

Relaxation Behavior of Network Polymers with Random Connectivity

Hiroshi Sasaki

Toagosei Co., Ltd.

October 20, 2023

1 Introduction

- Adhesive Bonding Technology as a Key to Multi-Materialization
- Theoretical Models for Rubber
- Objectives

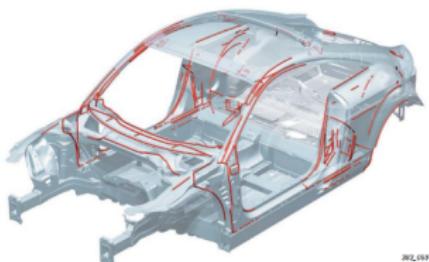
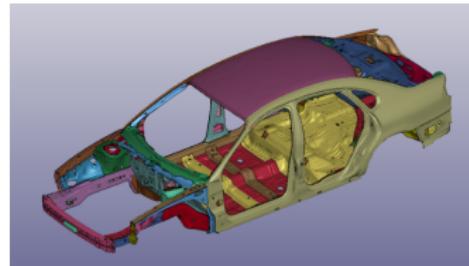
2 Simulation

- Generation Recipe of Random Networks
- Phantom and KG Chains as Strands
- Simulation Conditions

3 Results

- Networks with Phantom Chains
- KG Chain Networks
- Relaxation in KG Networks

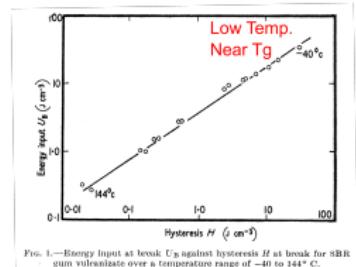
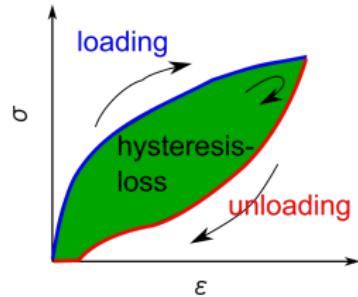
Adhesive Bonding Technology



- For Energy conservation
 - weight reduction of cars
 - **multi-materialization**
 - **adhesive bonding** technology is a key
- durability in long-term use is important
 - Especially for alertfatigue tests
 - **reliability of polymer materials** is still ambiguous

Mechanical Hysteresis Loss and Fracture Energy

- Mechanical Hysteresis Loss
 - Reduced stress on unloading
 - Energy dissipation during cycle
 - Positive correlation with fracture energy^a
- The origin of Hysteresis Loss^b
 - Viscoelastics
 - Crystallization
 - Derived by added filler



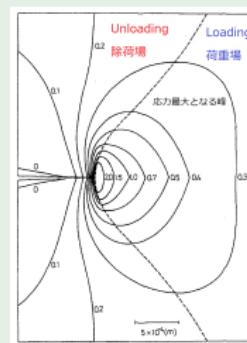
^aK.A.Grosch, J.A.C.Harwood, A.R.Payne,
Rub. Chem. Tech., 41, 1157(1968)

^bA.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

Andrews Theory for Rubber Toughness

Andrews Theory

- Focused on stress field around the crack^a
 - Stress Loading zone
 - Unloading one
 - divided by stress maximum line
- On the progress of the crack,
 - stress field is transit
 - Hysteresis Loss \Rightarrow Energy Dissipation
 - The progress of Crack is Suppressed
- Bigger Hysteresis Loss results in Higher Toughness.



^aE.H.Andrews, Y.Fukahori, J. of Mat. Sci. 12, 1307 (1977)

Classical Theory of Rubber Elasticity

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 Points fluctuation

Affine Network Model ^a

$$G_{affine} = \nu k_B T$$

ν : Number density of strands in the system

Phantom Network Model ^a

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

f : Functionality of Junction Points

^aP.J. Flory, Principles of Polymer Chemistry, (1953)

^aH.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.



Effect of other strands (Combination of G_c and G_e)

- Suppress the fluctuation of Junction Point
 - Deviate from Phantom Network Model and higher G_c
- Strands Entangles each other
 - Works as a Junction Point
 - Generate additional G_e

Storage modulus G is combination of G_c and G_e

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.



