ABSTRACT

SOLID ROCKET FUEL CONSTITUTIVE THEORY AND POLYMER CURE

ROBERT REAM

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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:

Robert Ream

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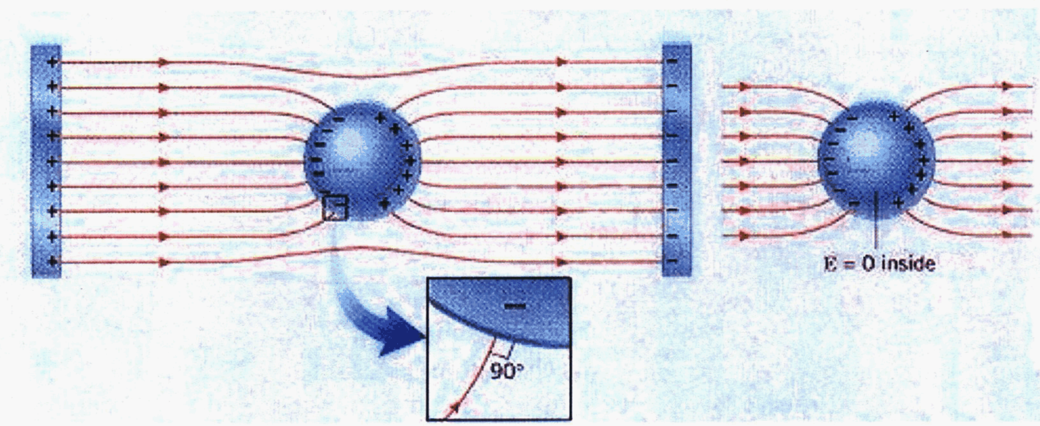
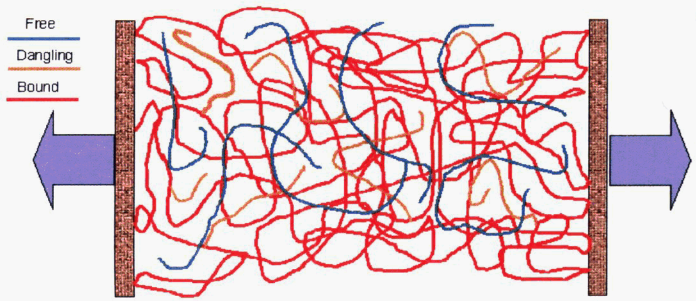
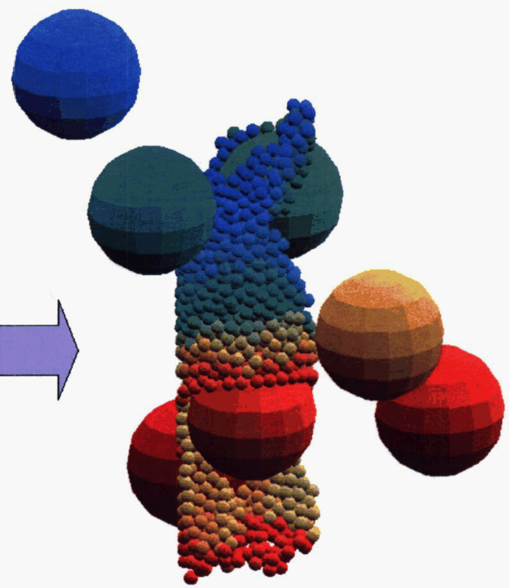
Constitutive Theory for Solid Rocket Fuel

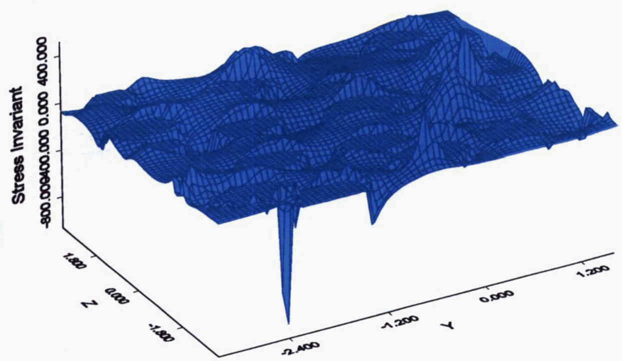
- $\sigma_{ij}=c_{ijkl}e_{kl}$
- c_{ijkl} is the elastic stiffness
- Rigid spheroids in a stress field
- Similar to conductors in an electric field



- Polymer Mechanics + Particle Packing = Constitutive Relation



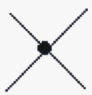
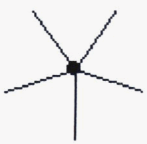




