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Coefficient of diffusion

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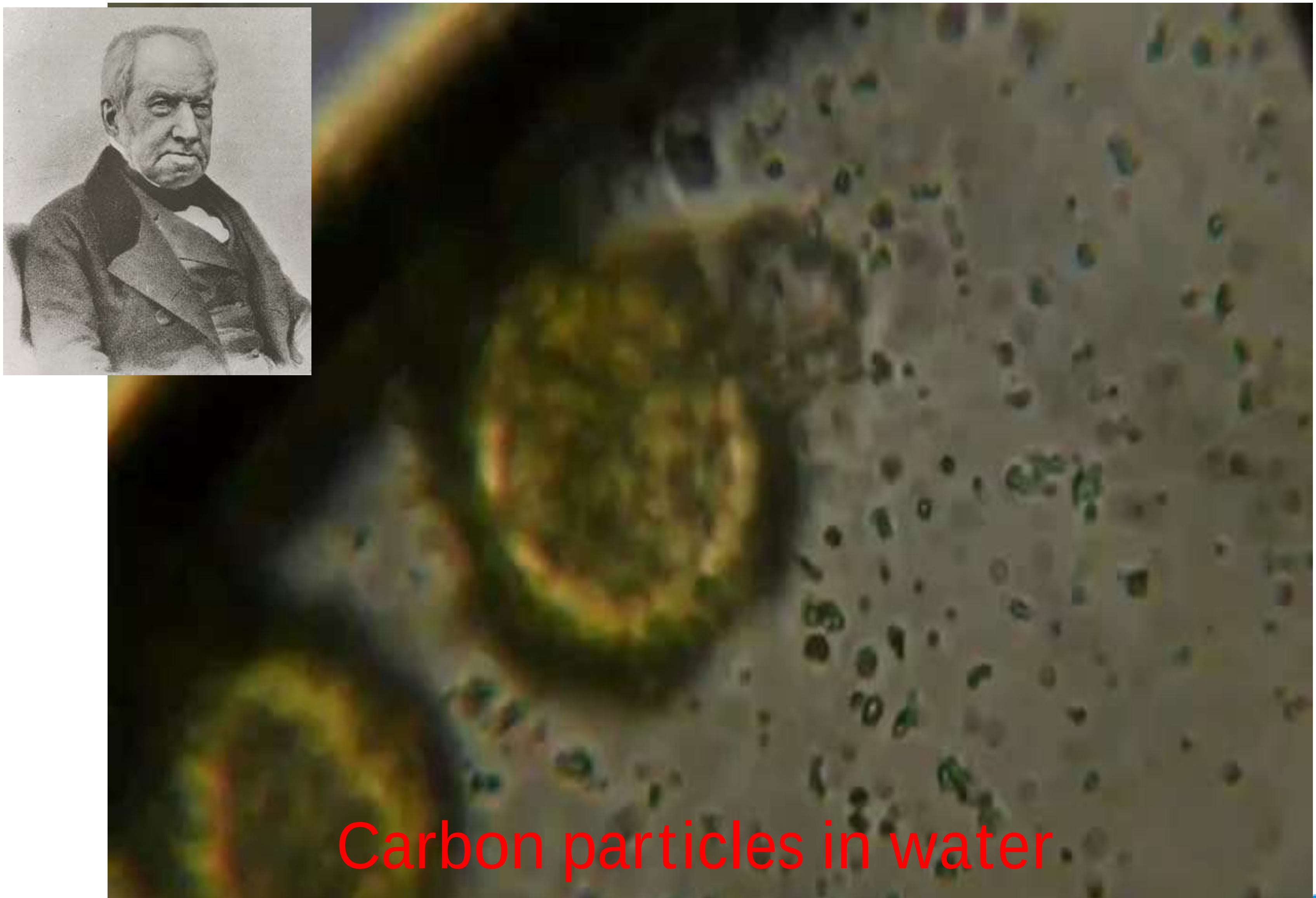
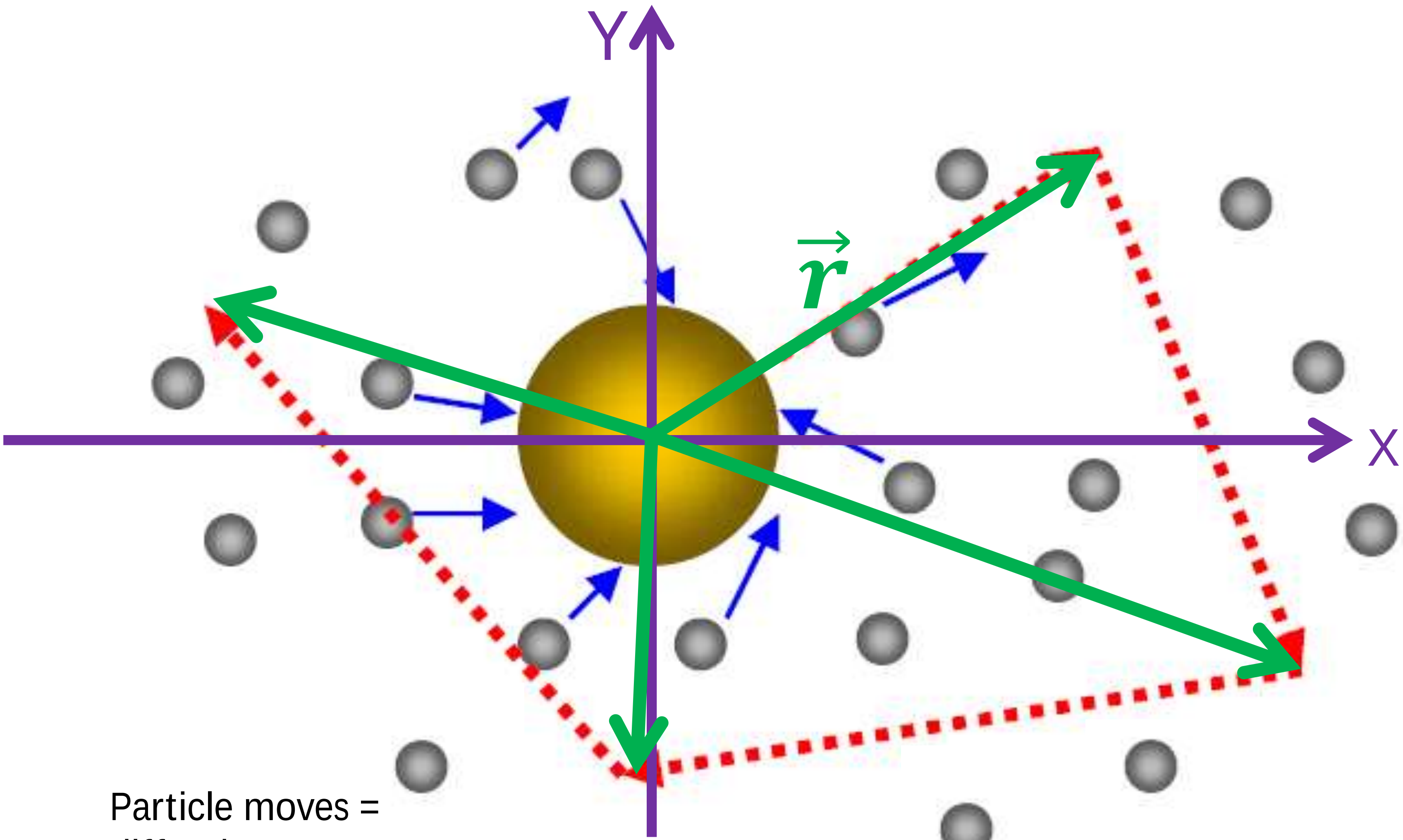
Assignment

Using a microscope, observe the Brownian motion of a particle of the order of micrometer in size. Investigate how the coefficient of diffusion depends on the size and shape of the particle.

