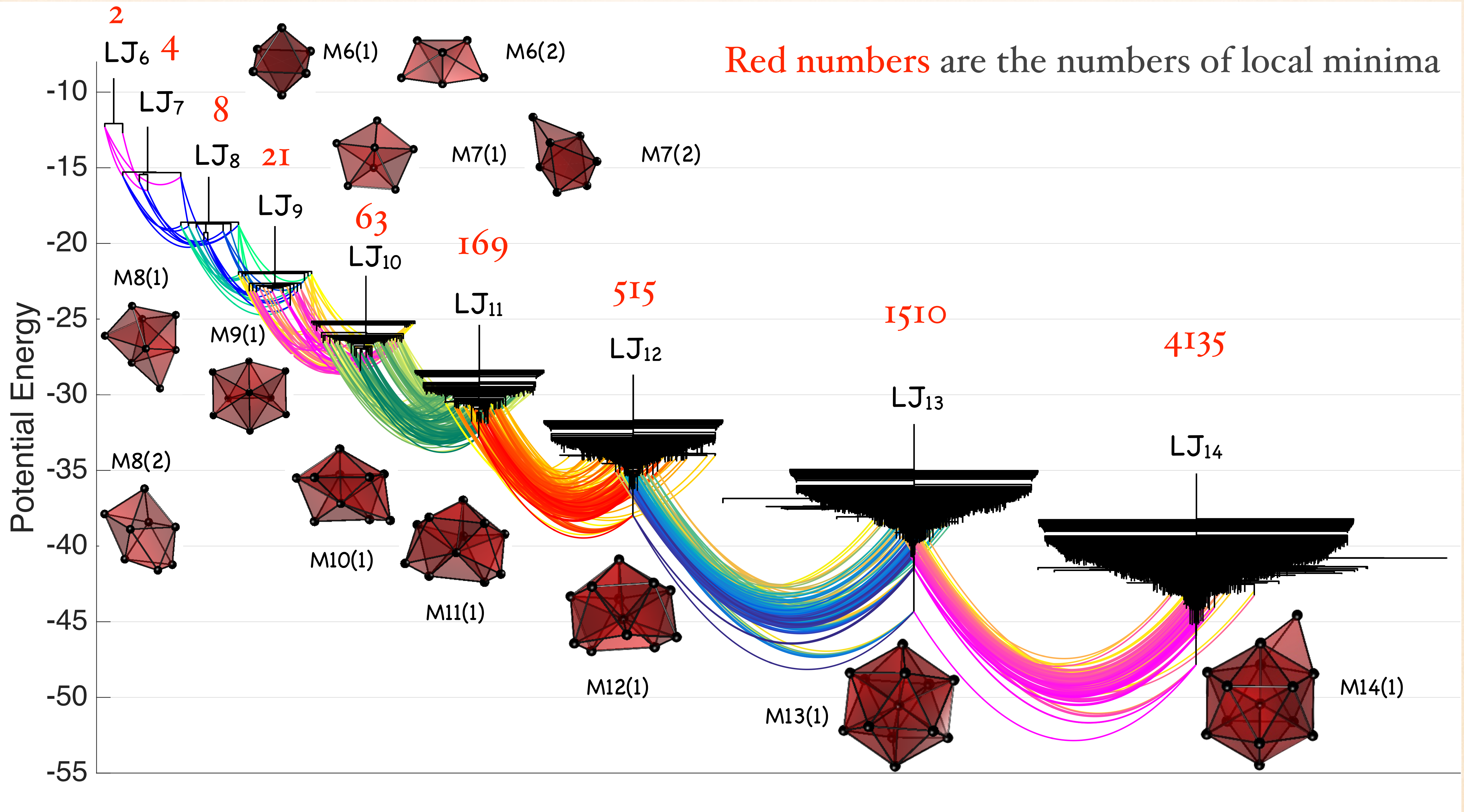
Aggregation of LJ particles





V
LJ6
-12.0
-13.0
-14.0
-15.0
-16.0
Transition rate from minimum i to minimum j via saddle ij on LJN
$$L_{i\to j} \approx \frac{O_i}{O_{ij}}\frac{\omega_{ij}}{2\pi}\sqrt{\frac{\det H_i}{|\det H_{ij}|}}e^{-(V_{ij}-V_i)/(k_BT)}$$
0.23058
0.20956
0.55986
0.99984
0.00016
Transition probabilities from minima of LJN to minima of LJN+1
LJ7

