絡み合いとプラトー弾性率

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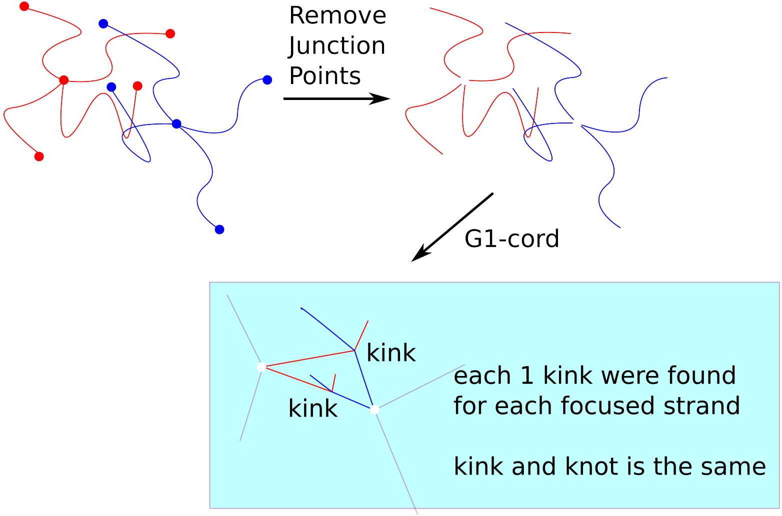
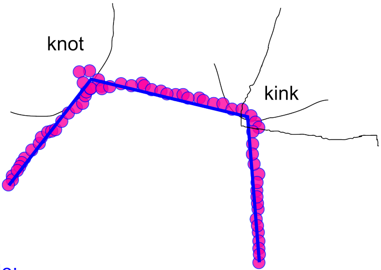
Z1 code


Remove
Junction
Points
G1-cord
kink
kink
each 1 kink were found
for each focused strand
kink and knot is the same

Comparison of Z1 vs. PPA

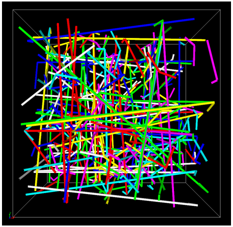
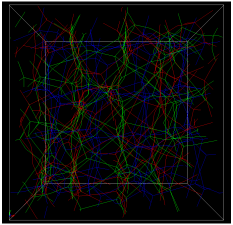
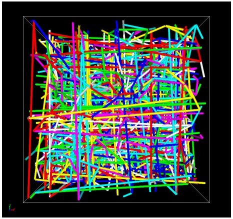
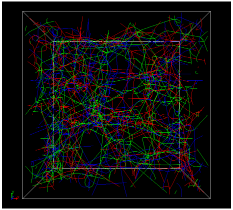
- 右図のような比較から、二倍程度は妥当かと。
- 次ページにあるネットワークでの比較でも明らかに PPA 由来の経路長は長い
- これと、プラトー弾性率との関係はよくわかりません。



Z1code:
1. Using G1 cord algorithm, strand is shrunked as a straight line preserving kinks.
2. Calc. z bycounting kinks on each strand
3. Calc. Me by deviding Number of segments by z.

PPA:
1. Shrink every bond preserving kinks and knots.
2. Calc. contour length by summing each bond length.
3. Calc. l_k from contour length

Example for NW

	Z1 cord	PPA
NPT 絡み合い小		
NVT 自然な絡み合い		

Classical Theory of Rubber Elasticity

Free Energy Density of Rubbers against Strain invariant

$$\frac{F}{V} = W = C_0 + \underbrace{C_1(I_1 - 3) + C_2(I_2 - 3)}_{Mooney-Rivlin Model} + \sum_{i,j=1}^{\infty} C_{ij}(I_1 - 3)^i (I_2 - 3)^j$$

Neo-Hookean Model

$W = C_1(I_1 - 3)$

against Uniaxial elongation

$$\sigma_{nom} = 2C_1\left(\lambda - \frac{1}{\lambda^2}\right) = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

