Tracer diffusion in polymer solutions

Peter Košovan[1] **Olaf Lenz**[1] **Christian Holm**[1]
Apostolos Vagias[2] **Kaloian Koynov**[2] **George Fytas**[2]

1. Institute for Computational Physics, University of Stuttgart
2. MPI for Polymer Research, Mainz

ESPResSo Summer School, Stuttgart, 12.10.2012

Diffusion – how and why?

- Diffusant in an environment
- Drug release, chemical reaction kinetics
- Biology

Methods to study diffusion in solutions

- Particle tracking
- Scattering of light, neutrons, X-rays ...
- PFG NMR
- Fluorescence recovery after photobleaching (FRAP)
- ...

Diffusion – how and why?

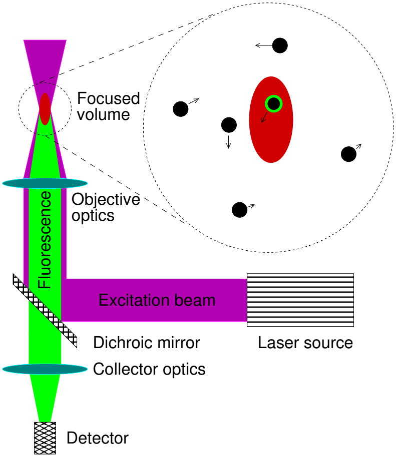
- Diffusant in an environment
- Drug release, chemical reaction kinetics
- Biology

Methods to study diffusion in solutions

- Particle tracking
- Scattering of light, neutrons, X-rays …
- PFG NMR
- Fluorescence recovery after photobleaching (FRAP)
- …
- **Fluorescence Correlation Spectroscopy**

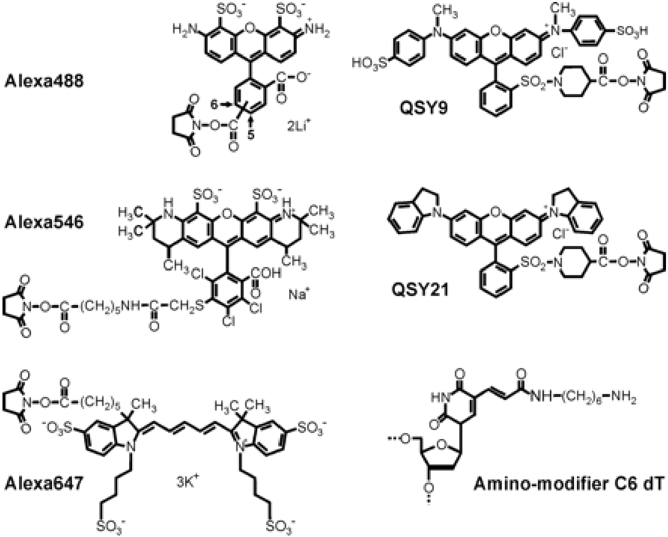
Fluorescence correlation spectroscopy (FCS)

- *Fluorophores* (fluorescent tracers)
- Selectivity
- Single-molecule sensistivity
- Sub-micron sized focal spot
- Tracer diffusion in its environment
- Popular in biosciences
- Works also *in vivo*



Schematic representation of experimental setup

Typical FCS tracers



W. Chiuman, Y. Li, Nucl. Acids Res. (2007) 35 (2): 401-405 doi: 10.1093/nar/gkl1056

Analysis of FCS experiments

- Autocorrelation of fluorescence intensity fluctuations

$$G(t) = \frac{\langle \delta I(t_0) \delta I(t_0 + t) \rangle}{\langle \delta I(t) \rangle^2}$$

- Inverse problem – solved by curve fitting

Analysis of FCS experiments

- Autocorrelation of fluorescence intensity fluctuations

$$G(t) = \frac{\langle \delta I(t_0) \delta I(t_0 + t) \rangle}{\langle \delta I(t) \rangle^2}$$

