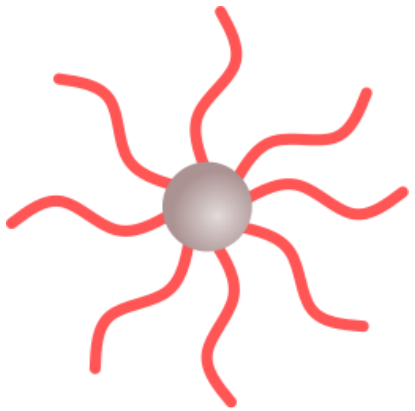
JÜLICH
FORSCHUNGSZENTRUM

Star polymers: a light scattering study

Yi Liu
Institute of Complex System (IBI-4)

Star-shaped polymers

- A broad class of macromolecular architecture
- linear “arms” + central branching point “core”
  - number of arms
  - length of arms
  - chemical nature of core
  - size-, and chemical distribution of arms
- a crossover between linear polymers and soft colloids
- Application
  - Interfacial stabilizing agent
  - Drug delivery
  - Gene therapy



Scope

light scattering in bulk

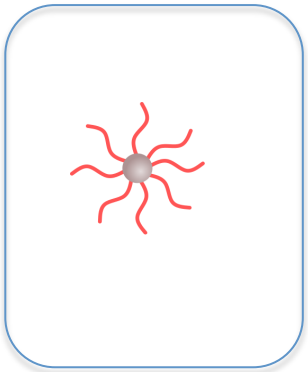
- DLS
- D_0, R_H
- Polydispersity
- SLS

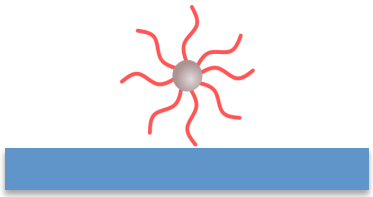
Dynamics at liquid-glass interface

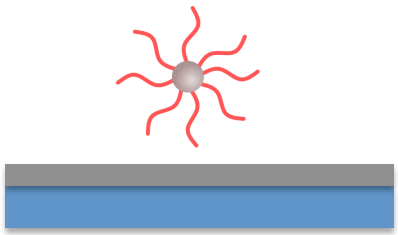
- 3 penetration depth
- parallel scan
- perpendicular scan

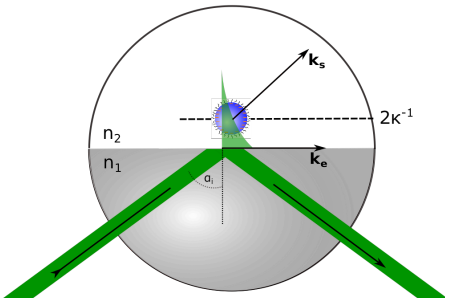
Dynamics at liquid – coated glass interface

- Coating of glass
- absorbing - desorbing

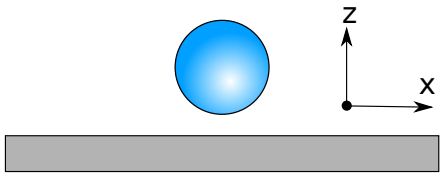


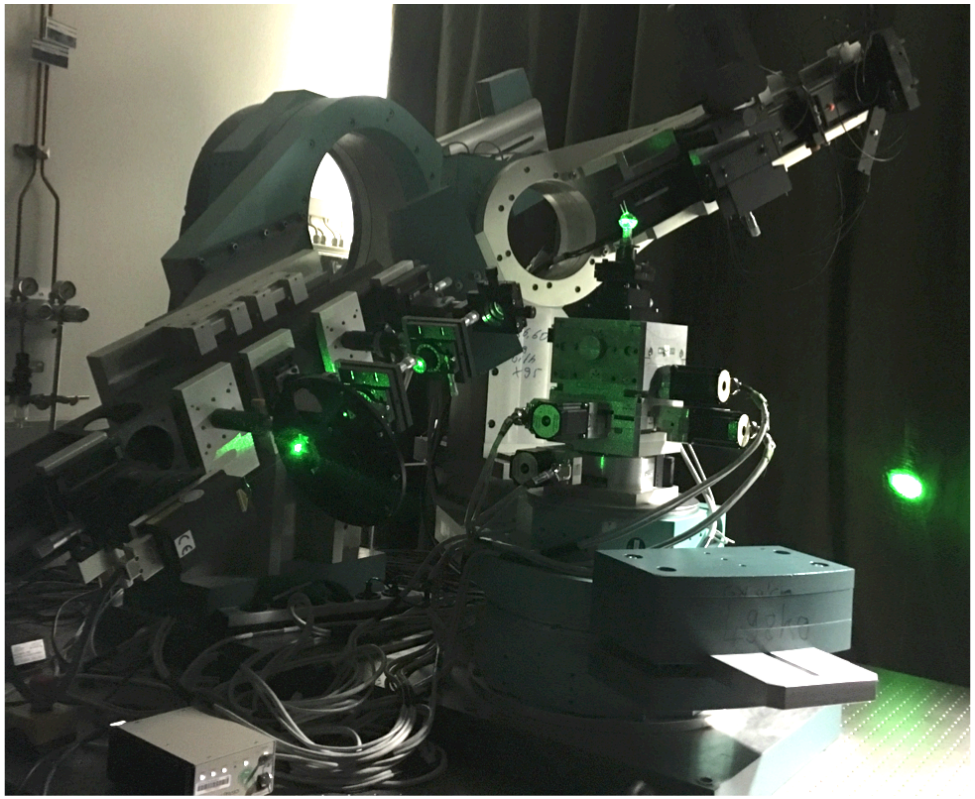


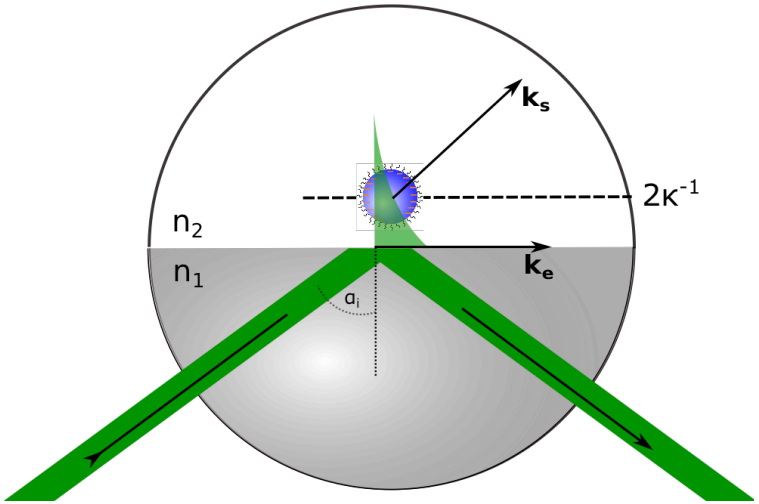




EWDLS for interface dynamics

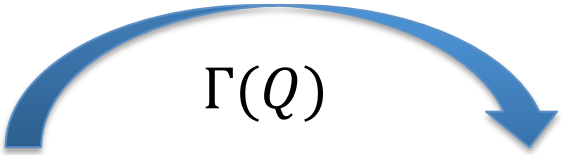


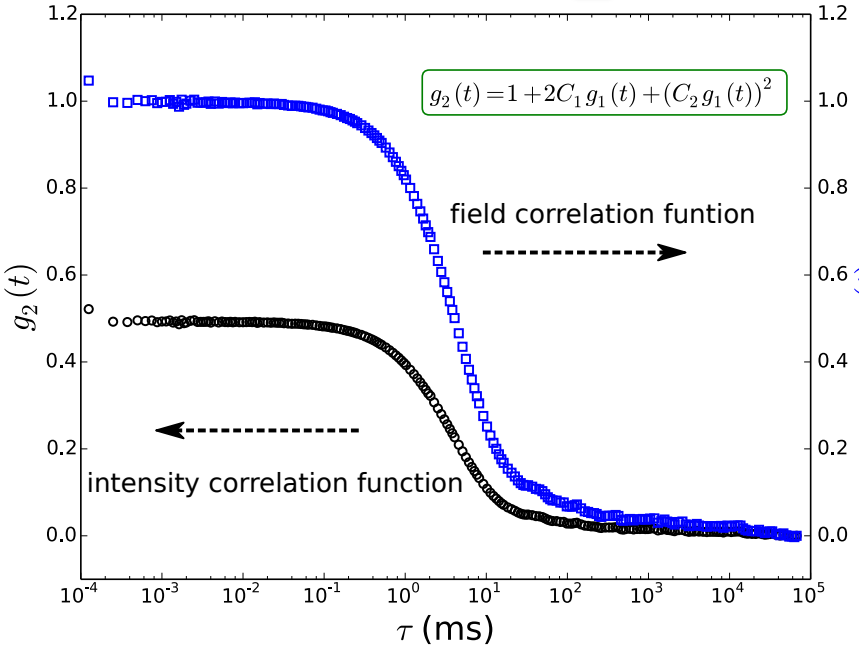


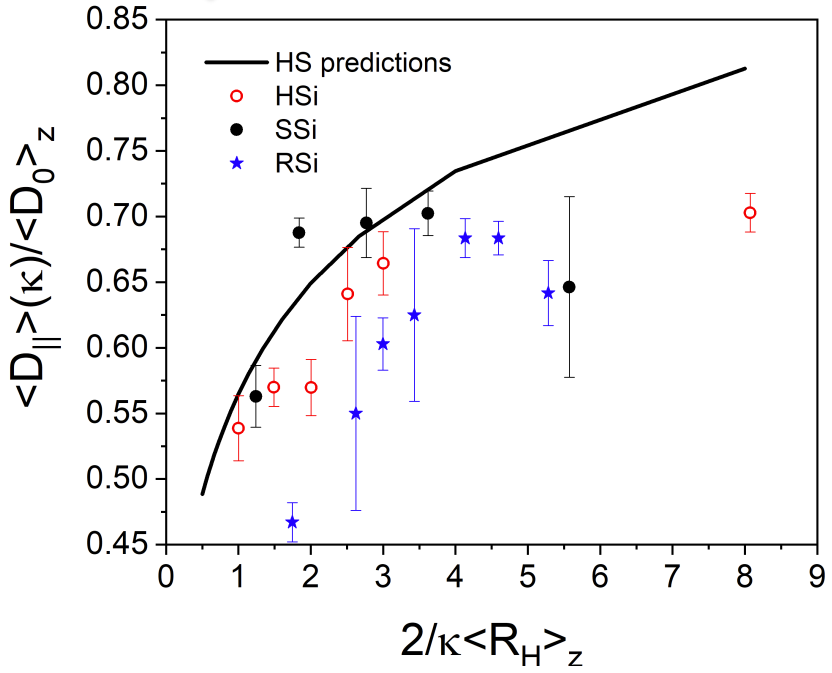


$$\mathbf{Q} = \mathbf{k_s} - \mathbf{k_e}$$

$$2\kappa^{-1} = \frac{\lambda_0}{2\pi\sqrt{(n_1 \sin\alpha_i)^2 - n_2^2}}$$







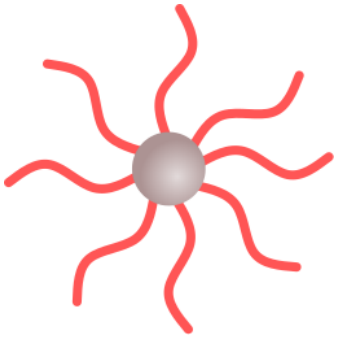
Generality

- Particles are slowed down at interface due to hydrodynamic interaction.
- The larger the penetration depth, the weaker the slow-down effect.

