From Small Carbon Fragments to Self-Assembled Fullerenes in Quantum Chemical Molecular Dynamics

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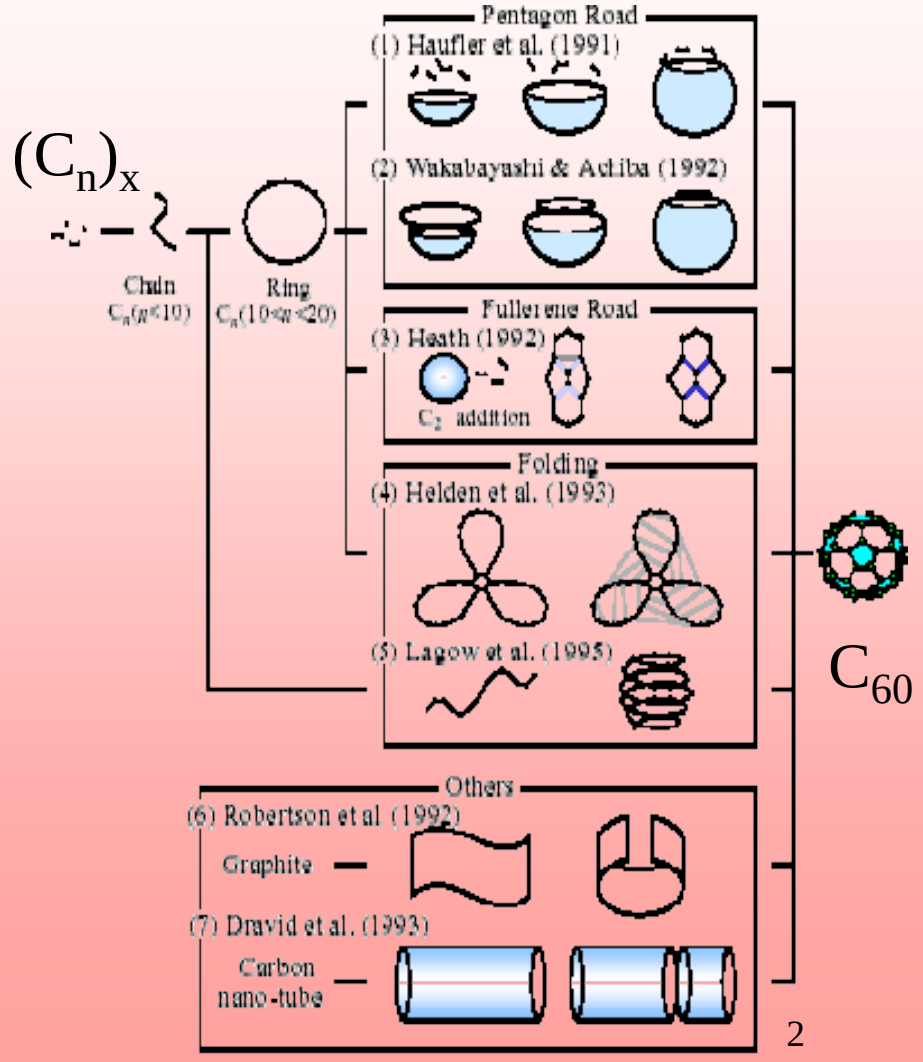
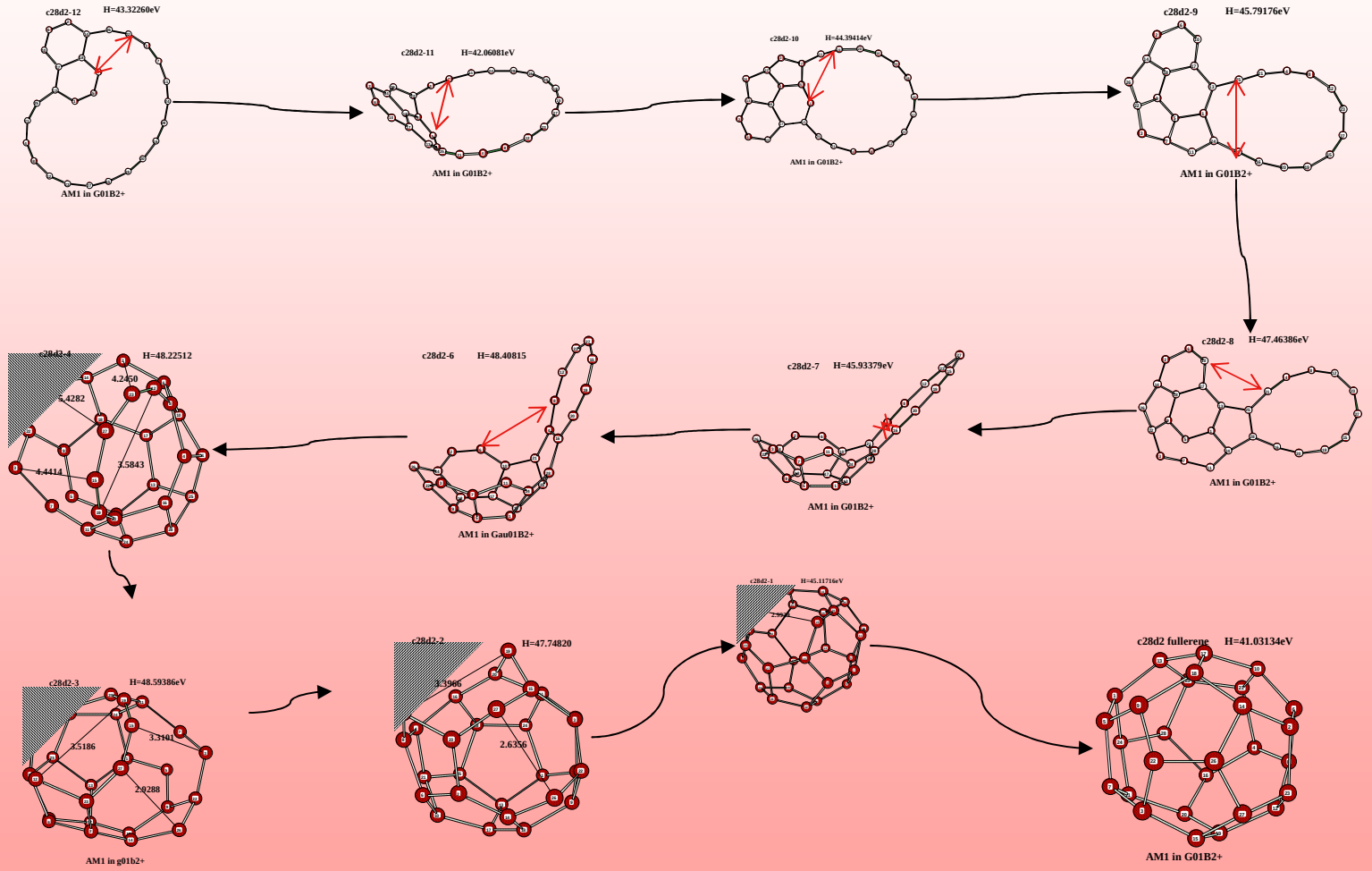
Overview: Proposed Fullerene Formation Mechanisms

- **Hypothetical mechanisms** relying on more or less sound assumptions; **no intermediate species confirmed so far.**
- Underlying **assumption of structural order**: Systematic "construction" from smaller fragments or collapse of highly pre-organized structures.
- **No experimental or theoretical verification !**