Effect of other strands (Combination of G_c and G_e)

- Constrained Junction Model
 - G approaches to G_c .^a
- Topological relationships
 - Contribution of entanglement.^b

$$G_e = T_e G_N^0$$

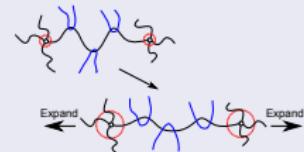


Figure 4. Three topological relationships between two closed loops.
(a) not entwined, (b) once entwined, (c) twice entwined.

^aP.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

^bD.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.^a
- Nonaffine Tube Model
 - Improved model of "Edwards' Tube Model".^b
- Slip-tube Model
 - A pairwise interaction of chains is introduced.^c

^a A. Kloczkowski, J.E. Mark, B. Erman, *Macromol.*, 28, 5089 (1995)

^b M. Rubinstein, S. Panyukov, *Macromol.*, 30, 25, 8036 (1997)

^c M. Rubinstein, S. Panyukov, *Macromol.*, 35, 6670 (2002)

Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model
 - Confining potential affect all points along the chain.^a
- Nonaffine Tube Model
 - Improved model of "Edwards' Tube Model".^b
- Slip-tube Model
 - A pairwise interaction of chains is introduced.^c

$$f^*(\lambda^{-1}) = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$
$$G_c = \nu k_B T \left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7} \nu k_B T L$$

where ν is the number density of network chains,
 L is the number of slip-links per network chain

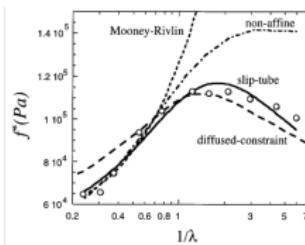


Figure 5. Fit of the data by Pak and Flory¹⁰ on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney-Rivlin expression (dotted line), nonaffine tube model (dash-dotted line), and the slip-tube model (solid line).

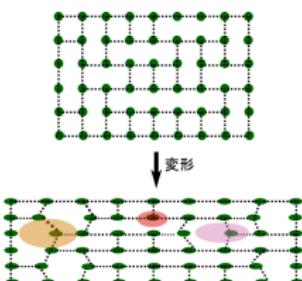
^a A. Kloczkowski, J.E. Mark, B. Erman, *Macromol.*, 28, 5089 (1995)

^b M. Rubinstein, S. Panyukov, *Macromol.*, 30, 25, 8036 (1997)

^c M. Rubinstein, S. Panyukov, *Macromol.*, 35, 6670 (2002)

Random Networks as a key for PNM

- Introduction of Random Connectivity.
- Criteria for PNM is fulfilled^a.
 - the mean values \bar{r} of strands are fluctuate
 - fluctuations $\Delta r = r - \bar{r}$ are Gaussian
 - the mean-square fluctuations depend only on structure
- Previous Work for Random Network
 - Random endcrosslink for telechelics^b
 - Primitive Chain Network Simulation^c



^aP. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)

^bG.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)

^cY. Masubuchi, Nihon Reoroji Gakkaishi, 49, 2, 73 (2021)

Objectives

- Recent approach for rubber elasticity models are based on Phantom Network Model.
- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
 - ① Employing phantom chain, basics for PNM is examined.
 - ② Changing the chain to KG Chain, constraints effects are investigated.
 - Excluded Volume Effect
 - No mutual crossing of Strands

1 Introduction

- Adhesive Bonding Technology as a Key to Multi-Materialization
- Theoretical Models for Rubber
- Objectives

2 Simulation

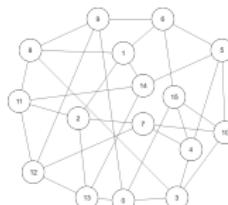
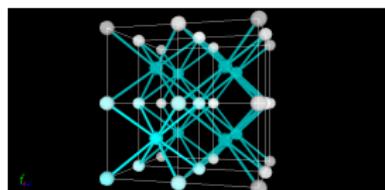
- Generation Recipe of Random Networks
- Phantom and KG Chains as Strands
- Simulation Conditions

3 Results

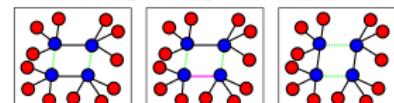
- Networks with Phantom Chains
- KG Chain Networks
- Relaxation in KG Networks

Generation of Initial Structure of Random Networks

- ① 8-Chain Model is used as starting structure in **Real space**.
 - Randomly selected edge is removed until desired functionality.
 - Topological model is generated.
- ② Randomness is introduced in **topological space**.
 - By **edge exchange**, random connectivity is introduced for each node.
- ③ Corresponding real space structure is generated.
- ④ According to e2e distance of strand, system size and multiplicity are set.



