A Study within the Nanosystem Architecture Domain: Self-assembly of Graphene

NKS 2007 Conference
Wolfram Science

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July 13, 2007

Tonight's Topic

- This talk is intended to demonstrate the application of the shape grammar-cellular automata (SG→CA) methodology in the study of nanosystem self-assembly, specifically to gain insights for nanosystem architecting of graphene.
- Introduction to system architecture
  - Motivation
- Introduction to shape grammar and the SG→CA methodology
- Nanosystem architecture: Graphene self-organization modeled by SG→CA

Current Discipline of System Architecture is in part Limited by

- Too few concept alternatives considered
  - Limited time and budget
- Dominance of paradigms, subjective personalities, political positions and financial influencers (*The Structure of Scientific Revolutions,* Thomas Kuhn, 1970*)*
  - Individuals
  - Teams
  - Enterprises
- Insufficient interaction of concept design and selection with stakeholders to elicit their true wants
- Compulsion to do rather than think, create alternatives, evaluate and rank alternatives, iterate system architectures with stakeholders

Motivation

- **System architecture**

1. To generate a creative space of system architectures that are physically legitimate and satisfy a given specification inspired by nature's bottom-up self-generative processes
   - using a shape grammar and cellular automata approach SG→CA
2. Expanding the application of the SG→CA approach to a study in the nanosystem domain – system architecting of graphene
   - modeling complex, nonlinear physical phenomena; Science → Application

Shape Grammar

- Based on transformational grammars [N. Chomsky 1957] , which generate a language of one dimensional strings
- Shape grammars (Stiny, 1972; Knight, 1994, Stiny 2006)
  - are systems of rules for characterizing the composition of designs in spatial languages (nondeterminant)
  - The grammar is unrestricted having the capability of producing languages that are recursively enumerable
  - defined by a quadruple SG = {V_T, V_M, R, I)}, generate a language of two or even three dimensional objects that are composed of an assemblage of terminal shapes, where
    - V_T is a set of terminal shapes (i.e., terminal symbols)
    - V_M is a set of markers (i.e., variables)
    - R is a set of shape rules (addition/subtraction and Euclidean transformations), u→v is the shape rule (i.e., productions; a production set of rules specifies the sequence of shape rules used to transform an initial shape to a final state and thus constitutes the heart of the grammar)
      - u is in $(V_M \cup V_T)^+$ and v is in $(V_M \cup V_T)^*$
    - I is the initial shape to which the first rule is applied (i.e., start variable)

The System Architecture Generative Algorithm in Stages: SG→CA

Given: Specification of function, constraints, requirements and "ilities" in solution neutral form

Stages 1: Developing the design system to describe the system architecture

2: Adapting the shape grammar to a cellular automaton neighborhood

3: Developing the computational system to generate the system architecture

4: (Optional) Narrowing the creative or solution space of system architectures

5: (Optional) Configuring the complete system architecture

6: Selecting from the creative or solution space of system architectures

Motivation for a Domain Study into Nanosystems

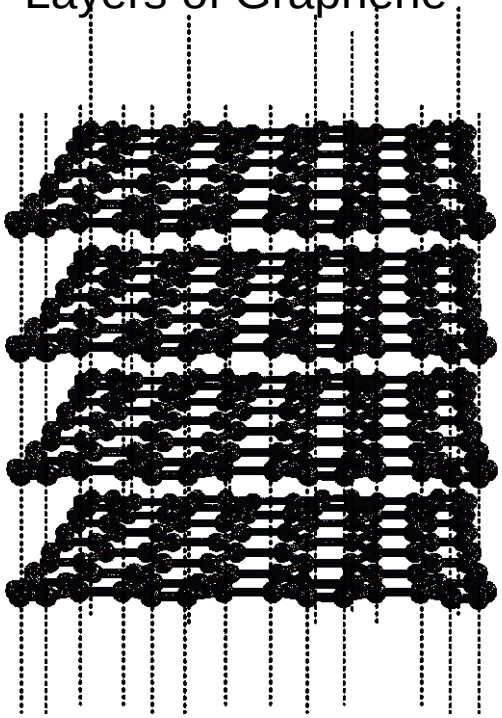
- Nanosystem architecting is a new science that could be the next technological surge in human advancement
- Problem: A number of architectural achievements have been made in nanoscience but mostly in the laboratory, characterized by very low volume production, high cost per "unit" situations, and a slow process
- Need-Want: A "manufacturing" advancement is required in order to produce nanosystems economically at large-scale
- Another problem identified in the literature regarding graphene, and even more widely as pertains nanosystems, is the inability to predictably model and then facilitate the self-assembly of nanostructures economically at large-scale using the physical laws of nature.
- Being able to model the self-assembly of nanosystem architectures could move progress toward better understanding the physics controlling the behavior of nanosystems and for predicting this behavior more accurately through the construction of nanosystem architectures for later empirical verification.
- The SG→CA methodology may prove a useful means for the conceptualization of solutions to these problems.

