Knots and Random Walks in Vibrated Granular Chains

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Motivation

Topological constraints, entanglements:
- Reduce accessible phase space
- Involve large relaxation time scales
- Affect dynamics, flow
  \[ \eta \sim \tau \sim N^3 \]

Relevance:
- Polymers: melts, rubber, gels
- DNA, biomolecules

Difficulties:
- Hard to observe directly
- Slow dynamics
- Finite size effects
Granular “Polymers”

Mechanical bead-spring:

\[ U(\{R_i\}) = v_0 \sum_{i \neq j} \delta(R_i - R_j) + \frac{3}{2b^2} \sum_i (R_i - R_{i+1})^2 \]

- Beads interact via hard core repulsions
- Rods act as springs (nonlinear, dissipative)
- Inelastic collisions: bead-bead, bead-plate
- Vibrating plate supplies energy

Advantages:

- Number of "monomers" can be controlled
- Topological constraints: can be prepared, observed directly
Vibrated Knot Experiment

- $t = 0$: knot placed at chain center
- Parameters:
  - Number of monomers: $30 < N < 270$
  - Minimal knot size: $N_0 = 15$
- Driving conditions:
  - Frequency: $\nu = 13 \text{Hz}$
  - Acceleration: $\Gamma = A\omega^2/g = 2.4$
- Only measurement: opening time $t$

Questions

1. Average opening time $\tau(N)$?
2. Survival probability $S(t, N)$?
   Distribution of opening times $R(t, N)$?
The Average Opening Time

\[ \tau(N) \sim (N - N_0)^\nu \quad \nu = 2.0 \pm 0.1 \]

Opening time is diffusive
The Survival Probability

- $S(t, N)$ Probability knot “alive” at time $t$
- $R(t, N)$ Probability knot opens at time $t$

$$R(t, N) = -\frac{d}{dt}S(t, N)$$

- $S(t, N)$ obeys scaling

$$S(t, N) = F(z) \quad z = \frac{t}{\tau(N)}$$

$\tau$ only relevant time scale
Theoretical Model

Assumptions:

- Knot $\equiv$ 3 exclusion points
- Points hop randomly
- Points move independently (no correlation)
- Points are equivalent (size $= N_0/3$)

3 Random Walk Model:

- 1D walks with excluded volume interaction
- first point reaches boundary $\rightarrow$ knot opens
Diffusion in 3D

\[ 1 < x_1 < x_2 < x_3 < N - N_0 \quad \rightarrow \quad 0 < x < y < z < 1 \]

\[ \frac{\partial}{\partial t} P(x, y, z, t) = \nabla^2 P(x, y, z, t) \]

- **Boundary conditions**
  
  **Absorbing:** \( P \big|_{x=0} = P \big|_{z=1} = 0 \)
  
  **Reflecting:** \( (\partial_x - \partial_y) P \big|_{x=y} = (\partial_y - \partial_z) P \big|_{y=z} = 0 \)

- **Initial conditions** \( P \big|_{t=0} = \delta(x-x_0)\delta(y-x_0)\delta(z-x_0) \)

- **Survival probability**

\[ S_3(t) = \int_0^1 dx \int_x^1 dy \int_y^1 dz \ P(x, y, z, t) \]

3 walks in 1D \( \equiv \) 1 walk in 3D
Product Solution

• Product of 1D solutions

\[ P(x, y, z, t) = 3! p(x, t)p(y, t)p(z, t) \]

• 1D solution \( p|_{x=0} = p|_{x=1} = 0 \quad p|_{t=0} = \delta(x-x_0) \)

\[ p_t(x, t) = p_{xx}(x, t) \]

• \( m \) interacting walks survival probability

\[ S_m(t) = [s(t)]^m \]

• 1 walk survival probability \( s(t) = \int_0^1 dx \, p(x, t) \)

\[ s(t) = \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{\sin[(2k+1)\pi x_0]}{2k+1} e^{-(2k+1)^2 \pi^2 t} \]

Reduced to noninteracting problem
Experiment vs. Theory

- Work with scaling variable $z = t/\tau$ ($\langle z \rangle = 1$)
- Combine different data sets (6000 pts)
- Fluctuations $\sigma^2 = \langle z^2 \rangle - \langle z \rangle^2$

$$\sigma_{\text{exp}} = 0.62(1), \sigma_{\text{theory}} = 0.63047 \ (< 2\%)$$

No fitting parameters!

Excellent quantitative agreement
Large Exit Times

- Largest decay time dominates
- Large time tail is exponentially small

\[ F(z) \sim e^{-\beta z} \quad z \to \infty \]

- Decay coefficient

\[ \beta_{\text{exp}} = 1.65(2) \quad \beta_{\text{theory}} = 1.66440 \quad (1\%) \]
Small Exit Times

- Exponentially small (in $1/\tilde{z}$) tail

\[ 1 - F(\tilde{z}) \sim \tilde{z}^{1/2} e^{-\alpha/\tilde{z}} \quad \tilde{z} \to 0 \]

- Decay coefficient

\[ \alpha_{\text{exp}} = 1.2(1) \quad \alpha_{\text{theory}} = 1.11184 \quad (10\%) \]
Heuristic Argument (short times)

- Use scaling form

\[ S(t, N) \sim F \left( \frac{t}{N^2} \right) \]

- Smallest exit time \( t = \frac{N}{2}, 1 - S \sim 2^{-N/2} \)

\[
1 - F \left( \frac{2}{N} \right) \sim e^{-\alpha N} \quad N \to \infty
\]

\[
1 - F(z) \sim e^{-\alpha/z} \quad z \to 0
\]

Analytic Calculation

- Laplace transform of exact solution

\[
s(q) = \int dt \ e^{-qt} s(t) = \frac{1}{\cosh(\sqrt{q}/2)}
\]

- Steepest descent \( s(q) \sim e^{-\sqrt{q}/2} \) as \( q \to \infty \)

\[
1 - F(z) \sim z^{1/2} e^{-\alpha/z} \quad z \to 0
\]
Off-Center knots = ruin problem

- Knot survival probability is equivalent to ruin problem with 3 players whose must maintain a hierarchy of assets

- Average opening time $D \nabla^2 T(x) = -1$

- Average opening probability $\nabla^2 E(x) = 0$

Fluctuations diverge near boundary
Conclusions

- Knot governed by 3 exclusion points
- Exponential tails (large & small exit times)
- Macroscopic observables \((t, S(t))\) reveals details of a topological constraint

**Predictive Power?**

- \(\tau(N) \approx \tau_3(N - N_0)^2/D \Rightarrow N_0, D\)
  \(N_0 = 15.2, D = 11Hz\)
- \(S(t)\) gives number of constraints \(m\)
  \(m = 1\) for a small ring
- Off-center: ruin problem / \(\nabla^2 P = 0\)
- Complicated constraints: \(\tau, \sigma \sim 1/\ln m\)
- Are the cross links correlated?
  no, beyond some correlation length \((\xi \approx 4)\)
Granular Chains