Molecular dynamics study of ideal polymer chains with variable persistence length

Results 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: $\zeta\ [\frac{\text{mass}}{\text{time}}]$, $\eta\ [\frac{\text{mass}}{\text{time}*\text{distance}}]$
- 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: $\tau_0 = \frac{3\pi^2 \tau_R}{N^2}$

Definitions, notations, units

Notations and definitions:

- index "e" for variables referring end-monomer of the chain: m_e, ζ_e

Conventions:

- Confidence interval specification: $\pm 3\sigma$

Common simulation settings and values

- Only bonded beads interract (ideal chain)
- Chain parameters: 64 monomers, monomer mass $m = 1$
- Ensemble size ≥ 500 chains
- Environment parameters: $\zeta = 1$
- Time step 0.0025 LJ

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

$$\langle R^2 \rangle = N_b l_b^2 \quad (1)$$

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

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

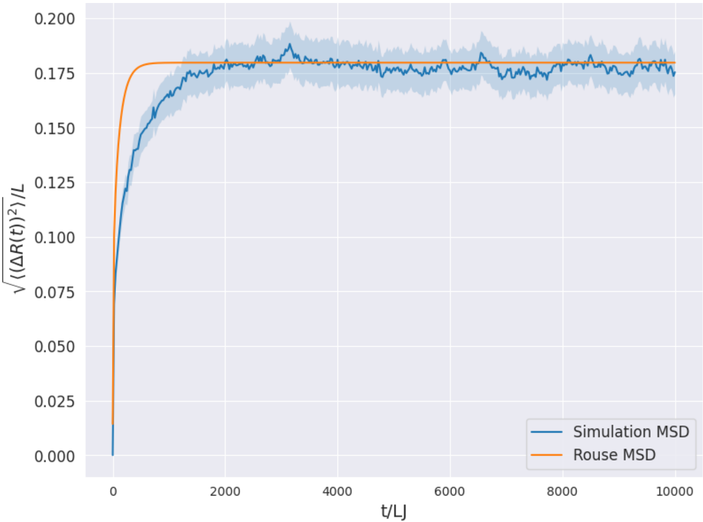


Figure: MSD - compare simulation and Rouse model with τ_R calculated analytically.

Experiment 1: Fully flexible chain

τ_R as free parameter

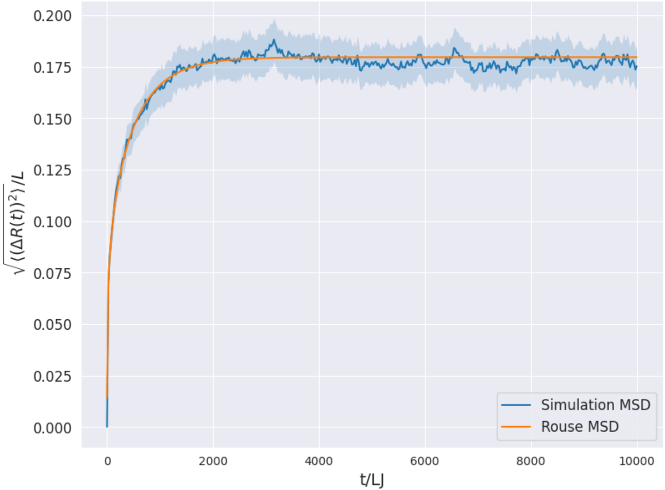


Figure: MSD - compare simulation and Rouse model with τ_R estimated from fit of $g_4(t)$ to simulation data.

Experiment 1: Fully flexible chain

τ_R as free parameter

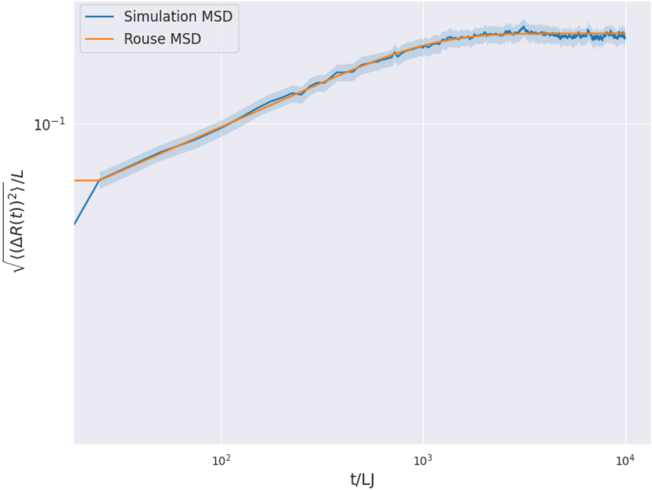


Figure: MSD - compare simulation and Rouse model with τ_R estimated from fit of $g_4(t)$ to simulation data.