Motivation for a Domain Study into Graphene

- Basic Carbon element in many inanimate and artificial systems, and all biotic systems
- Graphene was isolated only recently in 2004 by Novoselov, Geim
  - Considered a new material, a condensed-matter system
    - Graphene belongs to the carbon allotrope chemical class called fullerenes and is an sp^2 covalent bond carbon structure with a hexagonal (honeycomb) lattice shape.
  - Covalent bonds are stronger than diamond bonds (in fact, the strongest lattice bonds in the periodic table), providing a material that exhibits very high tensile strength and elasticity
  - No band gap, massless, waveform electron semiconductor property, similar to nanotubes with armchair chirality, which could be useful for electronic nano devices such as switches for logic or memory purposes
    - Electrons in graphene have been found to move ballistically at room temperature over large distances without being scattered, due to the delocalized, unbound p orbital electrons above and below the single atom layer of graphene
  - See Geim, *Nature* 2007 for a current survey of graphene science

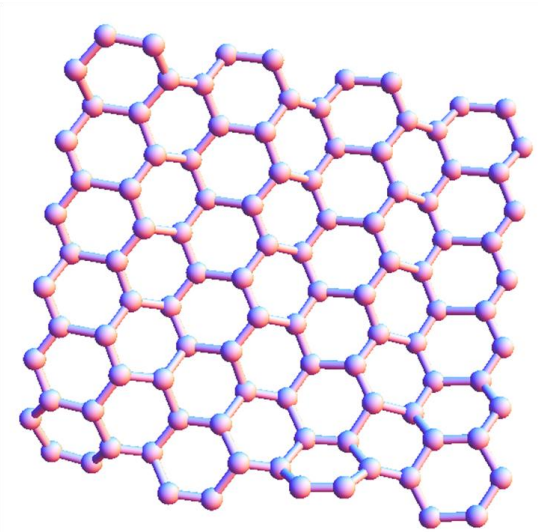
Introduction to Graphene

Graphite Composed of Layers of Graphene

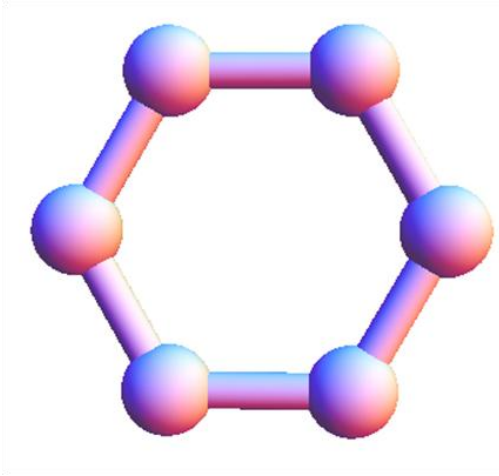


(The dashed lines are van der Waals forces weakly bonding the graphene layers together.)