Polymer Mechanics

- 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,

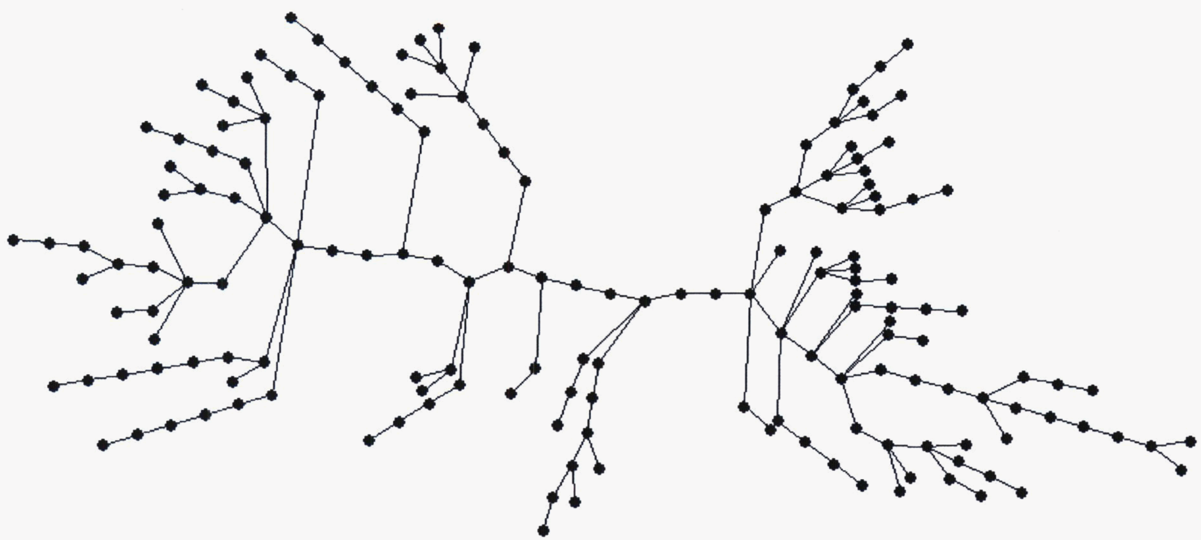
  J_2 extenders,

  J_3 1-branchers,

  J_4 2-branchers,

  J_5 3-branchers

When given probabilities of choosing η_1, η_2, η_3, η_4 , η_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

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

  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 a 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 1325151111 311251111 3125151111 3125151111 32515151111 32515151111 32515151111

9 configurations

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    4      5    4     5      6
4       3456 3456 34567 3456 3456 34567 3456 34567 345678
```

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+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.

	1	2	3	4	5	6	7	8	9	10
	0	1	0	0	0	0	0	0	0	0
3	0	1	1	0	0	0	0	0	0	0
2	2	2	1	0	0	0	0	0	0	0
5	0	0	0	5	3	1	0	0	0	0
4	0	0	9	9	9	9	4	1	0	0
3	0	41	41	41	32	23	14	5	1	0

2*41+3*41+4*41+5*32+6*23+7*14+8*5+9 = 814 configurations

- Old time: $$(2+J_2+2J_3+3J_4+4J_5)\frac{(2+J_2+2J_3+3J_4+4J_5)!}{(2+J_3+2J_4+3J_5)!J_2!J_3!J_4!J_5!}$$
- New time: $$(2+J_3+2J_4+3J_5)(J_2+J_3+J_4+J_5)\frac{(J_2+J_3+J_4+J_5)!}{J_2!J_3!J_4!J_5!}$$
- Old/New: $$\frac{(2+J_2+2J_3+3J_4+4J_5)}{(2+J_3+2J_4+3J_5)(J_2+J_3+J_4+J_5)}\frac{(2+J_2+2J_3+3J_4+4J_5)!}{(2+J_3+2J_4+3J_5)!(J_2+J_3+J_4+J_5)!}$$
- For a chain of 1-branchers

	1	2	3	4	5	6	7	8	9	10
	0	1	0	0	0	0	0	0	0	0
3	0	1	1	0	0	0	0	0	0	0
3	0	2	2	1	0	0	0	0	0	0
3	0	5	5	3	1	0	0	0	0	0
3	0	14	14	9	4	1	0	0	0	0
3	0	42	42	28	14	5	1	0	0	0

Catalan's Triangle

Catalan Number * # ways extenders go in

$$\frac{2(1+2J_3)!}{(2+J_3)!J_3!}\frac{(1+J_2+2J_3)!}{(1+2J_3)!J_2!}=\frac{2(1+J_2+2J_3)!}{(2+J_3)!J_2!J_3!}$$

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