- 初期状態は、黒色のボンドと潜在的な緑色のボンド（8-Chain のときに存在）
- 任意のボンド（ピンクのボンド）を一つ選択：真ん中の状態
- そのボンドを含んだ平行四辺形のトポロジーを探す。
- 二本毎にセット（黒色のボンドと緑色のボンド）で入れ替える。



Phantom and KG Chains as Strands

- Phantom Chain:
 - No Excluded Volume is set (no segmental interaction).
 - "Force Cap LJ" is set as Angle Potential to enumerate e2e length of KG Chains.
 - Harmonic bond ($k=1000$)
- KG Chain:
 - Excluded Volume is set by Repulsive LJ Potential.
 - Bond Potential is set to FENE.
 - Because of above two potentials, No Chain crossing will occur.

Relaxation of Initial Structure in KG Network

KG Network: KG chain as strand

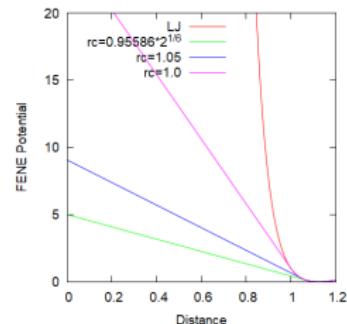
- Relaxation of initial structure is important.

$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

Initial Structure Relaxation

- According method of Auhl^a
 - Using force-capped-LJ pot.
 - relaxed by Slow Push Off

$$U_{FCLJ}(r) = \begin{cases} (r - r_{fc}) * U'_{LJ}(r_{fc}) + U_{LJ}(r_{fc}) & r < r_{fc} \\ U_{LJ} & r \geq r_{fc} \end{cases}$$



^aR. Auhl et al. J. of Chem. Phys., 119, 12718 (2003)

- force-capped-LJ Pot.
- gradually entangled

1 Introduction

- Adhesive Bonding Technology as a Key to Multi-Materialization
- Theoretical Models for Rubber
- Objectives

2 Simulation

- Generation Recipe of Random Networks
- Phantom and KG Chains as Strands
- Simulation Conditions

3 Results

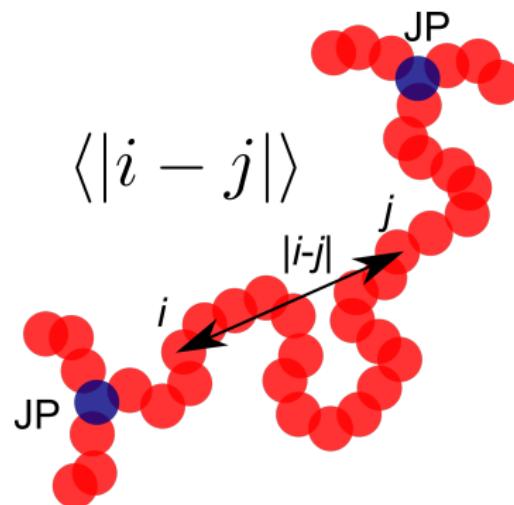
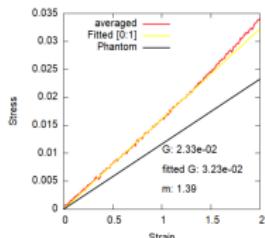
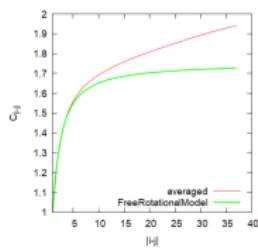
- Networks with Phantom Chains
- KG Chain Networks
- Relaxation in KG Networks

Phantom Chain NW ($f=4$, $N=36$)

- Strand-length is set to Equilibrated length ($N=36$)
- Multiplicity is 3 to keep $\rho = 0.85$