Experiment 1: Fully flexible chain

τ_R analytcal/free values

Analytical: $\tau_R = 130.16$, $\tau_0 = 0.941$
Free parameter: $\tau_R = 582.3 \pm 28.6$, $\tau_0 = 4.21 \pm 0.07$

Define adjustment factor $\alpha := \frac{\tau_{0,\text{empirical}}}{\tau_{0,\text{analytical}}} \approx 4.47$

Experiment 1: Fully flexible chain

Conclusions / Results

- Boundary conditions of Rouse model must be adjusted to describe dynamics on short/interim time-scales.
- Rouse model with τ_R as free parameter is introduced to account for boundary conditions. Based on τ_R estimate the adjustment factor for τ_0 is calculated. This allows to use the model on chains with different number of segments.

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:

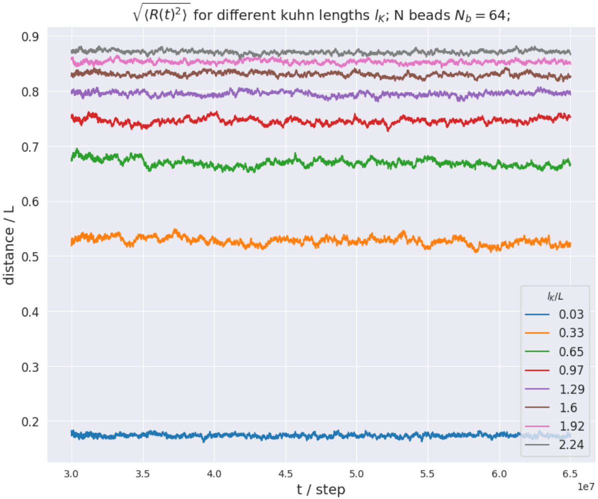
$$N_K = \frac{L}{l_K} \tag{4}$$

Rouse time:

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

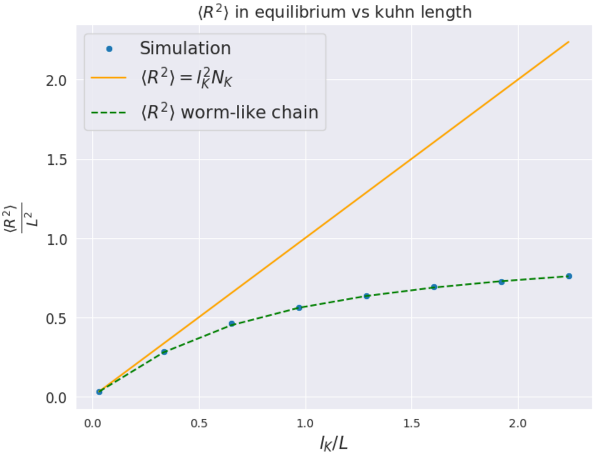
Experiment 2: Semi-flexible chain, vary persistence length

