Exp. Determination of Diffusion Coefficients

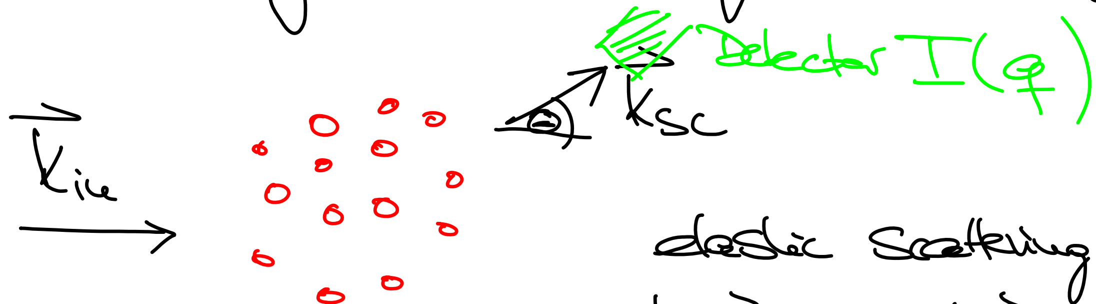
large particles: $x(t)$

$$\langle \Delta x^2(t) \rangle = 2D \cdot t \qquad \left(= 2 \cdot d \cdot D \cdot t \right) ✓$$

(dimensions → d)

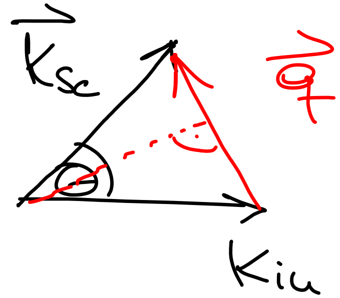
small particles:

dynamical light scattering



elastic scattering

$$\frac{2\pi}{\lambda} = |\vec{k}_{in}| = |\vec{k}_{sc}|$$



$$q = \frac{4\pi}{\lambda} \cdot \sin\left(\frac{\theta}{2}\right)$$

$I(q) \propto S(q)$

↑ **Static** structure factor

$$S(q) = 1 + n \int e^{i\vec{q}\vec{r}} \, g(\vec{r}) \, d^3r$$

Static → dynamics

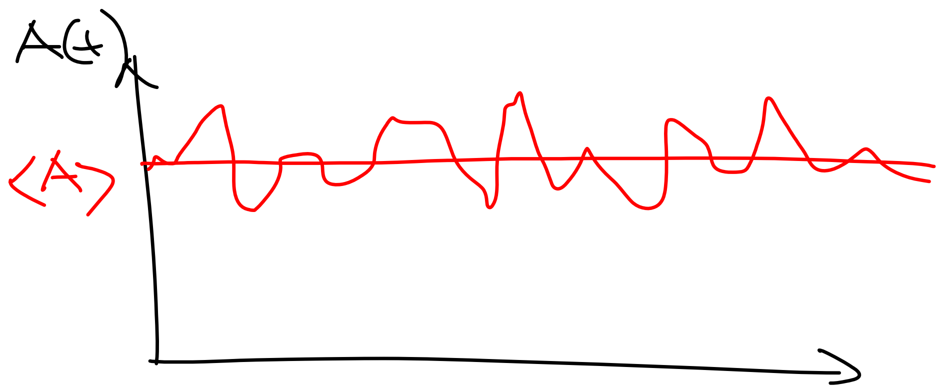
$S(q,t)$ ~~→ Fourier transform of $S(\vec{q},t)$~~

van - ~~Hove~~ - correlation function $G(\vec{r},t)$ ← $\langle I(t) \cdot I(t+$

$$G(\vec{r},t) = \frac{1}{N} \sum_{i=1}^{N} \delta\left[\left(\vec{r}_i(t) - \vec{r}_i(0) - \vec{r}\right)\right]$$