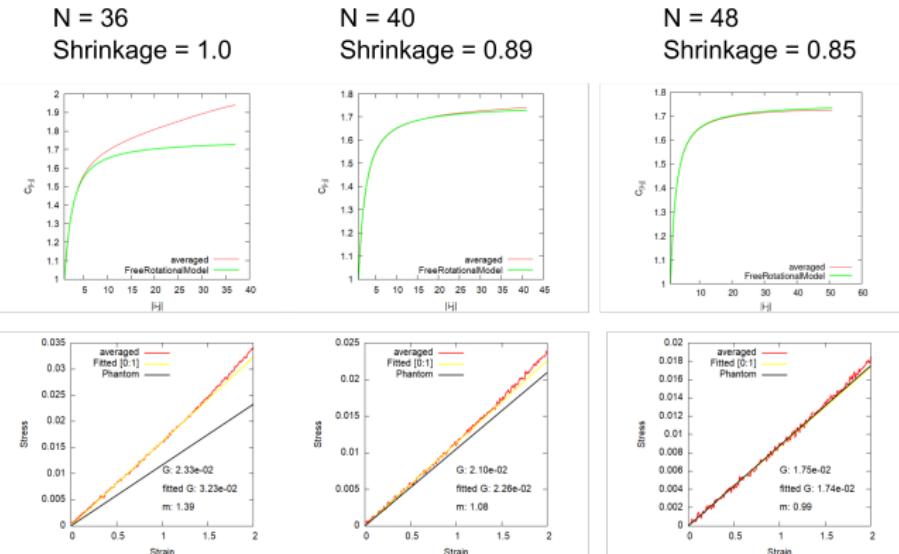
$N = 36$

Shrinkage = 1.0



Strand length Effect for Phantom Chain NW

- Strand-length is varied from 36 to 48 for $f=4$
- System size is reduced to keep $\rho = 0.85$



Strand Length Comparison for Shear Stress

Comparison of Functionality ($f = 3, 4, 6$)

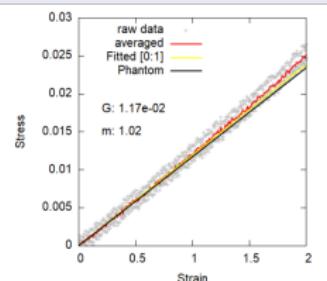
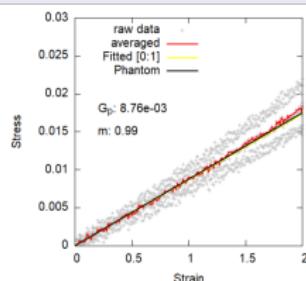
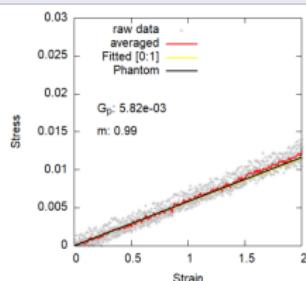
For Varied Functionalities

- With proper strand length
- Modulus changed according to theory

$f = 3$
 $N = 48$
multi = 4

$f = 4$
 $N = 48$
multi = 3

$f = 6$
 $N = 48$
multi = 2

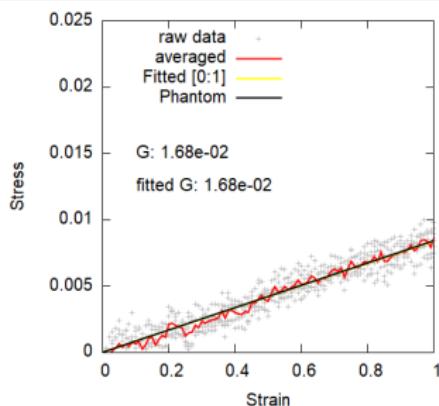


Mechanical Response for KG Chains($f=4$, $N=48$)

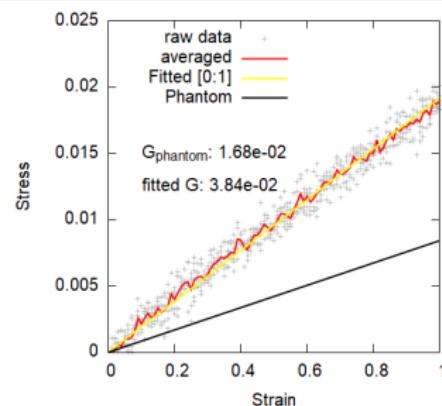
4-Chain Random Network with KG Chain

- Excluded Volume Effect by non-bonding LJ Potential.
- No strands mutual crossing by FENE bond.