Limitation

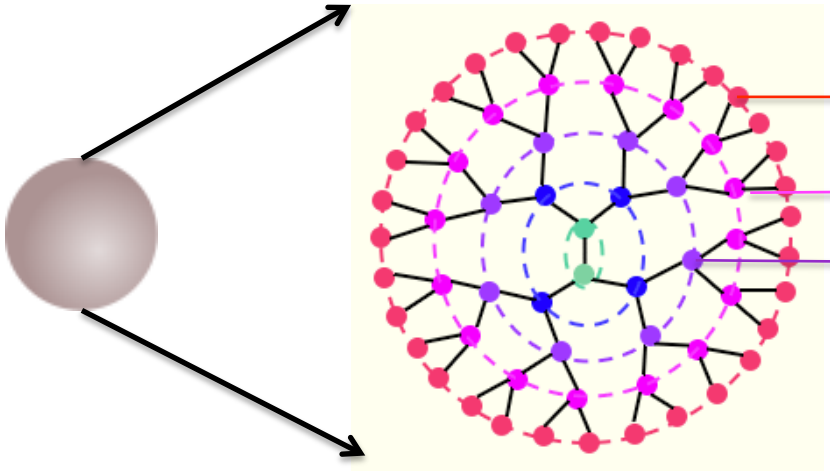
- The correlation function is the only source of information
- Dynamic behavior is impacted by static properties
- Static information cannot can not be directly discerned from dynamic information.

Model system



Model star polymers:

- core: dendrimer fractal
- arm: polystyrene chain
- varying arm length and number

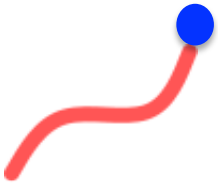


32 nodes, 32 arms grafted

16 nodes, 16 arms grafted

8 nodes, 8 arms grafted

Bifurcation process



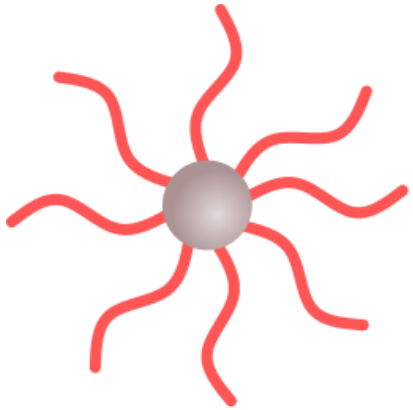
Polystyrene chains of different length
Grafted to the end point of dendrimer core

With increasing generation / arm number, the structure is more compact and the surface is more defined.

Systems

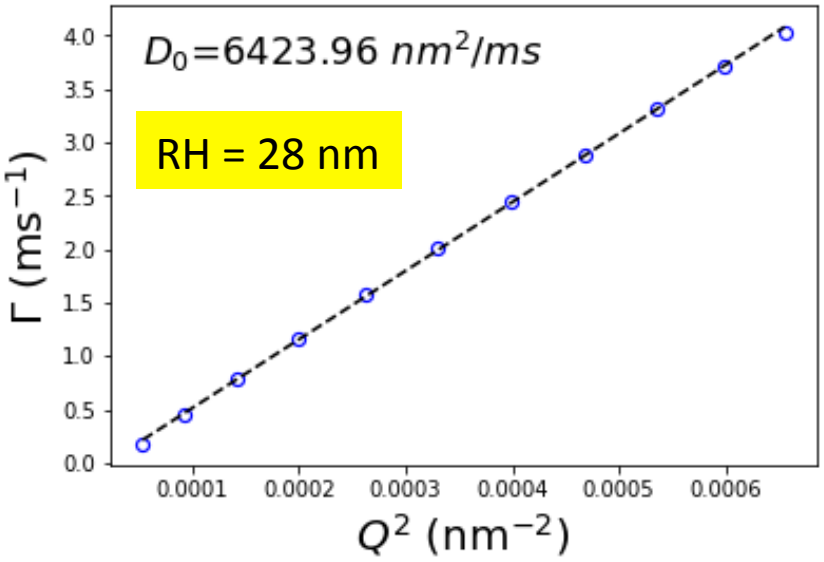
- 7 samples, received as powder
- Solvent: 1,4 dioxane (organic), dispersed over night
- Concentration: ca. 1mg/mL, far below overlapping

code	No. of arms	arm length kDa	Mw kDa
64-52k	64	52	3328
64-80k	64	80	5120
64-140k	64	140	8960
32-52k	32	52	1664
32-80k	32	80	2560
32-140k	32	140	4480
8-57k	8	57	456

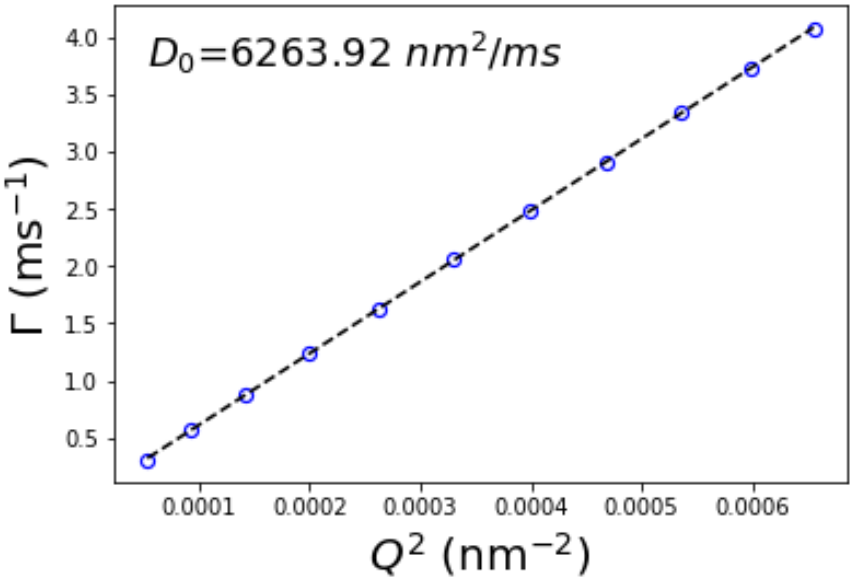


Light scattering in Bulk

64-52k

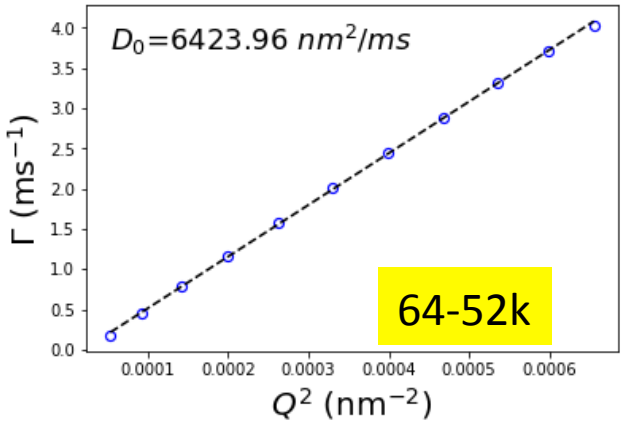


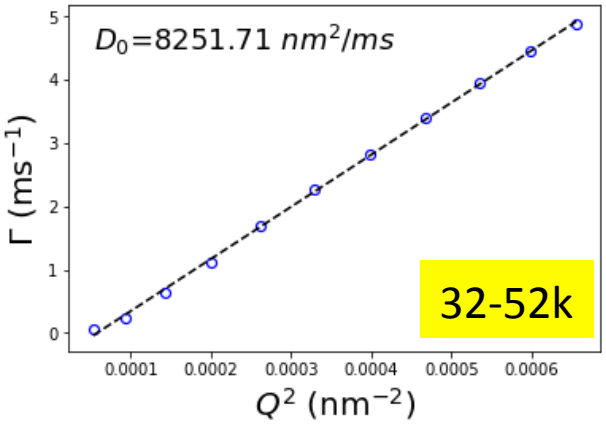
bulk DLS before EWDLS measurement



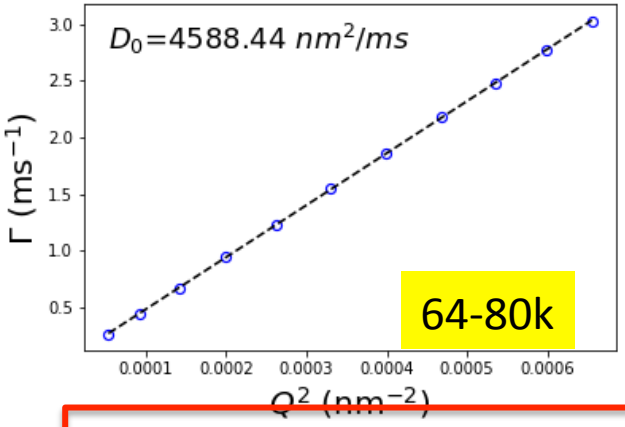
bulk DLS after EWDLS measurement

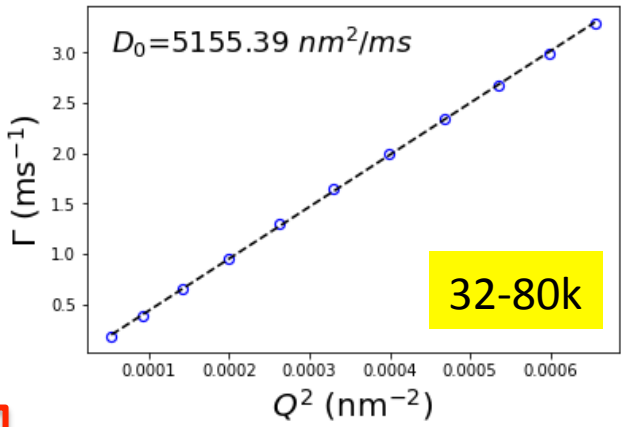
- Stretched exponential fit is applied first to estimate the size and polydispersity.
- DLS is done before and after EWDLS measurement.
- Sample is in general well dispersed, relatively monodisperse and stable over time.
- An exact PDI is calculated with cumulant analysis.

