Solid Rocket Fuel is a complex composite material for which no general constitutive theory, based on first principles, has been developed. One of the principles such a relation would depend on is the morphology of the binder. A theory of polymer curing is required to determine this morphology. During work on such a theory an algorithm was developed for counting the number of ways a polymer chain could assemble. The methods used to develop and check this algorithm led to an analytic solution to the problem. This solution is used in a probability distribution function which characterizes the morphology of the polymer.
Solid Rocket Fuel Constitutive Theory and Polymer Cure

Presented by:
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Constitutive Theory for Solid Rocket Fuel

- $\sigma_{ij} = c_{ijkl} e_{kl}$
- $c_{ijkl}$ is the elastic stiffness
- Rigid spheroids in a stress field
- Similar to conductors in an electric field
- Polymer Mechanics + Particle Packing = Constitutive Relation
Polymer Mechanics

- Free, Dangling and Bound strand length distributions are needed to determine the constitutive relation for a polymer.
- Develop a cross-linking model which allows those length distributions to be computed throughout the curing process.
Curing

- Model the polymer as links with 1, 2, 3, or 4 functionality
  - terminators
  - extenders
- 1-brancher
- 2-brancher
- 3-brancher
What is the probability of having a chain with $2+J_3+2J_4+3J_5$ terminators,

- $J_2$ extenders,
- $J_3$ 1-branchers,
- $J_4$ 2-branchers,
- $J_5$ 3-branchers

When given probabilities of choosing $\eta_1$, $\eta_2$, $\eta_3$, $\eta_4$, $\eta_5$?

- $J_1=58$
- $J_2=76$
- $J_3=10$
- $J_4=14$
- $J_5=6$
\[ \psi(J_2, J_3, J_4, J_5) = \frac{2(1 + J_2 + 2J_3 + 3J_4 + 4J_5)!}{(2 + J_3 + 2J_4 + 3J_5)!J_2!J_3!J_4!J_5!} \eta_1^{2+J_3+2J_4+3J_5} \eta_2^{J_2} \eta_3^{J_3} \eta_4^{J_4} \eta_5^{J_5} \]

- (# of ways they can go together) ◇
  (probability of choosing those links)
- Each chain can be identified with a sequence of 1’s, 2’s, 3’s and 4’s which must satisfy the condition

\[ 2 + \sum_{i=1}^{n} (a_i - 2) > 0 \quad \forall n < 2 + J_2 + 2J_3 + 3J_4 \]

in order to represent a valid chain.
- How many sequences satisfy this condition?
Enter the Computer

- Using 55...544...433...322...211...1 as an initial sequence check all permutations against the previously given condition.

- Compute \( \frac{(2 + J_2 + 2J_3 + 3J_4 + 4J_5)!}{(2 + J_3 + 2J_4 + 3J_5)!J_2!J_3!J_4!J_5!} \) sums of length 2+J_2+2J_3+3J_4+4J_5

- By developing an algorithm to determine the number of ways terminators can be added to an ordered sequence of 2's, 3's, 4's, and 5's. The number of computations is reduced to \( \frac{(J_2 + J_3 + J_4 + J_5)!}{J_2!J_3!J_4!J_5!} \)

- Assuming this algorithm takes an amount of time similar to a sum of length 2+J_2+2J_3+3J_4, the computation time can be reduced significantly.
An efficient algorithm for counting the number of ways one-hooks can be added to a pre-determined sequence of links.

Consider building a chain by starting with a terminated chain of two one-hooks, at each step tag enough one-hooks onto the end of the chain to terminate with the next link. Now count how many ways the next link can go in, while maintaining order.

Example: 325

```
  11
  .1.11

  1311  3111
  13.1.1  3.1.1.1

  13121  13211  31121  31211  32111
  1312.1111  132.1.1111  3112.1111  312.1.1111  32.1.1.1111

  131251111  1325151111  311251111  3125151111  32515151111  32515151111
```

There are two important observations.

1st: If a given configuration has n trailing terminators, then adding a h-link link will create n new configurations.

2nd: Moreover, those n configurations will have h-1,h,...,n+h-2 trailing terminators.
These observations can be used to create a counting scheme.

Example: 32543
The numbers in this tree represent a configuration with that many trailing terminators.
The tree is built from observation 2, and the answer obtained through observation 1.

```
  2
 3  2  3
2  1  2  1  2  3
5  4  4  5  4  5  4  5  6
4  3456 3456 3456 3456 3456 3456 3456 3456 3456
```

Now sum to get the number of ways the last 3 can go in

3+4+5+6+3+4+5+6+3+4+5+6+7+3+4+5+6+3+4+5+6+7+3+4+5+6+7+8 = 198 configurations

It is easy to see that the above will become a cumbersome array of ghastly proportions in a very short period of time for this reason we will merely keep track of the number of configurations with a given number of trailing terminators.

Example: 325432
Again observation 2 is used to build the table and observation 1 gives the answer.

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2*41+3*41+4*41+5*32+6*23+7*14+8*5+9 = 814 configurations
- Old time: \[
\frac{(2 + J_2 + 2J_3 + 3J_4 + 4J_5)}{(2 + J_3 + 2J_4 + 3J_5)!J_2!J_3!J_4!J_5!}
\]

- New time: \[
\frac{(2 + J_2 + 2J_3 + 3J_4 + 4J_5)(J_2 + J_3 + J_4 + J_5)}{J_2!J_3!J_4!J_5!}
\]

- Old/New: \[
\frac{(2 + J_2 + 2J_3 + 3J_4 + 4J_5)}{(2 + J_3 + 2J_4 + 3J_5)(J_2 + J_3 + J_4 + J_5)} \times \frac{(2 + J_3 + 2J_4 + 3J_5)!}{(J_2 + J_3 + J_4 + J_5)!}
\]

- For a chain of 1-branchers

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Catalan’s Triangle

Catalan Number * # ways extenders go in

\[
\frac{2(1 + 2J_3)!}{(2 + J_3)!} \times \frac{(1 + J_2 + 2J_3)!}{J_3!} \times \frac{2(1 + J_2 + 2J_3)!}{(2 + J_3)!J_2!} = \frac{2(1 + J_2 + 2J_3)!}{(2 + J_3)!J_2!J_3!}
\]
\[
\psi(J_2, J_3, J_4, J_5) = \frac{2(1 + J_2 + 2J_3 + 3J_4 + 4J_5)!}{(2 + J_3 + 2J_4 + 3J_5)!J_2!J_3!J_4!J_5!} \eta_1^{2+J_3+2J_4+3J_5} \eta_2^{J_2} \eta_3^{J_3} \eta_4^{J_4} \eta_5^{J_5}
\]