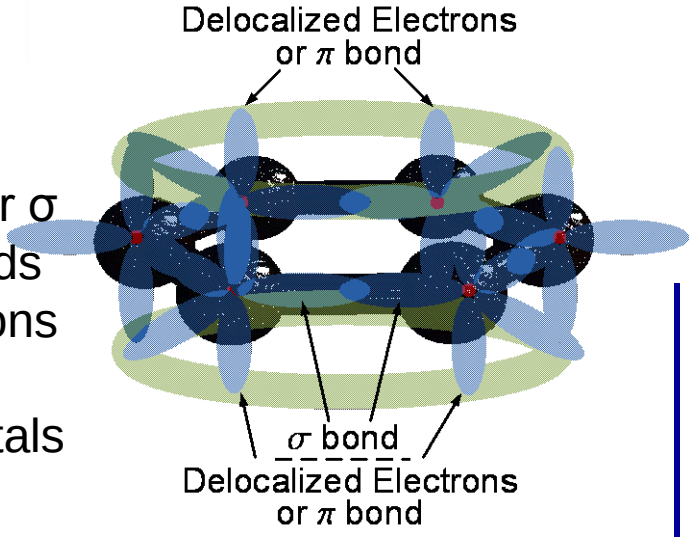
Hexagonal Six Carbon Lattice Structure



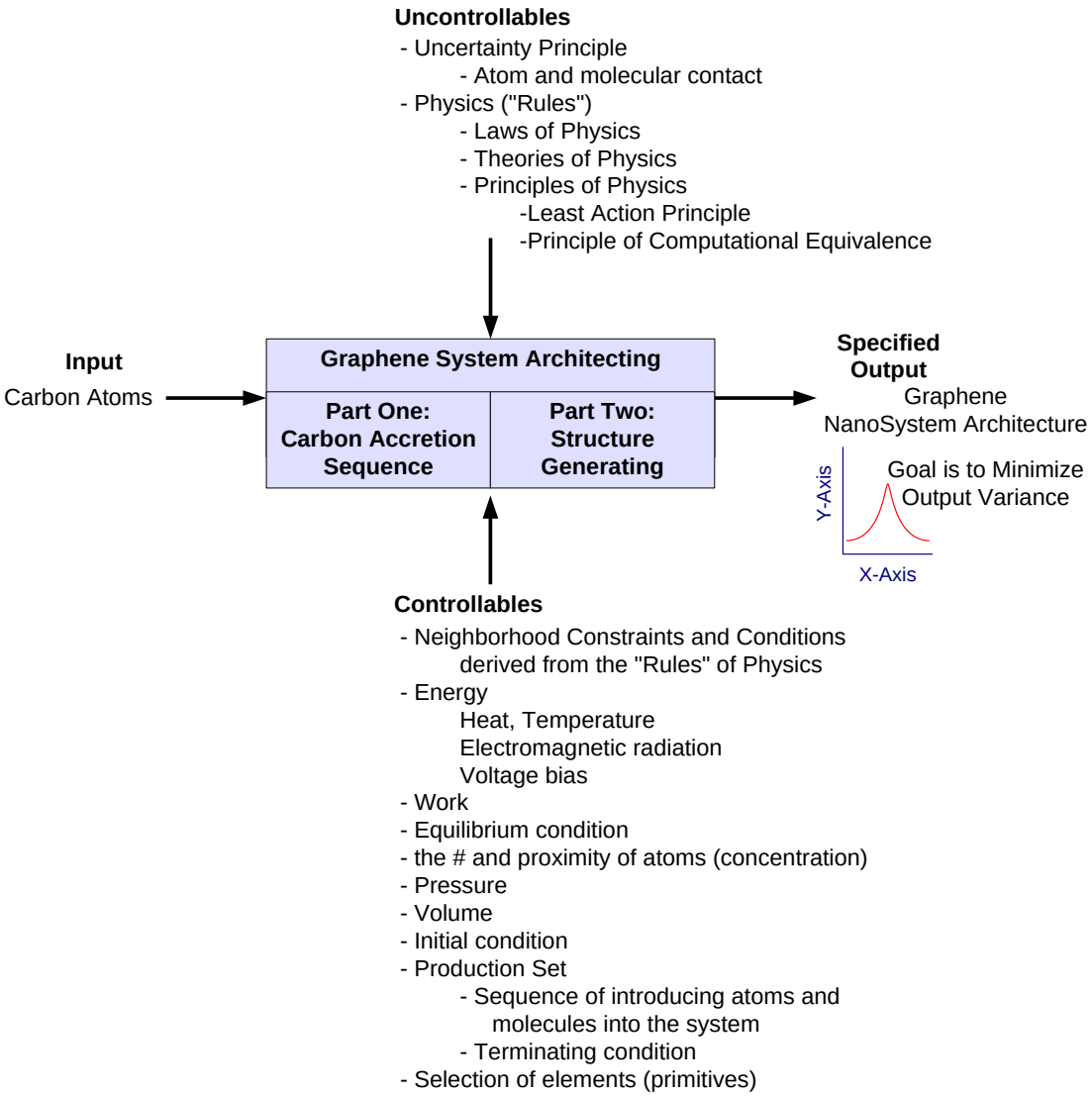
Hexagon Shape (the spheres are carbon atoms and the cylinders are covalent bonds)



Electron Orbitals in their σ Covalent in-plane Bonds and Delocalized Electrons (as in Graphene) or Available π Bonds Orbitals



p-diagram of Graphene System Architecting



Graphene Shape Grammar-Cellular Automata Models[1] (SG→CA)

- The given specification
  - Self-assemble graphene
- Shape Grammar
  - Shape variables:= {Primitives, Modules, Markers}
  - Rules of neighborhood interaction
  - Initial condition is empty space with:
    - Carbon atoms can be directed into a precisely controlled atmosphere via a carbon atom vapor to deposit loosely over a heated metallic substrate so that the carbon atoms can diffuse, come into neighborhood proximity, and then combine covalently into increasingly larger structures
    - Graphene does not appear to form as a stable structure in free space, a substrate is required to attract and maintain alignment of the planar or two-dimensional arrangement of carbon atoms. Ribbons of nickel may be used in this manner as its metallic surface attracts the growing graphene structure by means of van der Waals forces resulting from the delocalization of the carbon electron in the perpendicular (p_z) orbital above and below the graphene layer.
- The generating machine is a two-dimensional cellular automaton
  - Transcribe the shapes into symbols, then
  - Compute generatively the system architectures by computing with the symbolically represented shapes
- Translate back to shape and provide graphical visual output

[1] Described in Speller, T.H., Jr., D. Whitney, and E. Crawley, *Using Shape Grammar to Derive Cellular Automata Rule Patterns. Complex Systems, 2007.* ***17: p. 79-102.***

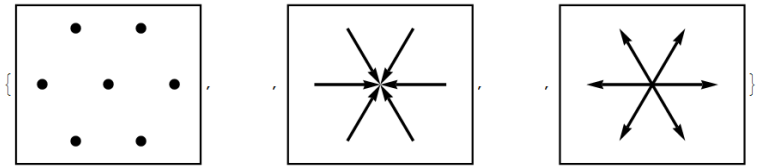
Part One: Carbon Atom Aggregation

- **Stages 1 and 2 – Shape grammar and neighborhood development for carbon atom accretion**
  - The shape grammar for graphene self-organization was developed after review of chemical representation schemes and consideration of the Lewis[1] and "Electron Cloud" Repulsion Theory (Valence Shell Electron Pair Repulsion, VSEPR)[2] methods, also known as the "AXE" notation, for representing and predicting by means of rules the proper bonding and geometry of molecular systems.
  - The fact that a carbon atom can be represented as a tetrahedron led to the representation of three of the four carbon valences as the vertices of an equilateral triangle when the tetrahedron is projected onto a two-dimensional space, the fourth electron being allowed to become delocalized between the graphene plane and the substrate.

1. Lewis, G.N., *THE ATOM AND THE MOLECULE.* J. Am. Chem. Soc., 1916. **38**(4): p. 762-785.
2. Gillespie, R.J., *The VSEPR model revisited.* Chemical Society Reviews, 1992. **21**: p. 59 - 69.