ETE in equilibrium



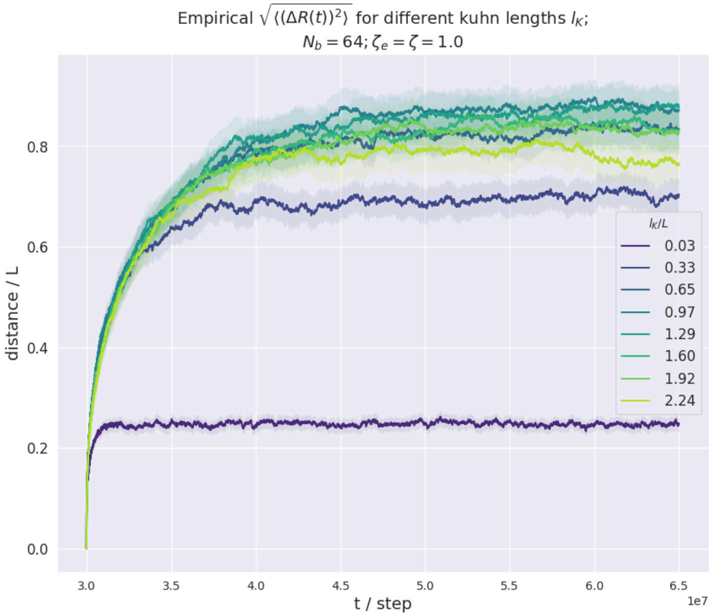
Experiment 2: Semi-flexible chain, vary persistence length

ETE vs Kuhn length



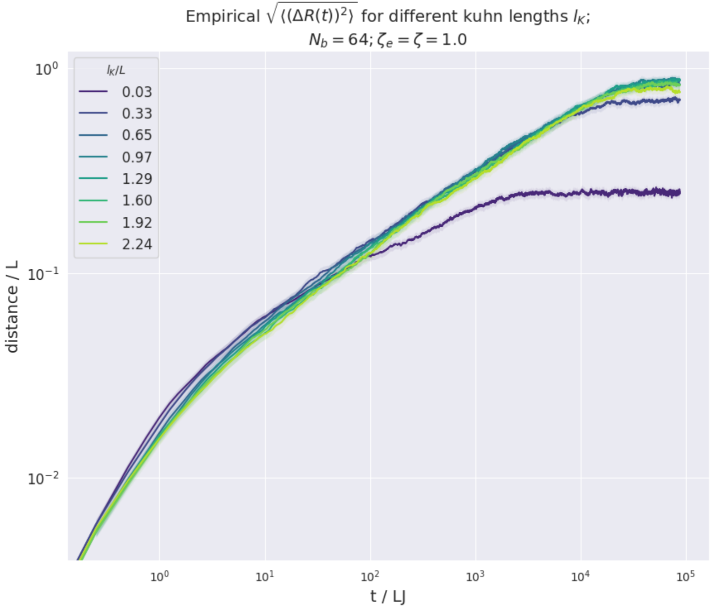
Experiment 2: Semi-flexible chain, vary persistence length

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



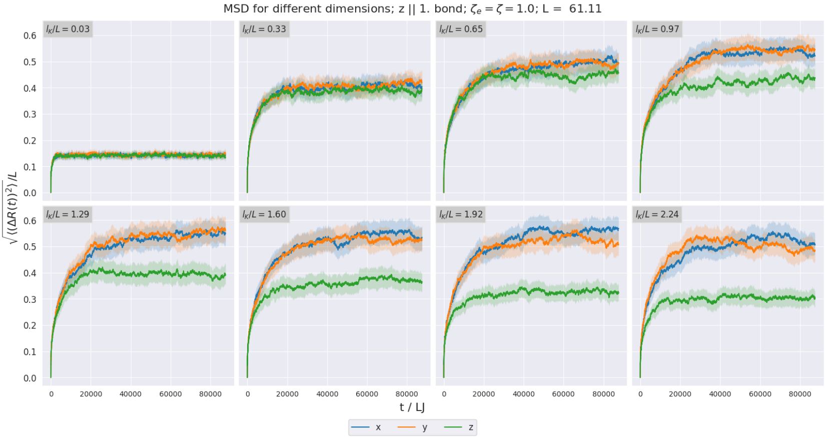
Experiment 2: Semi-flexible chain, vary persistence length