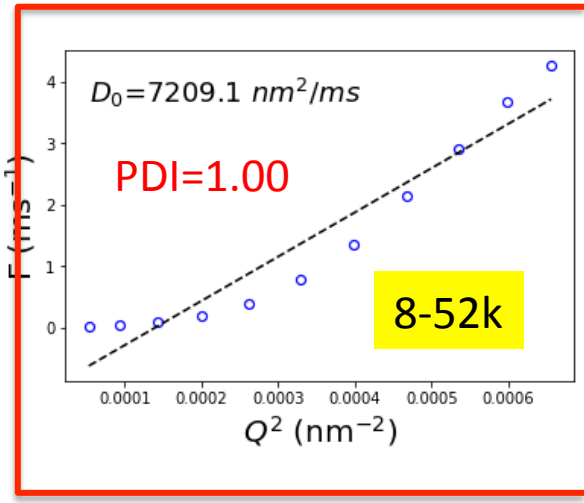


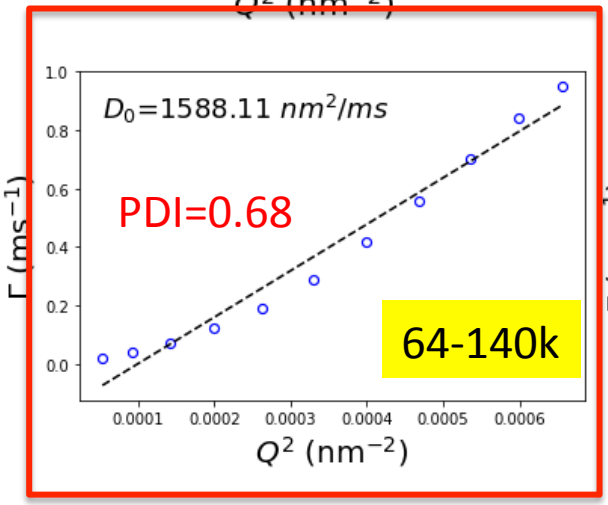


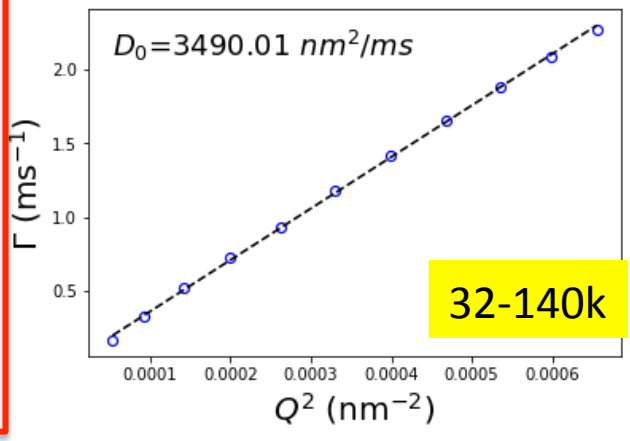
DLS
stretched exponential
analysis





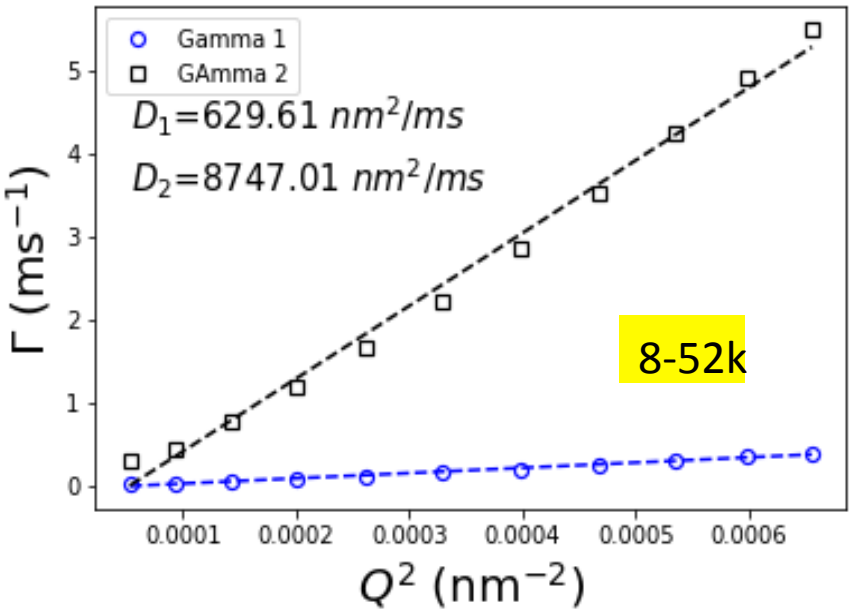


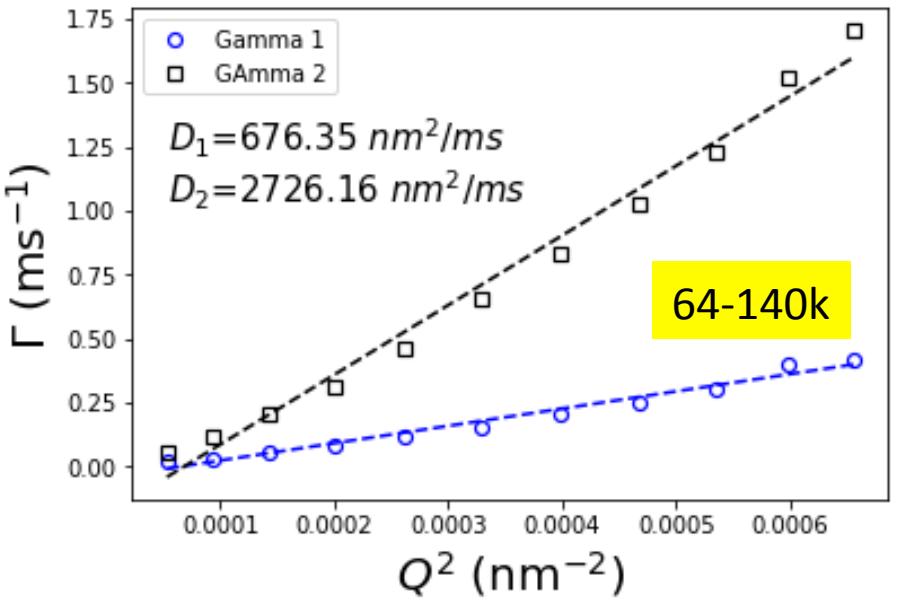




Two outlets

Analysis considering two relaxations

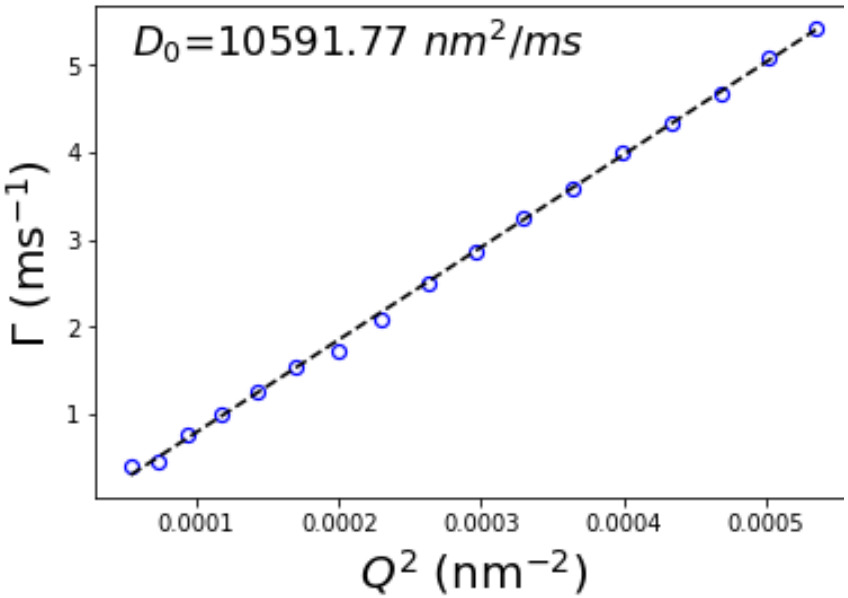


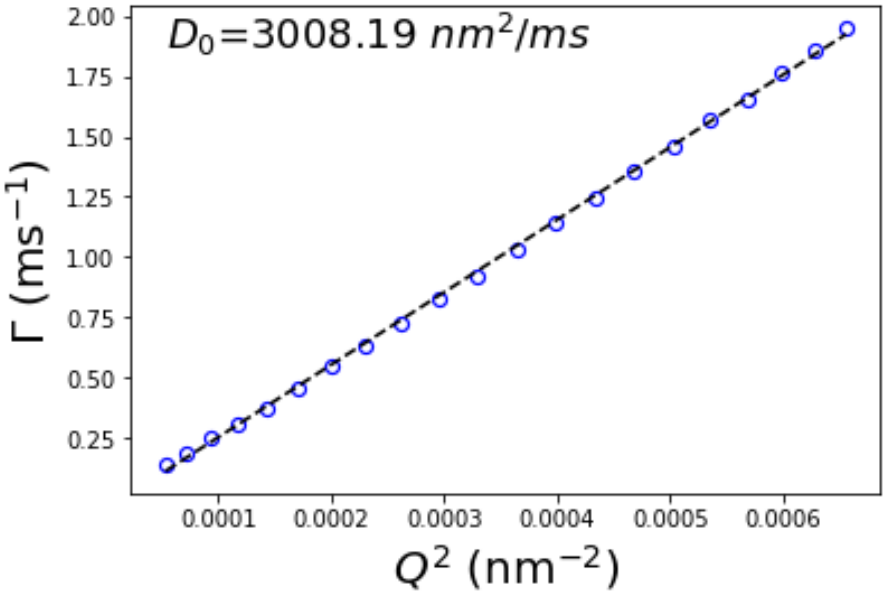


The fit suggests two species:

- the smaller one reflects the expected size;
- the bigger one might come from aggregation.

sample	$D_{0,1}$ nm^2/ms	$D_{0,2}$ nm^2/ms	$R_{H,1}$ (nm)	$R_{H,2}$ (nm)
64-140k	676	2726	269	67
8-57k	630	8747	289	20



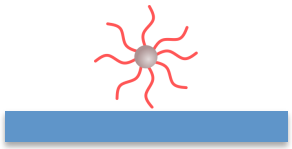


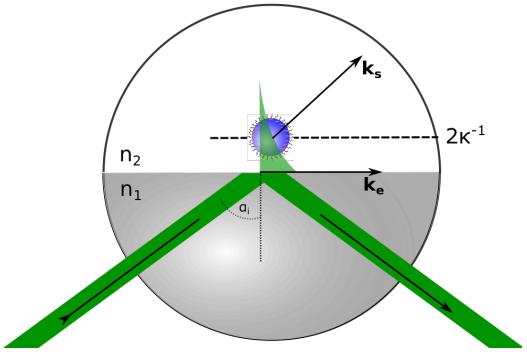
Summary of bulk light scattering

sample	Mw (kDa)	R_H (nm)	D_0 nm^2/ms	PDI
64-52k	3328	28	6424	0,011
64-80k	5120	39	4588	0,0022
64-140k	8960	113	1588	0,68
				0,197iio
32-52k	1664	22	8252	0,096
32-80k	2560	35	5155	0,0055
32-140k	4480	51	3490	0,047
8-57k	456	25	7209	1,00
				0,09322

sample	$D_{0,1}$ nm^2/ms	$D_{0,2}$ nm^2/ms	$R_{H,1}$ (nm)	$R_{H,2}$ (nm)
64-140k	676	630	269	289
8-57k	2726	8747	67	20