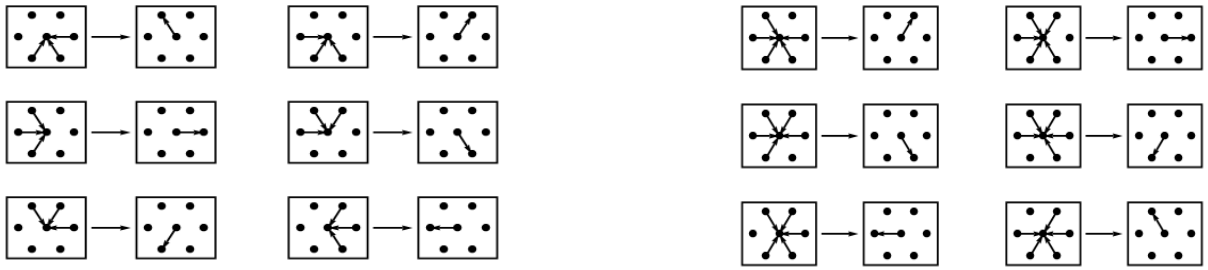
Stages 1 and 2: Developing a Shape Grammar and Neighborhood for a Graphene Specification

- Shape Variables for the Dynamic Accretion Grammar:
  - 1 empty shape (no atom present), symbolically: {0}
  - Shape variables: seven points of a star graph, six orientations of an arrow (or line) to indicate all incoming and outgoing atom and molecule momentum vectors (mass, velocity, direction),
    - symbolically: {1, 2, 3, 4, …, n}, where n is the number of atoms introduced in the controlled atmosphere



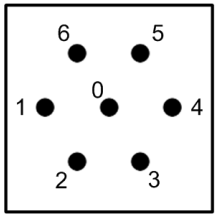
Entry/exit Location Points | All Incoming Vectors for Atoms and Molecules | All Outgoing Vectors after Combining

  - 0 shape markers
- 64 rules: the formal simple relationships of form-function symbolically expressed according to local neighborhood conditions



Stage 3 – Developing the Cellular Automaton, Combinatorics and Algorithm for the Carbon Accretion

Shape Variable



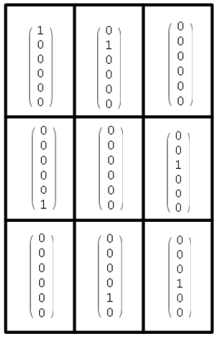
Hexagonal Neighborhood Positions Schema

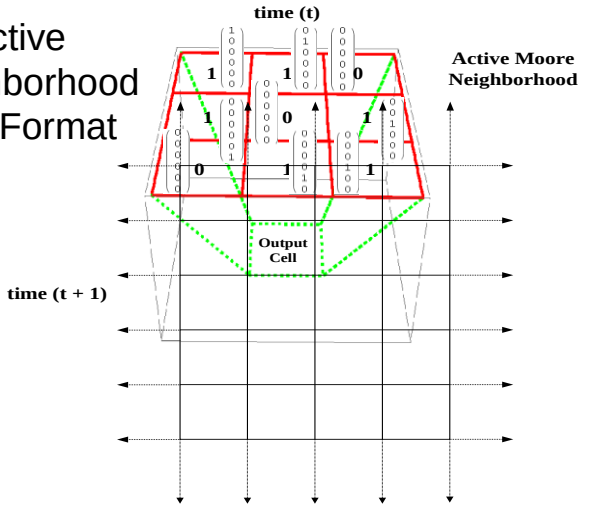
6	5	0
1	0	4
0	2	3

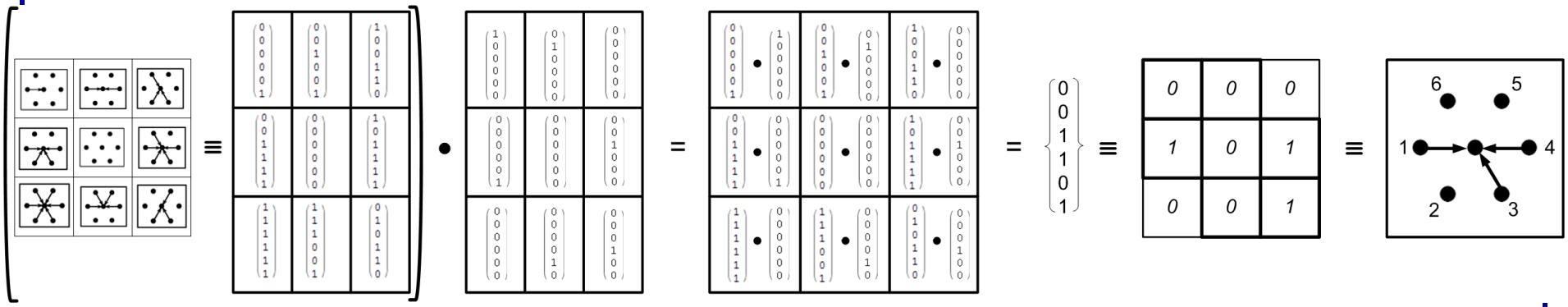
Active Conditional Neighborhood for the Accretion Experiment

