Graph Theory Capstone

Applications of Graph Theory to the Physical Sciences

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Outline

Kinetic Graph

- Mechanisms of chemical reactions were first "graphed" in 1950s, by Christiansen.
- A modified version of his procedure creates the kinetic graph.

Kinetic Graph

- Edges represent reaction steps.
- Vertices represent intermediates.

Example Reaction

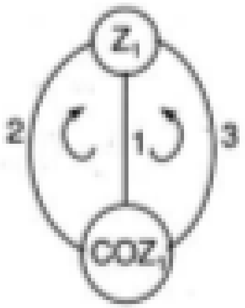
Reaction steps:

$$C + H_2O + Z_1 \rightleftharpoons H_2 + COZ_1 \quad (1)$$
$$COZ_1 \rightleftharpoons CO + Z_1 \quad (2)$$
$$COZ_1 + CO \rightleftharpoons CO_2 + C + Z_1 \quad (3)$$

For Z_1, COZ_1 intermediates; C, H_2O, CO, CO_2, and H_2 terminal species.

Example Kinetic Graph

Figure: A kinetic graph for the reaction steps.



Reaction Routes

- From kinetic graph, reaction routes can be realized.
- "Stoichiometric number," v_s, can be determined.
- Not unique - in case of example reaction, here are some example sets of v_s:

$$
\begin{aligned}
v_s^{I} &= (1,1,0)\\
v_s^{II} &= (1,0,1)\\
v_s^{III} &= v_s^{I} - v_s^{II} = (0,1,-1)\\
v_s^{IV} &= v_s^{I} + v_s^{II} = (2,1,1)
\end{aligned}
$$

Reaction Routes

$$C + H_2O \rightleftharpoons H_2 + CO \qquad \text{(I)}$$
$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \text{(II)}$$
$$CO_2 + C \rightleftharpoons 2CO \qquad \text{(III)}$$
$$C + 2H_2O \rightleftharpoons 2H_2 + CO_2 \qquad \text{(IV)}$$

Reaction Routes

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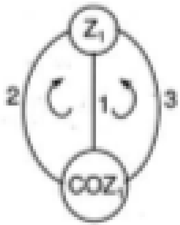
Kinetic Graph



Determining Linearly Independent Routes

- The number of linearly independent reaction routes, P, is determined by $P = S - I$, where S is the number of reaction steps and I is the number of linearly independent intermediates.
- I is determined based on the stoichiometric numbers.
- For example reaction, $P = 3 - 1 = 2$. Then, combinations of reaction routes (each from a set of v_s) are able to completely describe the reaction.

Example Reaction

$$C + 2H_2O + CO \rightleftharpoons 2H_2 + CO + CO_2 \qquad \text{(I)+(II)}$$
$$2C + 2H_2O + CO_2 \rightleftharpoons 2H_2 + CO_2 + 2CO \qquad \text{(III)+(IV)}$$

Outline

Reaction Network

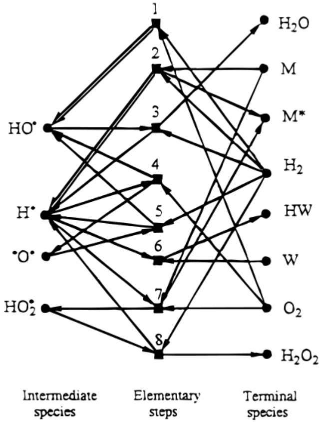
- A reaction network is a graph with 3 partite sets (intermediates, reaction steps, terminal species).
- Direction is assigned to edges to show whether a species is consumed or created by a reaction step.

Example Reaction Steps

$$H_2 + O_2 \rightarrow 2HO^\bullet$$
$$H_2 + M \rightarrow 2H^\bullet + M^*$$
$$H_2 + HO^\bullet \rightarrow H^\bullet + H_2O$$
$$H^\bullet + O_2 \rightarrow HO^\bullet + {}^\bullet O^\bullet$$
$$H_2 + {}^\bullet O^\bullet \rightarrow H^\bullet + HO^\bullet$$
$$H^\bullet + W \rightarrow HW (\text{W= wall})$$
$$H^\bullet + O_2 + M \rightarrow HO_2^\bullet + M^*$$
$$HO_2^\bullet + H_2 \rightarrow H^\bullet + H_2O_2$$

Where $HO^\bullet$, $H^\bullet$, ${}^\bullet O^\bullet$, and $HO_2^\bullet$ are intermediates and H_2O, M, M^*, H_2, HW, W, O_2, and H_2O_2 are terminal species.