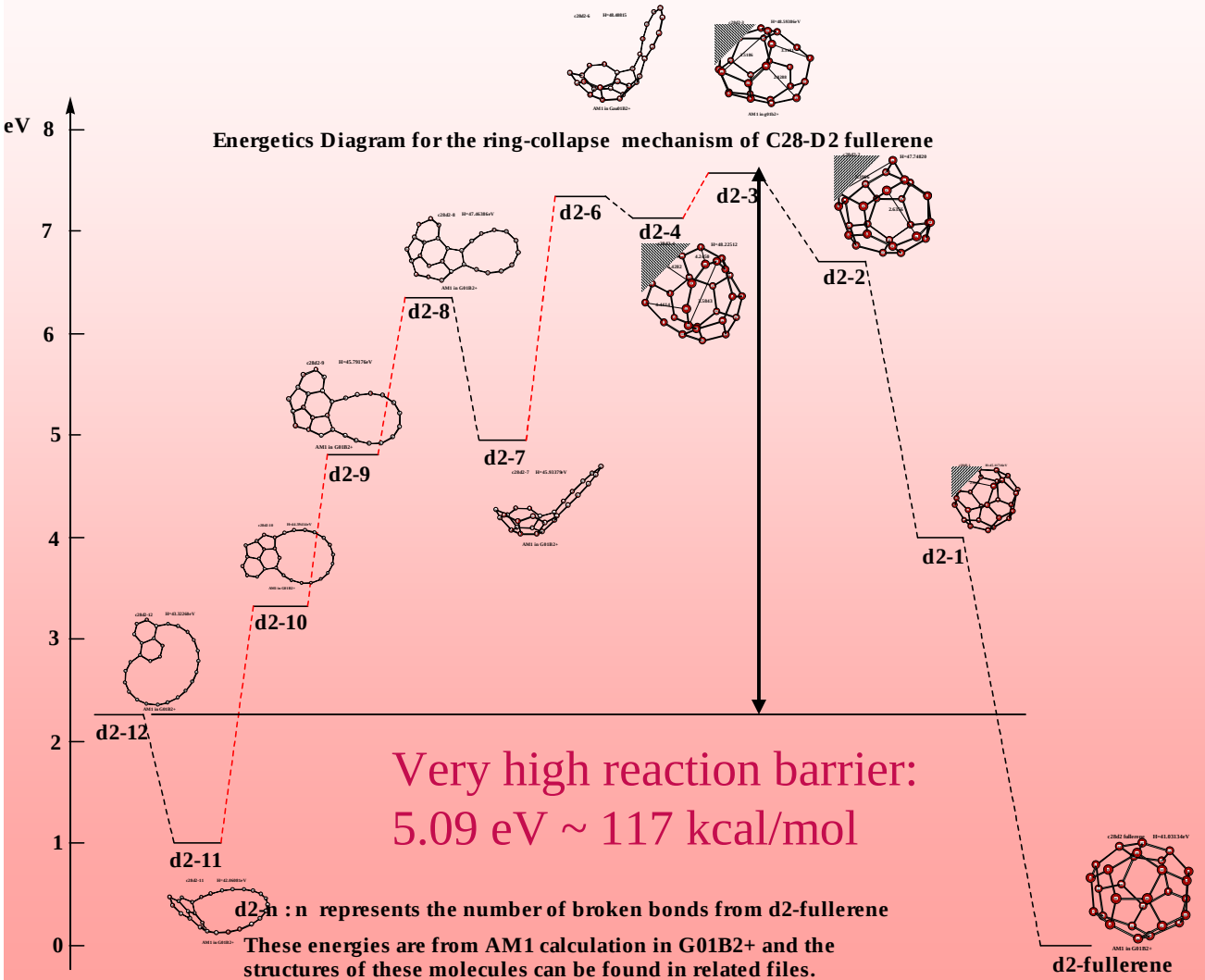
Scheme from: Yamaguchi, T.; Maruyama, S. *JSME* **1997**, *63-611B* 2398

One Possible "Designed" Pathway to C_{28} - Structures



AM1 calculation including all transition states and intermediates of a "ring collapse mechanism" in the spirit of Mishra, R. K.;Lin, Y.-T.; Lee, S.-L. *J. Chem.Phys.* **2000**, 112, 6355-6364

One Possible "Designed" Pathway to C_{28} - Energetics



Very high reaction barrier:
5.09 eV ~ 117 kcal/mol

Large barrier associated with ring strain.

Energy stabilization in final steps through 3D-π-aromaticity

Need for Reactive Molecular Dynamics Simulations

1. High temperature (1000 - 5000 K) → reduced relevance of thermodynamically favorable pathways. Can sample structures of high potential energies.

2. High-dimensionality prohibits systematic determination of structures and energies of intermediates and transition states.

⇨ **Need high temperature molecular dynamics (MD) approach.**

⇨ **Need inexpensive method for calculating potential energy function which allows bond breaking/formation:**

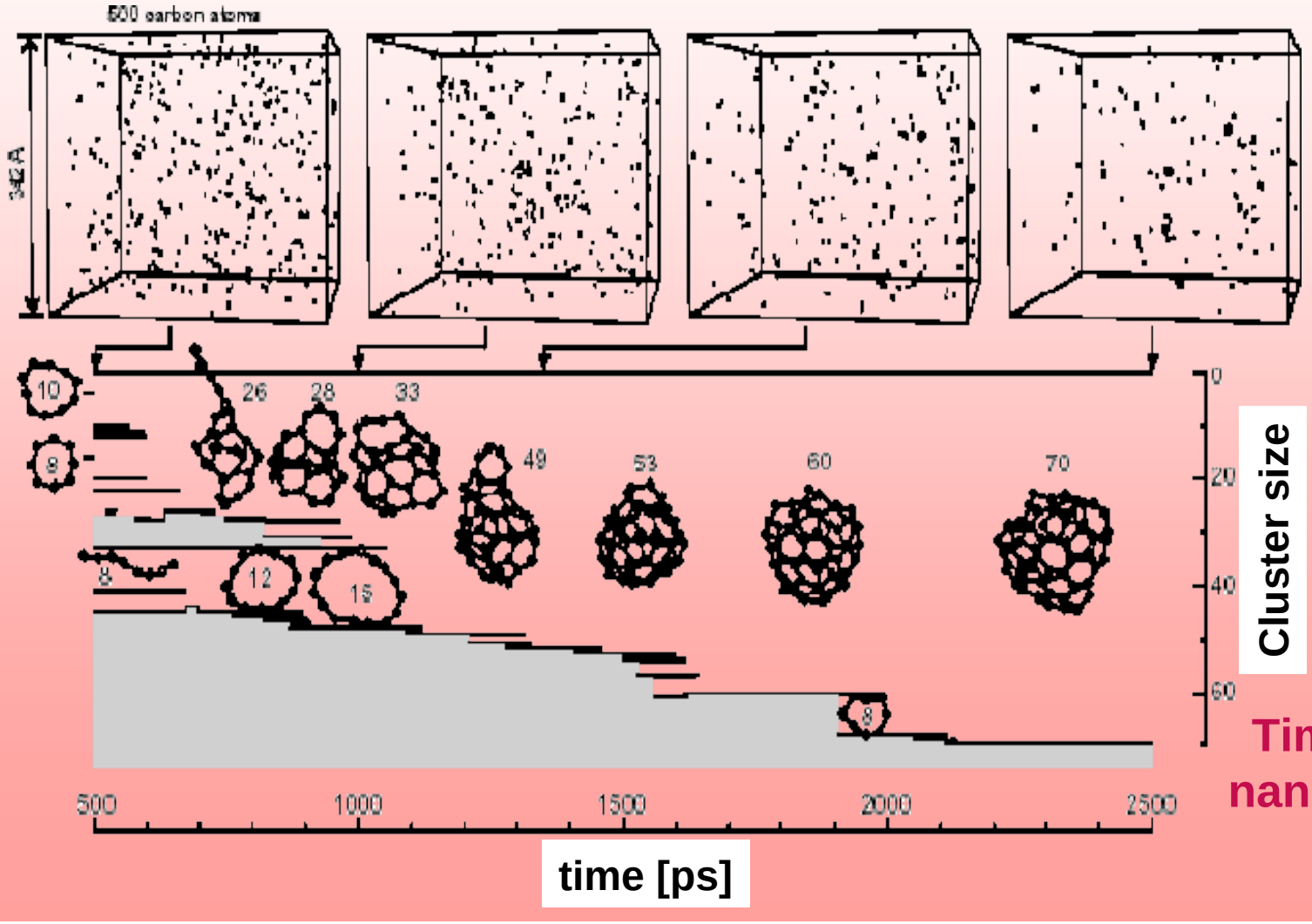
1. **Semiclassical** Brenner REBO (Reactive empirical bond-order) **molecular force field** potential, (e.g., Brenner et al, *Phys. Rev. B* **1990**, *42*, 9458, for simulation od diamond)

2. **Semiempirical quantum chemical** methods (AM1, PM3, DFTB)

Brenner-Potential MD Simulation of the Fullerene Formation Process - Time Scale

Yamaguchi, Y.; Maruyama, S. *Chem.Phys.Lett.*, **1998**, *286*, 336-342

T=1500 K



Time scale: nanoseconds

Brenner-Potential MD vs. Quantum Chemical Potential

REBO Force Field is several orders of magnitude **faster** than semiempirical quantum chemical methods, in addition: scaling ~ N^2 vs. N^3

REBO Force Field was developed for vapor decomposition of graphite under high pressure to form diamond; can only describe σ–**bond** formation/breaking processes.