1	1	0
1	0	1
0	1	1

Equivalent Active Conditional Neighborhood in List Structure Format

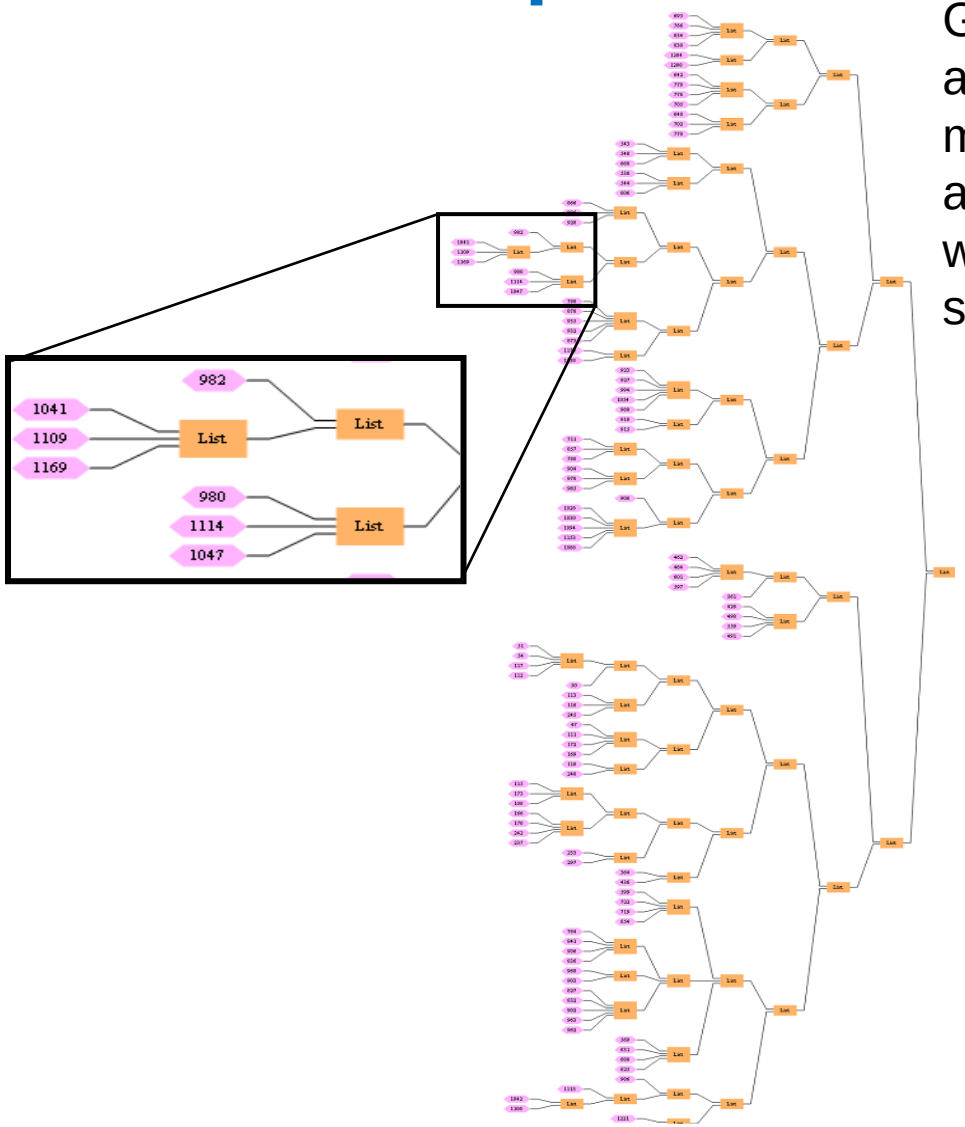






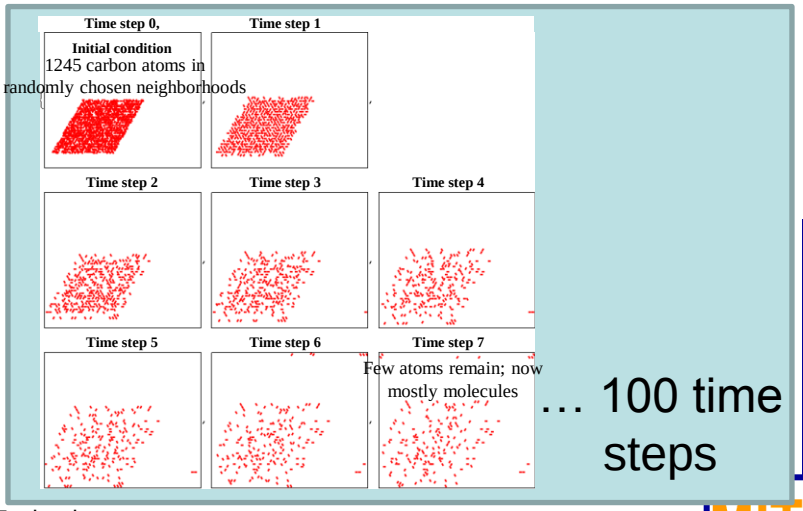
$$\left(\begin{pmatrix}\text{Entire Moore Neighborhood}\{3\,\text{rows},3\,\text{columns}\}\\(\text{sample pictures})\end{pmatrix} * (\text{Active Moore Template})\right) = lhs\,Rule$$

Accretion Sequence Combinatoric Tree Graph



Groups of carbon atoms by sequence of attachment to the self-generating molecular system after 100 cellular automaton time steps (largest sequence was chosen for Part Two, graphene structure generating.