Mooney-Rivlin Model

$W = C_1(I_1 - 3) + C_2(I_2 - 3)$

against Uniaxial elongation

$$\sigma_{nom} = 2\left(C_1 + C_2\frac{1}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right)$$

With or without Junction Poinits fluctuation

Affine Network Model [a]

$G_{affine} = \nu k_B T$

ν: Number density of strands in the system

[a] P.J. Flory, Principles of Polymer Chemistry, (1953)

Phantom Network Model [a]

$$G_{phantom} = \nu k_B T\left(1 - \frac{2}{f}\right)$$

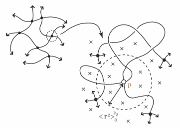
f: Functionality of Junction Points

[a] H.M. James, E.J. Guth, Chem. Phys., 21, 6, 1039 (1953)

Constraint Factors for Junction Points and Strands

Vicinity of Junction Point

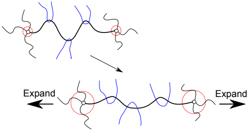
- Junction points are surrounded by many of adjacent strands(x in fig.).
- Fluctuation of junctions are suppressed.



Storage modulus G is combination of G_c and G_e

- Constrained Junction Model
  - Constraints are reduced and G approaches to G_c.[a]
- Topological relationships
  - Contribution of entanglement.[b]

$$G_e = T_e G_N^0$$



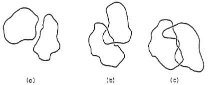


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

[a] P.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

[b] D.S.Pearson and W.Graessley, Macromol., 11, 3, 528 (1978)

Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model
  - Confining potential affect all points along the chain.[1]
- Nonaffine Tube Model
  - Improved model of "Edwards' Tube Model".[2]
- Slip-tube Model
  - A pairwise interaction of chains is introduced.[3]

$$f^*(\lambda^{-1}) = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$

$$G_c = \nu k_B T\left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7}\nu k_B T L$$

L is the number of slip-links per network chain

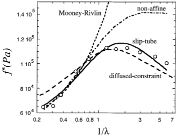


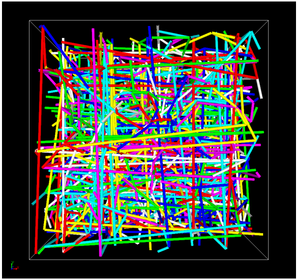
Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

[1] A. Kloczkowski, J.E. Mark, B. Erman, Macromol., 28, 5089 (1995)

[2] M. Rubinstein, S. Panyukov, Macromol., 30, 25, 8036 (1997)

[3] M. Rubinstein, S. Panyukov, Macromol., 35, 6670 (2002)

ランダムネットワークの絡み合い解析: Z1-code



Z1-code での絡み合い

ホモポリマーとの比較

- Z は一本鎖あたりの絡み合い
- 今回のネットワークは、
  ホモポリマーと同等

	Homo	4 Chain NW
Segments	50	48
Chains	200	768
Entanglements	204	800
Entangled Chains	134	557
$< Z >_{Z1}$	1.02	1.04

Z1-code とは

- 絡み合いを可視化するアルゴリズム[a]

[a]M. Kröger, Comput. Phys. Commun. 168, 209 (2005)

絡み合いの効果について

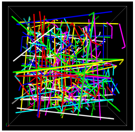
Entanglement in Slip-tube Model

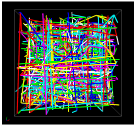
Rubinstein らの先行研究 [a]

$$G_c = \nu k_B T \left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7} \nu k_B T L$$

and L is the number of slip-links per network chain

[a] M. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)





	NPT	NVT
Chains, ν	768, 0.018	
$G_c = \nu \times (1 - 2/4)$	0.009	
Entanglements	278	800
Entangled Chains	249	557
L	278/768=0.36	800/768=1.04
$G_e = 4/7 \times \nu \times L$	0.004	0.011
$G_{calcd.} = G_c + G_e$	0.013	0.020
$G_{measd.}$	0.013	0.022