ランダムな接続性のファントム鎖ネットワークのMD シミュレーション

MD Simulations of Phantom Chain Networks with Random Connectivity

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ABSTRACT

Existence of mechanical hysteresis is believed to be one of a key to achieve high durability for rubber materials. For hysteresis cycle, added fillers are believed to play an important roll in meso-scale region response against local stress. Our question is "Is there any other mechanism to enhance durability in micro-scale region such as size of polymer chains?".

"Phantom Network Model", in which fluctuation of junction point is rather high, seems to be a good candidate for micro-scale energy dissipation. Introducing random connectivity for network junctions, we successfully presented "Phantom Network Model" in molecular dynamics simulations.

Introduction

Classical Theory of Rubber Elasticity

With or without Junction Poinits fluctuation

Affine Network Model[1]

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

ν: Number density of strands

Phantom Network Model[2]

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

f: Functionality of Junction Points

Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model[3]
  - Confining potential affect all points along the chain.
- Nonaffine Tube Model[4]
  - Improved model of "Edwards' Tube Model".
- Slip-tube Model[5]
  - A pairwise interaction of chains is introduced.

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

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

L is the number of slip-links per network chain

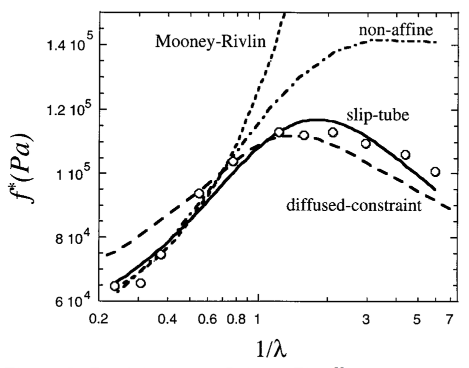
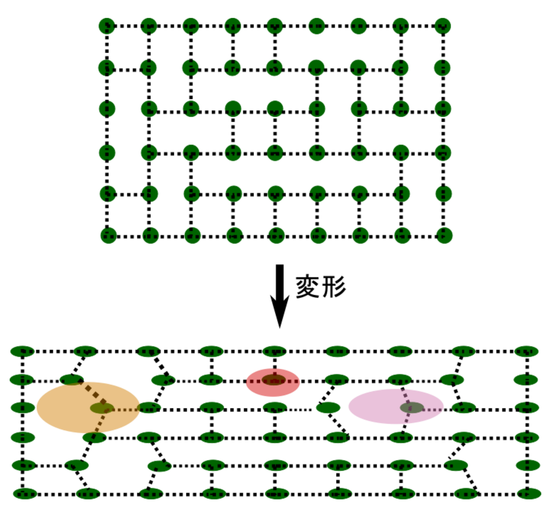


Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

Random Connectivity[6]

- Regular Structure as Initial Structure
  - Same strand length for easy understanding
  - Easy to monitor the strand length distributions
- Irregular Connectivity for each Junction Point
  - Random Connectivity
  - Fluctuations of Junction Points are secured
- Phantom Network Requirement by Flory is fulfilled



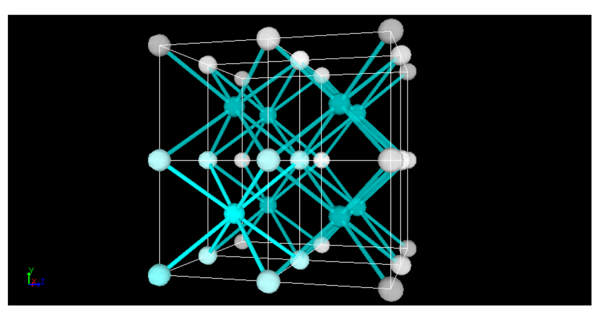
OBJECTIVE

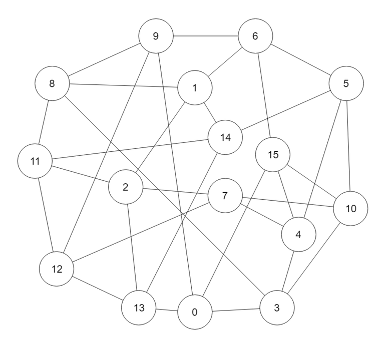
- Recent approach for rubber elasticity models are based on Phantom Network Model.
- To investigate the criteria for Phantom Network Model, employing phantom chain as strand and introducing random connectivity, MD simulation studies were carried out.