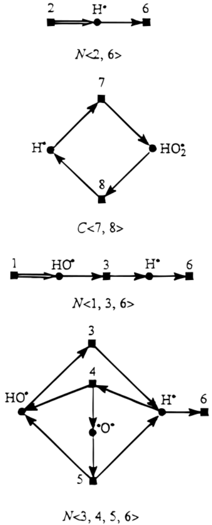
Example Reaction Network



Types of Submechanisms

- Each reaction network contains submechanisms which can be independent of one another or interdependent.
- They are labeled two types, C and N.
- The types of submechanisms involved in a reaction mechanism determine whether the reaction is catalytic (C type only), noncatalytic conjugated (N type only), or a chain reaction (both C and N types).
- In example case, both types are present.

Submechanisms for Example

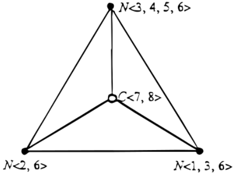


Submechanism Graph

- Vertices represent submechanisms (open circle denotes C type, close denotes N type).
- Edges connect two vertices if they share either a step or intermediate - meaning they are strongly related and require one another.
- In example case, K_4 is obtained, since all submechanisms are related to one another directly.

Example Submechanism Graph

Figure: The submechanism graph for the example reaction steps, where the vertices are associated submechanisms.



Summary: Kinetic and Submechanism Graphs

- The kinetic graph helps realize reaction routes.
- The submechanism graph, which is an extension of the kinetic graph, gives more detailed information about submechanisms in a reaction.
- The submechanism graph also helps categorize a reaction by type (catalytic, noncatalytic, chain).

Outline

Cold Dark Matter

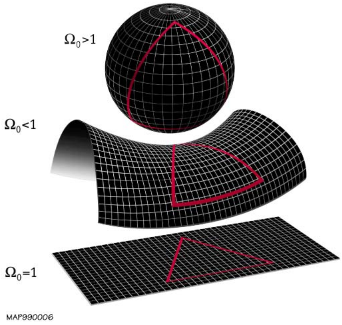
- CDM does not produce visible radiation, so it cannot be viewed directly by traditional methods.
- This model of universe provides density parameter, Ω.

Ω

$$\Omega = \frac{\rho_{avg}}{\rho_{ced}} \tag{4}$$

Where ρ_{avg} is the average density of the universe, and ρ_{ced} is the critical energy density, or the density required for a universe to be flat. Ω_0 is the density parameter today, since it is not necessarily constant.

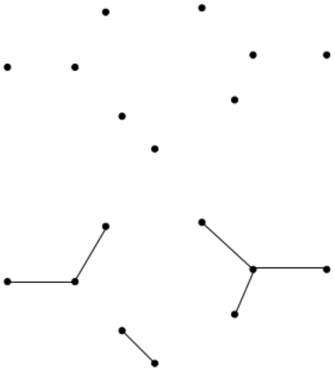
Ω_0



Outline

Example Constellation Graph

Figure: An example dataset and its constellation graph.

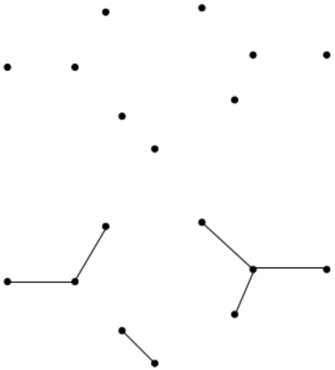


Constellation Graph

- Vertices represent galaxies (or stars/ other data).
- Edges are added by connecting each vertex to its nearest neighbor, in no specific order.
- Some vertices have one edge, some have many edges.
- For large data sets, the constellation graph is disconnected.

Example Constellation Graph

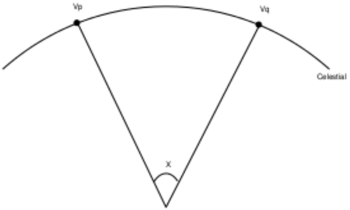
Figure: An example dataset and its constellation graph.



Edge Angle

- To give weight to edges, and "edge angle" is assigned, based on the arc length between two vertices.