Observation

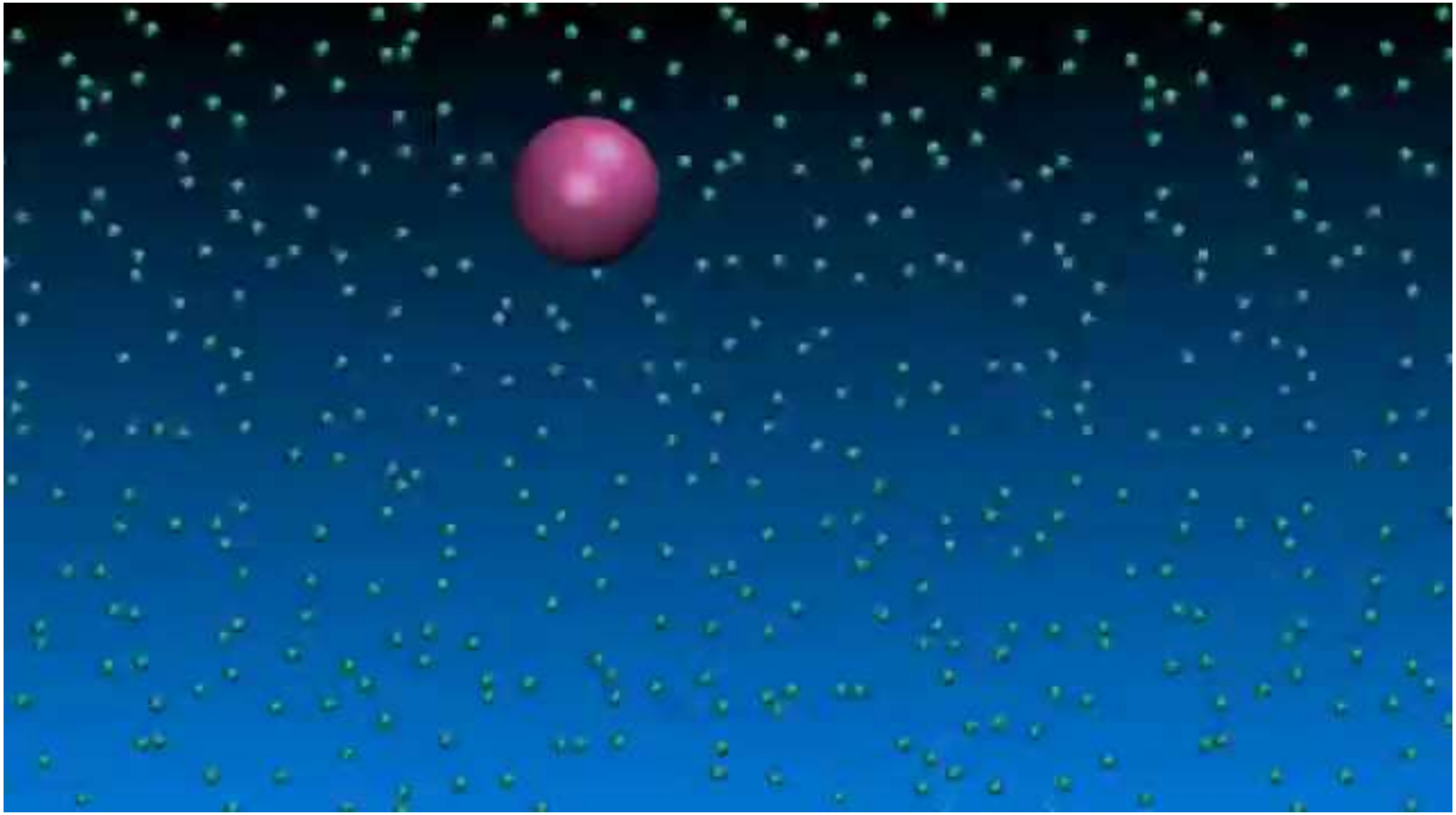


What is the Brownian motion



Particle moves = diffunds

What is the Brownian motion? Simulation 2D



Source:
http://www.rpgroup.caltech.edu/courses/aph162/2006/Protocols/diffusion.pdf