- Inverse problem – solved by curve fitting
- Single-component diffusion

$$G(t) = \frac{1}{N} \left(1 + \frac{4Dt}{w^2}\right)^{-1} \left(1 + \frac{4Dt}{s^2 w^2}\right)^{-0.5}$$

Analysis of FCS experiments

- Autocorrelation of fluorescence intensity fluctuations

$$G(t) = \frac{\langle \delta I(t_0) \delta I(t_0 + t) \rangle}{\langle \delta I(t) \rangle^2}$$

- Inverse problem – solved by curve fitting
- Single-component diffusion

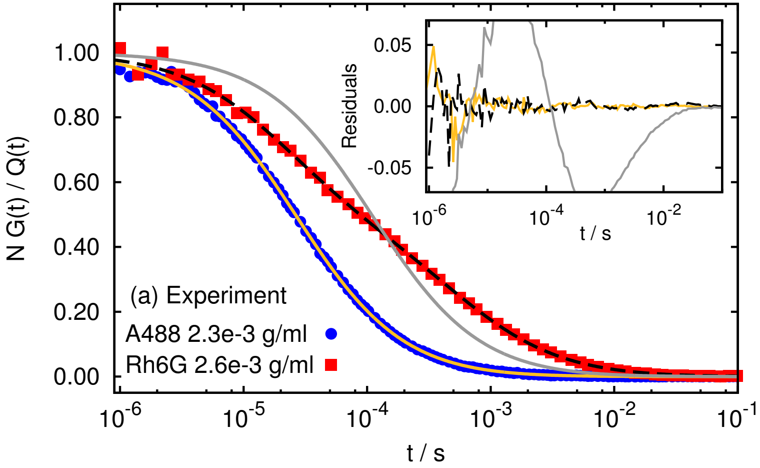
$$G(t) = \frac{1}{N} \left(1 + \frac{4Dt}{w^2}\right)^{-1} \left(1 + \frac{4Dt}{s^2 w^2}\right)^{-0.5}$$

- Multi-component diffusion + photophysical relaxation

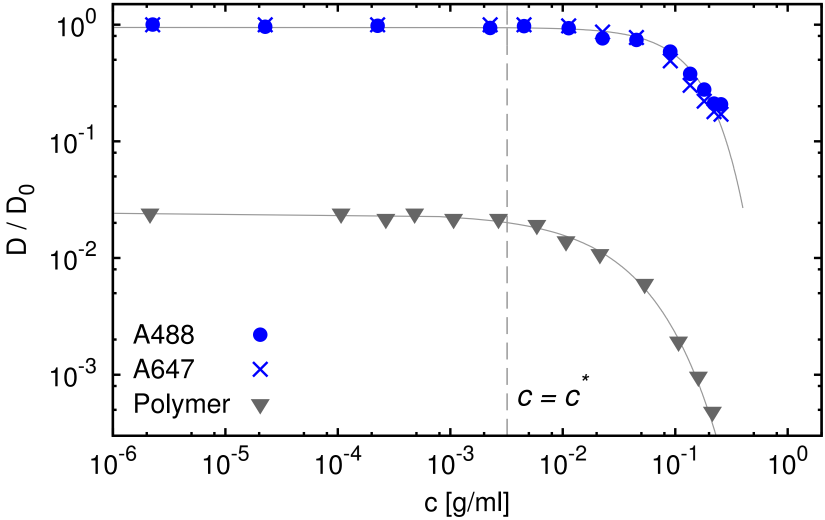
$$G(t) = \frac{Q(t)}{N} \sum_{i=1}^{n} F_i \left[\left(1 + \frac{4D_i t}{w^2}\right)^{-1} \left(1 + \frac{4D_i t}{s^2 w^2}\right)^{-0.5} \right]$$