Quantum chemical all valence electron approaches include naturally directionality, i.e. π–**bond** formation/breaking.

Quantum chemical potential includes naturally **aromaticity**, π–conjugational stabilization, C sp $\rightarrow$ C sp^3 hybridization

Density Functional Tight Binding (DFTB)

Seifert et al., *Int. J. Quant, Chem.* **1996**, *92*, 185

Extended Hückel type method using atomic parameters from DFT (PBE), diatomic repulsive potentials from B3LYP

- Seifert, Eschrig (1980-86): STO-LCAO; 2-center approximation

$$E = \sum_{A>B}^{atom} V_{AB} + \sum_{k}^{orb} n_i \varepsilon_i$$

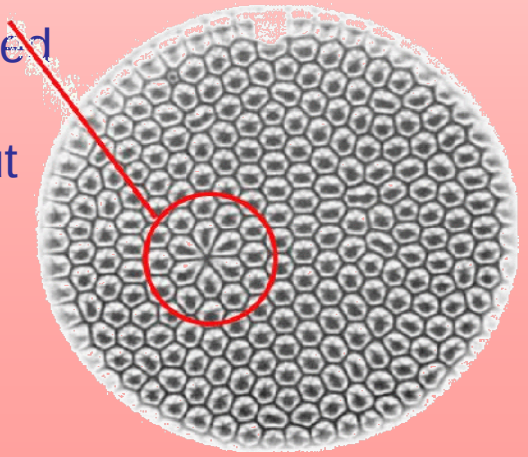
- Porezag *et al.* (1995): efficient parameterization scheme
- Elstner *et al.* (1998): charge self-consistency: *SCC-DFTB*

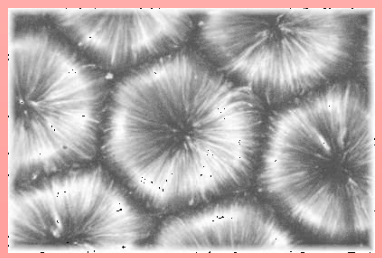
→ *"approximate DFT"*

Only time consuming step: Matrix diagonalization

Order out of chaos? Ensembles of C_2 molecules as starting structures for DFTB/MD simulations

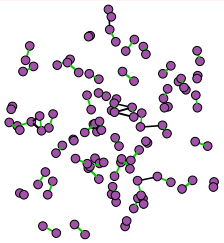
- Experimental conditions of fullerene formation: Many carbon clusters available in great abundance under great heat and normal pressure
- **Non-equilibrium dynamics** with large kinetic energy and carbon cluster material fluctuations: Monomolecular approach may not be valid.
- More realistic starting point for DFTB/MD simulations: Ensembles of randomly oriented C_2 molecules under ~ 2000 K, providing steady supply of additional C_2 molecules: *Open exchange of energy and carbon material*, **NO SINGLE POTENTIAL ENERGY SURFACE**
- Example for order created dynamically out of chaos: Dissipative structures (e.g. Rayleigh-Benard convection cells) without associated single potential energy function





Adding More C2's is a key to formation of fullerenes

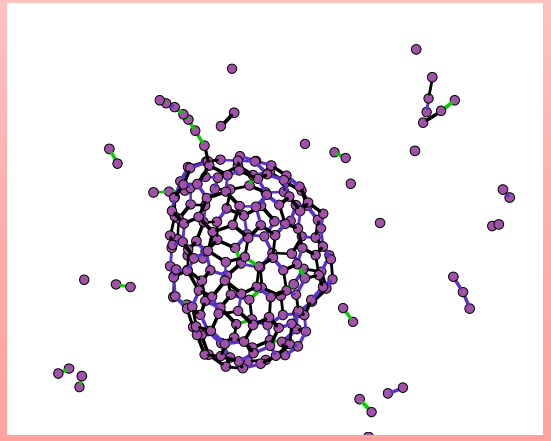
"S2" to "S5"



60 C_2s in 30Å cubic box 0.7g/cm

6ps 2000K → add 10 more C_2 → 6ps 2000K → add 10 more C_2 → 6ps 2000K → add 10 more C_2 → 6ps 2000K → add 10 more C_2 → 6ps 2000K → add 10 more C_2 → 6ps 3000K → add 10 more C_2 → 10-48ps 3000K

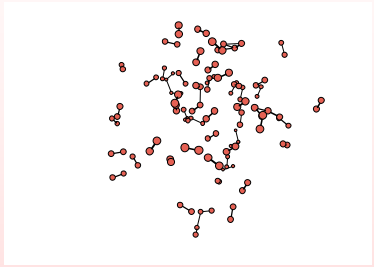
2000K preferred for earlier stage



DFTB/MD on *n* C_2 in 30Å periodic boundary box (I)

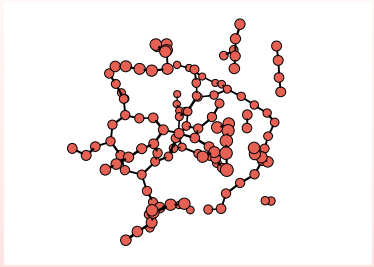
S1

0.00ps



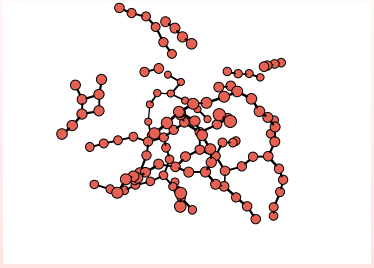
Initial state

0.24ps



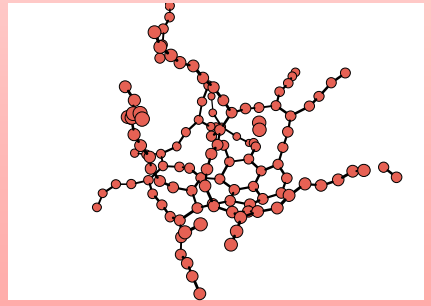
Long entangled chains

0.29ps



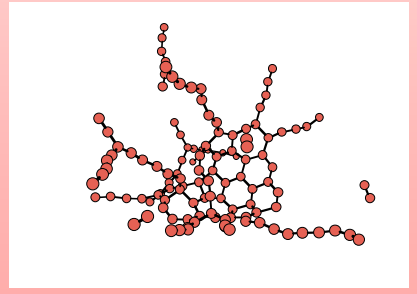
First big rings

3.86ps



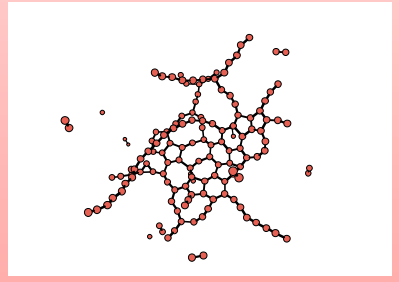
Big rings collapse into smaller rings

6.05ps



More smaller rings created by ring collapse

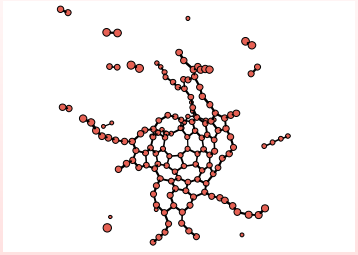
12.1ps



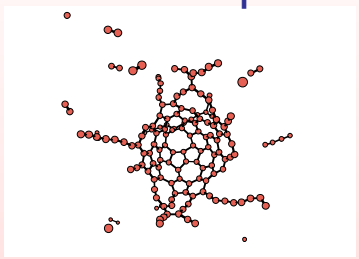
Many long chains at the edges

DFTB/MD on *n* C_2 in 30Å periodic boundary box (II)

14.54ps

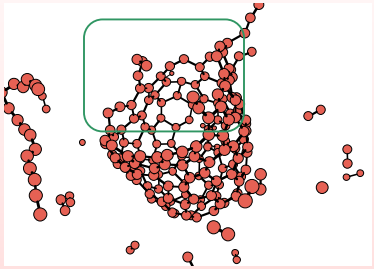


22.07ps



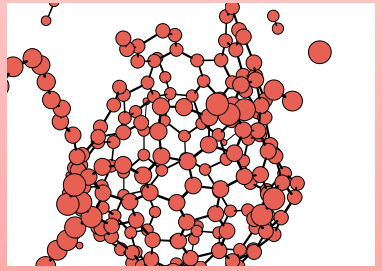
Growth by collapse
of chains on edges

39.78ps



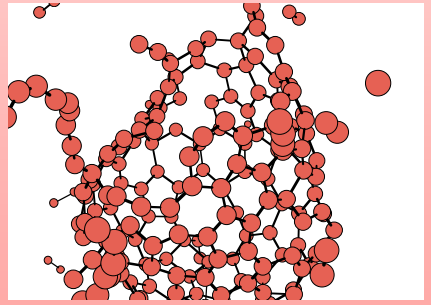
Short chain
connect with
another long chain