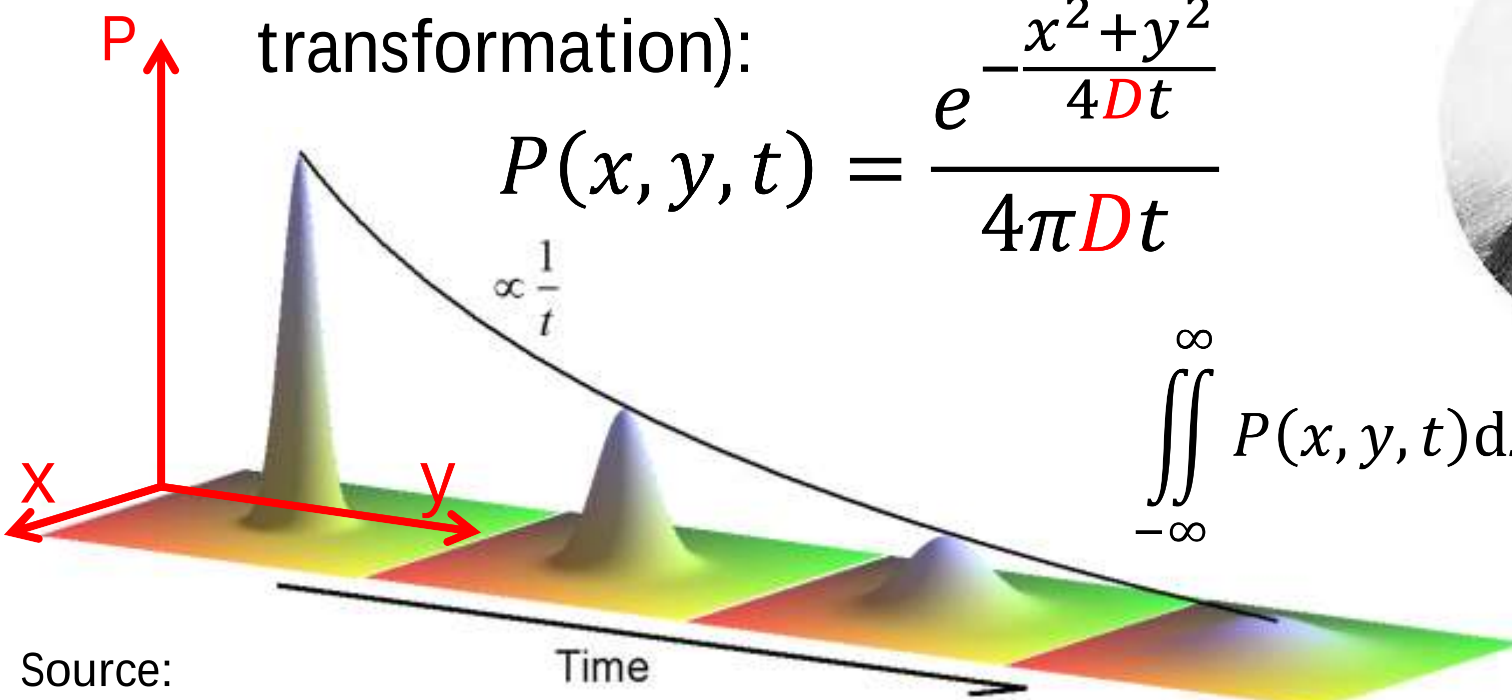
Diffusion equation in 2D

$$D\nabla^2 P = \frac{\partial P}{\partial t} \qquad \Leftrightarrow \qquad D\left(\frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2}\right) = \frac{\partial P}{\partial t}$$