JOINT AGGREGATION/DEFORMATION LJ6-14 NETWORK



STATS FOR LJ_N NETWORKS

LJ_6:
N vertices = 2
N edges = 3

LJ_7:
N states = 4
N edges = 10

LJ_8:
N states = 8
N edges = 21

LJ_9:
N states = 21
N arcs = 61

LJ_{10}
N states = 63
N edges = 938

LJ_{11}
N states = 169
N edges = 756

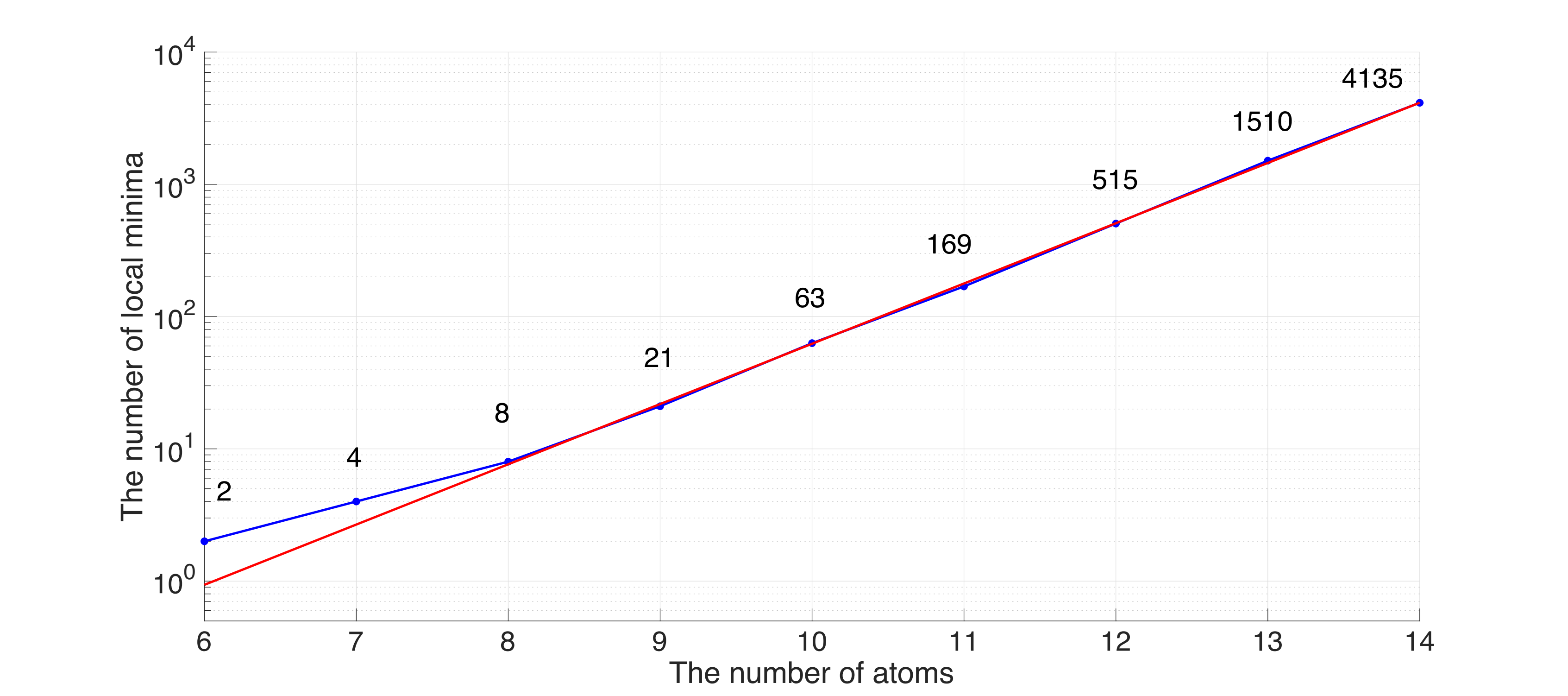
LJ_{12}
N states = 515
N edges = 1582

LJ_{13}
N states = 1510
N edges = 4660

LJ_{14}
N states = 4135
N arcs = 13049

Least squares fit:

$$N_{min} = 1.7 \cdot 10^{-3} \cdot e^{1.04N}$$



TECHNICAL CHALLENGES IN BUILDING LENNARD-JONES AGGREGATION/DEFORMATION NETWORKS

Vertices

- Finding the set of local energy minima for each LJ_N. Local minimizer: trust region BFGS. Minima of LJ_N are found by: (1) minimization starting from random configuration, (2) adding an extra atom to LJ_{N-1}, (3) descending from found saddles

Edges & rates in LJ_N

- Finding the set of Morse index one saddles for each LJ_N. Saddle search starting from each local minimum by a technique combining min-mode+dimer (S. Sousa, REU 2016)

- Finding point group orders (Y. Forman, REU 2016)

$$L_{i\to j} \approx \frac{O_i}{O_{ij}}\frac{\omega_{ij}}{2\pi}\sqrt{\frac{\det H_i}{|\det H_{ij}|}}e^{-(V_{ij}-V_i)/(k_BT)}$$

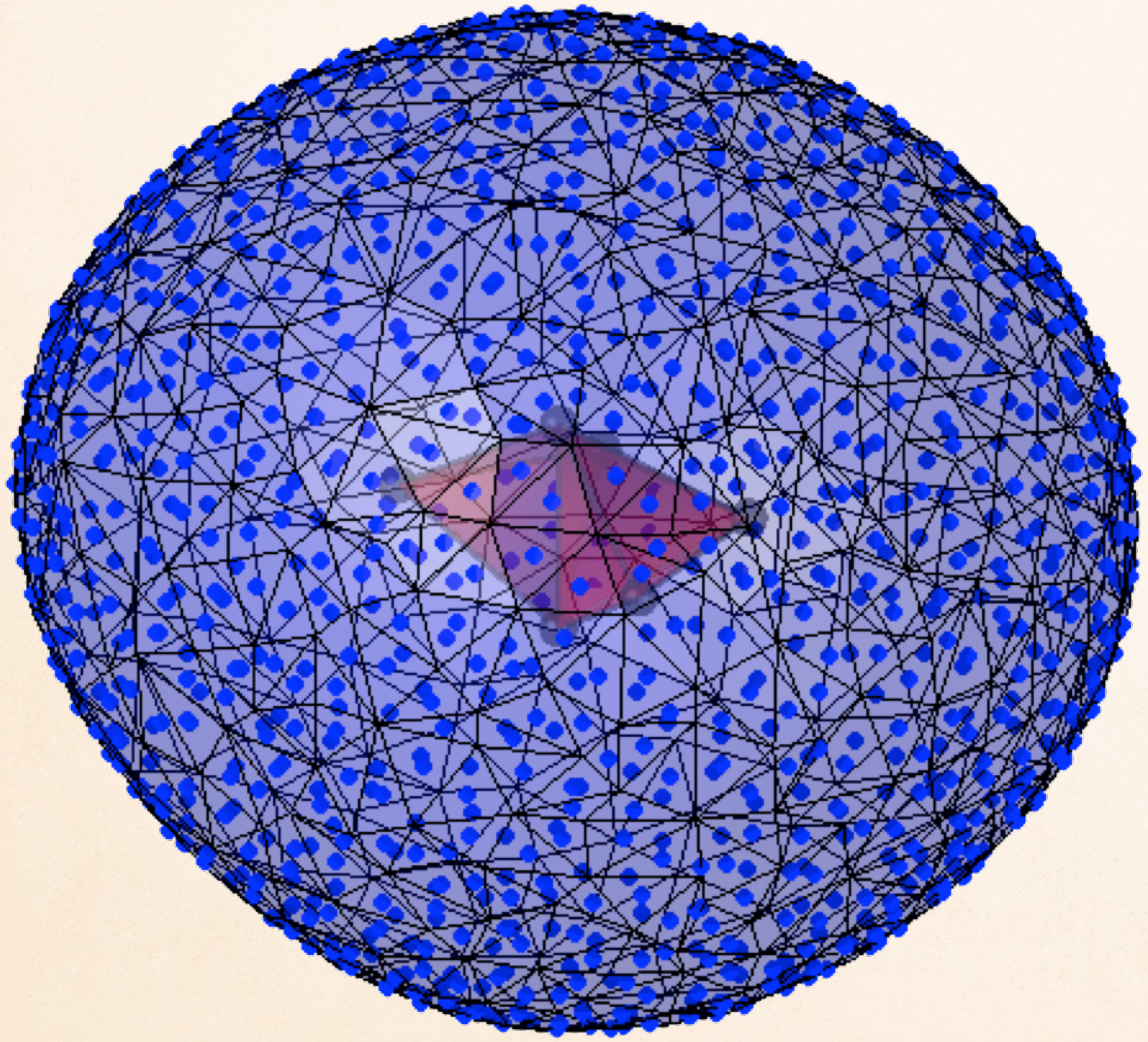
Edges & probabilities $LN_N \to LJ_{N+1}$