MSD: $\langle [\Delta R(t)]^2 \rangle$ on log-log scale



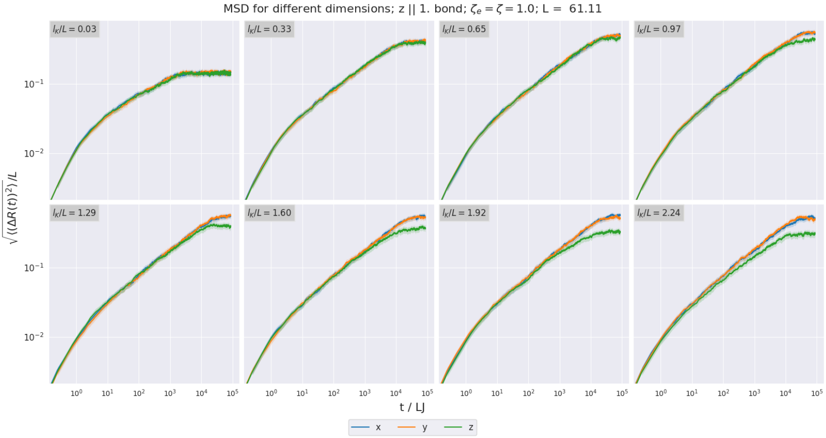
Experiment 2: Semi-flexible chain, vary persistence length

MSD: $\langle[\Delta R(t)]^2\rangle$ by dimension



Experiment 2: Semi-flexible chain, vary persistence length

MSD: $\langle [\Delta R(t)]^2 \rangle$ by dimension on log scale



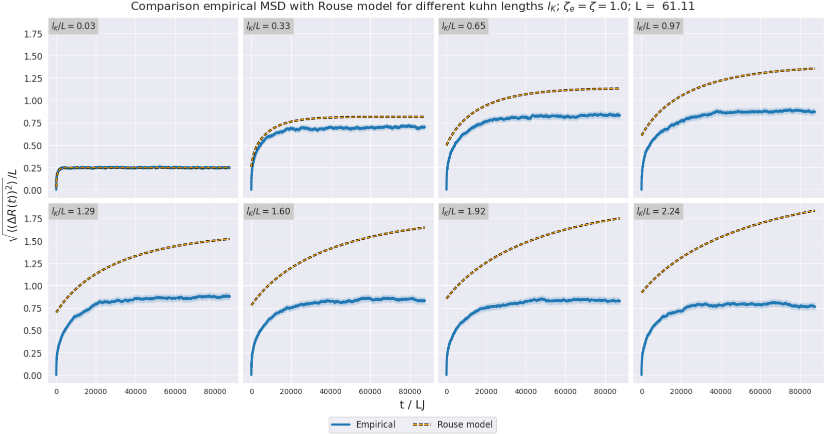
Experiment 2: Semi-flexible chain, vary persistence length

Conclusions 1

1. The behavior of MSD for different l_K is roughly the same for $l_K/L \gtrapprox 0.65$
2. The relaxation time grows non-linearly with rising l_K
3. MSD in z dimension is noticable different for $l_K \gtrapprox 0.97$.
   - The relaxation time in z dimension gets smaller relative to x,y dimensions with increasing l_K. Explanation: chain has less freedom along z axis with rising l_K.
   - MSD is in z is smaller then in x,y on longer time scales. Explanation: same.

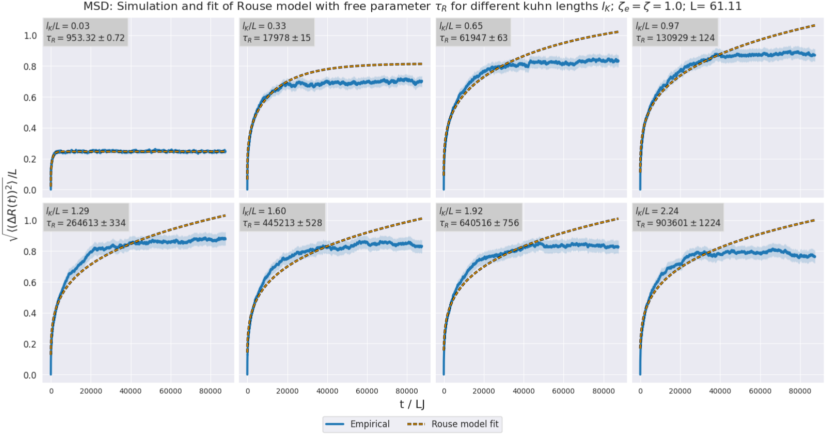
Experiment 2: Semi-flexible chain, vary persistence length