Solution (1. time used Fourier transformation):

$$P(x,y,t) = \frac{e^{-\frac{x^2+y^2}{4Dt}}}{4\pi D t}$$

$$\iint\limits_{-\infty}^{\infty} P(x,y,t)\mathrm{d}x\mathrm{d}y = 1$$



Source: http://www.rpgroup.caltech.edu/courses/aph162/2006/Protocols/diffusion.pdf

Diffusion equation in 2D

Position [x(t), y(t)] cannot be predicted but $\langle x \rangle$ and $\langle y \rangle$ can.

Logically:

$$\langle \boldsymbol{x} \rangle = \iint_{-\infty}^{\infty} \boldsymbol{x P(x, y, t) dx dy = 0}$$

$$\langle \boldsymbol{y} \rangle = \iint_{-\infty}^{\infty} \boldsymbol{y P(x, y, t) dx dy = 0}$$

The most probable position is [0, 0] - initial state

Using polar coordinates:

$$\langle r^2 \rangle = \int_0^{2\pi} \int_0^{\infty} r^2 P(x, y, t) r \mathrm{d}r \mathrm{d}\theta = \int_0^{2\pi} \int_0^{\infty} \frac{r^3}{4\pi \boldsymbol{D} t} e^{-\frac{r^2}{4Dt}} \mathrm{d}r \mathrm{d}\theta$$

$$\langle \boldsymbol{r^2} \rangle = 4 \mathrm{Dt}$$

Generally for *n* dimensions:

$$\langle \boldsymbol{r^2} \rangle = 2\mathrm{n}\boldsymbol{D}\mathrm{t}$$

Source: http://www.rpgroup.caltech.edu/courses/aph162/2006/Protocols/diffusion.pdf

Coefficient of diffusion

Calculation by Einstein (1905):

$$D = \frac{kT}{f}$$

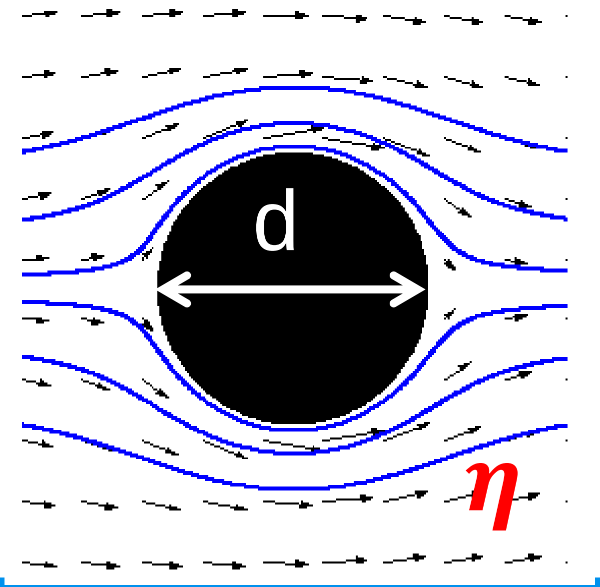
k - Boltzmann constant

T - thermodynamic temperature

$f = 3\pi\eta d$ – for spheres (Stokes)