- Gluing LJ_N and LJ_{N+1}. An isosurface approach (Y. Forman & M. Cameron)

GLUING LJ_N AND LJ_{N+1} NETWORKS

Equipotential surface

$$\Sigma := \{\mathbf{r} \in \mathbb{R}^3 \mid U(\mathbf{r}) = -0.1, \quad \min_{1 \le i \le N} |\mathbf{r} - \mathbf{r}_i| > 2^{1/6}\}$$



r = position of N+1-st atom

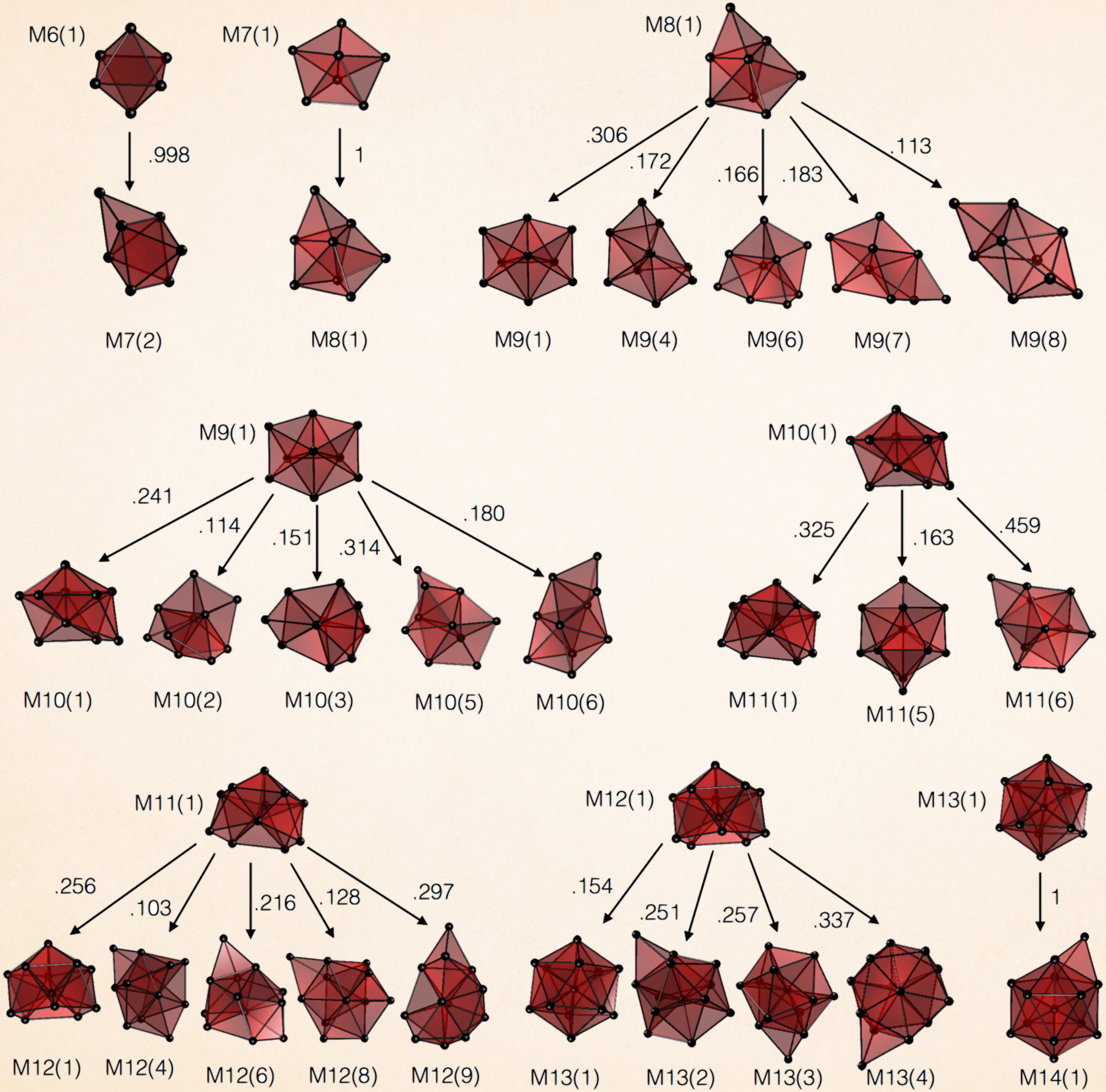
$$U(\mathbf{r}) = 4\sum_{i=1}^{N} |\mathbf{r} - \mathbf{r}_i|^{-12} - |\mathbf{r} - \mathbf{r}_i|^{-6}$$

