Molecular dynamics study of ideal polymer chains with variable persistence length

Short progress report

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Outline

Definitions, notations, units

Mostly: following [Svaneborg and Everaers, 2020]
Units: LJ
Notations and definitions:

- Contour length: L
- End to End distance (ETE): $\vec{R}$
- Change of ETE: $[\Delta R(t)]^2 := [\vec{R}(t) - \vec{R}(0)]^2$
- Friction coefficient of bead, viscosity: ζ $[\frac{\text{mass}}{\text{time}}]$, η $[\frac{\text{mass}}{\text{time}*\text{distance}}]$
- subscript "b" to denote bead specific properties to distinguish these from Kuhn units:
  - Kuhn lenght, bond length: l_K, l_b
  - Number of Kuhn segments, number of beads: N_K, N_b
- Friction coefficient of center of mass: $\zeta_{CM} = N_b\zeta$
- Rouse relaxation time [Svaneborg and Everaers, 2020]: $\tau_R = \frac{1}{3\pi^2}\frac{\zeta_{CM}\langle R^2\rangle}{k_B T} = \frac{1}{3\pi^2}\frac{\zeta N_b^2 l_b^2}{k_B T}$
- Relaxation time of single bead: $\tau_0 = \frac{\tau_R}{N^2}$

Assumptions

- Variation of 0.2% of l_b is neglectible [Svaneborg and Everaers, 2020]
  $\Rightarrow l_b = const$, $L = (N_b - 1) l_b$=const
- ...

Rouse model

$$\langle R^2 \rangle = N_b l_b^2 \tag{1}$$

$$g_4(t) := \langle (\Delta R(t))^2 \rangle = 2 N_b l_b^2 \left(1 - \frac{8}{\pi^2} \sum_{p=1,3,\ldots} e^{\frac{-tp^2}{\tau_R}}\right) \tag{2}$$

Experiment 1: Fully flexible chain

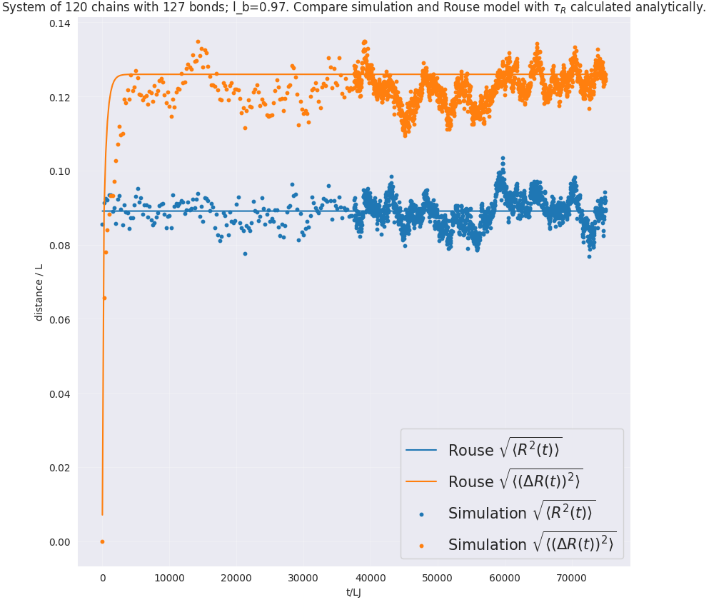
Settings

Same potentials used as in [Svaneborg and Everaers, 2020, Section 2.1], except:

- Bending potential: $U_{bend}(\theta) = 0$
- Only bonded beads interract

Experiment 1: Fully flexible chain

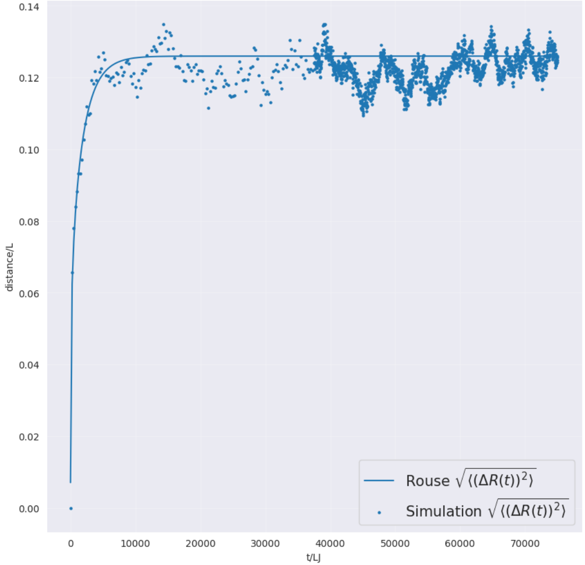
τ_R calculated analytically



Experiment 1: Fully flexible chain

τ_R as free parameter

System of 120 chains with 127 bonds; l_b=0.97. Compare simulation and Rouse model with τ_R estimated from fit of $g_4(t)$ to simulation data.