43.26ps



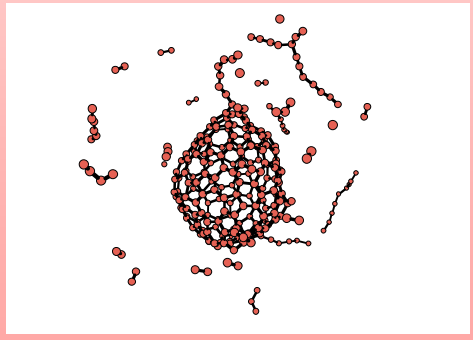
One more hexagon
Created by reaction
Between wobbling
C2 and C3

43.27ps



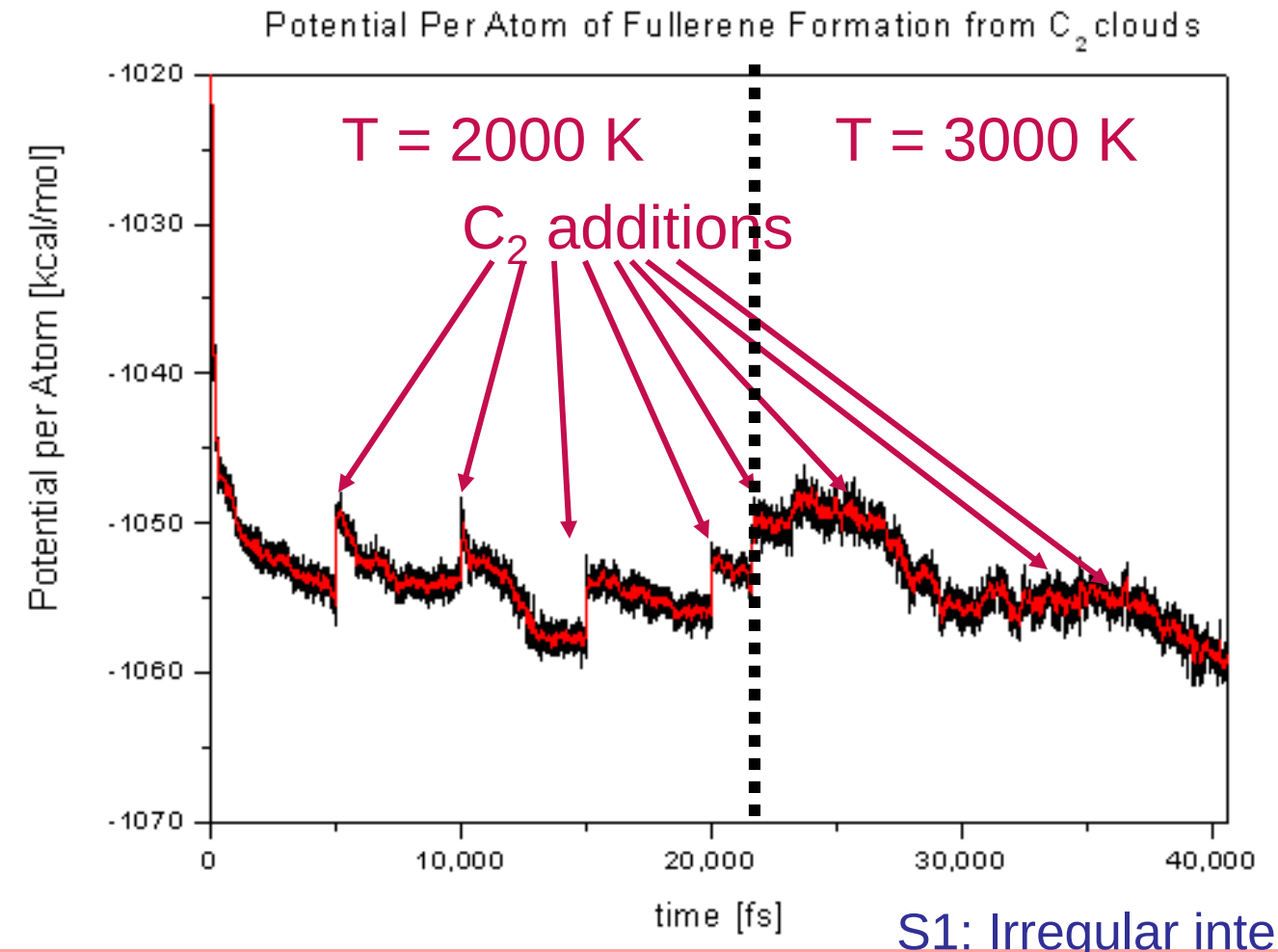
Cycloaddition between
Adjacent chains
On border similar to CNT

49.72ps



Fullerene with 26 penta
42 hexa, and 15 heptagons,
146 carbons in the cage

DFTB/MD on *n* C_2 in 30Å periodic boundary box (IV)



S1: Irregular intervals for C_2 addition,
S2-S4: regular intervals

DFTB/MD on *n* C_2 in 30Å periodic boundary box (V)

Irle et al., *Nano Lett*, 3, 1675 (2003)

S1

								tend [ps]	sf [ps]
start time [ps]	0.00	12.00	24.00	36.00	47.93	56.42	62.53	66.70	66.3
simulation time [ps]	12.00	12.00	12.00	11.93	8.49	6.11	6.19	6.19	
T [K]	2000	2000	2000	2000	2000	2000	3000		
# 5-ring	0	5	8	11	16	20	18	19	
# 6-ring	0	5	10	16	16	23	27	44	
# 7-ring	0	0	3	7	11	13	14	8	
C2 added	60	10	10	0	10	10	0	C_{146}	
# of C atoms	120	140	160	160	180	200	200		

S3

								tend [ps]	sf [ps]
start time [ps]	0.00	6.05	12.10	18.15	24.20	30.25	36.30	46.69	43.7
simulation time [ps]	6.05	6.05	6.05	6.05	6.05	6.05	10.39		
T [K]	2000	2000	2000	2000	2000	3000	3000		
# 5-ring	0	5	7	11	12	13	14	15	
# 6-ring	0	8	11	15	16	23	27	43	
# 7-ring	0	2	6	5	9	11	11	10	
C2 added	60	10	10	10	10	10	10	C_{146}	
# of C atoms	120	140	160	180	200	220	240		

S2

								tend [ps]	sf [ps]
start time [ps]	0.00	6.05	12.10	18.15	24.20	30.24	36.29	68.28	61.5
simulation time [ps]	6.05	6.05	6.05	6.05	6.04	6.05	31.99		
T [K]	2000	2000	2000	2000	2000	3000	3000		
# 5-ring	0	5	8	11	16	20	18	19	
# 6-ring	0	5	10	16	16	23	27	44	
# 7-ring	0	0	3	7	11	13	14	8	
C2 added	60	10	10	10	10	10	10	C_{184}	
# of C atoms	120	140	160	180	200	220	240		

S4

								tend [ps]	sf [ps]
start time [ps]	0.00	6.05	12.10	18.15	24.20	30.25	36.30	84.31	84.3
simulation time [ps]	6.05	6.05	6.05	6.05	6.05	6.05	48.01		
T [K]	2000	2000	2000	2000	2000	3000	3000		
# 5-ring	0	4	4	6	6	8	10	27	
# 6-ring	0	5	3	5	8	7	23	49	
# 7-ring	0	1	5	4	6	6	7	12	
C2 added	60	10	10	10	10	10	10	C_{208}	
# of C atoms	120	140	160	180	200	220	240		

Final structures: hexagon/pentagon ratio 1:0.5

20 “unsuccessful” (or better: unfinished) simulations

Ratio of success: 5/25 = 20% (similar to fullerene yield?)