$\vec{r}_i(t) - \vec{r}_i(0) = \vec{r}$

Time correlation functions



$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t')\, dt'$$

- $A(t) \neq A(t+\tau) \qquad \tau \neq 0$

for small τ : $A(t) \approx A(t+\tau)$

" $A(t)$ is correlated with $A(t+\tau)$ "

large τ : $A(t+\tau)$ uncorrelated with $A(t)$

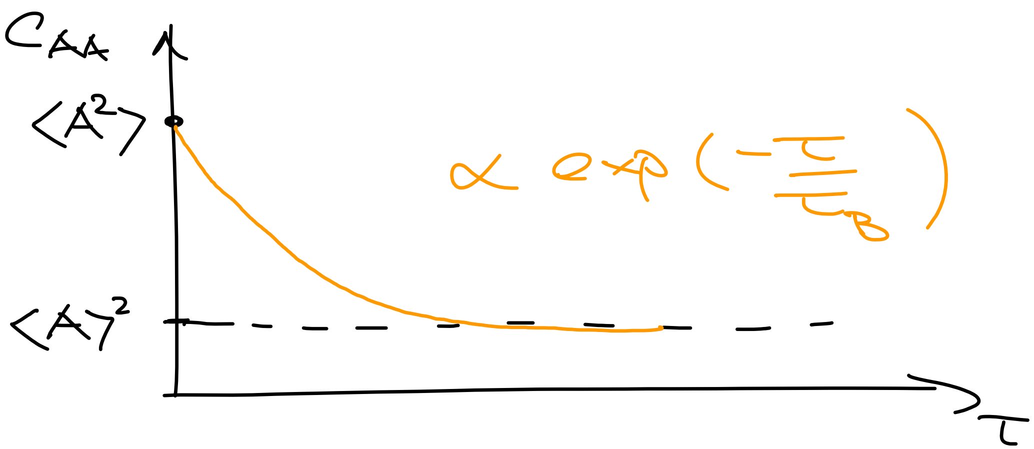
" independent of "

→ <u>Autocorrelation</u> function $\underline{C_{AA}}(\tau) \equiv \langle A(t) \cdot A(t+\tau) \rangle =$

$$\lim_{T \to \infty} \frac{1}{T} \int^{T} dt' \, A(t') \cdot A(t'+\tau)$$

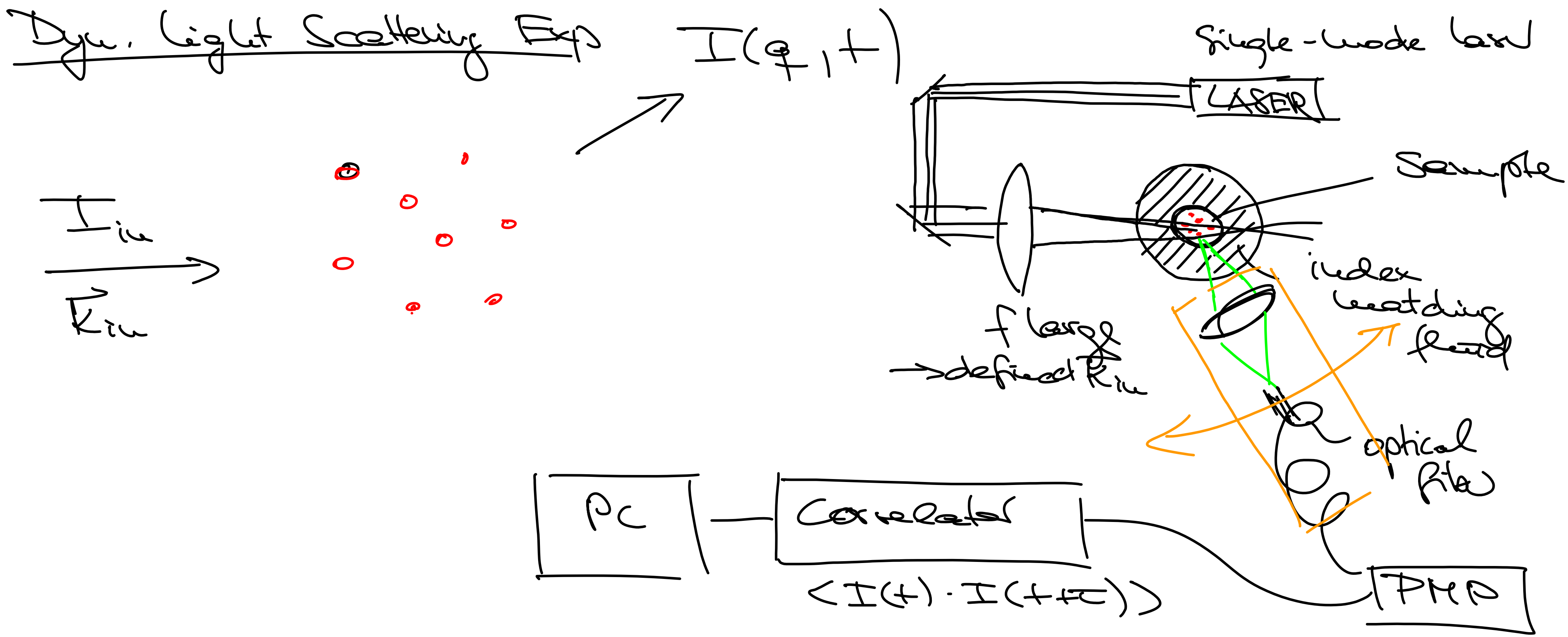
$$\tau = 0 \; : \; C_{AA}(0) = \langle A(t) \cdot \overset{0}{A}(t) \rangle = \langle A^2(t) \rangle$$