Triangulation of Σ:

$$\Sigma := \bigcup_{m=1}^{1000} \sigma_m$$

Transition probability from
min k of LJ_N
to min l of LJ_{N+1}

$$\gamma_{kl}^{N \to N+1} = \frac{\sum_{m=1}^{1000} A(\sigma_m)\delta_{kl}(m)}{A(\Sigma)}$$

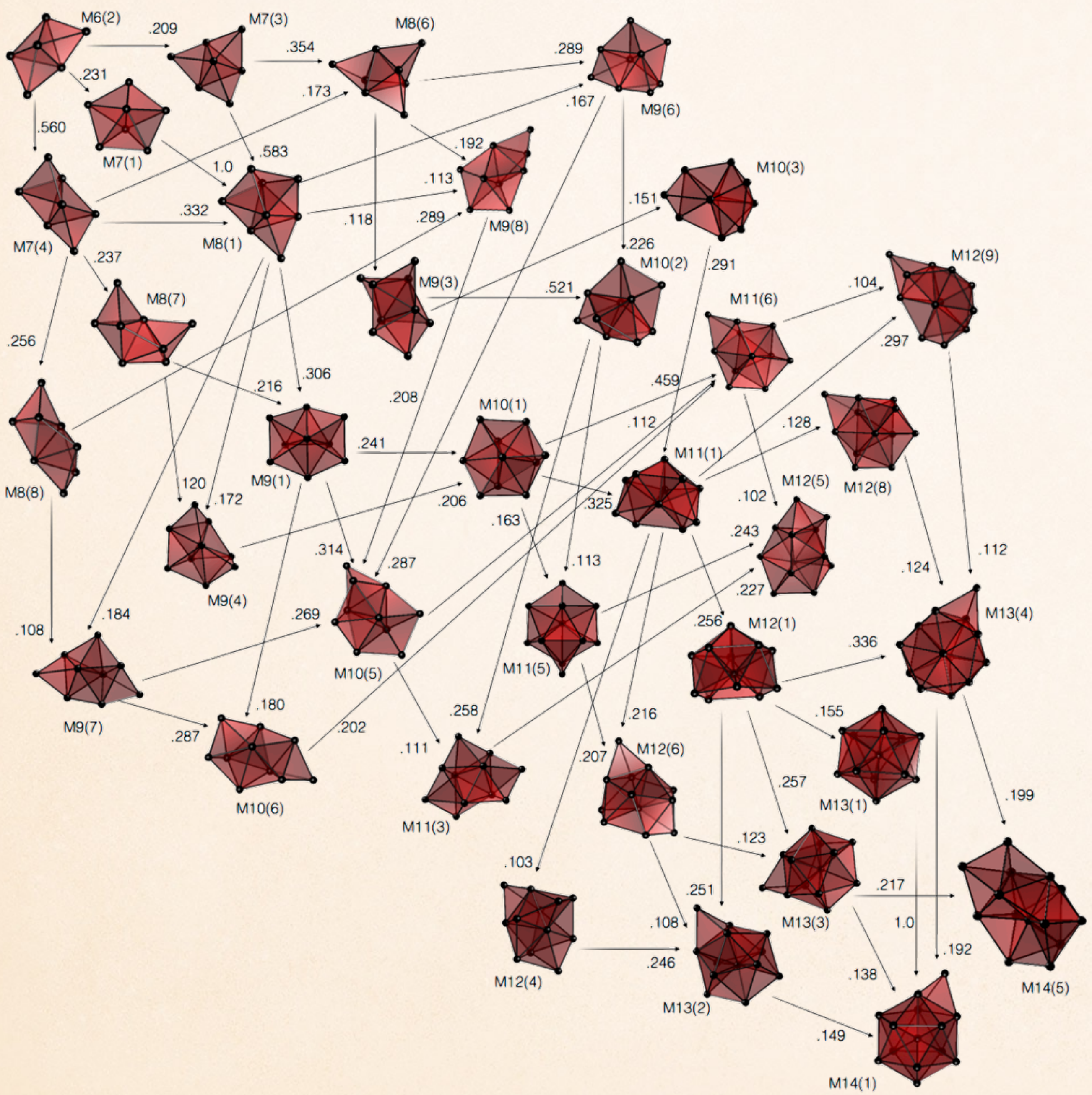


The most likely transitions from the global minima of LJ_N

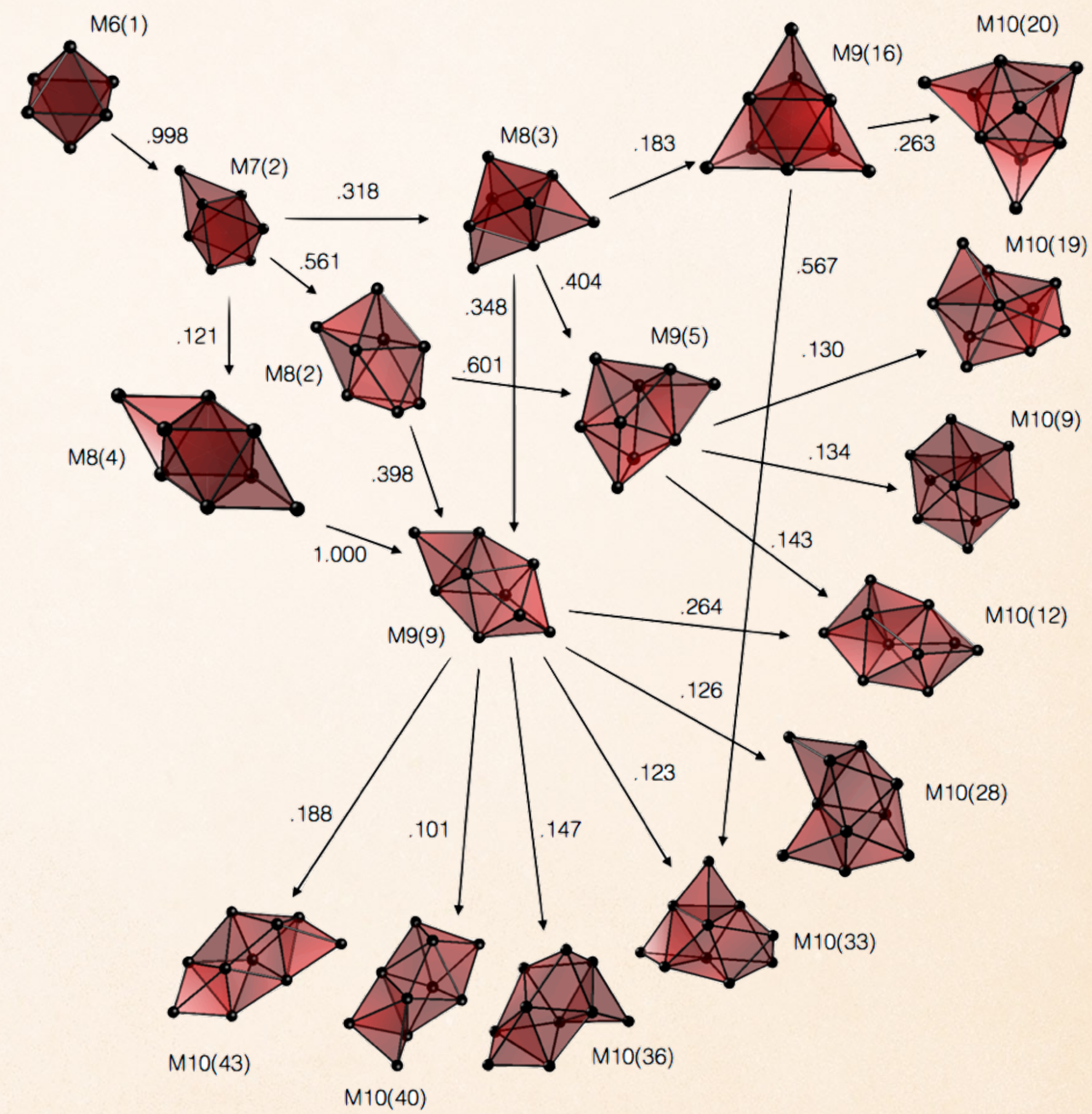