Conclusions for Self-Assembled Fullerenes from C_2's

Three Stages of Fullerene Growth in continued C_2 flow:

1. ***Nucleation:*** **Determined by C_2 density around 2000 K forming initial nucleus with high pentagon/hexagon ratio (similar to pentagon road)**
2. ***Ring collapse growth:*** **Ring collapse of chains growing at borders of nucleus which continue to grow by addition of C_2 (similar to ring collapse mechanism), driven by growing π-delocalization**
3. ***Cage closure:*** **Similar to CNT → fullerene formation, final stage is driven by reduction of unfilled valences in closing the cage orifice. Higher temperature seem to accelerate the activity.**

Temperature and initial density control nucleation. Addition of C fragments controls the growth.

A Serious Question Unanswered

All the fullerenes made here are large: C_{146} - C_{208}.

How are smaller fullerenes (C_{60} and others) formed?

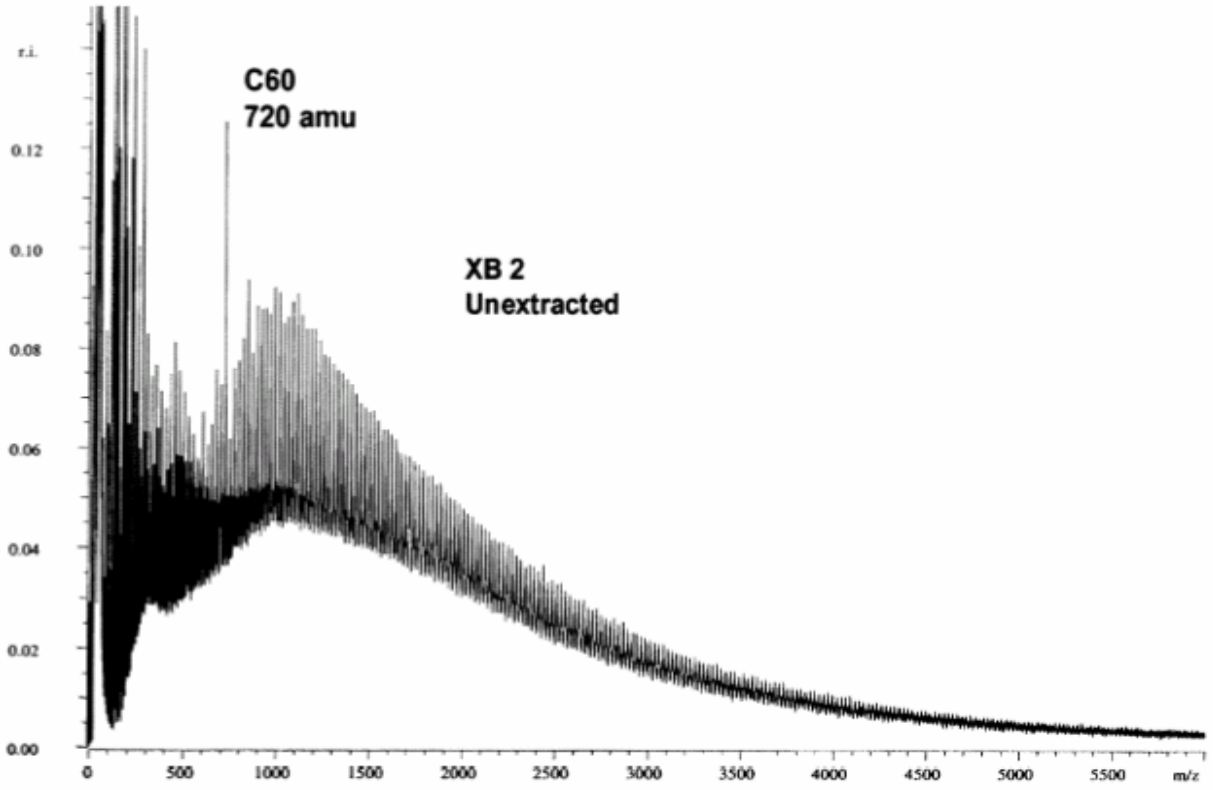


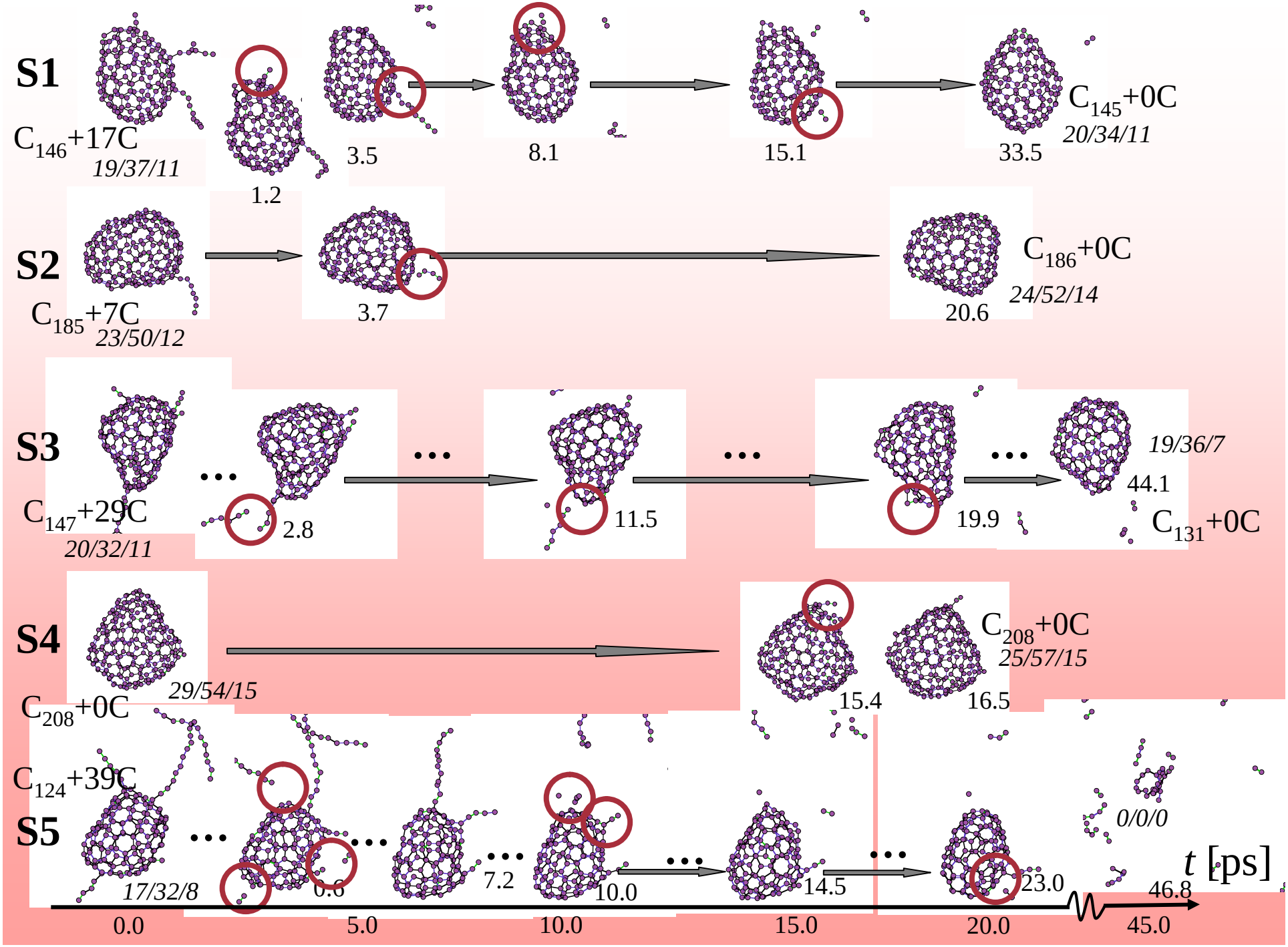
Fig. 4. XB2 MALDI mass spectrum showing C60 and higher fullerenes in carbon black soot.