$$\tau \to \infty : \lim_{\tau \to \infty} C_{AA}(\tau) = \lim_{\tau \to \infty} \langle A(t) \cdot A(t+\tau) \rangle = \langle A \rangle^2$$



Exp. Setup

Dyn. Light Scattering Exp



[illegible]

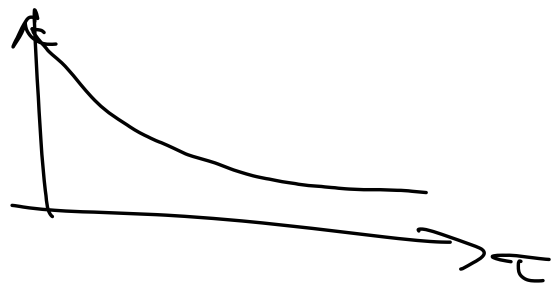
$$\langle I(t) \cdot I(t+\tau) \rangle_t \equiv G(\tau)$$

contains dynamical

<u>highly diluted suspensions</u>

$$\frac{\langle I(t) \cdot I(t+\tau) \rangle}{\langle I \rangle^2} = 1 + \exp\left(-2q^2 \cdot \underline{\underline{D_0}} \cdot \tau\right)$$

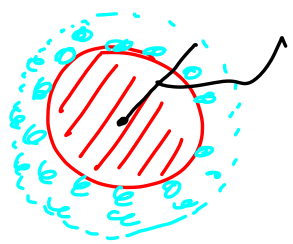
...