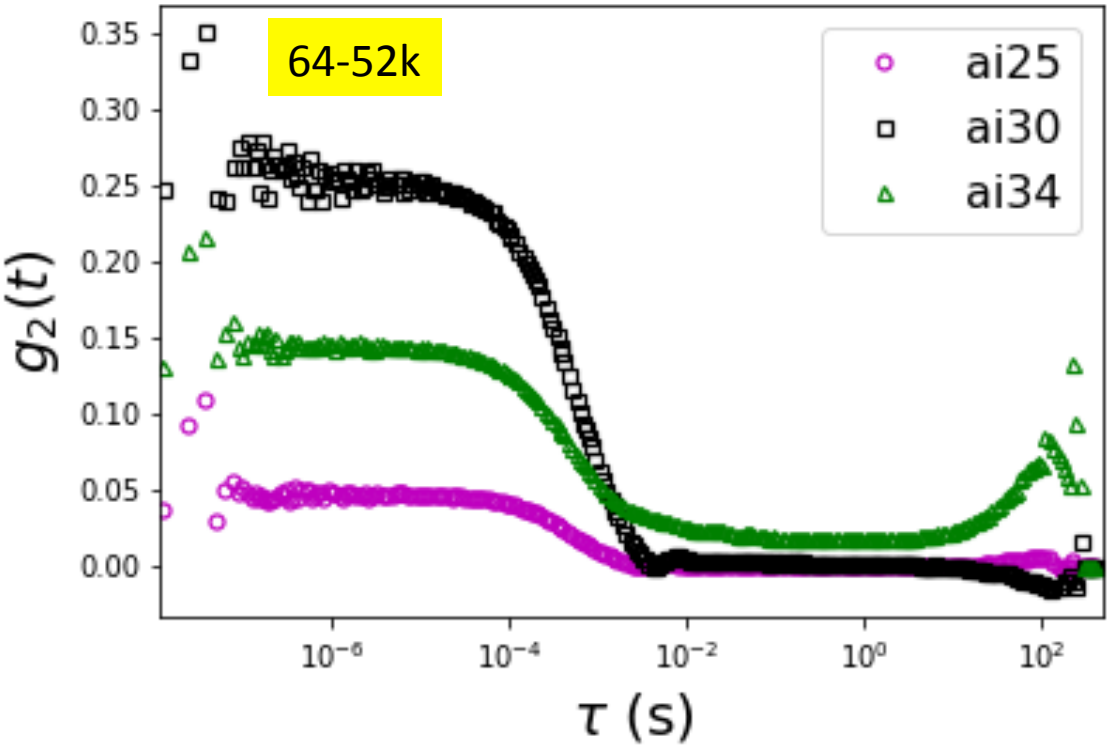
EWDLS : correlation function





ai = 25, PD = 126 nm
ai = 30, PD = 174 nm
ai = 34, PD = 386 nm

$$2\kappa^{-1} = \frac{\lambda_0}{2\pi\sqrt{(n_1 \sin\alpha_i)^2 - n_2^2}}$$



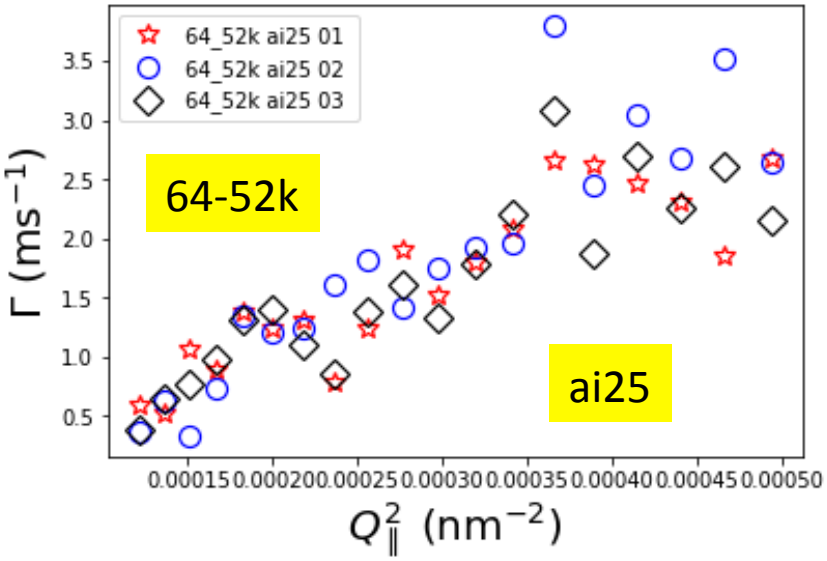
Protocol L

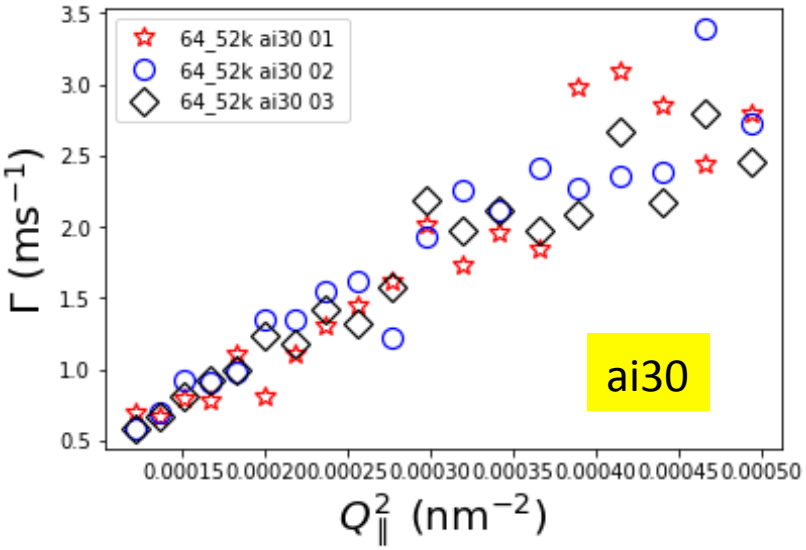
- 7 systems
- 3 penetration depth
- **parallel** and perpendicular scan
- 20 g_2(t) for each scan

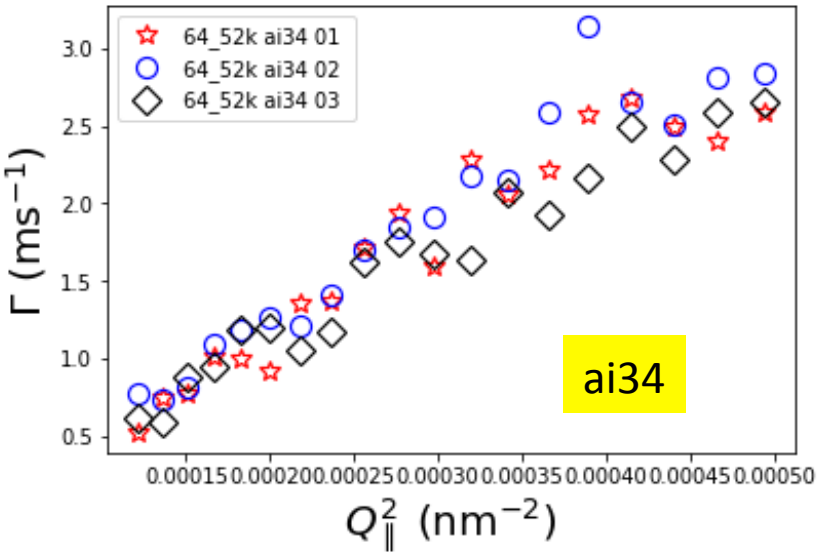
$$\Gamma(Q)$$

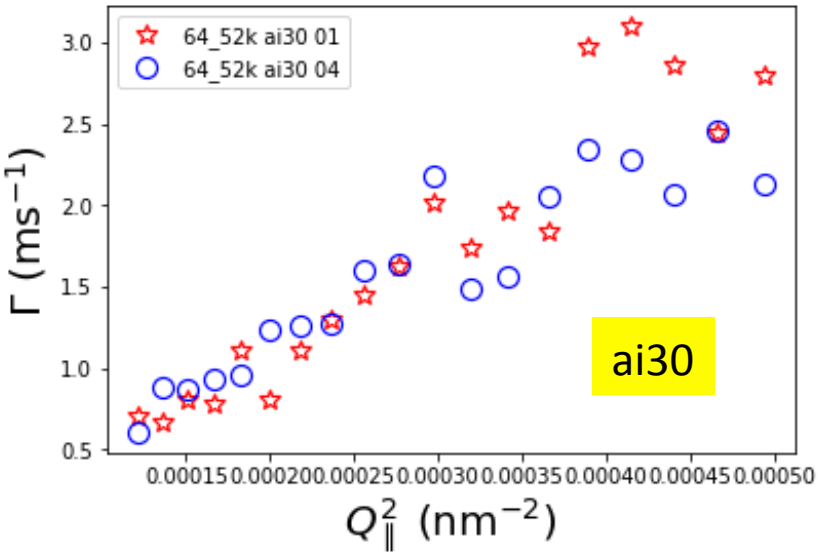
- each g_2(t) measured for 300 s and 3 times.

EWDLS: reproducibility and stability



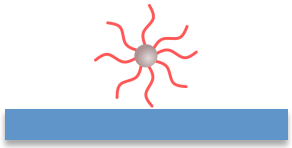




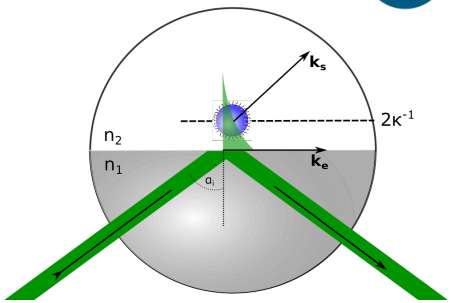


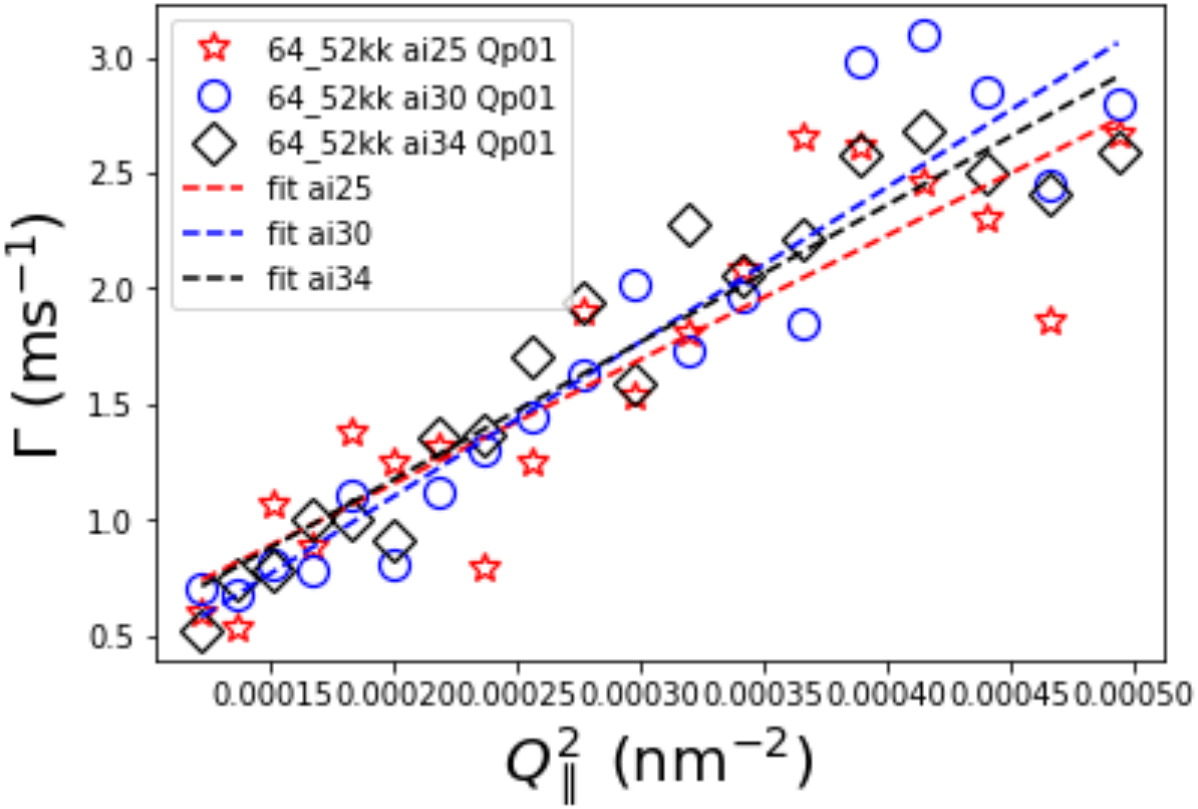
EWDLS measurement is reproducible. Each Dp is averaged over three repetitive runs.