Figure: Determining x for v_p and v_q.



Adjacency Matrix of Constellation Graph

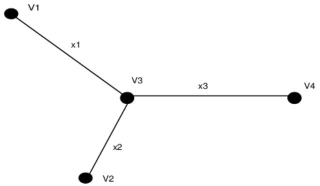
$$a_{pq} = \begin{cases} x^j & \text{if galaxy } v_p \text{ is adjacent to } v_q \\ 0 & \text{otherwise} \end{cases}$$

Example Adjacency Matrix for Constellation Graph

Adjacency Matrix

$$A = \begin{bmatrix} 0 & 0 & x_1^j & 0 \\ 0 & 0 & x_2^j & 0 \\ x_1^j & x_2^j & 0 & x_3^j \\ 0 & 0 & x_3^j & 0 \end{bmatrix}$$

Constellation Graph



Eigenvalues of A

$$e = 0, 0, -\sqrt{x_1^{2j} + x_2^{2j} + \ldots + x_n^{2j}}, \sqrt{x_1^{2j} + x_2^{2j} + \ldots + x_n^{2j}}$$

Where n is the number of edges.

Mean Deviation of Eigenvalues

$$D(j) = \frac{1}{N_e} \sum_{i=1}^{N_e} |e_i - \bar{e}|$$

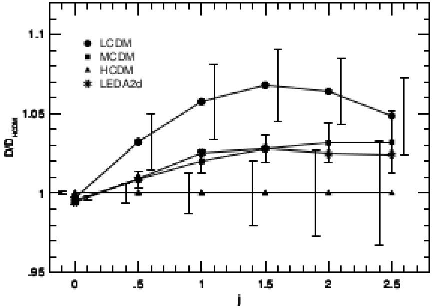
Where N_e is the number of eigenvalues and $\bar{e}$ is the mean of the eigenvalues.

LEDA2d Subsample and CDM Models

- The Lyon-Meudon Extragalactic Database (LEDA) provides images of galaxies distant and nearby.
- Images taken from LEDA (LEDA2d subsample - far universe) were compared to CDM simulations.
- The models chosen were LCDM, MCDM, and HCDM, which differ in their definition of Ω:
- $$\mathrm{LCDM} = 0.1 \tag{5}$$
  $$\mathrm{MCDM} = 0.5 \tag{6}$$
  $$\mathrm{HCDM} = 1.0 \tag{7}$$

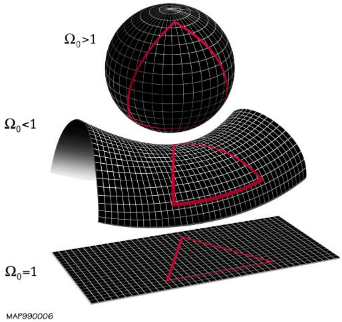
CDM Models vs. LEDA Data

Figure: Comparison of CDM models and LEDA2d subsample.



Bounds for Ω_0

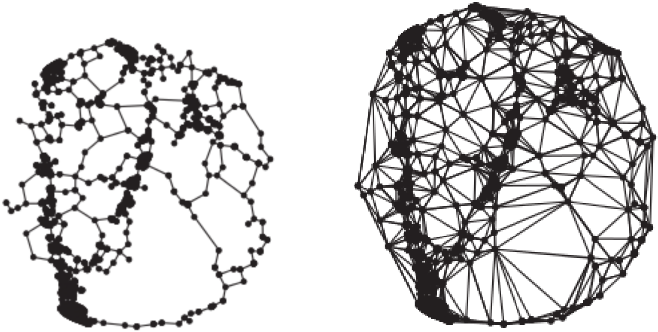
- A restriction is given instead of a concrete value for Ω_0.
- $0.1 < \Omega_0 < 1.0$



Outline

Delaunay Graph

Relative Neighborhood Graph



Bounds for Ω_0

- This time, the nearby structure of universe, not large-scale structure of universe was investigated.
- Only data for nearby galaxies was chosen.
- $0.1 < \Omega_0 < 0.5$

Summary: Bounds for Ω_0

- Analysis of the constellation graph gives bound $0.1 < \Omega_0 < 1.0$ for large-scale structure of the universe.
- Analysis of the nearest neighbor graph gives bound $0.1 < \Omega_0 < 0.5$ for structure of nearby universe.