Production set:
{3, 1, 3, 3, 7, 6, 19, 13, 59}



… 100 time steps

Part Two: Graphene Structure Generation

- **Four experiments were conducted**
  1. **Experiment 1 – random, one-by-one self-organization**
  2. **Experiment 2 – random, accretion group self-organization**
  3. **Experiment 3 – attraction force, one-by-one self-organization**
  4. **Experiment 4 – attraction force, accretion group self-organization**
- **Experiment 4 is described as an example**

Stages 1 and 2 – Shape Grammar and Neighborhood Development for Experiment 4 (attraction force, accretion group self-organization)

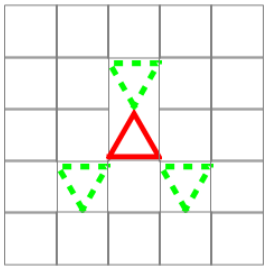
- Shape variables:
  - 1 empty shape, symbolically: {s0}
  - 4 shape variables, symbolically: {cd, cu, cdg, cug}
  - 0 shape markers: there are no boundary conditions; the space expands as atoms are accreted
- 122 rules: the formal simple relationships of form-function symbolically expressed according to local neighborhood conditions
- Production set: {3, 1, 3, 3, 7, 6, 19, 13, 59}, (per Accretion Sequence Combinatoric Tree Graph)
- The initial condition is empty.

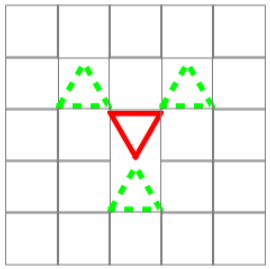
Experiment 4, Examples of "Basin of Attraction" Rules for Aggregated Atom Subgroups

Shape Variables with their Symbolic Equivalents

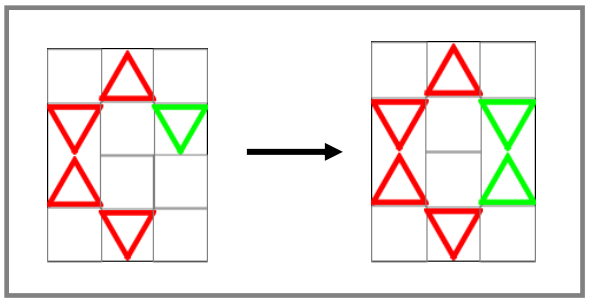
{ s0, cd, cu, cdg, cug}

Shape Rule Possibilities for Random Bonding to an Open Orbital

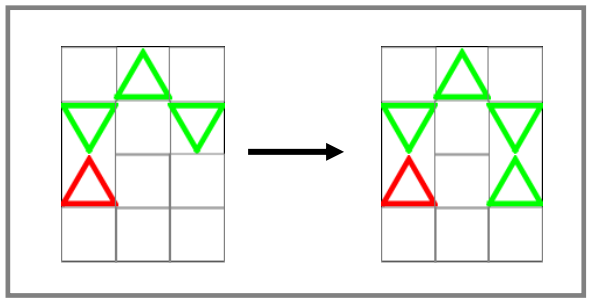




"Basin of Attraction"

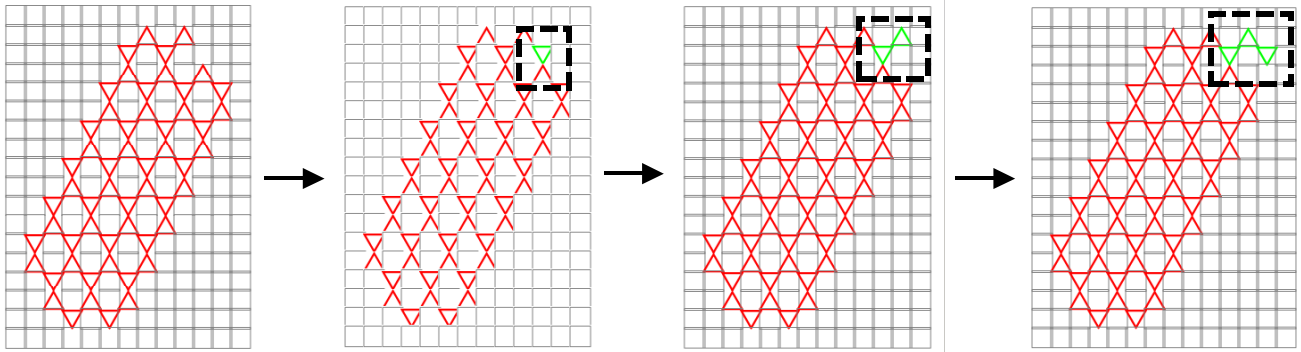


(adding an aggregated atom subgroup to a 5-carbon ring)



(adding an aggregated atom subgroup to a 4-carbon ring)

Experiment 4 Example of a Graphene Structure Produced by Basin of Attraction Shape Rules, Different Steps in the Progression

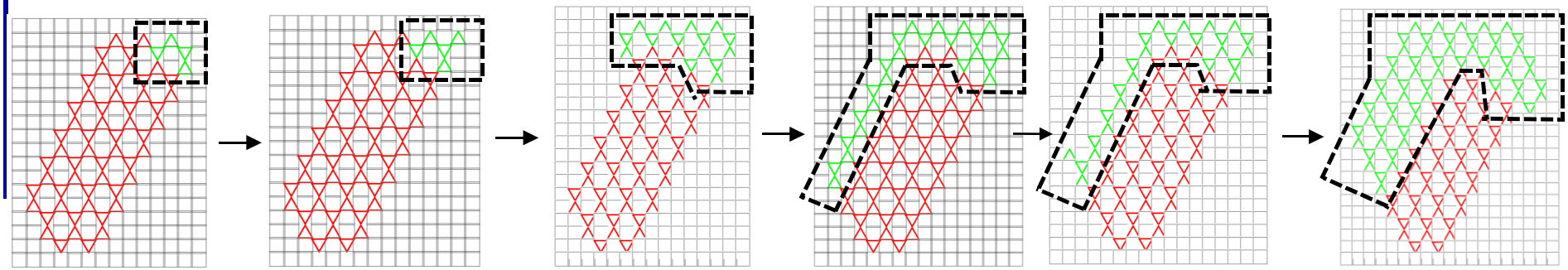


Structure (red) Prior To Attaching Next Subgroup

Attaching 1st Atom Of Next Subgroup (green)