Notation: $MN(i)$ is minimum i of LJ_N

AT THE FIRST GLANCE: HERITAGE CASCADES

Icosahedral



Non-icosahedral



ANALYSIS OF AGGREGATION/DEFORMATION LJ6-14 NETWORK

Y. Forman, 2016

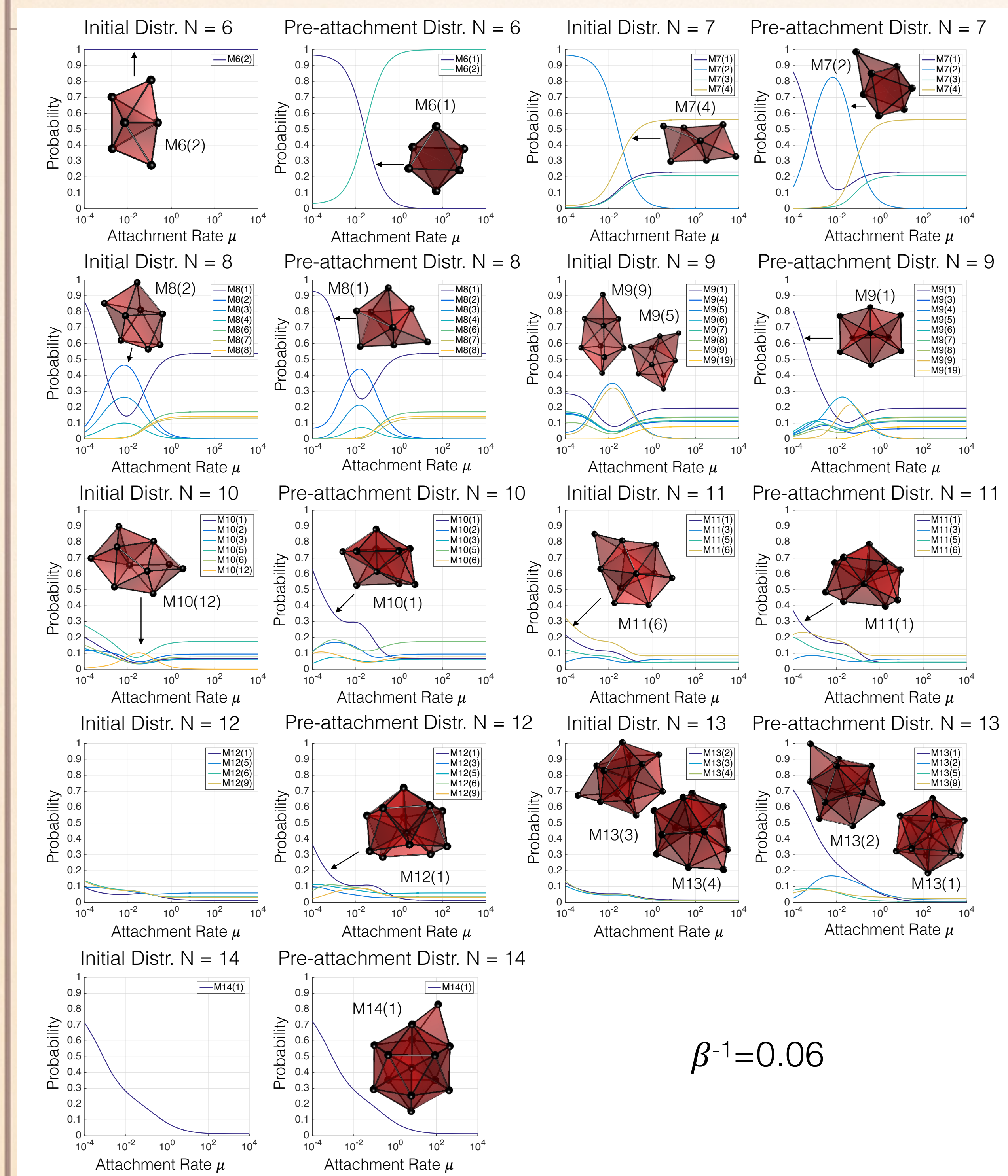
- In LJ_N, probability distribution evolves according to: $\frac{dp}{dt} = pL$
- Eigendecomposition of L_N:

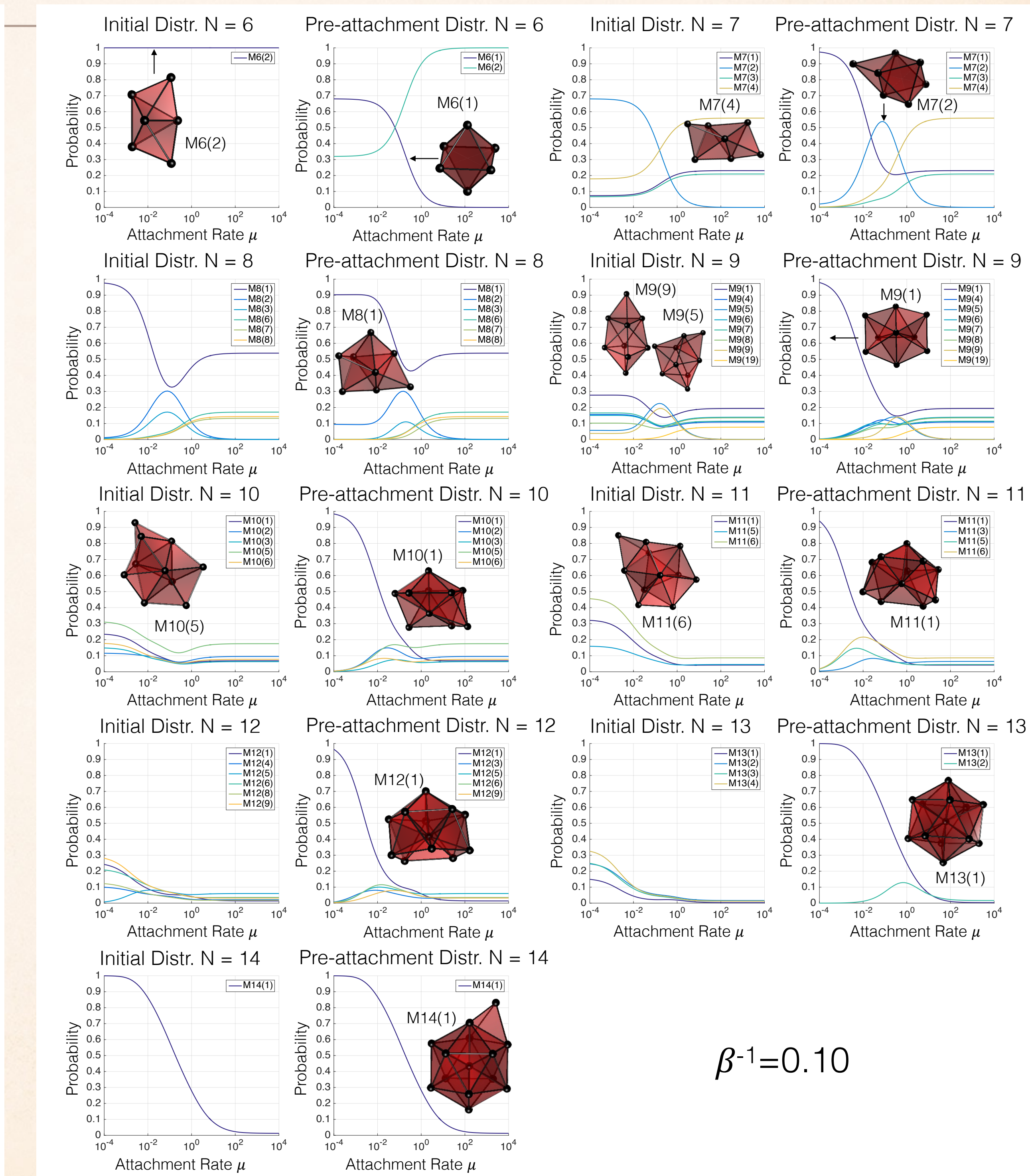
$$L_N = [\phi_N^0 \dots \phi_N^{N-1}] diag\{0, -\lambda_1, \dots, -\lambda_{N-1}\}[P_N\phi_N^0 \dots P_N\phi_N^{N-1}]$$