$$D_0 = k_B T / 6\pi\eta a_H$$

↑ particle radius

a > geometrical radius



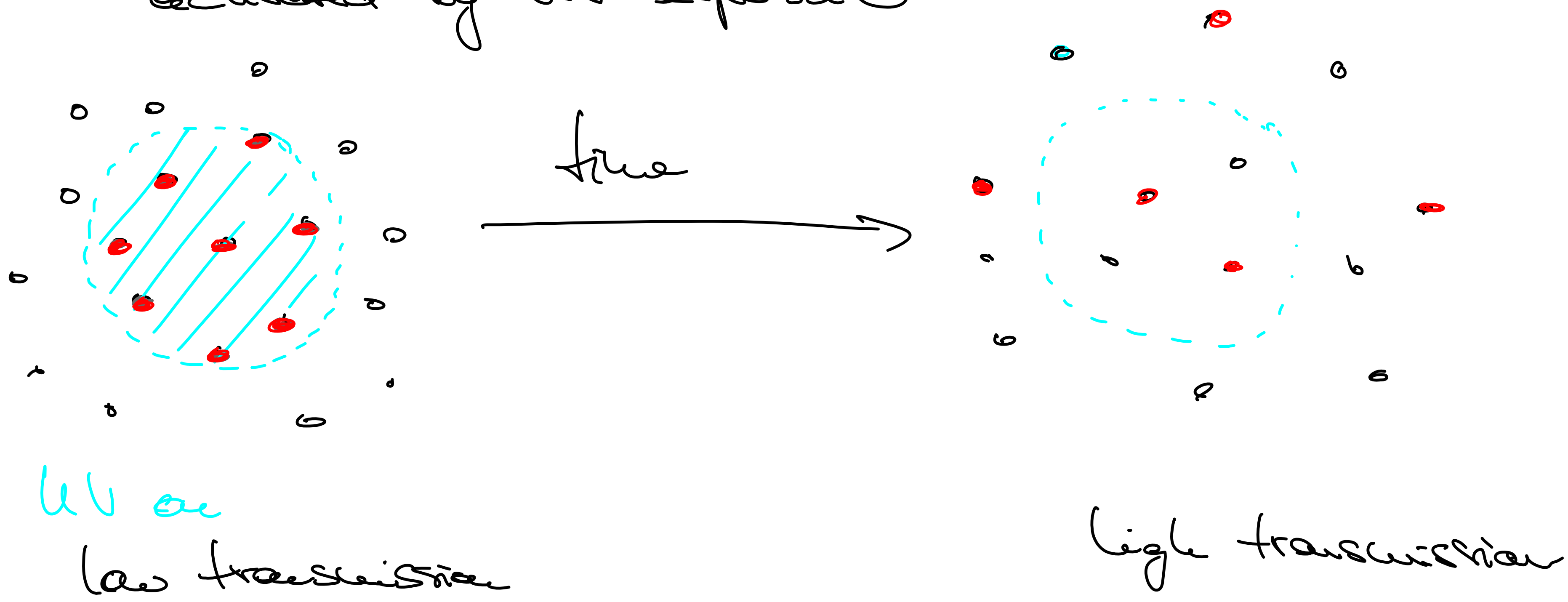
a_H : hydrodynamic radius

example : $a \approx 50\,nm$

$a_H \sim 55\,nm$

2) Forced Rayleigh Scattering (FRS)

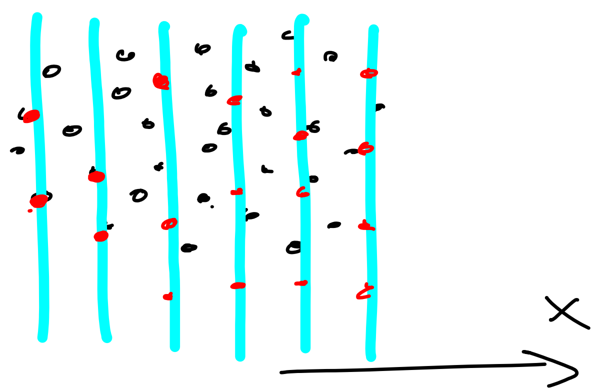
Principle: label few particles with dye, which can be activated by UV exposure

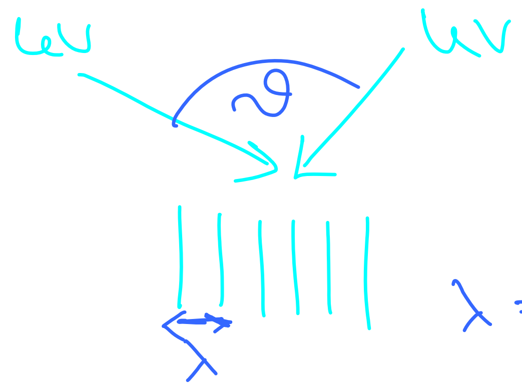


problem : for large particles $D < 1\frac{\mu m^2}{sec}$

→ long measuring time

Solution : intensity grating





$\lambda = \frac{2\pi}{q}$

$q = \frac{4\pi}{\lambda} \cdot \sin\frac{\vartheta}{2}$

absorption grating $\alpha(x, t=0) = A(\cos(qx + 1))$

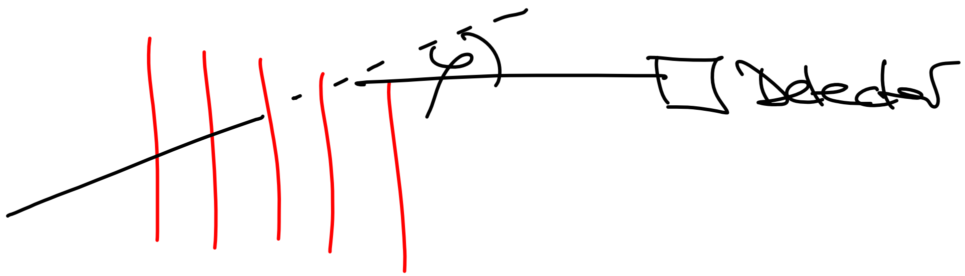
UV off : fading of the grating

Diff. equation: $$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}$$

ρ is prop. to the absorption coefficient

$$\frac{\partial \alpha(x,t)}{\partial t} = D \frac{\partial^2 \alpha(x,t)}{\partial x^2}$$