Phantom Chain



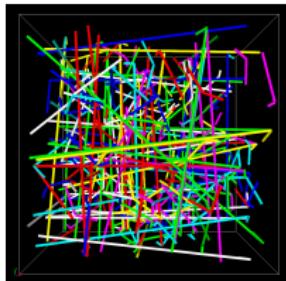
KG Chain



Reduced Entanglements by NPT Model

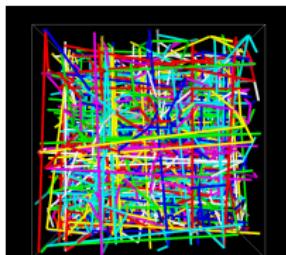
- 4-Chain-NPT

$$\langle Z \rangle_{Z1} = 0.36$$



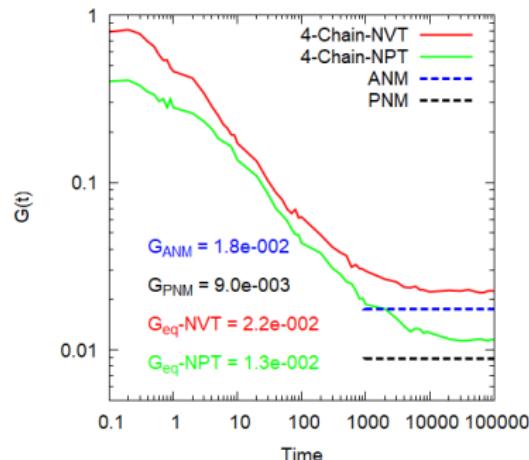
- 4-Chain-NVT

$$\langle Z \rangle_{Z1} = 1.04$$



$G(t)$

- Step Deformation ($\lambda = 2.0$)
- Reduced Modulus



Entanglement effect in Slip-tube Model

Entanglement in Slip-tube Model

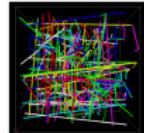
Theoretical model by Rubinstein^a

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

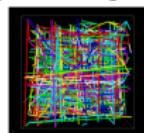
and L is the number of slip-links per network chain

^aM. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)

NPT
(less Entgld.)



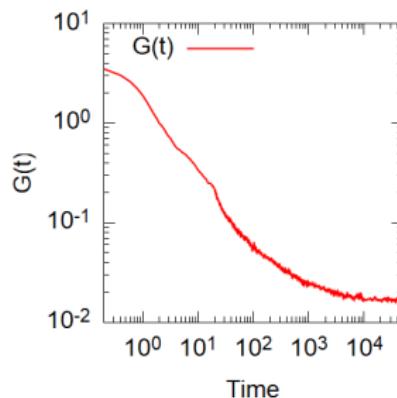
NVT
(well Entgld.)



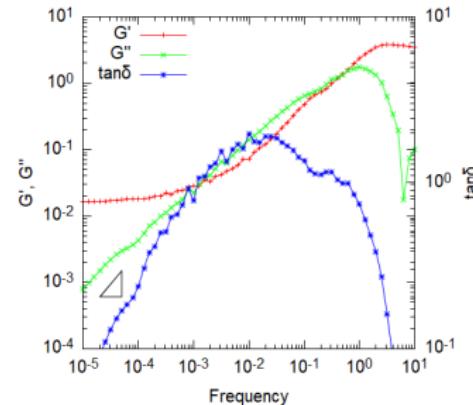
	Ensemble	NPT	NVT
$G_c = \nu \times (1 - 2/4)$		768, 0.018	
Entanglements	278	800	
Entangled Chains	249	557	
L	$278/768=0.36$	$800/768=1.04$	
$G_e = 4/7 \times \nu \times L$	0.004	0.011	
$G_{calcd.} = G_c + G_e$	0.013	0.020	
$G_{measd.}$	0.013	0.022	