Effect of penetration depth



ai = 25, PD = 126 nm
ai = 30, PD = 174 nm
ai = 34, PD = 386 nm

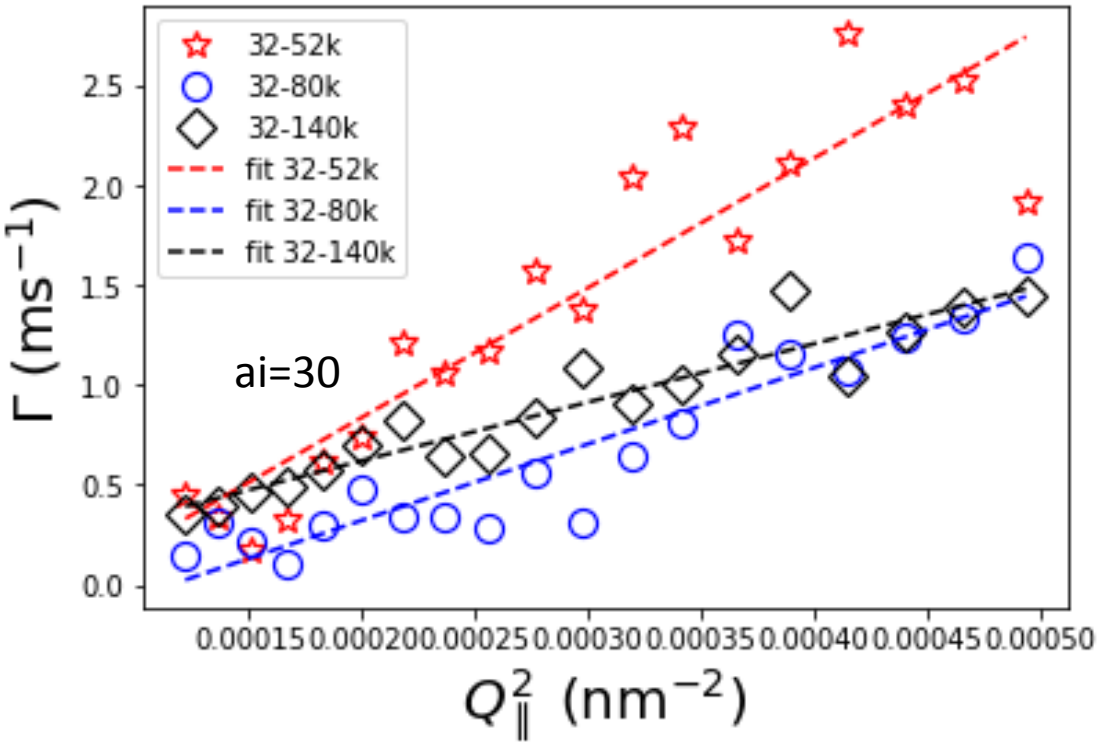




The effect of penetration depth is negligible in the current cases.

Effect of arm length

Arm number 32

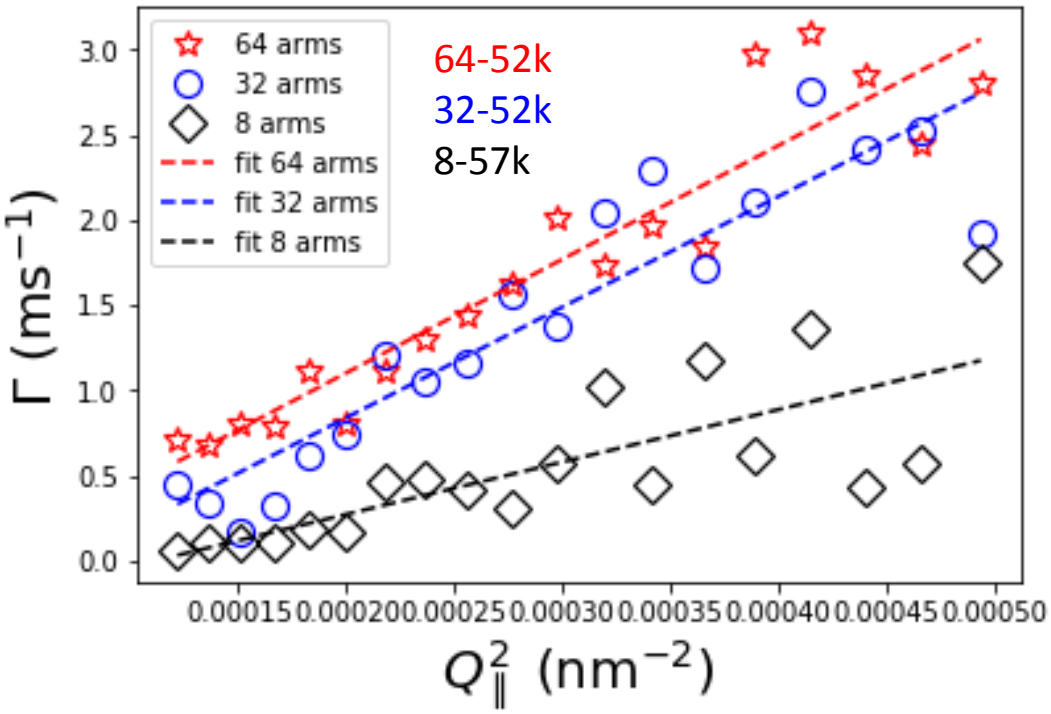


sample	D_0 nm^2/ms	D_p nm^2/ms	D_p/D_0
32-52k	8252	6296	0,76
32-80k	5155	3819	0,74
32-140k	3490	2928	0,84

At fixed arm number 32:
The diffusion of star polymers is slowed down by the interface.
However, the slow down effect of interface does not depend on arm length.

Effect of arm number

arm length 52 kDa



sample	D_0 nm²/ ms	D_p nm²/ ms	D_p/D_0
64-52k	6424	6180	0,96
32-52k	8252	6296	0,76
8-57k	7209	3072	0,43

At arm number 64, interface has no discernible effect on dynamic,
As arm number decreases to 32, a slow down effect of interface is observed,
The slow down effect seems to be more pronounced with decreasing arm number.
Note: 8-57 data is not reliable due to high polydispersity.

Summary of EWDLS

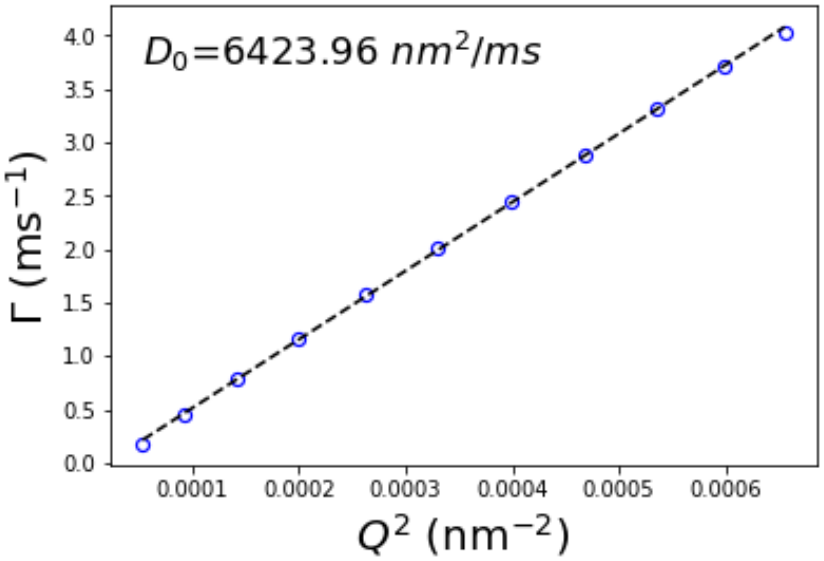
sample	PDI	D_0 nm^2/ms	D_p nm^2/ms	D_p/D_0
64-52k	0,001	6424	6180	0,96
64-80k	0,0022	4588	4224	0,92
64-140k	0,68	1588	355	0,22
32-52k	0,096	8252	6296	0,76
32-80k	0,0055	5155	3819	0,74
32-140k	0,047	3490	2928	0,84
8-57k	1,00	7209	3072	0,43

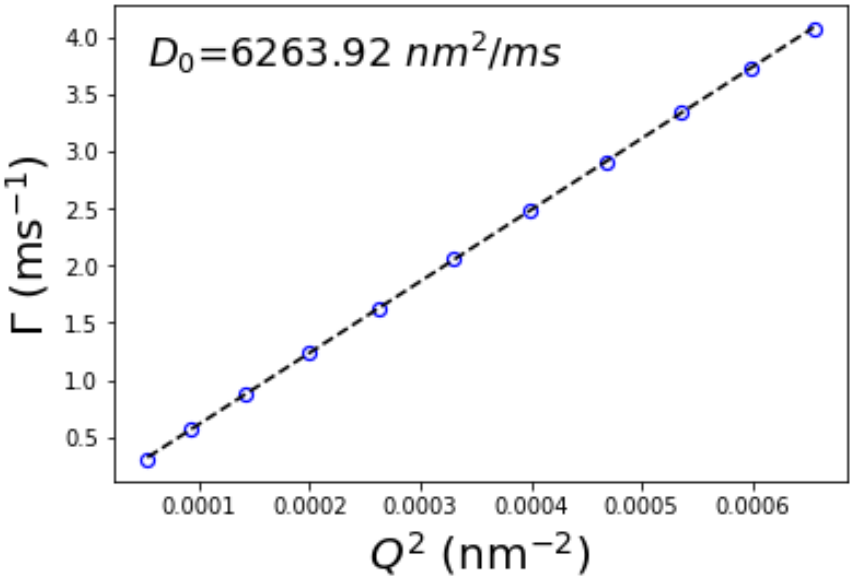
- At the same arm number, the wall effect does not depend on arm length.
- The wall effect depends heavily on arm number:
  - With 64 arms, the wall has no effect on the dynamic.
  - With 32 arms, the wall shows a slow down effect.