$$\alpha(x,t) = \alpha(x,t=0) \cdot \underbrace{\exp\left(-Dq^2 \cdot t\right)}_{\text{fading of grating}}$$



3) Polarized Fluorescence Recovery after Photobleaching (p-FRAP)

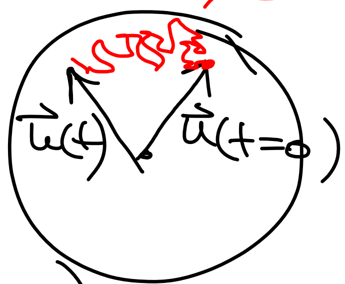
Determination of rotational diffusion coefficient

rotational diffusion:

$\vec{u}(t)$: unit vector

$$\langle \vec{u}(t) \cdot \vec{u}(t+\tau) \rangle = \exp\left(-2D_0^r \cdot \tau\right)$$

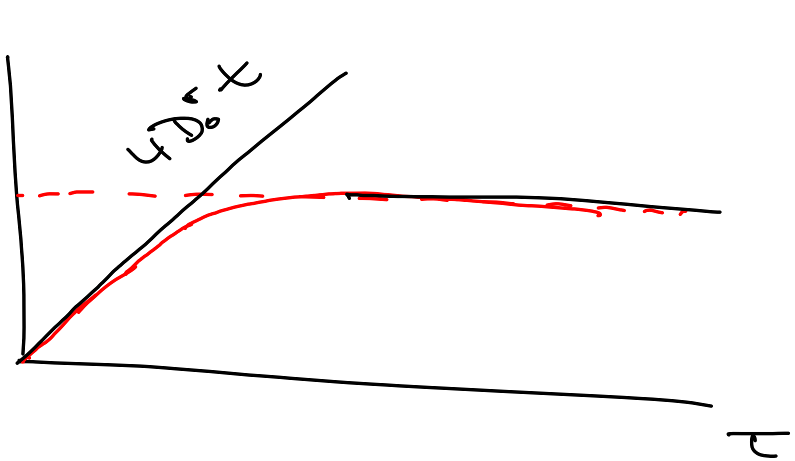
↑ rot. Diff. coeff.

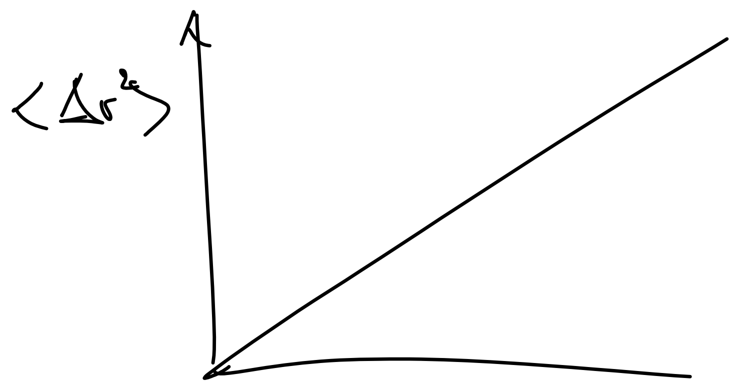


random walk on spherical surface

$\hat{=}$ 2D random walk on a unit sphere

$$\langle |u(t) - u(t+\tau)|^2 \rangle = 2 \cdot \left(1 - \exp\left(-2D_0^r \cdot t\right)\right)$$