Attaching 2nd Atom (green)

Attaching 3rd Atom (green)



Attaching 4th Atom (green)

Attaching 5th Atom (green)

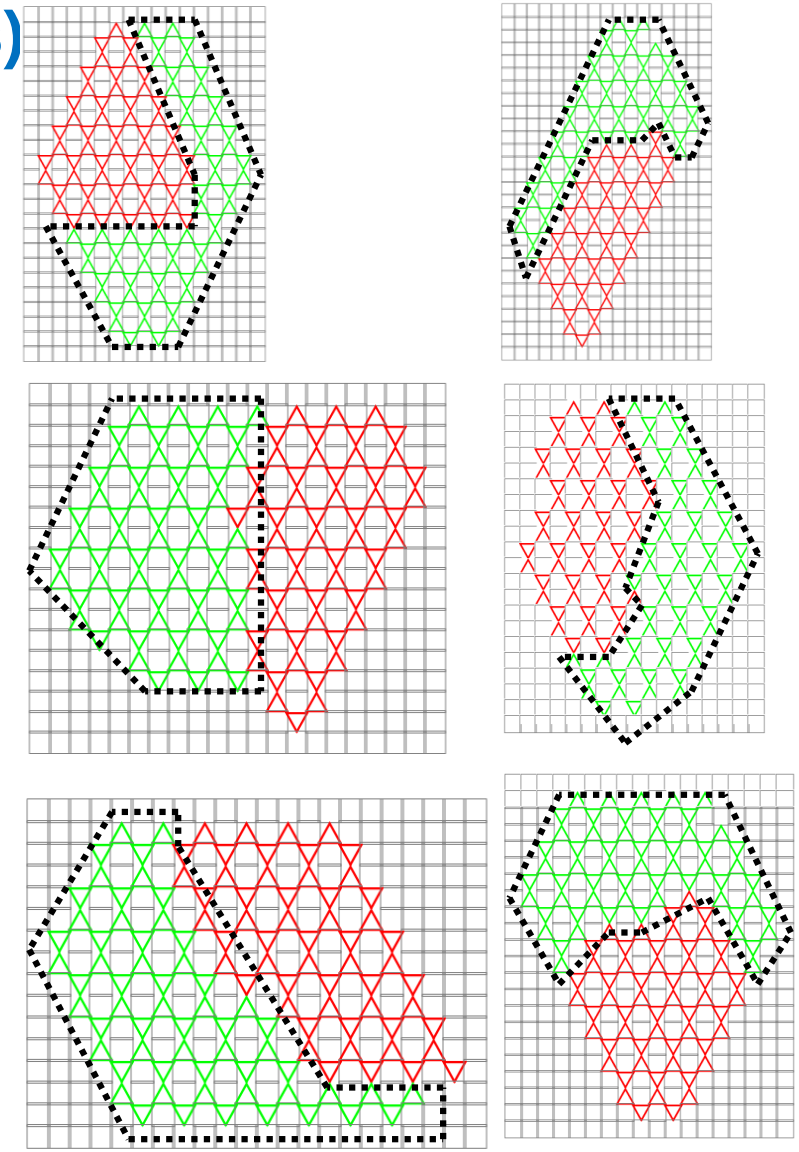
Attaching 15th Atom (green)

Attaching 25th Atom (green)

Attaching 26th Atom (green)

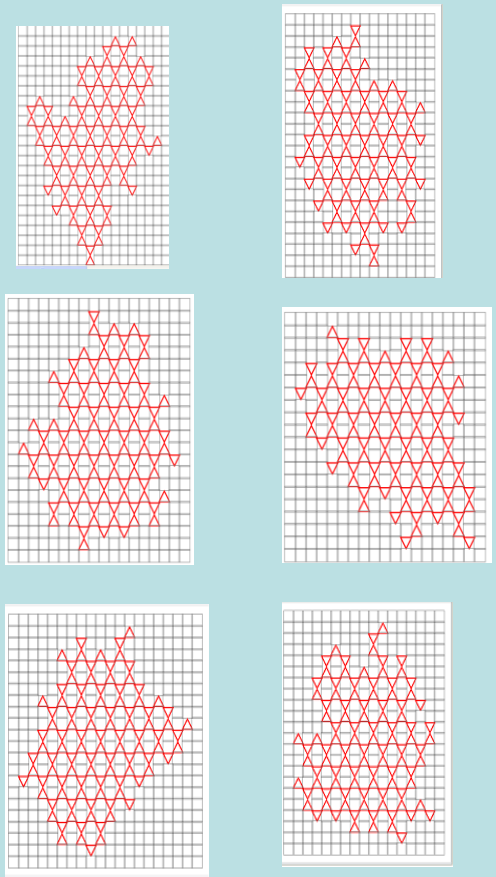
All 59 Atoms Of Last Subgroup Attached

Experiment 4 Examples of Final States of Graphene Structures Showing Last Subgroup (Basin of Attraction Rules for Self-Organization with Accretion Groups)