- 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:

$$\begin{aligned} p_{preatt}^N(s) &= \int_0^\infty \mathbb{P}^N(S = s|T = t) f_T(t) dt \\ &= \sum_{k=0}^{N-1} (p_0^N \phi_N^k) \left(\frac{\mu}{\mu + \lambda_k}\right) (P_N\phi_N^k)_s^T \\ &= \mu p_0^N (\mu I - L_N)^{-1} \end{aligned}$$

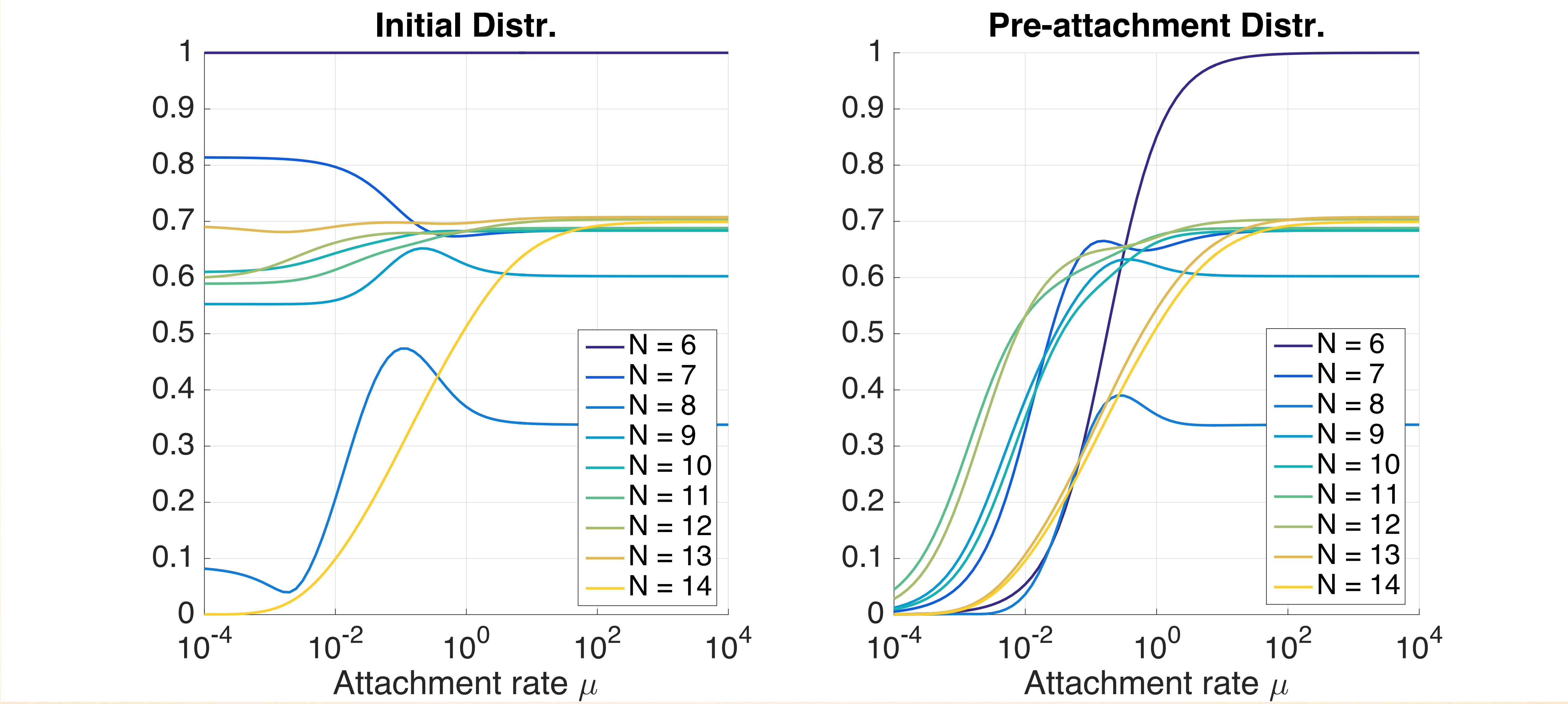
EXPECTED INITIAL AND PRE-ATTACHMENT DISTRIBUTIONS





ATTACHMENT DOES MIXING

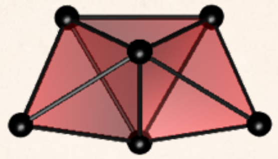
A normalized RMS deviations from the invariant distributions