Size-Down Roadmap

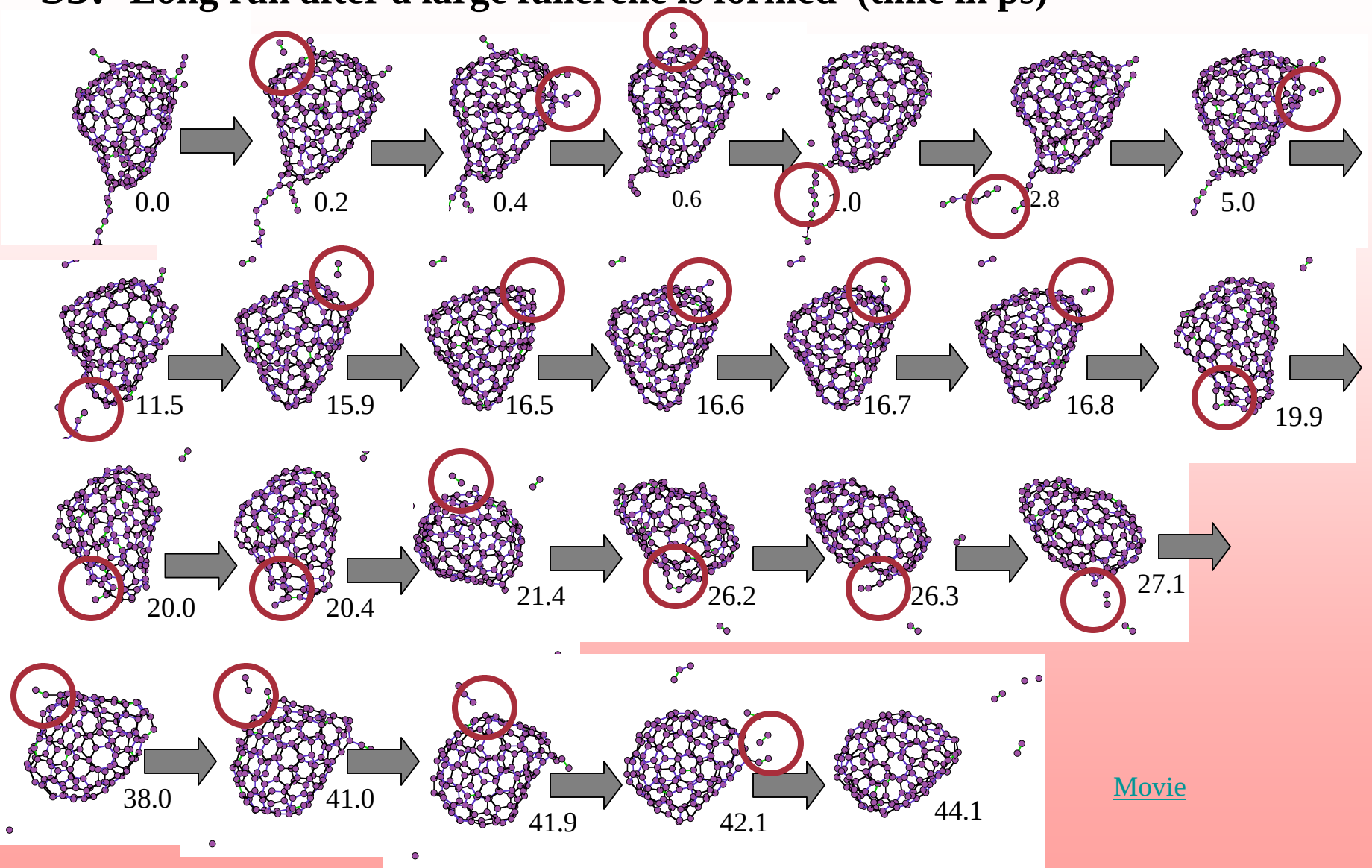
1. Larger fullerenes are made first, and later they become smaller. (Size-down approach)

- How do larger fullerenes become smaller?
- Dynamics after the formation of large fullerenes
  - Do they lose the branches?
  - Do they lose small C fragments or split into smaller fullerenes?
  - Are additional C fragments (or collision partners) needed?
  - What is the best temperature? How long does this take?

Follow up S1-S5, by running longer simulation


S1
C146+17C
19/37/11
1.2
3.5
8.1
15.1
33.5
C145+0C
20/34/11
S2
C185+7C
23/50/12
3.7
20.6
C186+0C
24/52/14
S3
C147+29C
20/32/11
2.8
11.5
19.9
44.1
19/36/7
C131+0C
S4
C208+0C
29/54/15
15.4
16.5
C208+0C
25/57/15
C124+39C
S5
17/32/8
0.6
7.2
10.0
14.5
23.0
0/0/0
46.8
t [ps]
0.0
5.0
10.0
15.0
20.0
45.0

S3: Long run after a large fullerene is formed (time in ps)



Movie

Size-Up Roadmap

All the fullerenes are large: C_{146} - $C_{208.}$

How are smaller fullerenes (C_{60} and others) formed?

2. Smaller fullerenes are formed directly from carbon fragments. (Size-up approach)

How can the growing cluster gain steep curvature efficiently?

A. Better concentration (pressure), or temperature?

B. Speed of addition of more C fragments?

C. Need some hidden catalyst?

Strategies to Make Smaller Fullerenes Directly

1. Larger carbon fragments (C_6 instead of C_2)
2. Lower carbon density, adding single C_2 and longer simulations
3. Higher carbon density, less C_2's

Larger Carbon Fragments (C_6 instead of C_2 units)

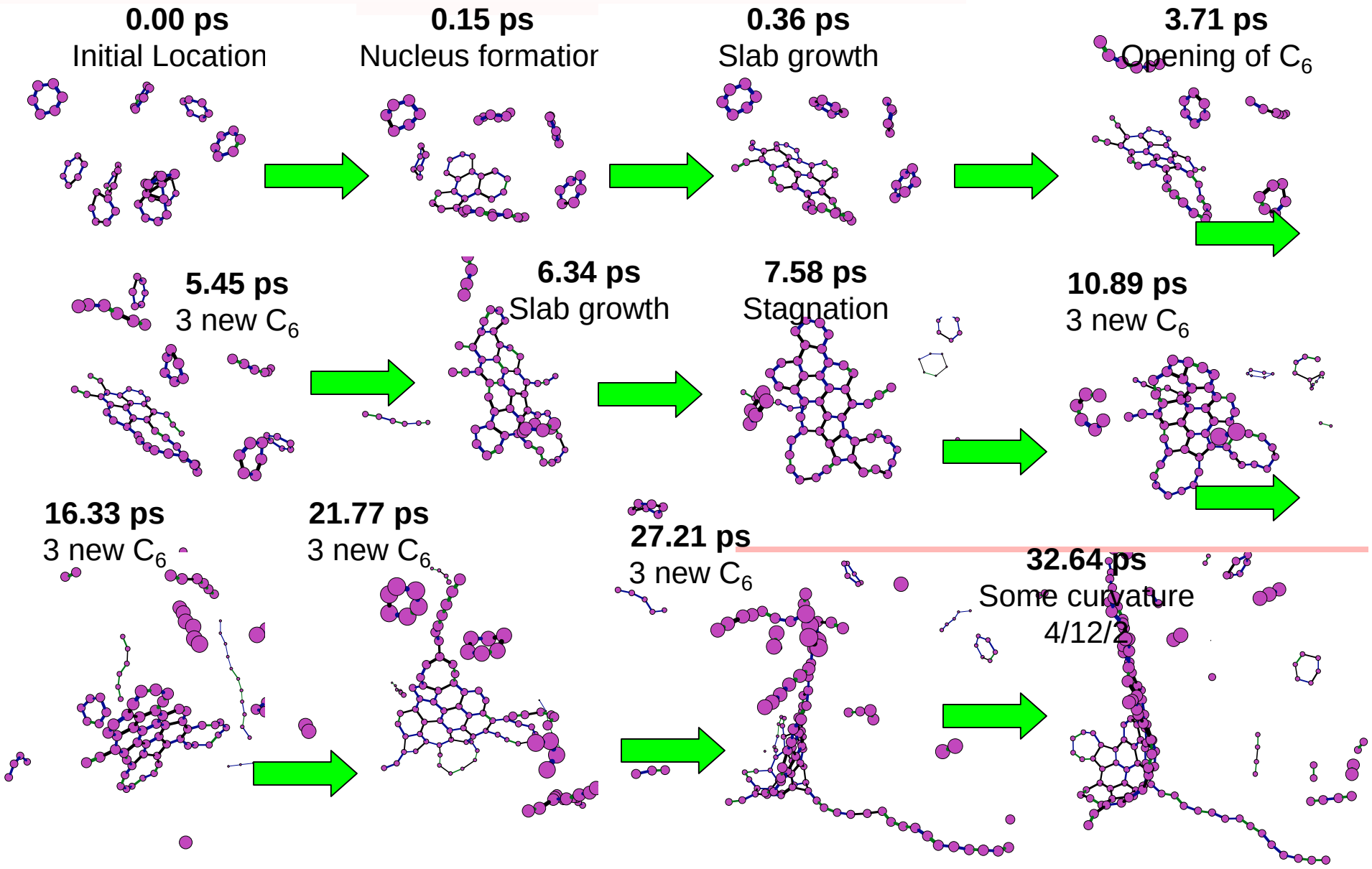
Reasoning:
Larger carbon fragments could become easier entangled in a more 3D-like structure.