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



Experiment 2: Semi-flexible chain, vary persistence length

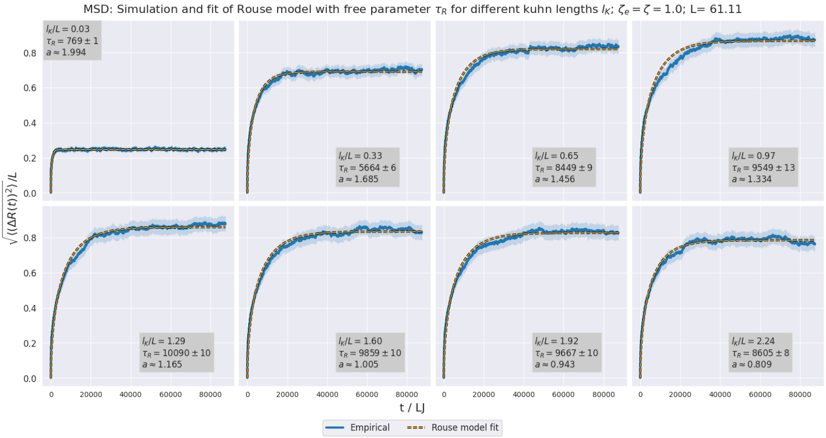
$\langle [\Delta R(t)]^2 \rangle$ vs Rouse with τ_R as free parameter



Experiment 2: Semi-flexible chain, vary persistence length

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

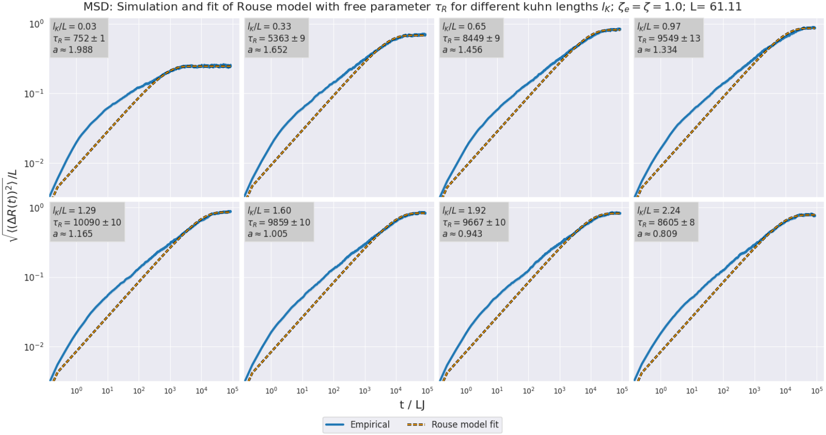
$$\langle[\Delta R(t)]^2\rangle = a\langle R\rangle[1 - \exp(-\frac{t}{\tau_R})]$$



Experiment 2: Semi-flexible chain, vary persistence length

$\langle[\Delta R(t)]^2\rangle$ vs Adjusted Rouse with τ_R, a as free parameter on log scale

$$\langle[\Delta R(t)]^2\rangle = a\langle R\rangle[1 - \exp(-\frac{t}{\tau_R})]$$



Experiment 2: Semi-flexible chain, vary persistence length

Conclusions 2

1. Rouse model is not able to describe semi-flexible chain with $\gtrapprox$ 3 segments even with rouse time adjusted for boundary conditions. (Continuum assumption violated; ETE of worm-like chain is different.)
2. Rouse model with free τ_R doesn't work for small number of kuhn segments.
3. Introducion of Adjusted Rouse model helps to describe dynamics on interim and large time scales, however it's inaccurate on short time scales.

Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

Settings

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

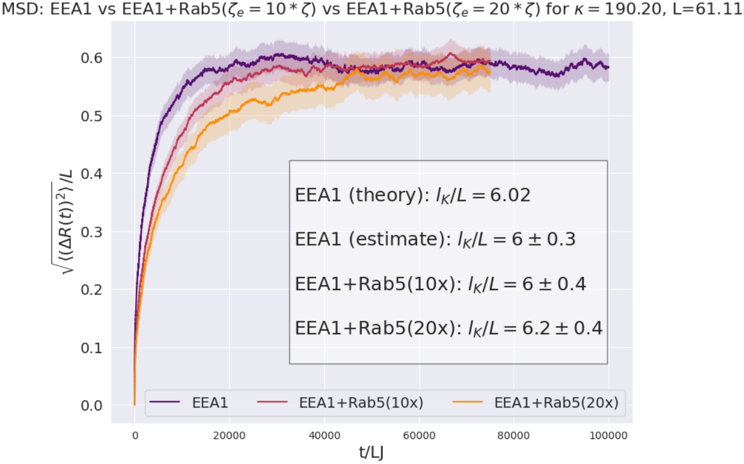
- Only bonded beads interract

Modelling EEA1 and EEA1+Rab5:

- EEA1: $\kappa = 190.2 \Rightarrow l_K/L = 6.02$
- EEA1+Rab5: $\zeta_e = 10\zeta, 20\zeta$; $m_e = 1.5m$

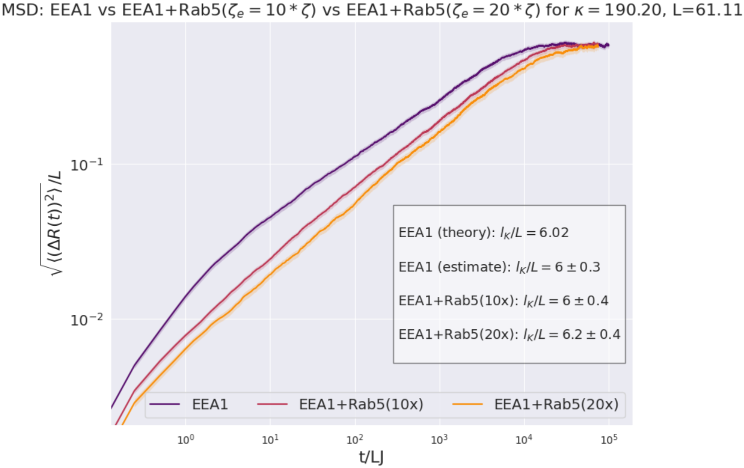
Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

MSD



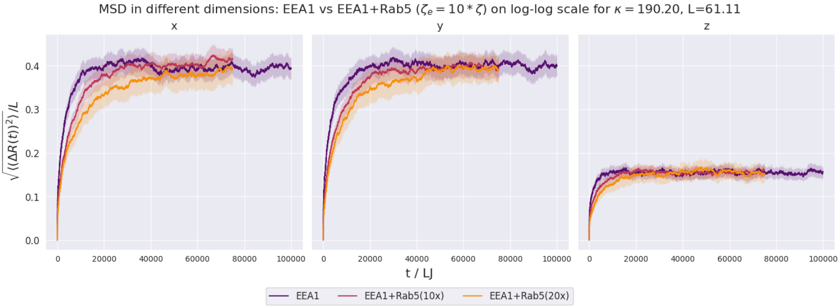
Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

MSD on log scale



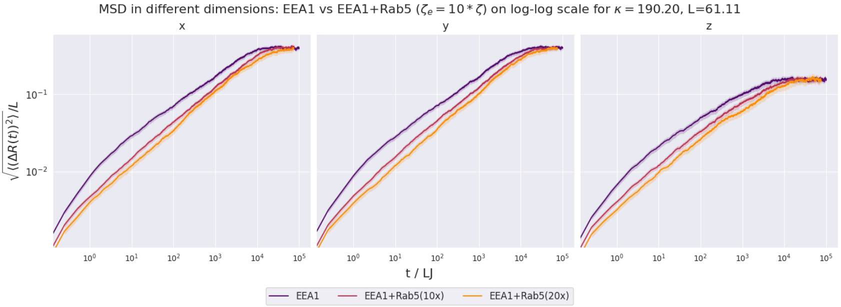
Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