A glimpse on experimental FCS data

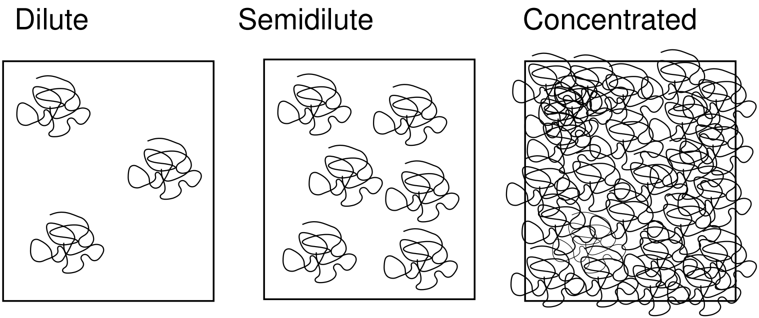
Two different tracers in dilute polymer solution



Crowding-induced slowdown



Concentration regimes in polymer solutions



- Overlap concentration:

$$c^* = \frac{N}{\frac{4}{3}\pi R_g^3} \sim \frac{N}{N^{-3\nu}} \sim N^{-2\nu} \approx N^{-1.2}$$

Diffusion of polymers in solution

Rouse: no hydrodynamics

- Real concentrated solutions
- Langevin thrermostat
- Rouse time

$$\tau_{\mathrm{R}} \sim \tau_0 N^{(1+2\nu)}$$

- Long time scales $\tau \gg \tau_{\mathrm{R}}$

$$D_{\mathrm{R}} = \frac{k_{\mathrm{B}}T}{\zeta_{\mathrm{R}}} = \frac{k_{\mathrm{B}}T}{N\zeta}$$

Zimm: hydrodynamics

- Real dilute solutions
- LB-fluid, DPD
- Zimm time

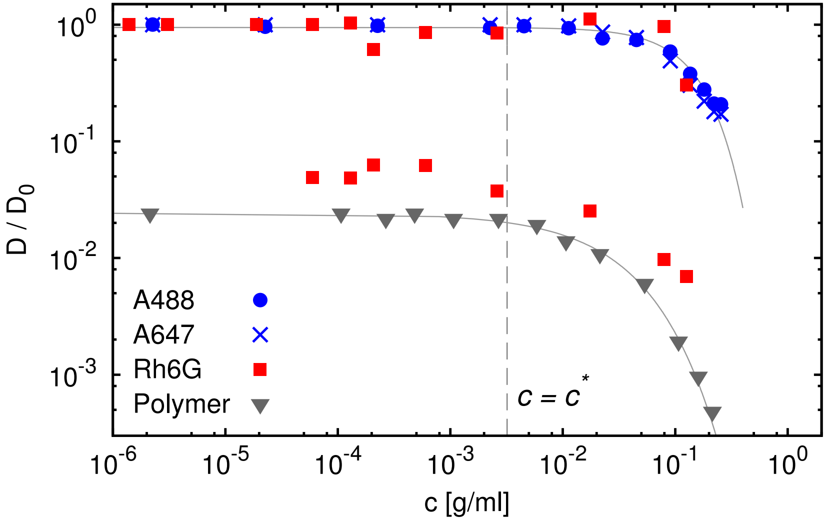
$$\tau_{\mathrm{Z}} \sim \tau_0 N^{3\nu}$$