Schematic:
30 Å periodic cube, initially 10 C_6, 3 C_6 units added every 5.43 ps for 6 times. First step at 1500 K, every following step 2000 K. 32 ps length. 18 Trajectories total.

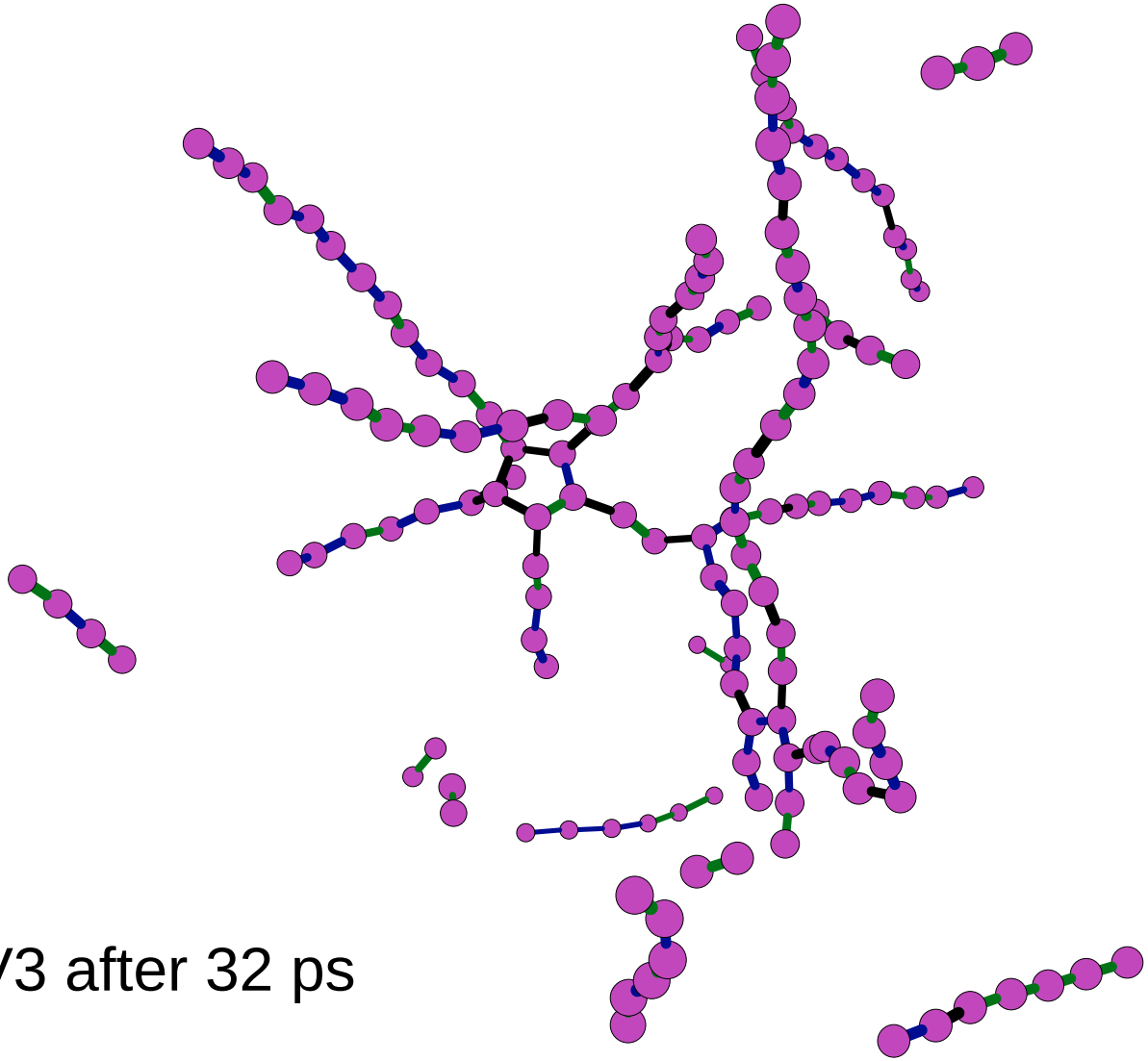
Results:
2 trajectories show slow slab formation
16 trajectories form only long chains and macrocycles

Possible Reason for Fullerene Formation Failure:
Initial carbon density too low, C_6 units initially too far away from each other

Larger Carbon Fragments (C_6 instead of C_2 units) v2



Larger Carbon Fragments (C_6 instead of C_2 units)

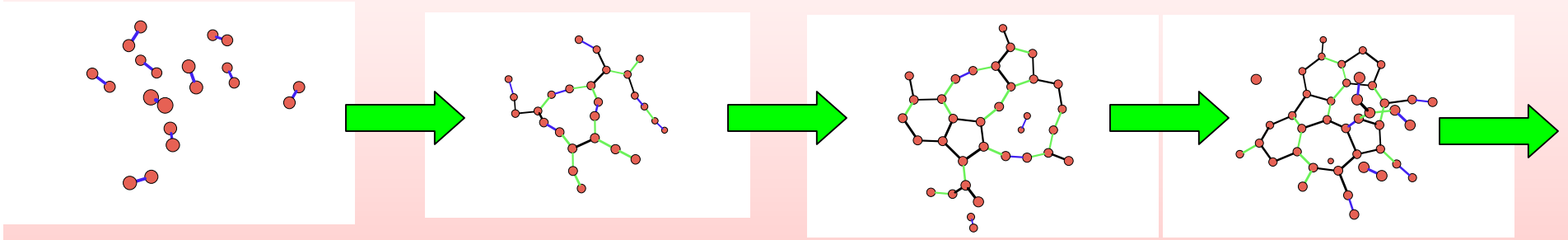


V3 after 32 ps

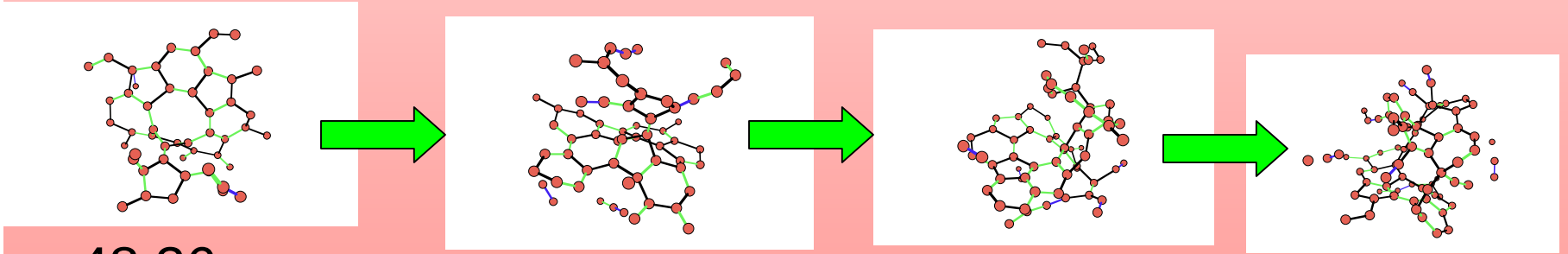
	5/6/7-rings
V2	4/12/0
V3	1/0/0
V4	0/1/0
V5	1/5/0
V6	4/10/1
V7	2/5/1
V8	1/0/0
V9	3/3/0
V10	2/4/0
V11	0/2/0
V12	2/3/0
V13	2/8/0
V14	2/2/0
V15	2/0/0
V16	3/0/0
V17	2/2/1
V18	1/1/0
V19	0/2/0

Longer Simulations, Lower Densities, Individual C_2's

Schematic: 10 C_2 units, 10 Å periodic box, 2000K. 1 C_2 added every 3 ps.