MSD by dimension



Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

MSD by dimension on log scale



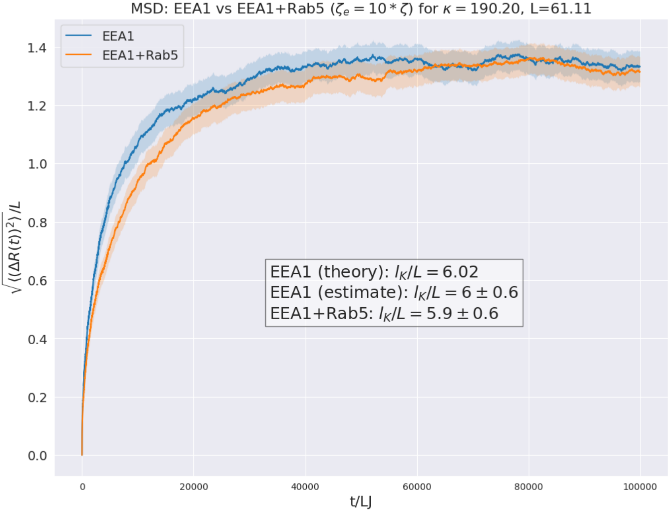
Experiment 3: EEA1/EEA1+Rab5-like chain, anchored

Conclusions / Results

- l_K of the EEA1-like- and EEA1+Rab5-like- anchored chain is the same.
- Increased diameter of end monomer changes short- and interim-time scale dynamics. Relaxation time of the chain increases. Likely because of slower diffusion of the end monomer and correspondingly of the part of the chain.

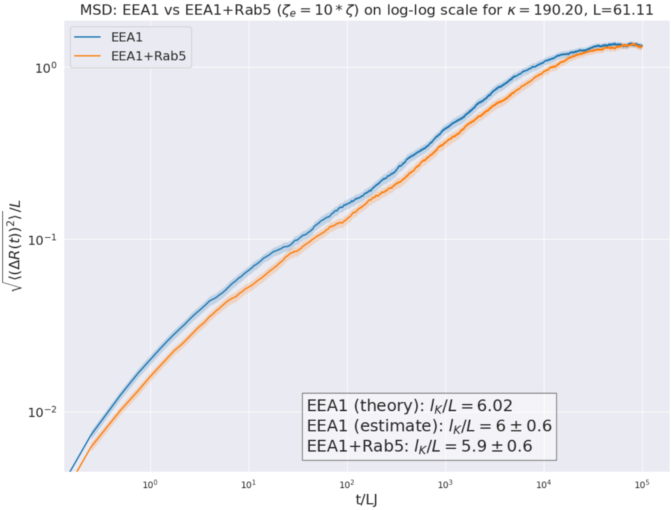
Experiment 4: EEA1/EEA1+Rab5-like chain, free

MSD



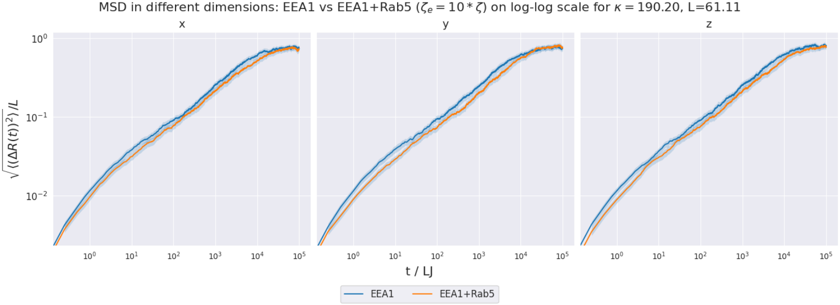
Experiment 4: EEA1/EEA1+Rab5-like chain, free

MSD on log scale



Experiment 4: EEA1/EEA1+Rab5-like chain, free

MSD by dimension on log scale



Experiment 4: EEA1/EEA1+Rab5-like chain, free

Conclusions / Results

- l_K of the EEA1-like- and EEA1+Rab5-like- free chain is the same.
- With increasing diameter of the end monomer short- and interim- time scale dynamics slightly changes. The relaxation time slightly uncreases. Change in relaxation time is smaller then in case of anchored chain.
- In difference to anchored chain - MSD in z direction does not differ from x,y.

Problems and Questions

1. No analytical model for experiment 3 and 4, therefore precise description of the difference in dynamics is not possible.

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.