Experiment 1: Fully flexible chain

τ_R analytcal/free values

Analytical: $\tau_R = 520.64$, $\tau_0 = 0.032$
Free parameter: $\tau_R = 2136.5 \pm 155.2$, $\tau_0 = 0.130 \pm 0.009$

Experiment 2: Semi-flexible chain, vary persistence length

Settings

Same potentials used as in [Svaneborg and Everaers, 2020, Section 2.1], except:

- Only bonded beads interract

Experiment 2: Semi-flexible chain, vary persistence length

Used equations

Kuhn length [Svaneborg and Everaers, 2020]:

$$l_K = l_b \frac{2\kappa + e^{-2\kappa} - 1}{1 - e^{-2\kappa}(2\kappa + 1)} \tag{3}$$

Number of Kuhn segments:

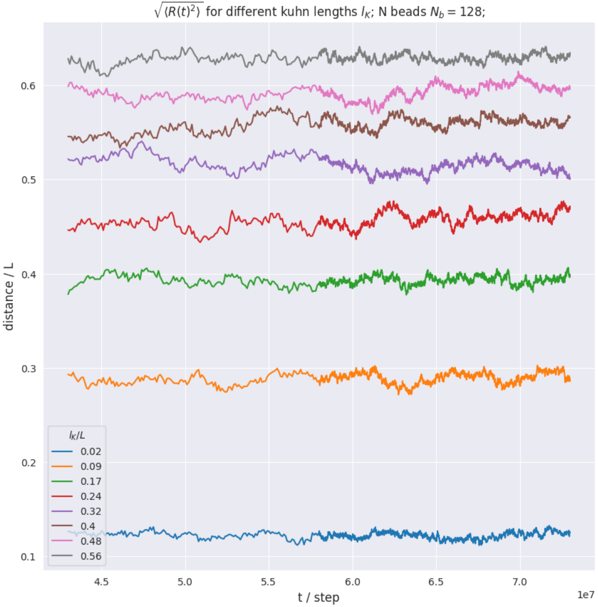
$$N_K = \frac{L}{l_K} \tag{4}$$

Rouse time with assumption $\zeta_{CM} = \zeta N_K$:

$$\tau_R = \frac{1}{3\pi^2} \frac{\zeta_{CM} \langle R^2 \rangle}{k_B T} = \frac{1}{3\pi^2} \frac{\zeta N_K^2 l_K^2}{k_B T} \tag{5}$$

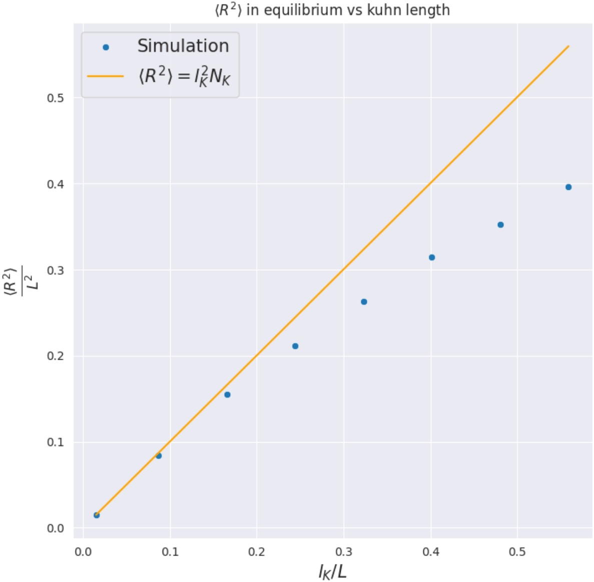
Experiment 2: Semi-flexible chain, vary persistence length

ETE in equilibrium



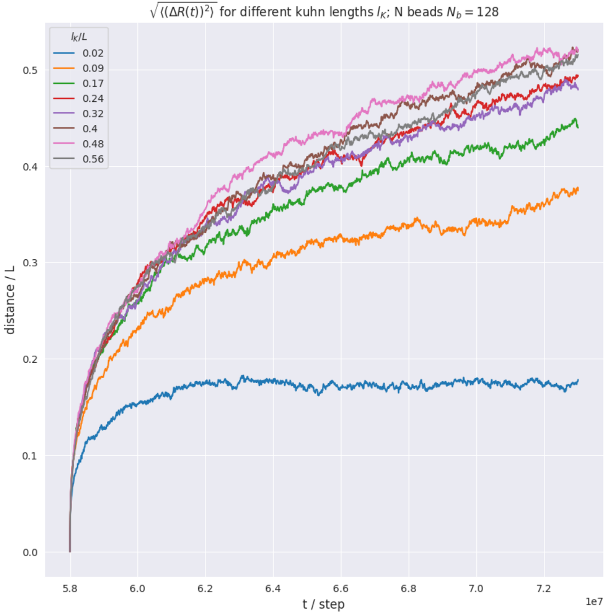
Experiment 2: Semi-flexible chain, vary persistence length