- Long time scales $\tau \gg \tau_{\mathrm{Z}}$

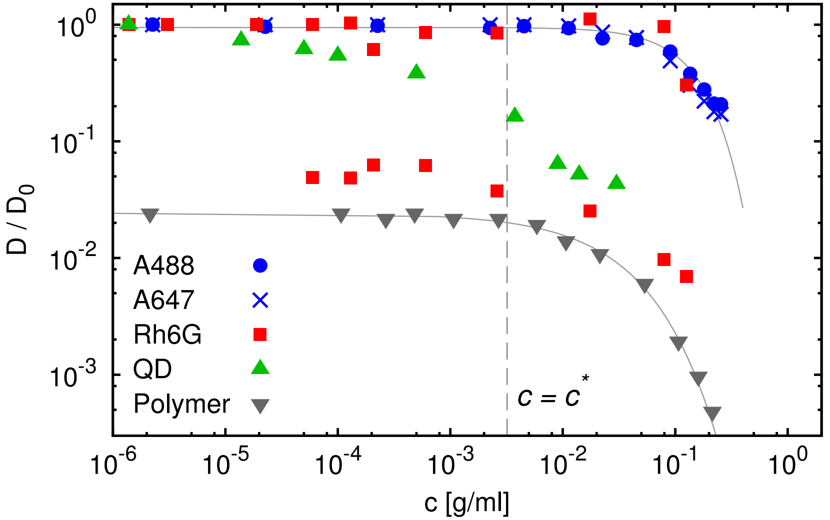
$$D_{\mathrm{Z}} = \frac{k_{\mathrm{B}}T}{\zeta_{\mathrm{Z}}} \sim\sim \frac{k_{\mathrm{B}}T}{\eta_{\mathrm{s}} b N^{\nu}}$$

- Zimm is faster than Rouse for the same N

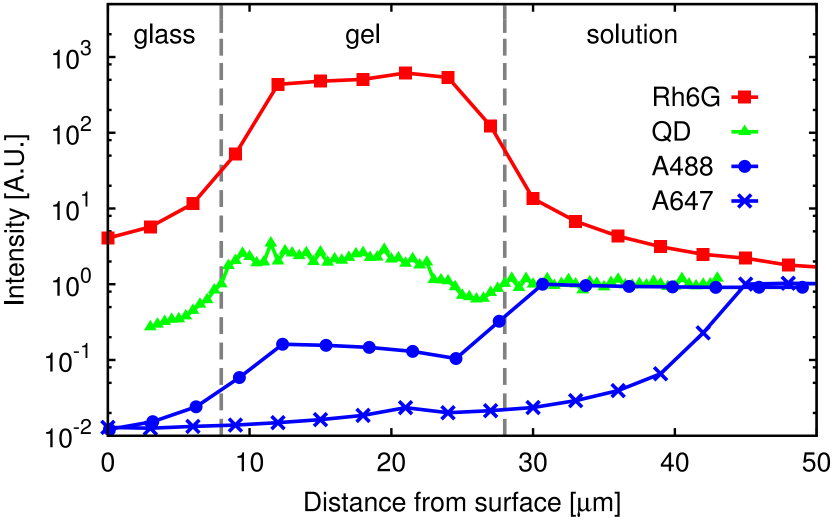
One more tracer



. . . and one more

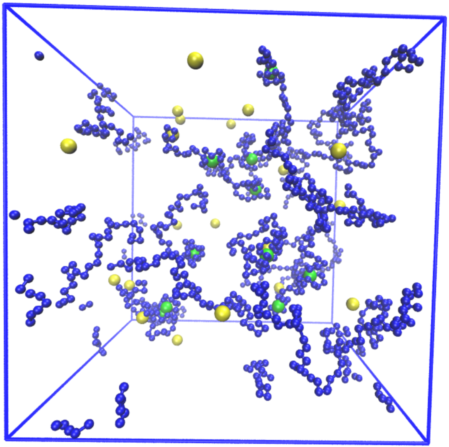

D / D$_0$
10^0
10^{-1}
10^{-2}
10^{-3}
A488
A647
Rh6G
QD
Polymer
$c = c^*$
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
c [g/ml]

Clue: polymer-tracer interactions



Model system setup

- 20 athermal polymers (WCA potential)
- Chain length $M = 50$
- 10 athermal tracers (WCA potential)
- 5 attractive tracers (LJ potential)
- Variation of ϵ_{LJ}
- Concentrations: $c/c^* \in [10^{-3} : 10^2]$
- $\sigma_{\mathrm{LJ}} = 1\,\mathrm{nm}$, $D_0 = D(Rh6G)$
- Langevin thermostat