β^{-1} = 0.10

PURE ATTACHMENT PROCESSES

$a_N = [1,0]\Gamma^{6\to 7}\ldots\Gamma^{N-1\to N}$



$b_N = [0,1]\Gamma^{6\to 7}\ldots\Gamma^{N-1\to N}$

$A_N := \{i \in \mathrm{LJ}_N \mid a_N(i) > b_N(i)\}$

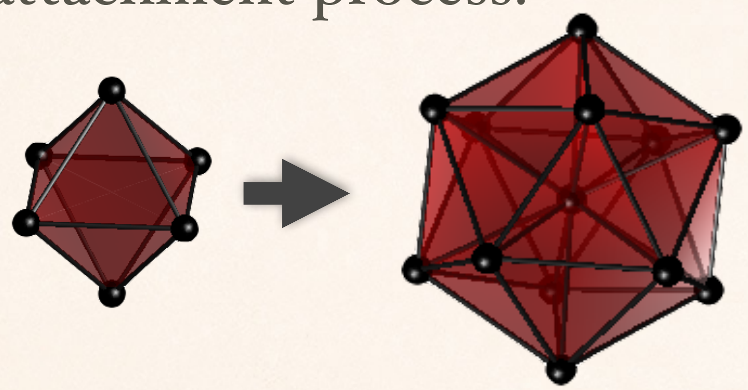
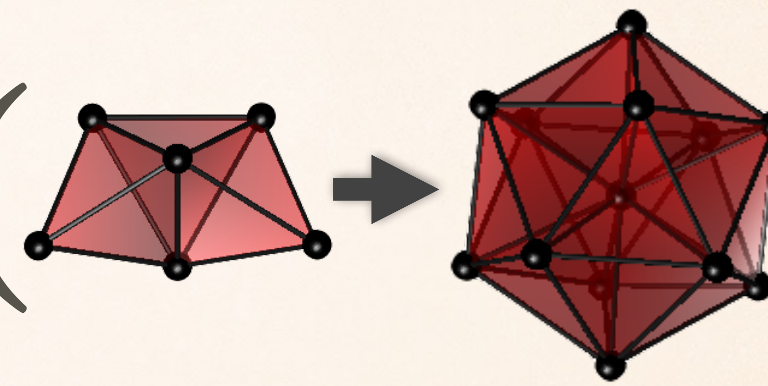
$B_N := \{i \in \mathrm{LJ}_N \mid b_N(i) > a_N(i)\}$

$\beta^{-1} = 0.10$

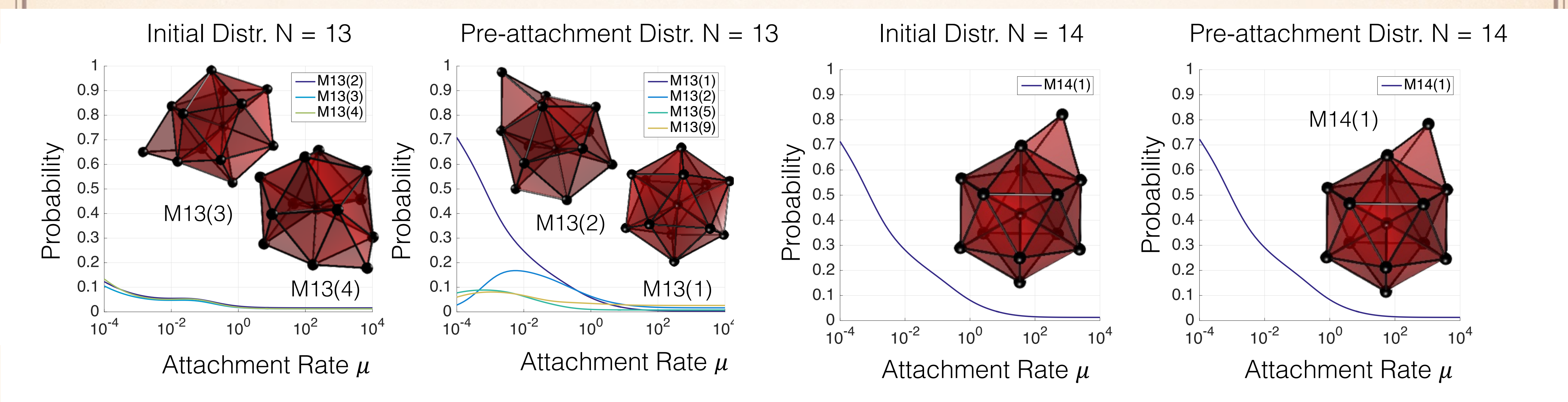
N	$\lvert A_N \rvert$	$P(A_N)$	$\lvert B_N \rvert$	$P(B_N)$
7	1	1.667E-02	3	9.833E-01
8	3	9.610E-02	5	9.039E-01
9	10	2.359E-03	11	9.976E-01
10	38	3.408E-04	25	9.996E-01
11	100	3.666E-04	69	9.996E-01
12	331	1	170	3.568E-06
13	1038	1	472	6.398E-13
14	2877	1	1257	3.514E-10

INTERESTING FACTS

- Both processes, relaxation and attachment, favor icosahedral packing in small clusters.
- For a pure attachment process:

Prob() > Prob()

- The 13-atom icosahedron has competitors, while the 14-atom capped icosahedron is the king

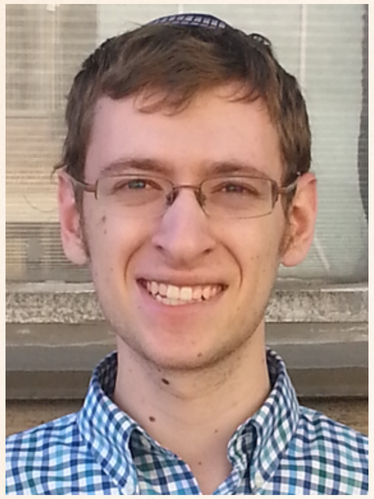


PERSPECTIVES

- Allow detachments. Will the 13-atom icosahedron be the dominant structure?
- Continue building network. Use an importance sampling for finding local energy minima.
- Let the temperature to be variable. Figure out conditions favoring the formation of desired configurations.
- Study aggregation processes for different kind of particles, e.g. sticky particles (there are lots of geometric peculiarities 😜)

ACKNOWLEDGEMENTS AND REFERENCES

- 2016 MAPS-REU students



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Univ. of Colorado, Boulder,

- NSF REU grant DMS1359307 at UMD (Host: Kasso Okoudjou)
- NSF CAREER grant DMS1554907

Refs:

- Y. Forman and M. Cameron, Modeling Aggregation Processes of Lennard-Jones Particles via Stochastic Networks, J. Stat. Phys. 2017, *online first*, DOI 10.1007/s10955-017-1794-y
- S. Sousa Castellanos and M. Cameron, Saddle Hunt, *in preparation*
- M. Cameron, Y. Forman, S. Sousa Castellanos, LJ6-14 dataset and MATLAB software package for building networks,

  https://www.math.umd.edu/~mariakc/lennard-jones.html