Simulation

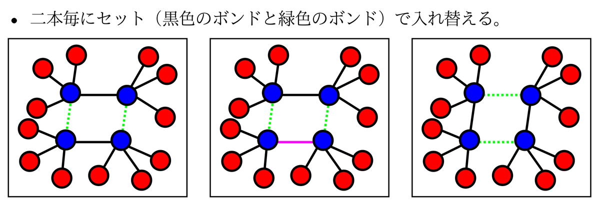
Initial Structure Generation[7]

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 as initial model.
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。



MD Simulation Conditions

1. Phantom Chain
   - No Excluded Volume is set (no segmental interaction).
   - "Force Cap LJ" is set as Angle Potential to enumerate KG Chain length.
   - Harmonic bond (k=1000)
2. Length and Multiplicity
   - Strand length in Initial Structure is set according to e2e distance of strand.
   - To set the system density ($\rho = 0.85$), network is multiplied as IPN.

Results

Strand Length (N = 36) and Shear Stress for 4-Chains

- System
  - Strand length N = 36
  - Multiplicity = 3
- Deformation
  - Shear mode (Lees-Edwards)
  - Shear rate = $1e^{-5}$

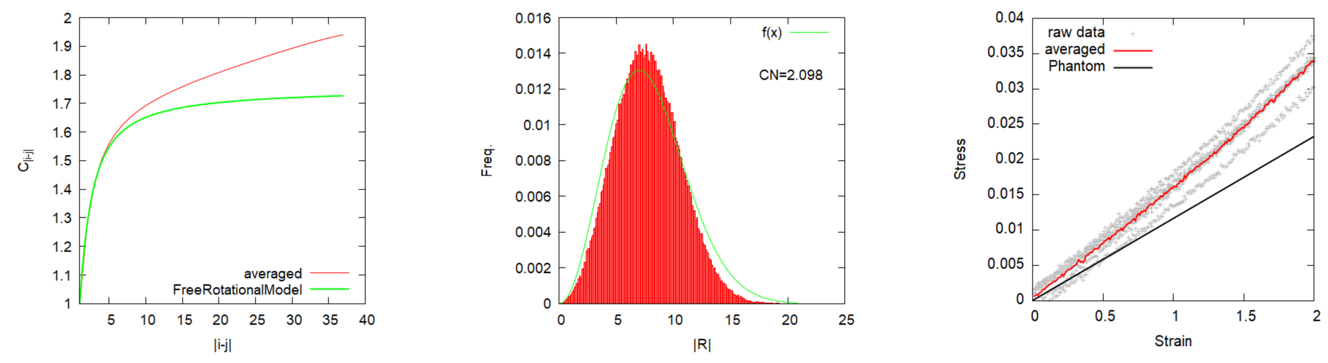


Fig. 1: Simulation results for 4-Chain model:N = 36, M = 3

Strand length Effect for 4-Chains