Relevant observables

- $G(t)$ from simulation trajectory

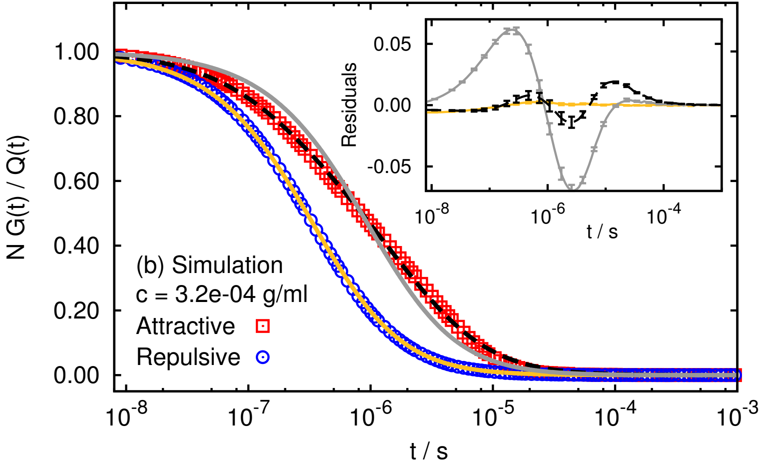
$$G(t) = \left\langle \exp\left(-\frac{\Delta x^2(t)}{w^2} - \frac{\Delta y^2(t)}{w^2} - \frac{\Delta z^2(t)}{s^2 w^2} \right) \right\rangle ,$$

F. Höfling *et. al.*, Soft Matter, 7, 1358–1363 (2011)

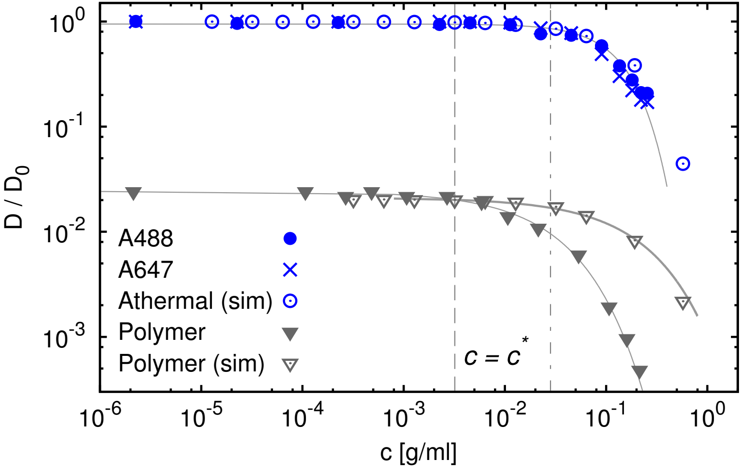
- Realization in ESPResSo:

```
set fcs [correlation new obs1 $tracer_positions \
         corr_operation fcs_acf $wx $wy $wz dt 1.0 \
         tau_max $tot_time tau_lin 16];
correlation $fcs autoupdate start
...
# integration loop
...
correlation $fcs finalize
correlation $fcs write_to_file "Gt.dat"
```