0.00ps 12.09ps 24.18ps 36.27ps

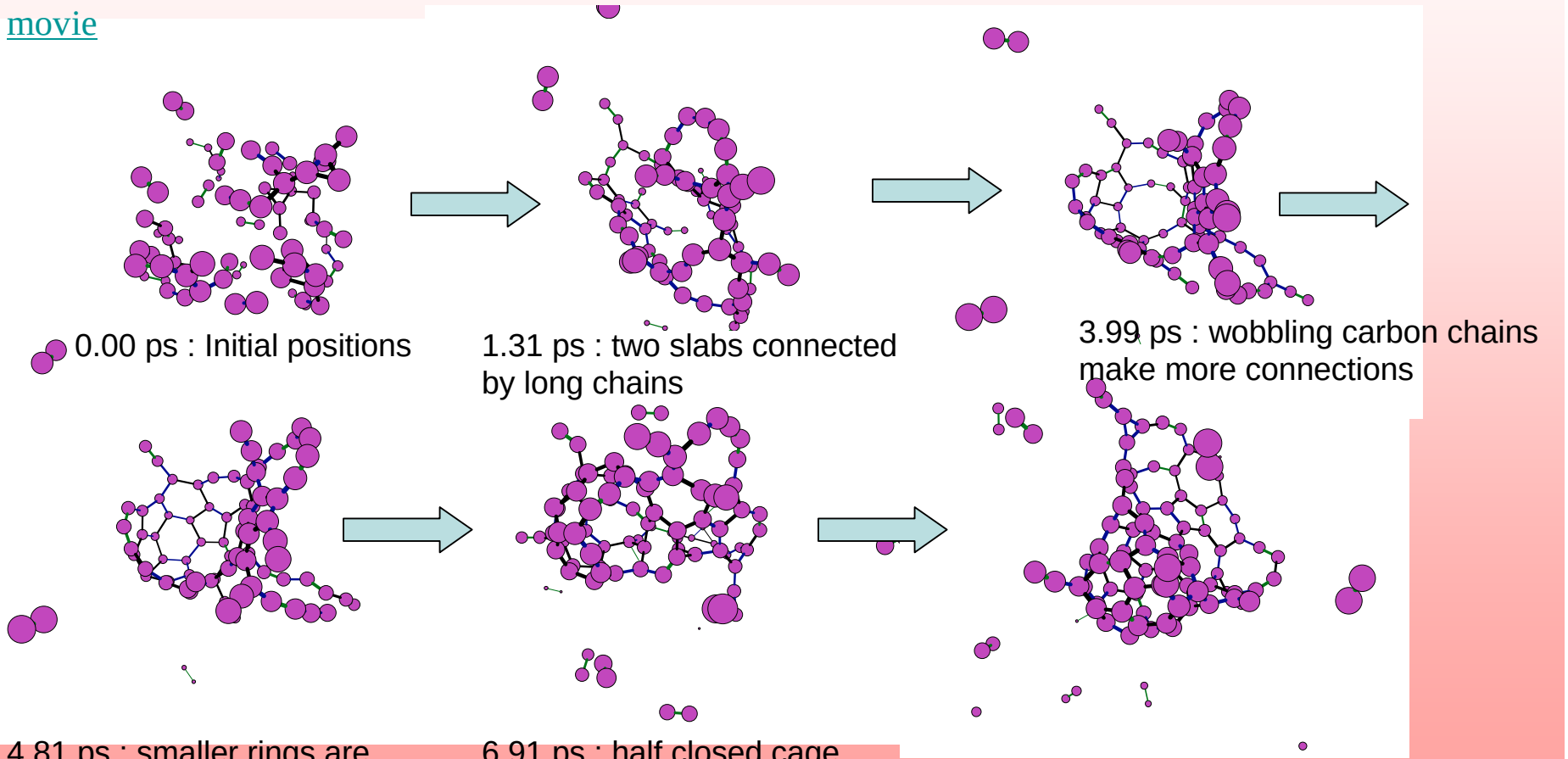


48.36ps 60.45ps 72.54ps 91.07ps

Higher Concentration of Initial C_2 Units (1.6g/cm^3)

w10: 40 C_2 units, 20 Å periodic box, 2000K. 10 C_2 added every 6.04ps.

movie



0.00 ps : Initial positions

1.31 ps : two slabs connected by long chains

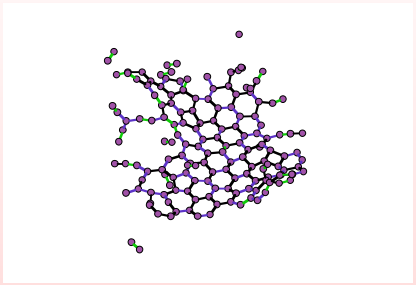
3.99 ps : wobbling carbon chains make more connections

4.81 ps : smaller rings are formed

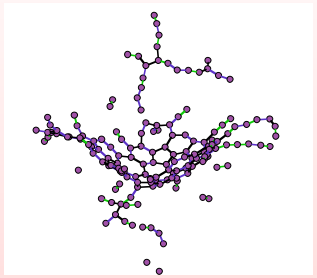
6.91 ps : half closed cage structure

7.87 ps : C_{54} fullerene forms with slab attached! (Frame 651)

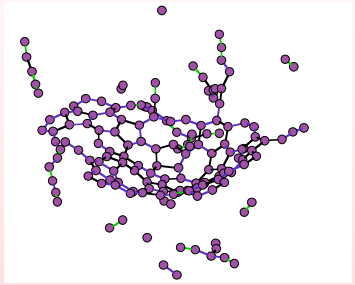
Higher Concentration of Initial C_2 Units (1.6g/cm^3)



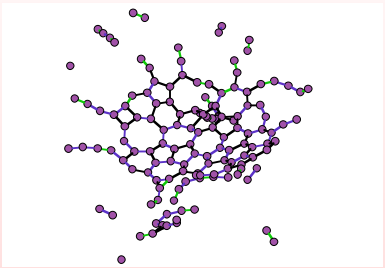
W1, 29.9ps



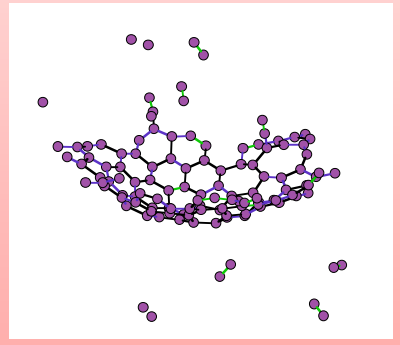
W2, 29.6ps



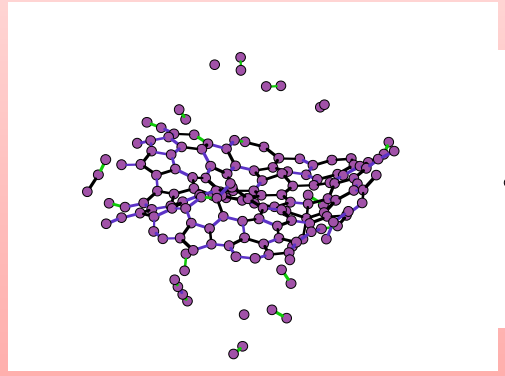
W4.29.6ps



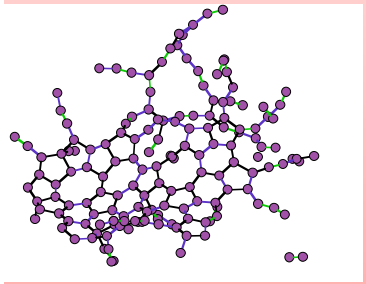
W5, 24.2ps



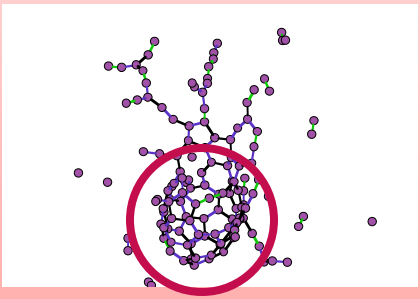
W6,18.1ps



W7.30.0ps



W8, 29.6ps



W9.24.1ps

Higher Concentration of Initial C_2 Units (0.2g/cm^3)

New Features of 5 successful trajectories (out of 103)

Three dimensional scaffold is built first.

The 3D open cage-like structure grows from the collapse of big rings

Smaller fullerenes grow **quicker** than before!! (<30 ps vs. > 40 ps)

W10: C92, W40: C74, W53: C82, W96: C96, W102: C95

Future Investigations

1. Simulated Annealing
   Including “Bombardment” with C_2 units, gradually reducing heat

2. Continue to perform high density trajectories for higher yield

3. Include cations as “3D-attractors”: Coulomb force is centro-symmetric, different from carbon atoms which tend to form slabs

4. Any wild ideas?
Any suggestion is welcome.

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Movies: http://euch4m.chem.emory.edu/nano