JÜLICH
FORSCHUNGSZENTRUM

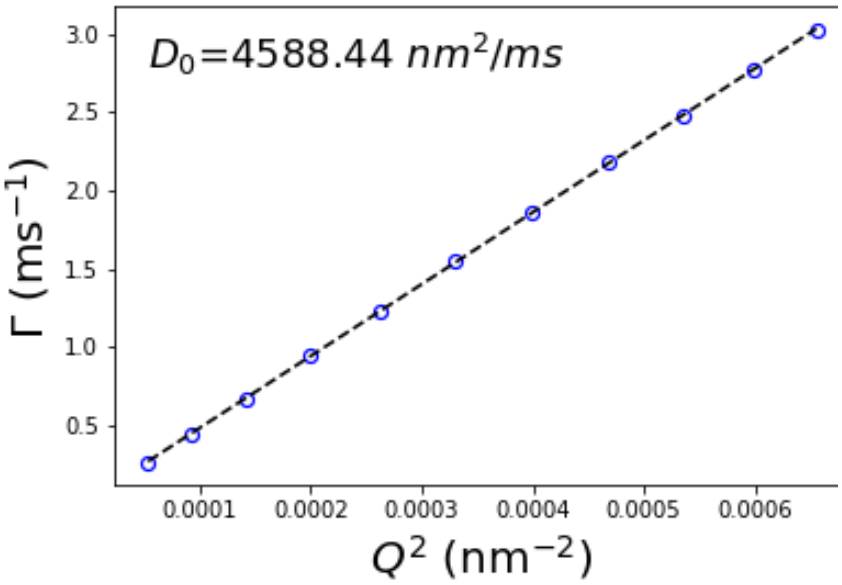
Appendix:

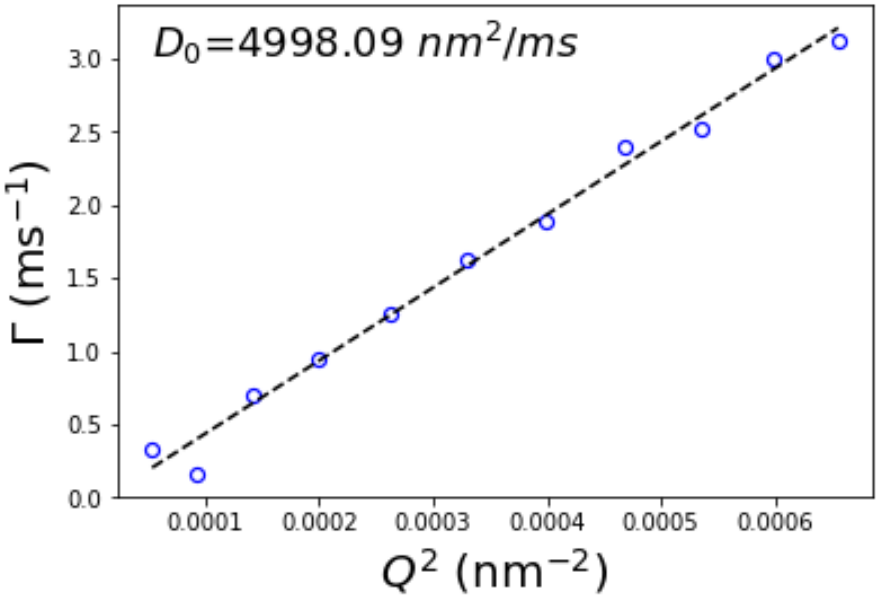
DLS 64-52k DLS





DLS 64-80k DLS

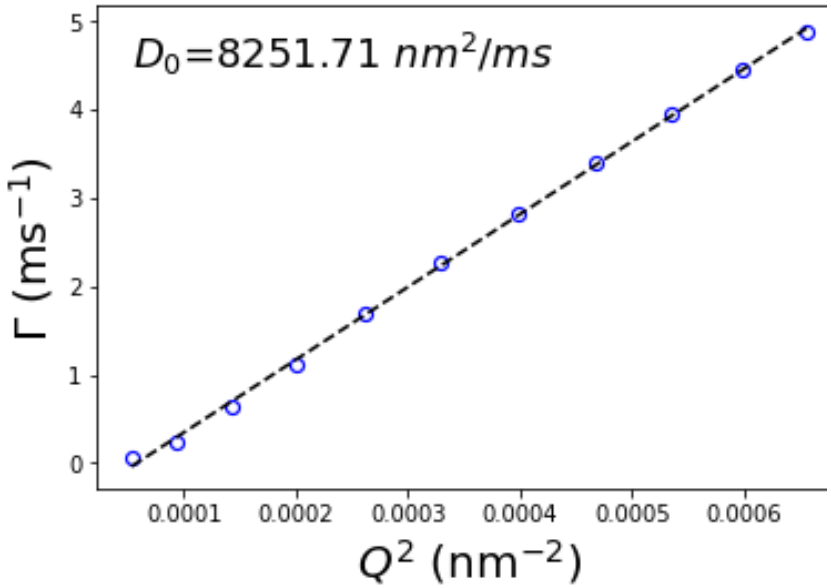




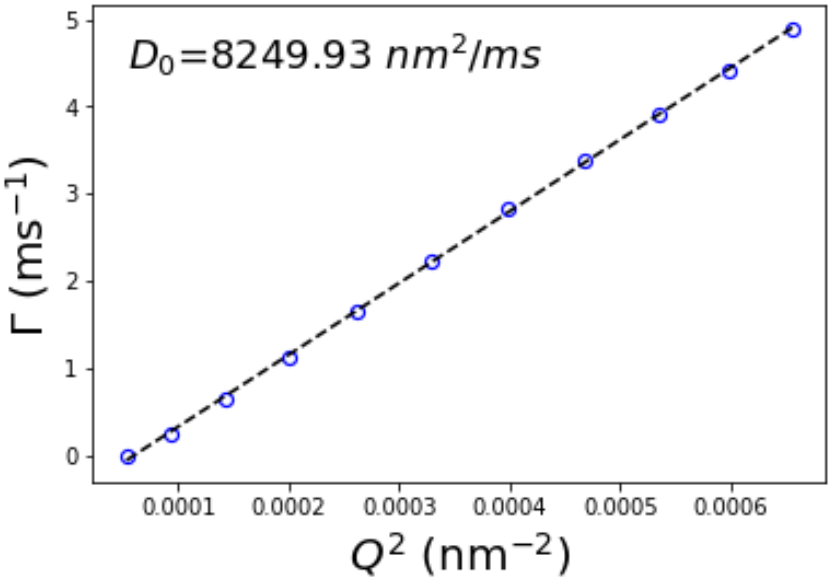
before EWDLS

after EWDSL

DLS 32-52k

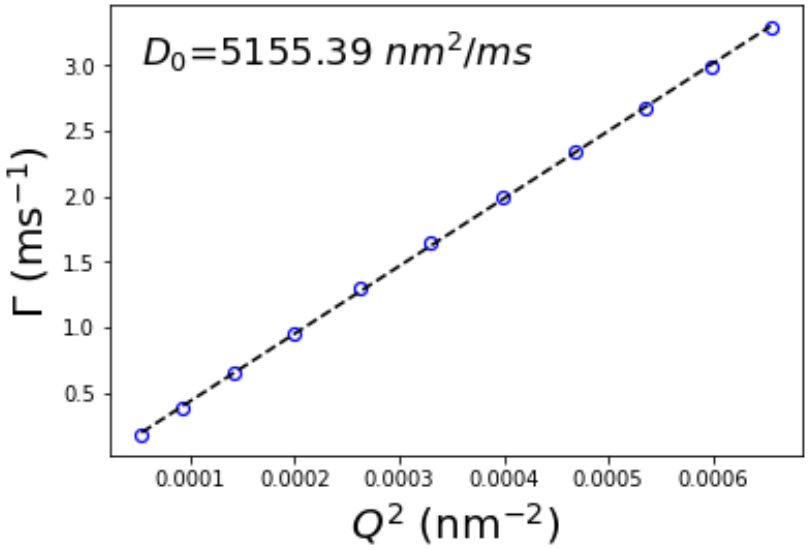


before EWDLS

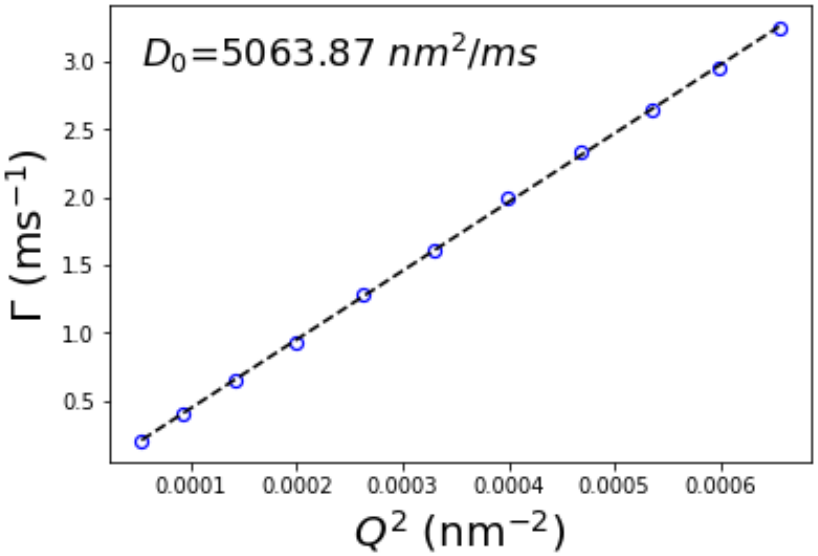


after EWDLs

DLS 32-80k

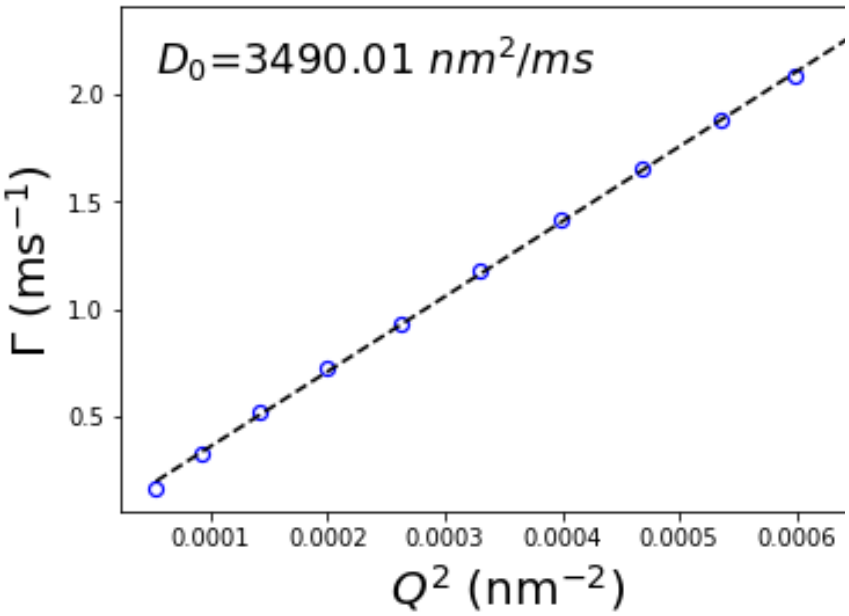


before EWDLS

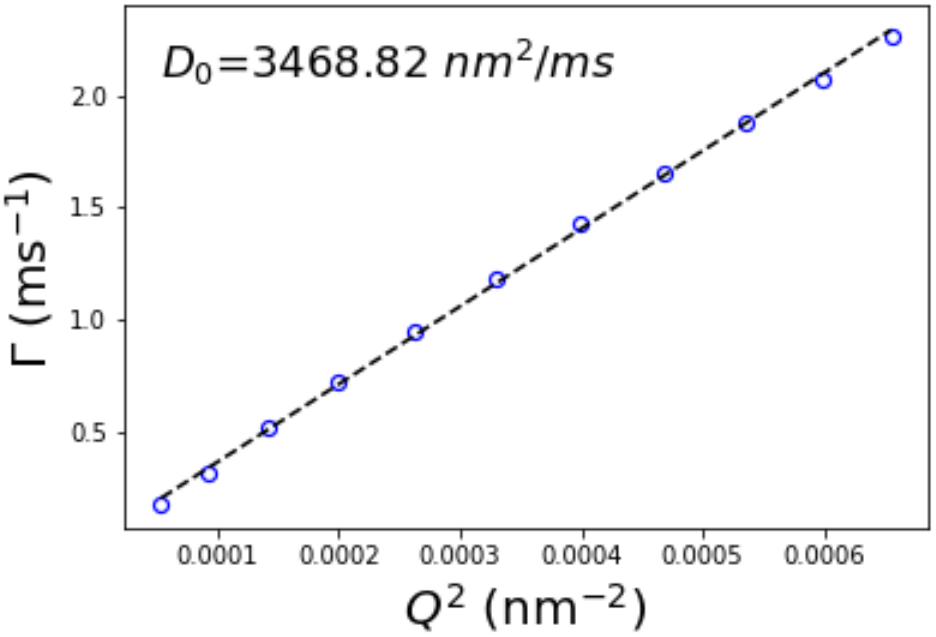


after EWDLS
The post ewdls sample was filtered again with PTFE

32-140k