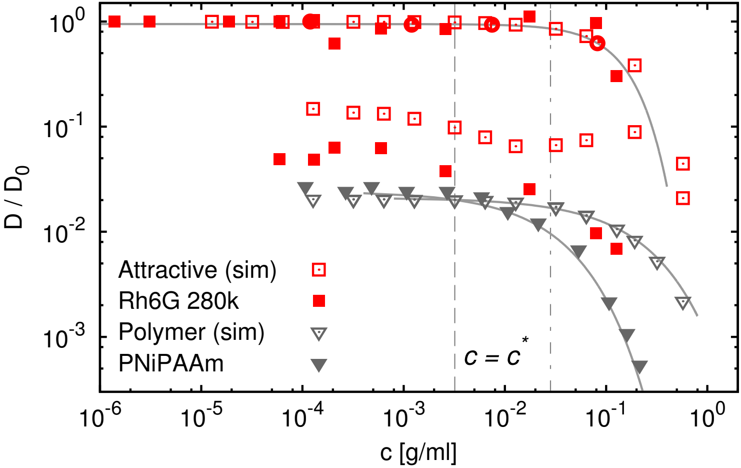
Fits to $G(t)$


N G(t) / Q(t)
1.00
0.80
0.60
0.40
0.20
0.00
(b) Simulation
c = 3.2e-04 g/ml
Attractive
Repulsive
Residuals
0.05
0.00
-0.05
10^-8
10^-6
10^-4
t / s
10^-8
10^-7
10^-6
10^-5
10^-4
10^-3
t / s

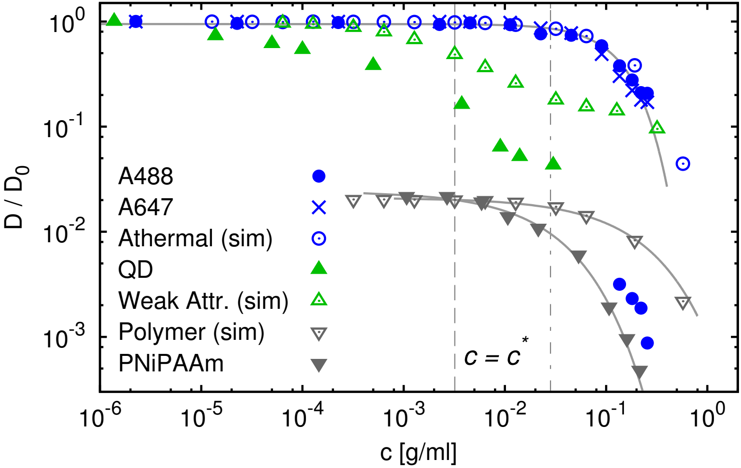
Athermal tracers: crowding-induced slowdown