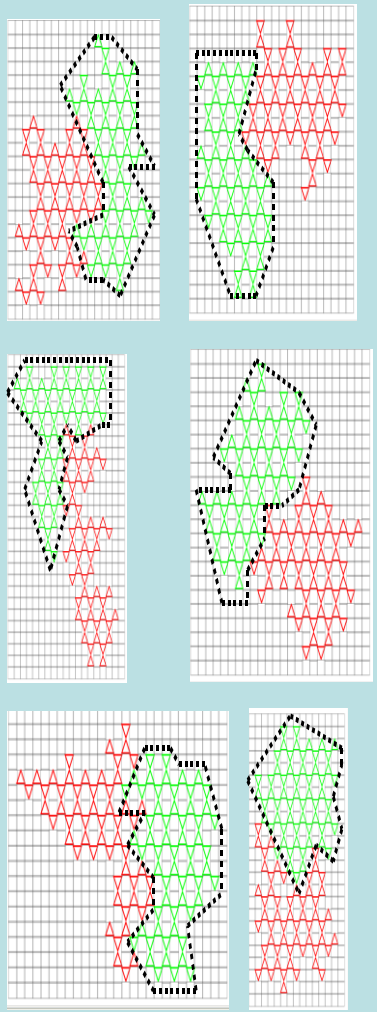


Experiments 1-4 Comparative Results

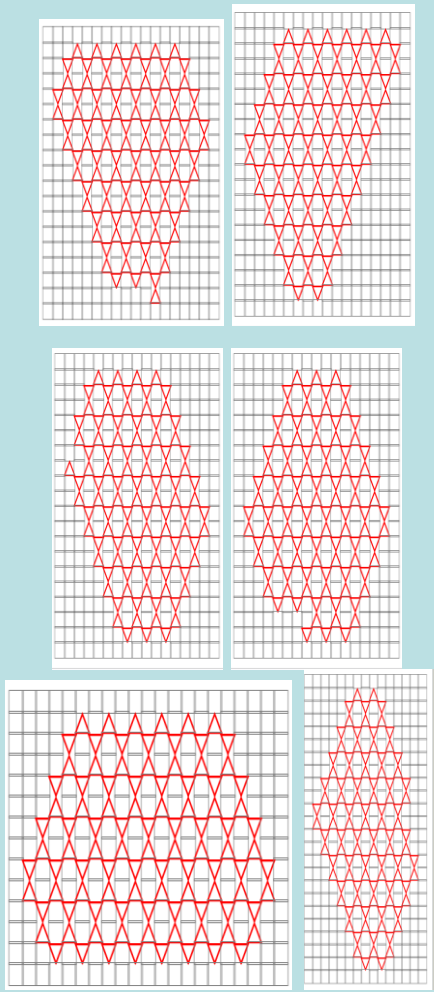
Experiment 1
random, one-by-one self-organization



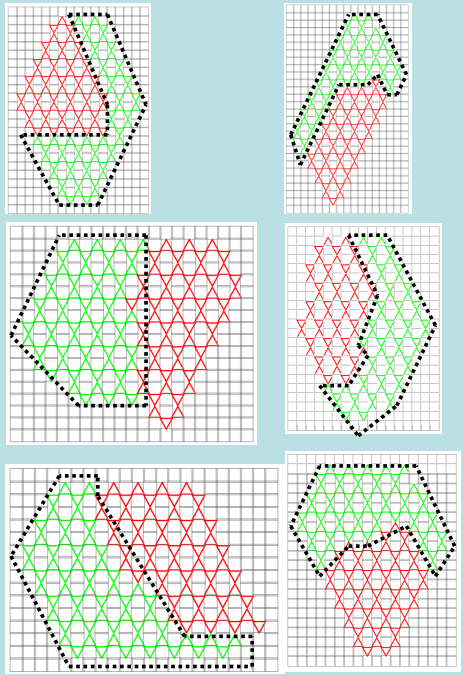
Experiment 2
random, accretion group self-organization



Experiment 3
attraction force, one-by-one self-organization



Experiment 4
attraction force, accretion group self-organization



Discussion of these Experiments

- All four models formed the graphene structure, although locally acting
- Allowing carbon to aggregate in separate subgroups should be avoided or minimized in the nanosystem architecting process of graphene.
  - While apparently ideal, creating graphene structures one atom at a time may not be feasible from a physical control standpoint.
- Therefore, in order to achieve more regular structures, one should try to control the number of atoms that combine into separate aggregations before bonding with each other. It would appear that the best graphene results would occur under conditions similar to Experiment 3, with methods utilized or devised to slow the carbon atom feed/deposition rate or induce nucleation at a single seed point on a substrate.
- This graphene study has demonstrated the potential use of the SG→CA methodology in an initial start for modeling the behavior of quantum systems. Many physical studies of nature's dynamics use numerical methods to try to calculate and predict chemical behavior. At the quantum scale this effort has been largely intractable computationally. However, emphasizing the SG→CA system architecting process as a computational grammar opens up the capability to study "in the computer" how physical systems might combine, therefore offering the ability to conduct system architecture experiments on the self-assembly of nanosystems.