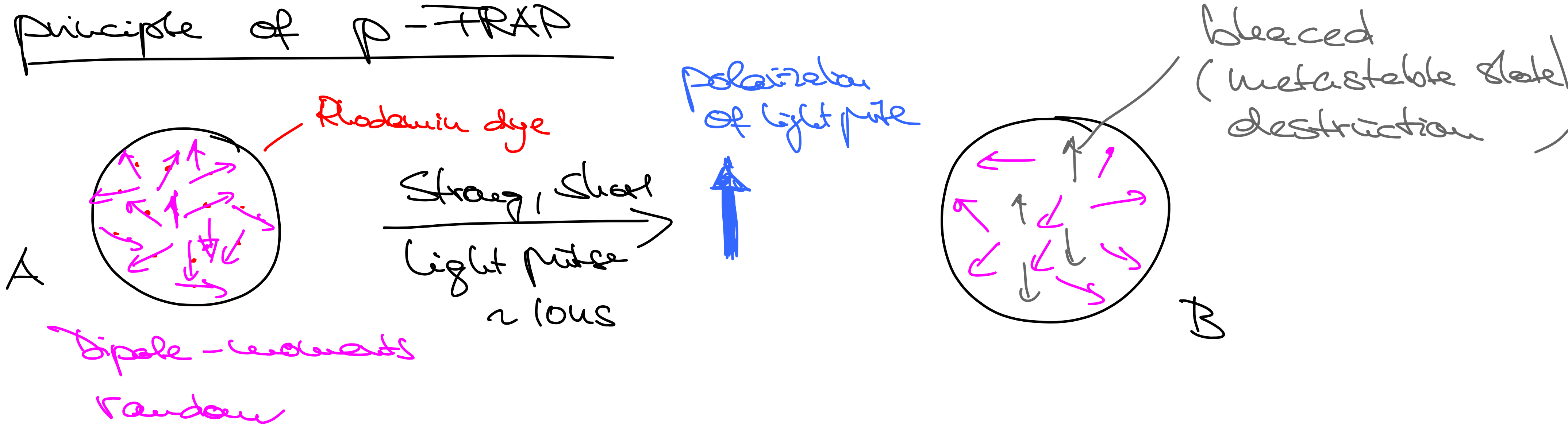
small t: $\langle \Delta u^2 \rangle = 4 D_0^r \cdot t$