Attractive ($\epsilon_{LJ} = 2.5$): two-component diffusion

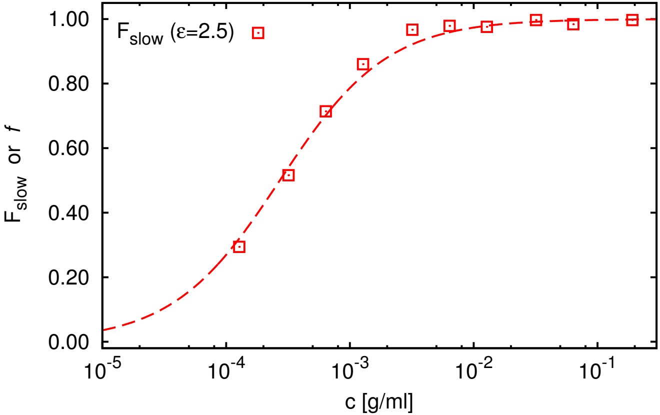


Attractive ($\epsilon_{LJ} = 2.0$): gradual slowdown



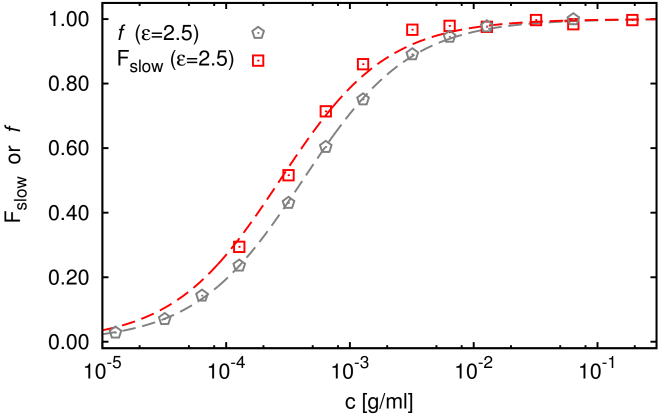
Amplitudes = fraction of bound tracers

$$K = \frac{[T][P]}{[TP]}$$



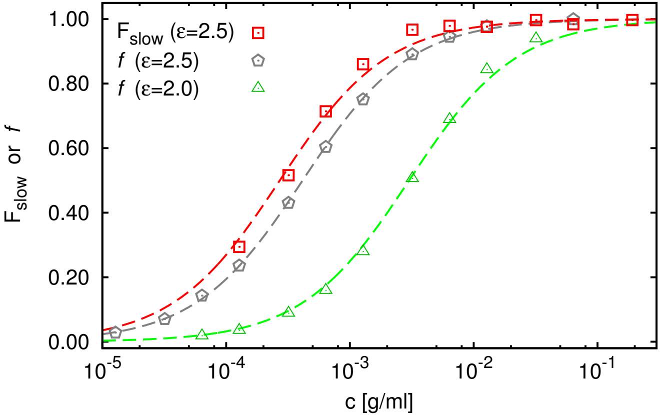
Amplitudes = fraction of bound tracers

$$K = \frac{[T][P]}{[TP]}$$



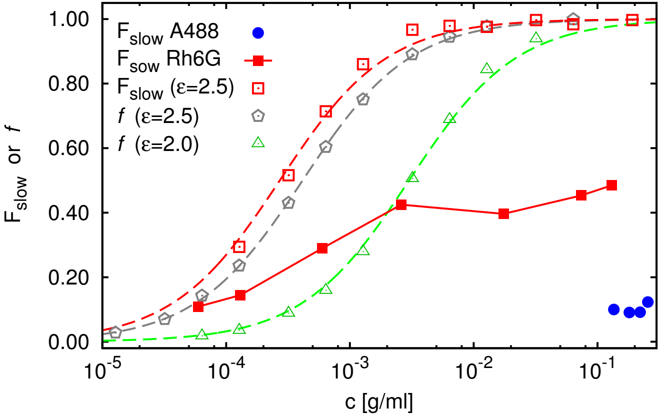
Amplitudes = fraction of bound tracers

$$K = \frac{[\mathrm{T}][\mathrm{P}]}{[\mathrm{TP}]}$$



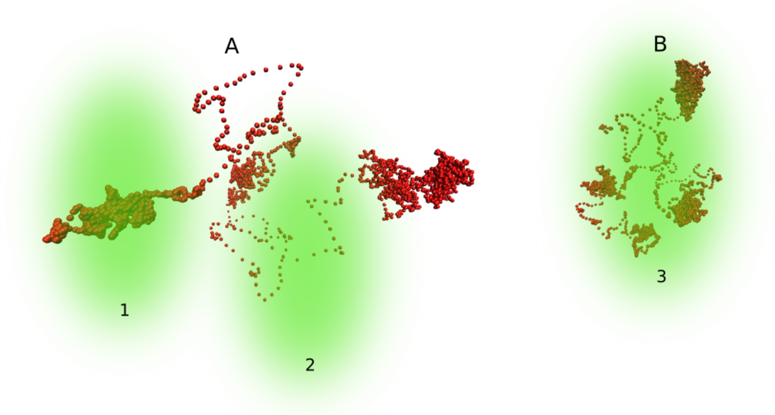
Amplitudes = fraction of bound tracers

$$K = \frac{[T][P]}{[TP]}$$



Comparing different length scales

Tracer trajectory ($\epsilon_{\mathrm{LJ}} = 2.5$) compared to different focal spot sizes