ETE vs Kuhn length



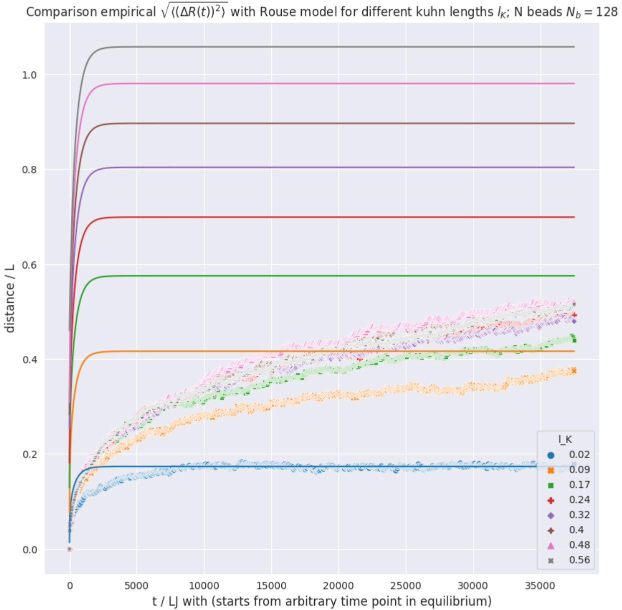
Experiment 2: Semi-flexible chain, vary persistence length

$\langle [\Delta R(t)]^2 \rangle$



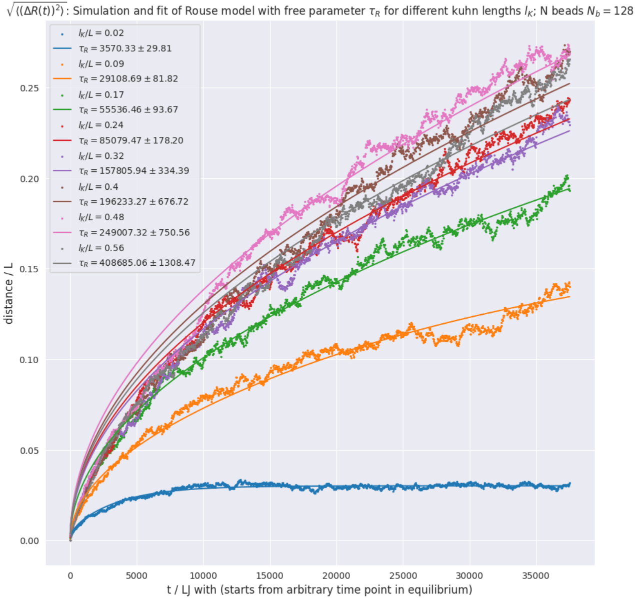
Experiment 2: Semi-flexible chain, vary persistence length

$\langle [\Delta R(t)]^2 \rangle$ vs Rouse with τ_R analytically



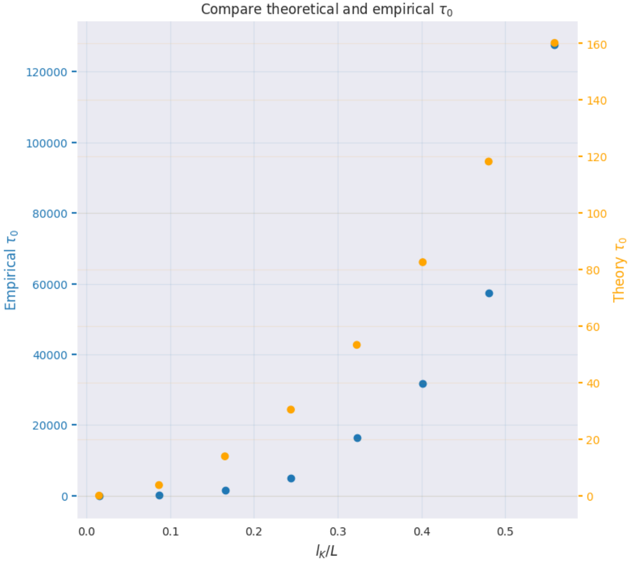
Experiment 2: Semi-flexible chain, vary persistence length

$\langle [\Delta R(t)]^2 \rangle$ vs Rouse with τ_R as free parameter



Experiment 2: Semi-flexible chain, vary persistence length

Analytical and empirical τ_0 vs Kuhn length



Problems and Questions

1. Eq. (5): Is the assumption correct? Intuitively: $\zeta_{CM} = \zeta_K N_K = \zeta \frac{N_b}{N_K} N_K = \zeta N_b$, but then [Svaneborg and Everaers, 2020, Eq. 15] is not proportional to N_K^2.
2. Empirical τ_0 are with factor $\approx 10^3$ larger then theoretical, why?

References

[Svaneborg and Everaers, 2020] Svaneborg, C. and Everaers, R. (2020).
Characteristic time and length scales in melts of kremer–grest bead–spring polymers with wormlike bending stiffness.
Macromolecules, 53(6):1917–1941.