large t: $t > \frac{1}{D_0^r}$ $\quad \langle \Delta u^2 \rangle = 2$

$$D_0^r = \frac{k_B T}{8 \pi \eta a^3}$$

$$D_0 = \frac{k_B T}{6 \pi \eta a}$$

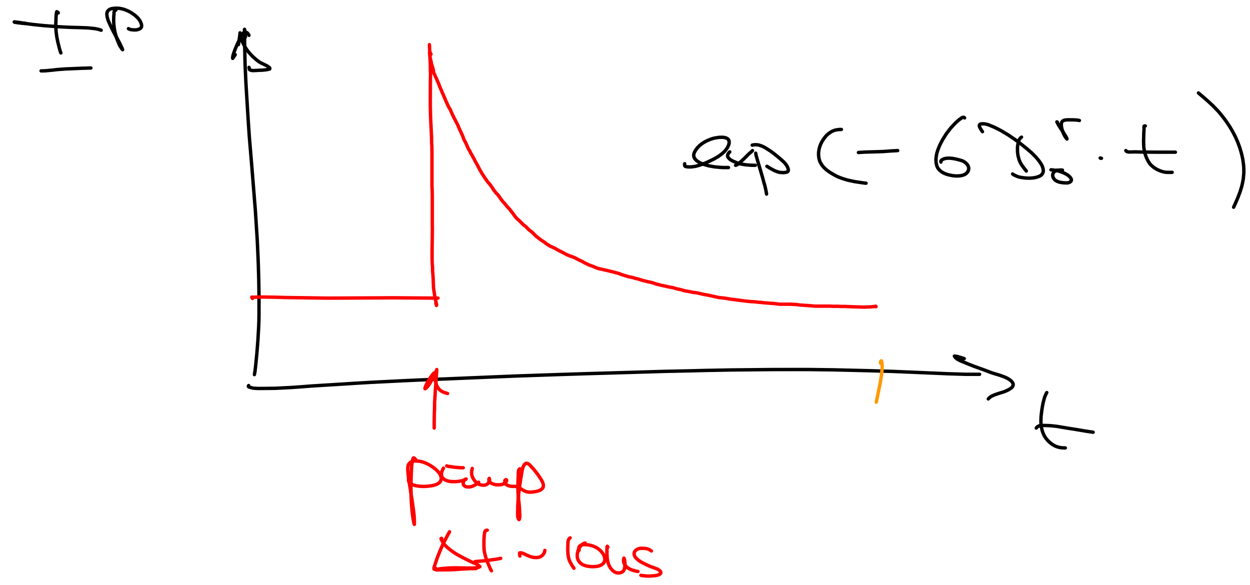
Principle of p-FRAP



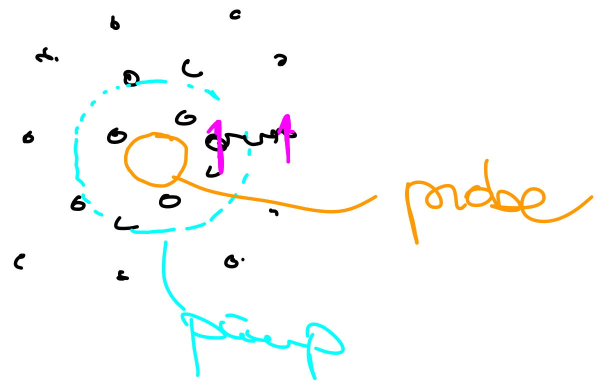
Pump - probe - technique

probe beam : same polarization, but much weaker

B : transmission of probe beam is much higher due to rot. diffusion → transmission of probe beam decreases → change of orientation of the dye molec.



time range: $1 - 10^{-6}$ s

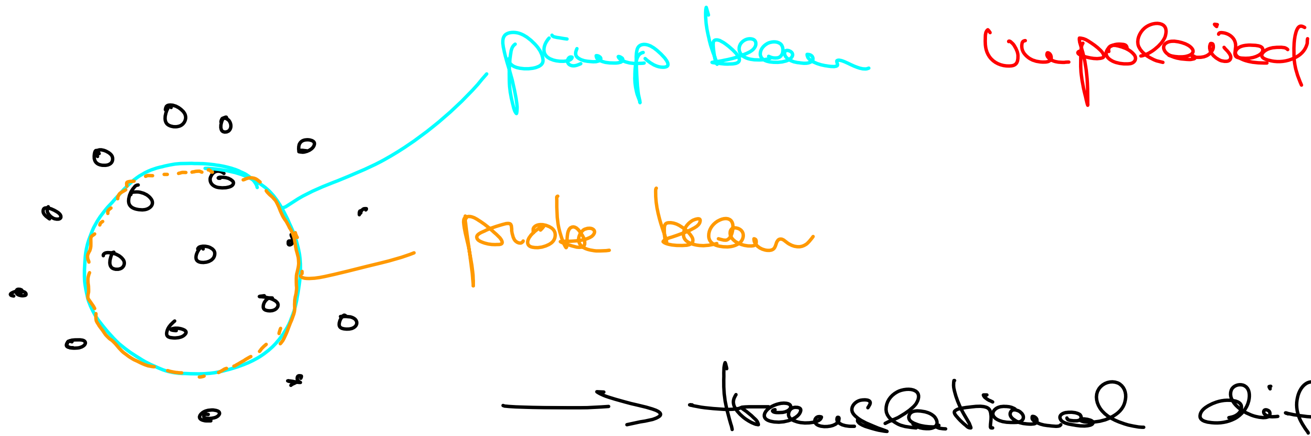


R^1 = pump ≈ 60 μm

R^2 probe ≈ 20 μm

technique can applied to transl. diffusion coeff

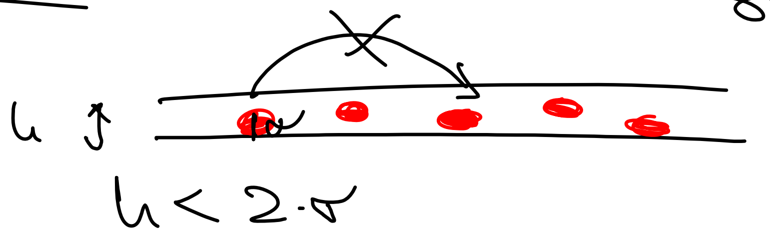
FRAP



→ translational diffusion coeff.

$$\langle x^2 \rangle = 2D \cdot t$$

$$\langle x^2 \rangle \propto t^{1/2}$$



single-file diffusion