$w \approx 30\,\mathrm{nm}$ $w \approx 100\,\mathrm{nm}$

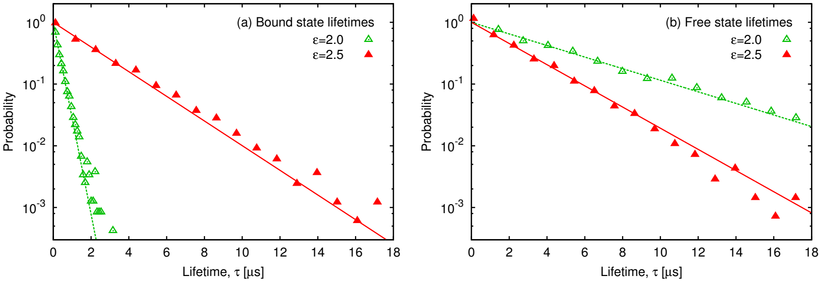
J. Enderlein, PRL 108, 108101 (2012)

History-dependent observable: binding lifetime

- Definition: time interval between two events (binding or unbinding)
- Event = change of a state
- Need to know the state in the past
- Realization in ESPResSo:

```
set bound_lft [observable new interaction_lifetimes \
              type $type_tr_att type $type_mon $cut 1];
...
for {set i 0} {$i < $maxi} {incr i} {
   integrates $nsteps;
   observable $bound_lft update
}
...
set lifetimes observable $bound_lft print;
```

Measuring the bound lifetimes



- Survival probability

$$P(t) = \exp(-t/\tau)$$

Quantitative comparison of length scales

$$L_{\text{bound}}^2 = 6D_{\text{bound}}t_{\text{bound}}$$
$$L_{\text{free}}^2 = 6D_{\text{free}}t_{\text{free}}$$

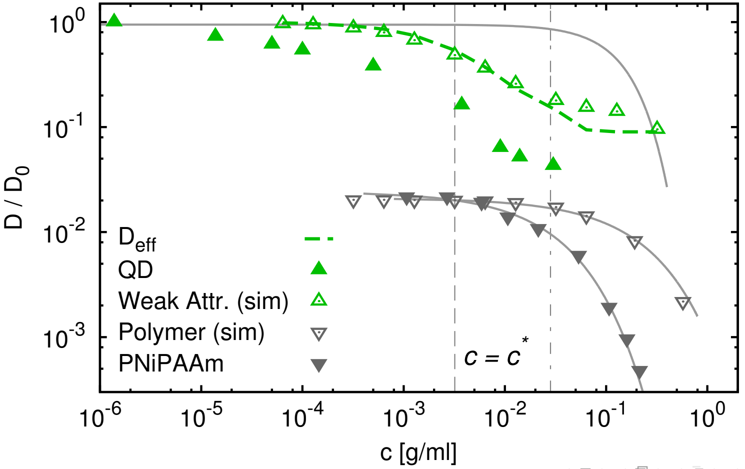
ϵ_{LJ}	t_{bound} [μs]	L_{bound} [nm]	t_{free} [μs]	L_{free} [nm]
2.0	0.45	11	4.63	101
2.5	2.17	54	2.53	75.0

$$\epsilon_{LJ} = 2.0: \; L_{\text{bound}} \ll w = 30\,\text{nm}$$

$$\epsilon_{LJ} = 2.5: \; L_{\text{bound}} \approx w$$

Effective diffusion coefficient ($\epsilon_{LJ} = 2.0$)

$$D_{\text{eff}} = fD_{\text{bound}} + (1 - f)D_{\text{free}}$$



Resolved issues

- Diffusion slowdown critically depends on polymer-diffusant interactions
- Universal behaviour for athermal diffusants
- Slowdown deep in the dilute solution for interacting diffusants
- FCS can resolve the two processes when attraction is strong enough
- It yields D_{eff} when attraction is weaker
- Clear comparison of length scales from simulations

Open questions

- Deviatoin of Rh6G slowdown from simple binding.
- Saturation of $F_{\text{slow}} \approx 0.5$
- Origin of slow A488 slow component at high c

Thanks and Acknowlegement

- Experimental collaborators:
  A. Vagias, K. Koynov, G. Fytas

$ DFG SPP 1259 *Intelligente Hydrogele*

Thank you for your attention!