$G(t)$ for Step Shear and Dynamic Rheo-Spectrum

$G(t)$ for Step Stretch



Dynamic Viscoelastics

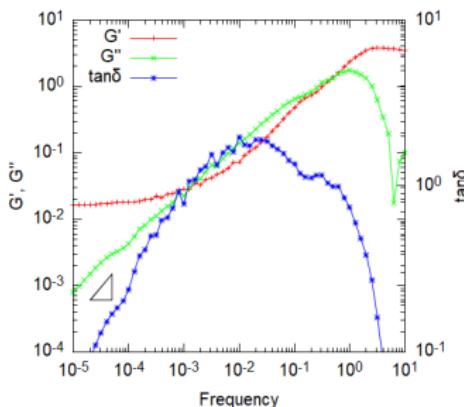


Conditions

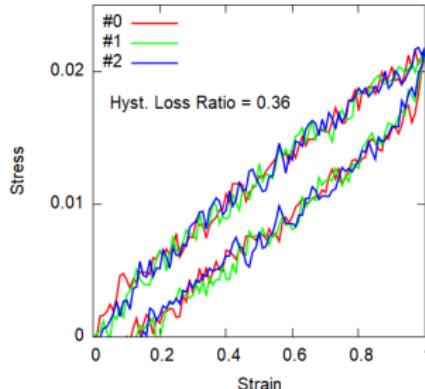
- 4-Chain KG-NW($N=50$)
- Step Stretch: $\lambda = 2$
- $G(t)$ is transformed to Dynamic Viscoelastic Spectrum

Mechanical Hysteresis Loss

Dynamic Viscoelastics



Hysteresis by Cyclic Shear



Conditions

- 4-Chain KG-NW($N=50$)
- Cyclic Shear: $\gamma = 1$, $\dot{\gamma} = 5e^{-5}$

ストランドの最長緩和時間

最長緩和時間 (τ) を評価

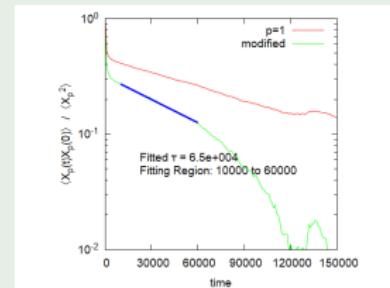
- ストランドのラウスマード ($p=1$) の自己相関関数 $C_p(t)$

$$C_p(t) = \langle X_p(t)X_p(0) \rangle / \langle X_p^2 \rangle$$

- 相関関数の振る舞い
 - 長時間極限で一定値に収束
 - 空間的な拘束のため
 - $C_p(\infty)$ を差し引いて評価

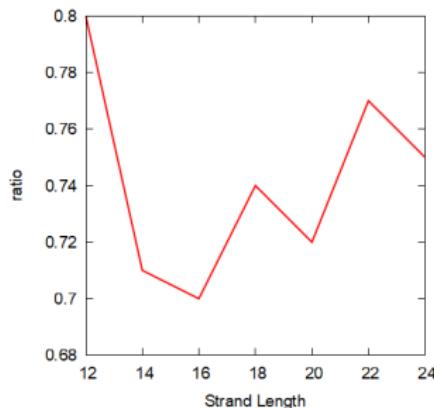
$$\tau \simeq 6.5e^4$$

ヒステリシスロスが消失する変形速度 ($\sim 1e^{-5}$) と対応

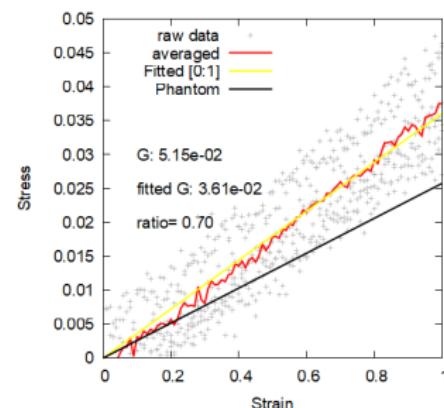


Effect of Strand Length for Shorter KG Chain

- For Phantom Chain
 - Longer Strand resulted in lower Modulus
- KG Chain
 - Proper Length was found for Low Modulus
 - which implies proper restriction for JP



Strand Length vs. Modulei ratio



Shear Stress for N=16

Conclusions

- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
 - Employing phantom chain, basics for PNM is examined.
 - Proper strand length is the key for PNM.
 - Functionality effect was confirmed.
 - Changing the chain to KG Chain, constraints effects are investigated.
 - Trapped Entanglement was explained by Slip-tube Model
 - Hysteresis