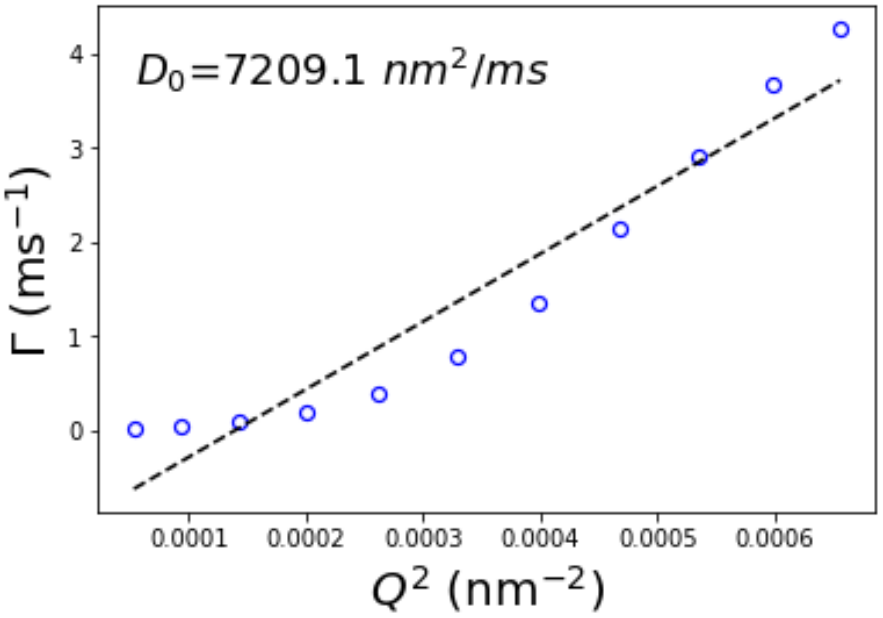


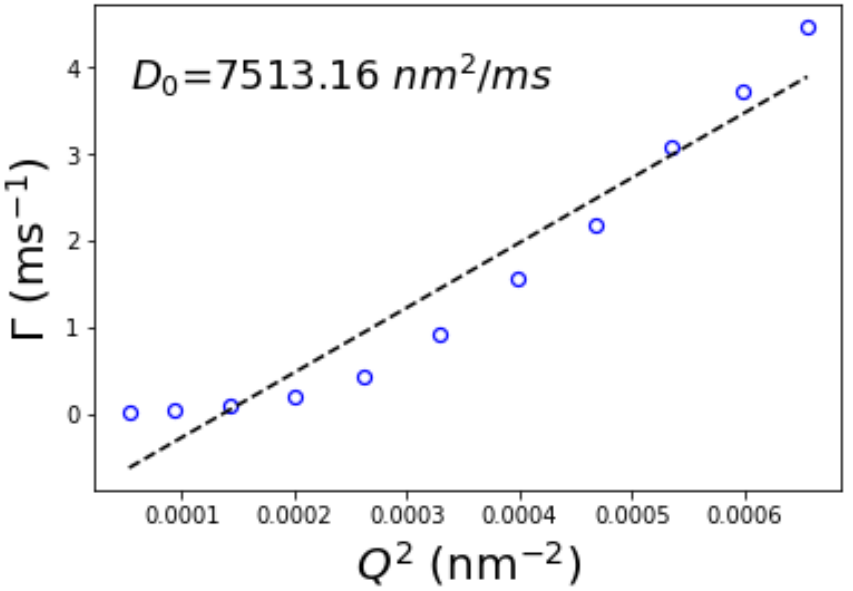
before EWDLS



after EWDLS
The post ewdls sample was filtered again with PTFE

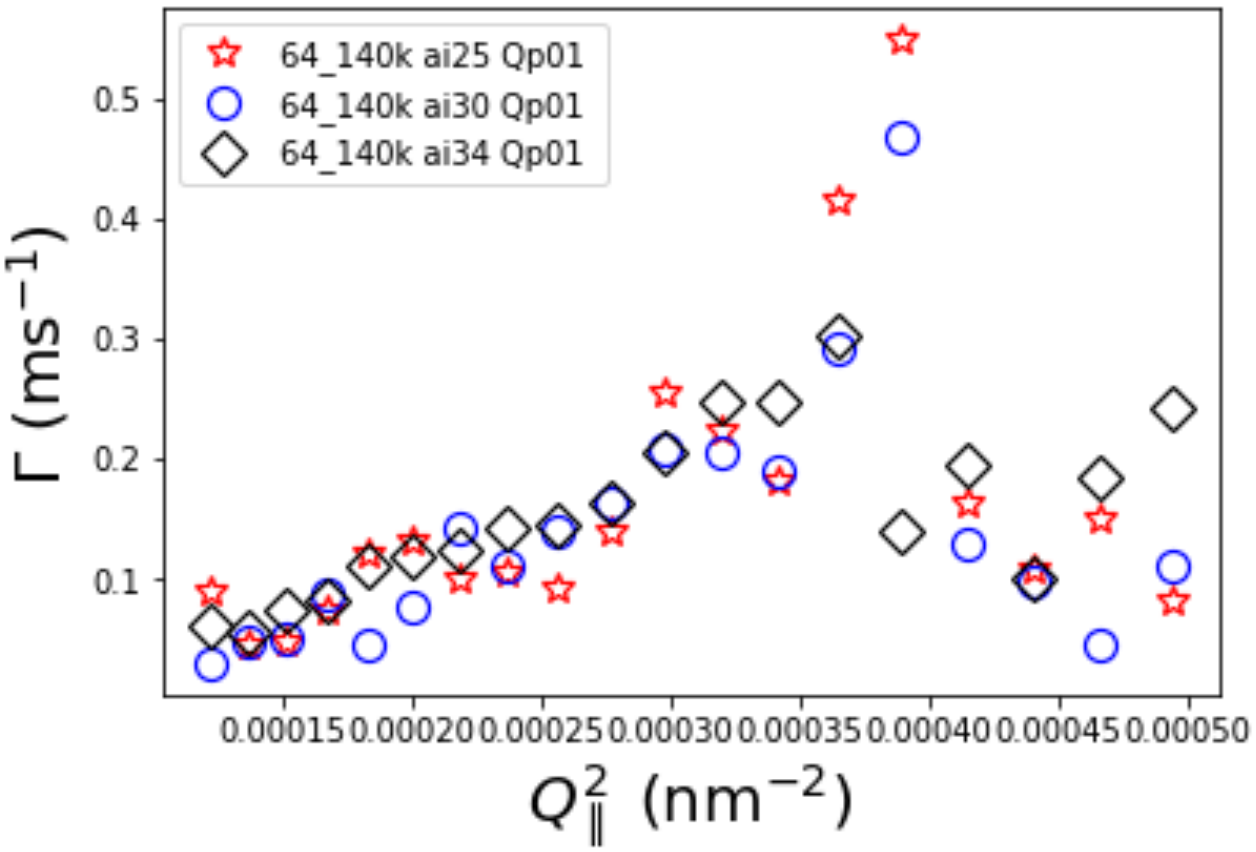
8-57k



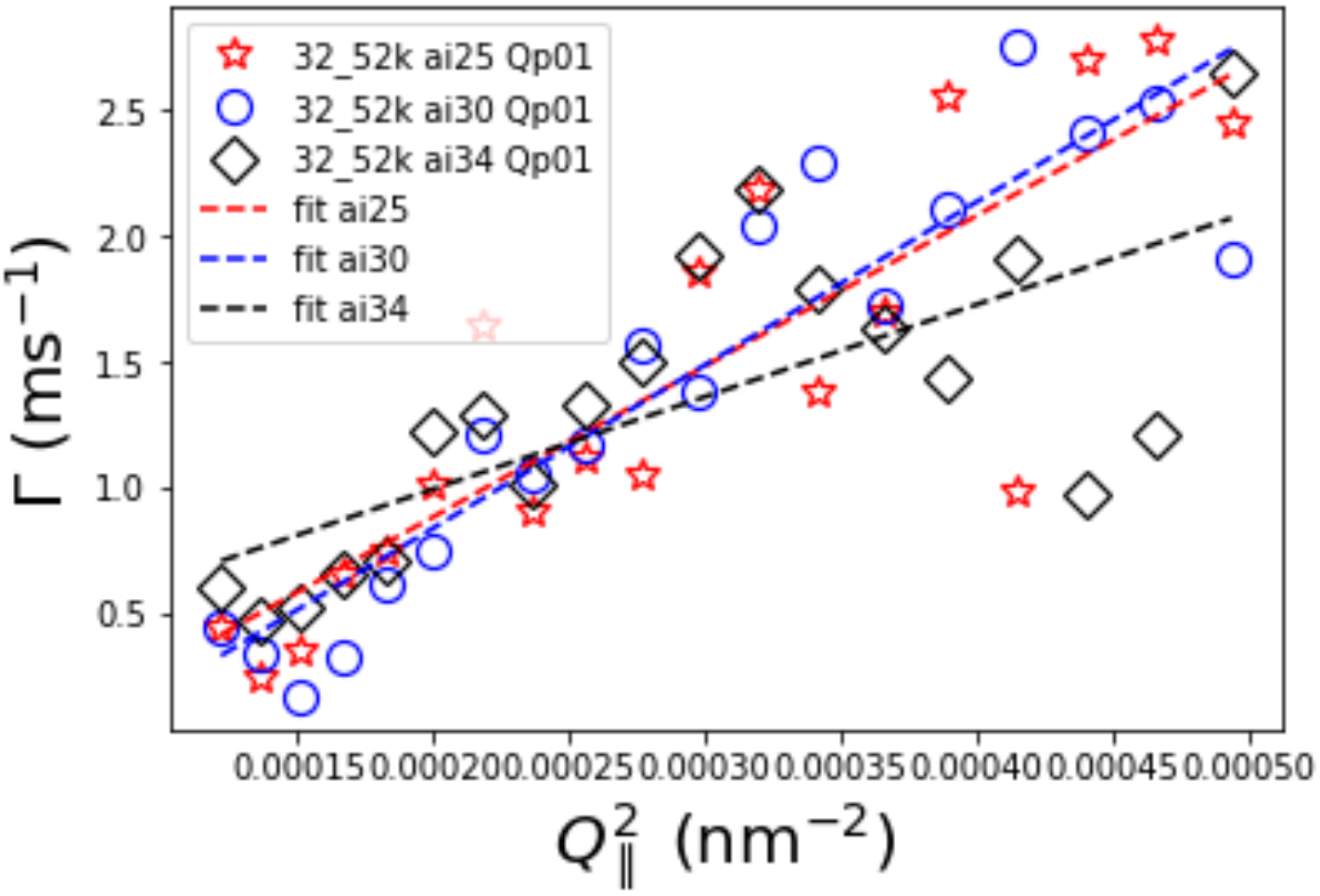


before EWDLS

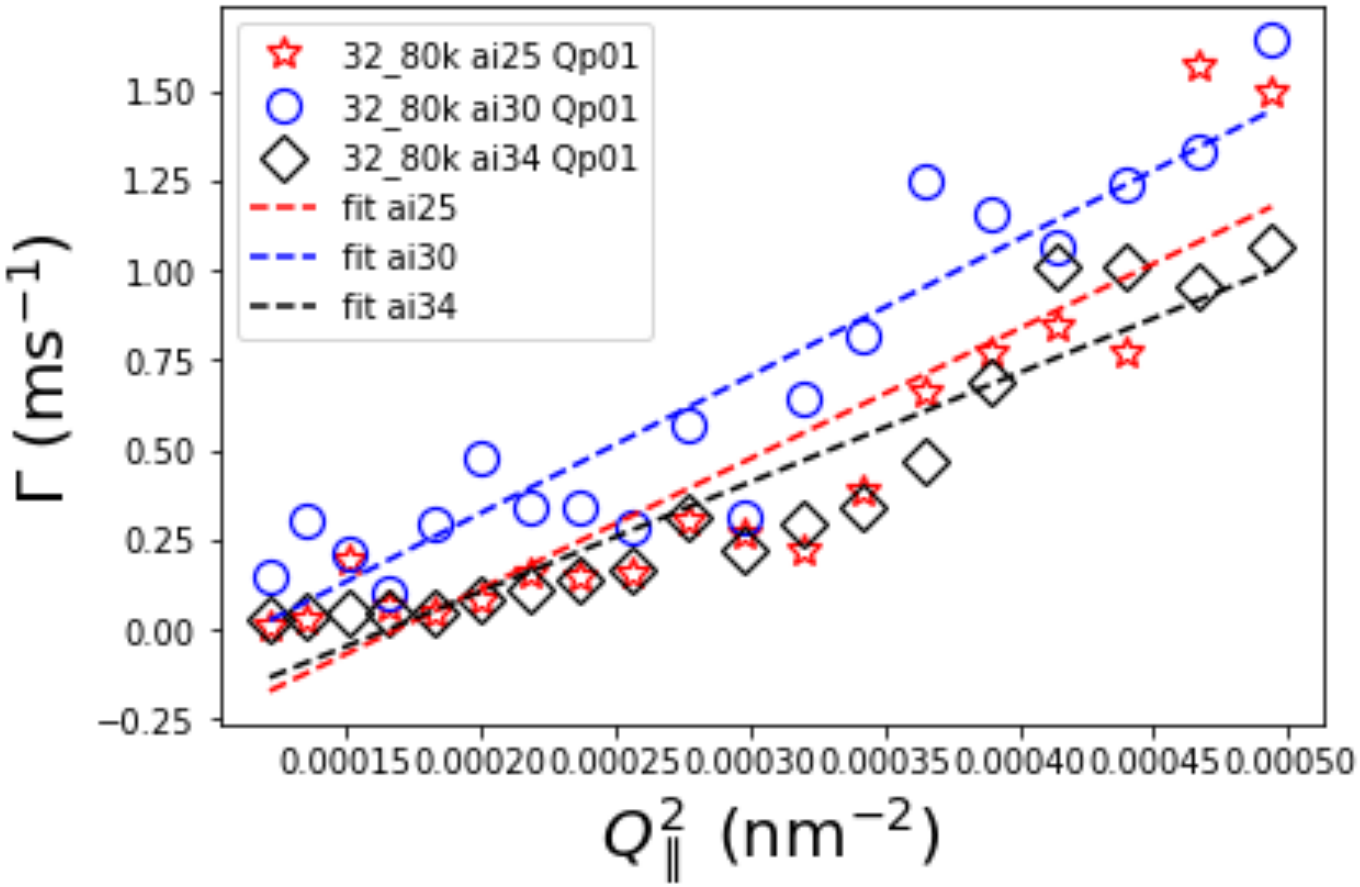
EWDLS 64-140k



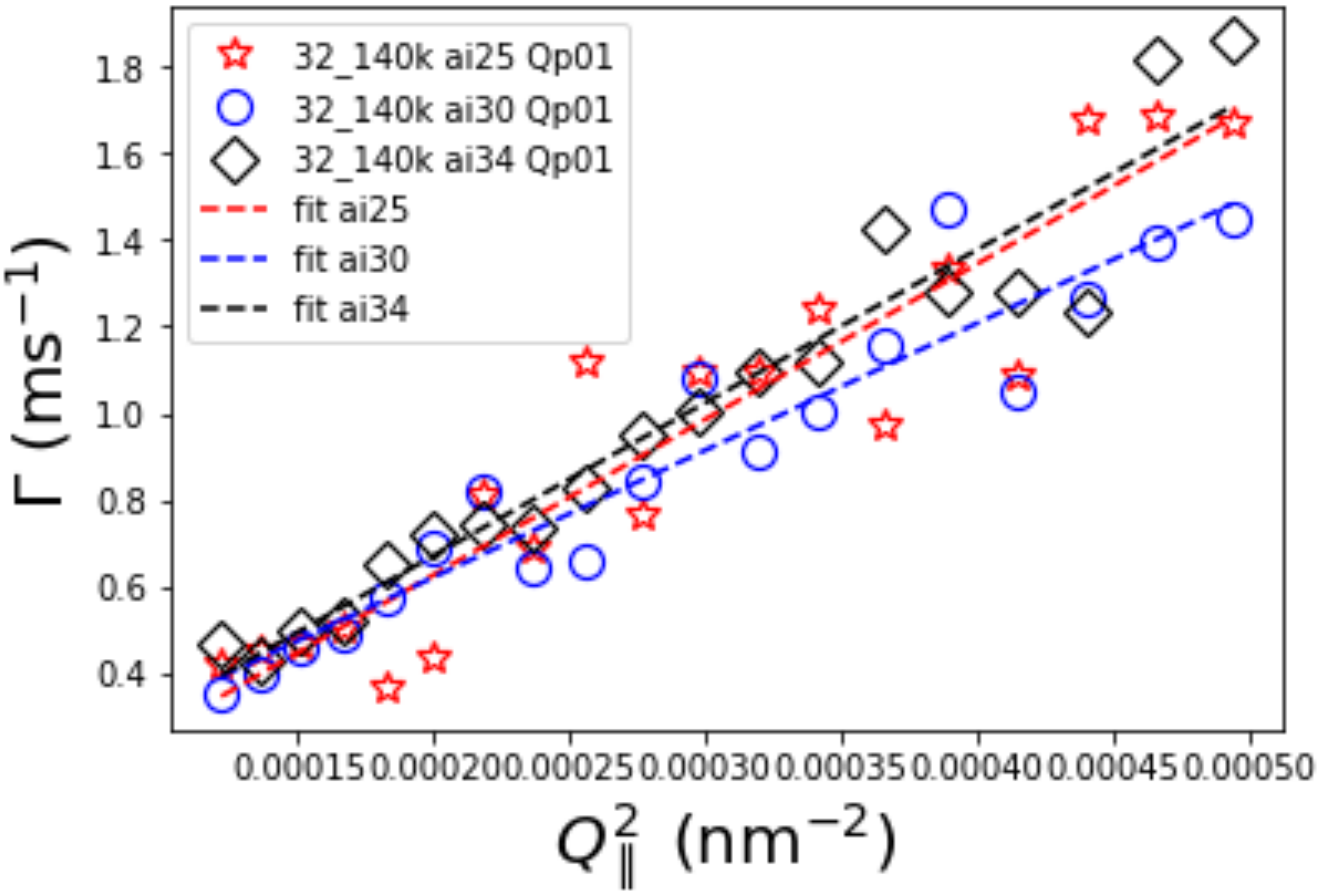
EWDLS 32-52k



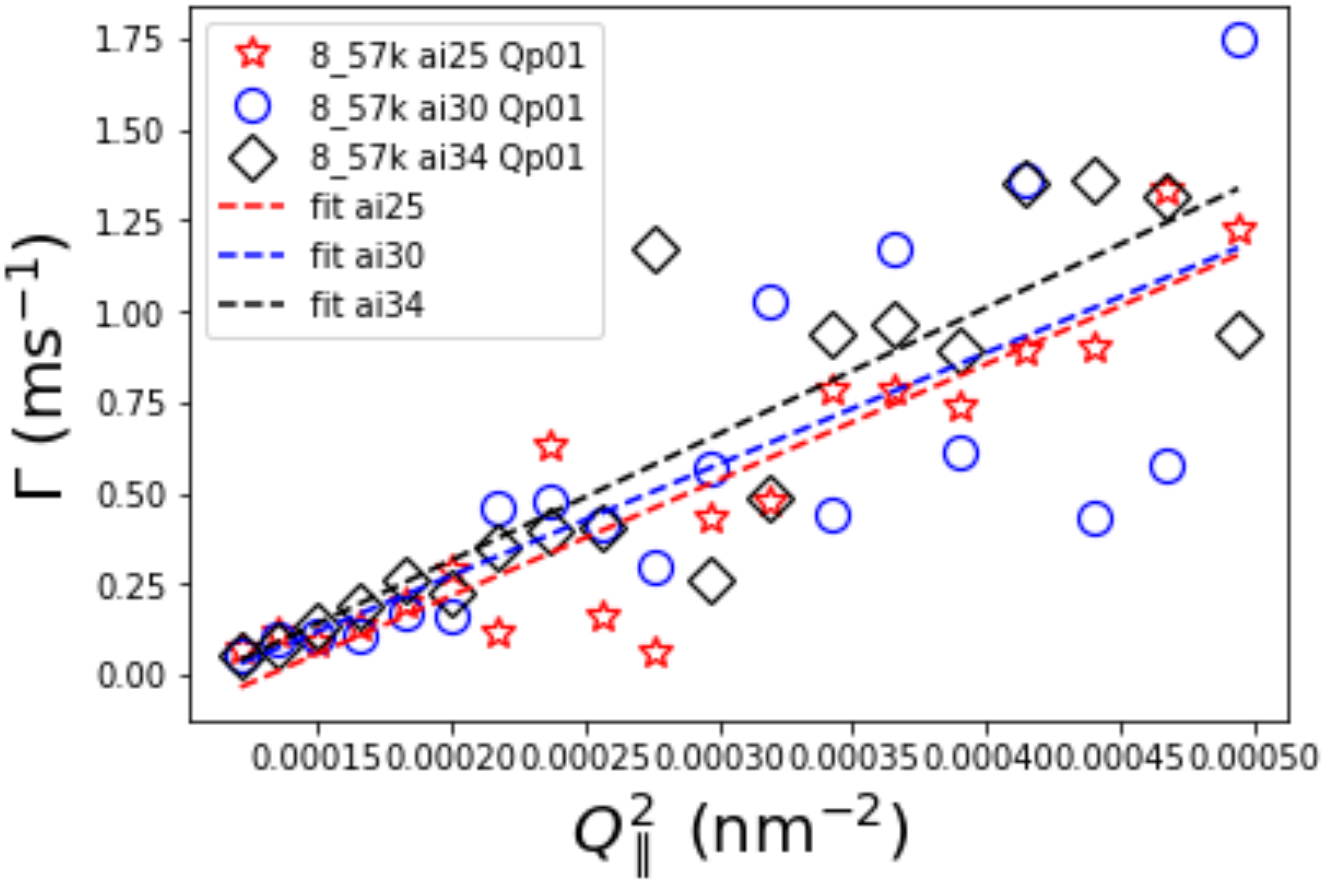
EWDLS 32-80k



EWDLS 32-140k



8-57k



same arm length Qn compare