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

N = 36 Shrinkage = 1.0 | N = 40 Shrinkage = 0.89 | N = 48 Shrinkage = 0.85

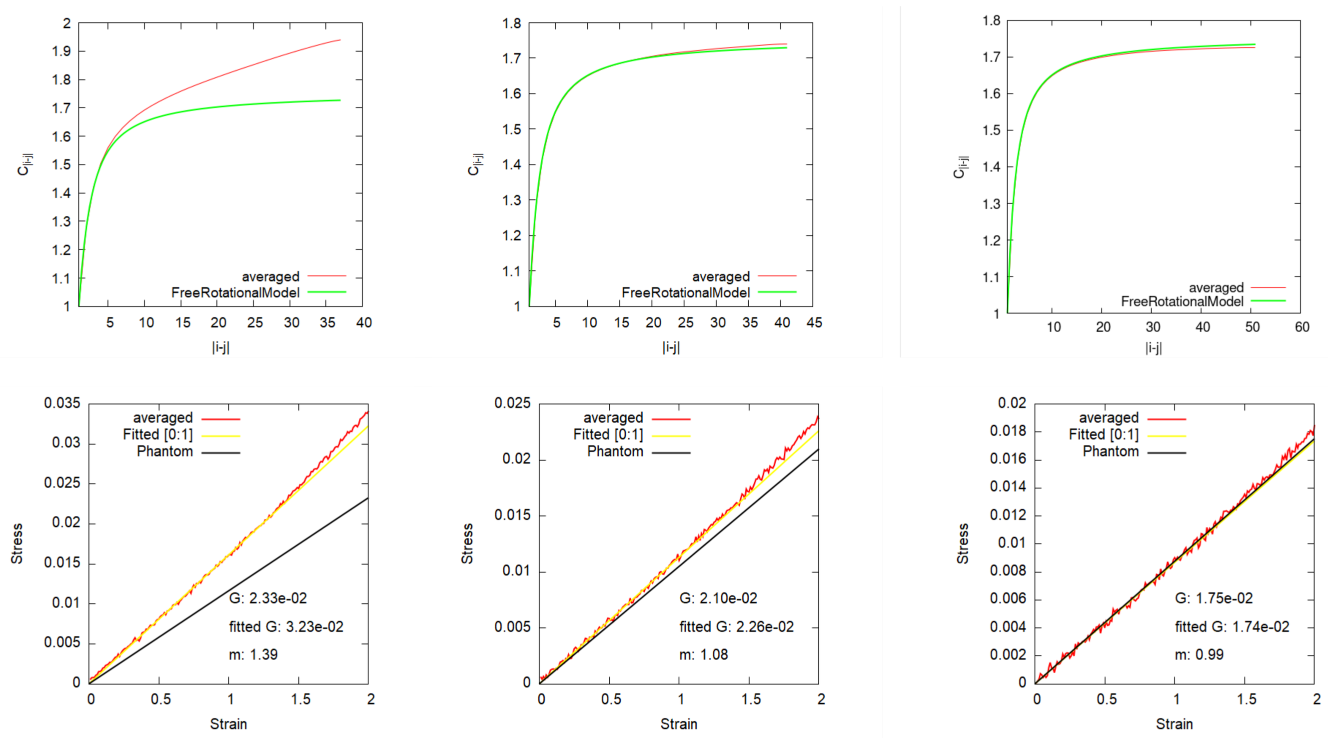


Fig. 2: Strand Length Comparison for N = 36, 40, 48

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

- Using same length of strand (N = 48), functionality effect was compared.

f = 3, N = 48, multi = 4 | f = 4, N = 48, multi = 3 | f = 6, N = 48, multi = 2

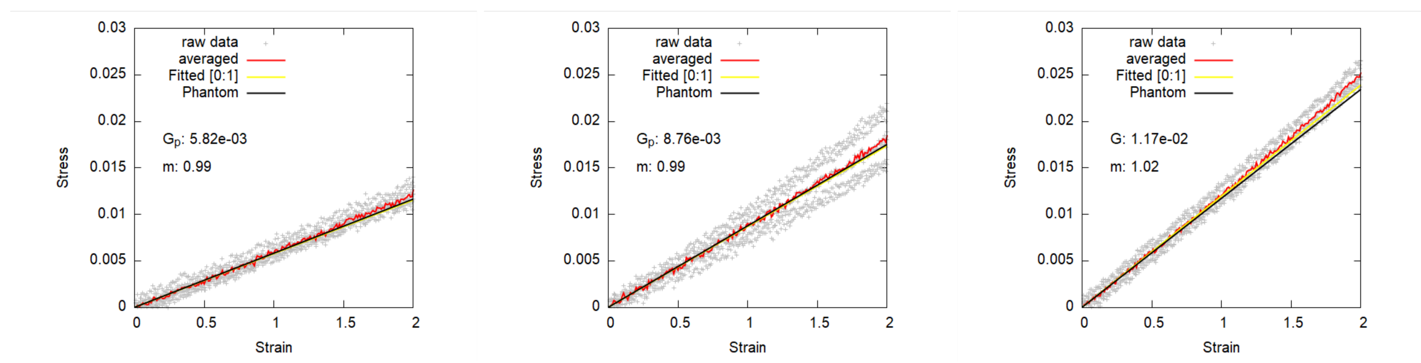


Fig. 3: Comparison of Functionality (f = 3, 4, 6)

Conclusions

- Employing phantom chain as strand, network model with random connectivity was examined.
- Setting the initial strand length as theoretical e2e length failed into expanded strand and higher stress compared with PNM.
- These results were explained by reduced fluctuation mobility of junction point.

References

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