η – dynamic viscosity of the fluid

d – diameter of the particle

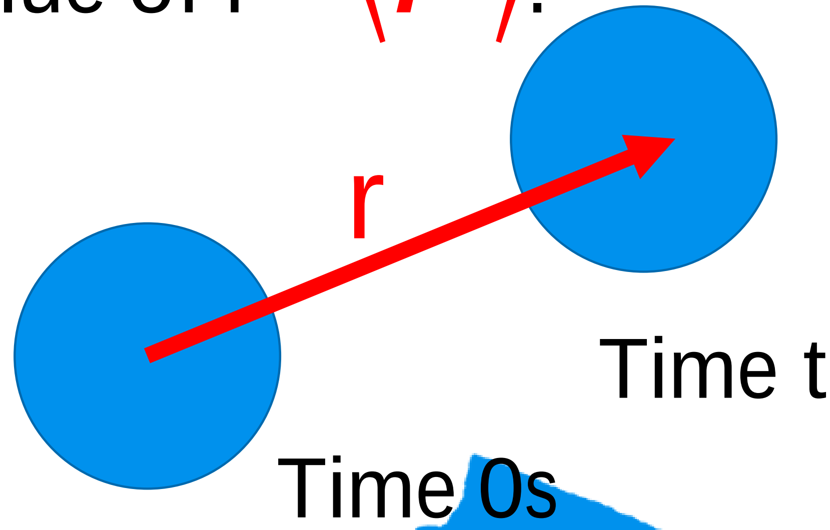


$$D(d) = \frac{kT}{3\pi\eta d}$$

How to measure D(d)?

1. Choose small time interval t (time between frames).
2. Determine square of particle displacement during t.
3. Repeat steps 1. and 2. as many times as possible.
4. Calculate average value of r² - $\langle r^2 \rangle$.
5. Calculate D.

$$D = \frac{\langle r^2 \rangle}{4t}$$



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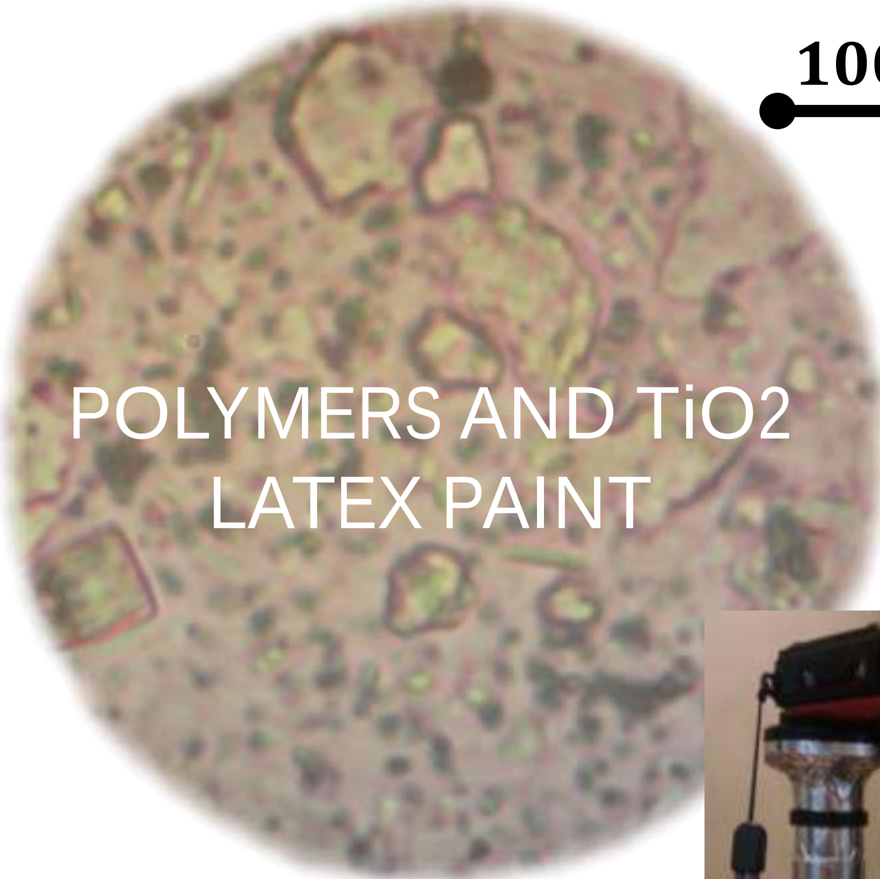
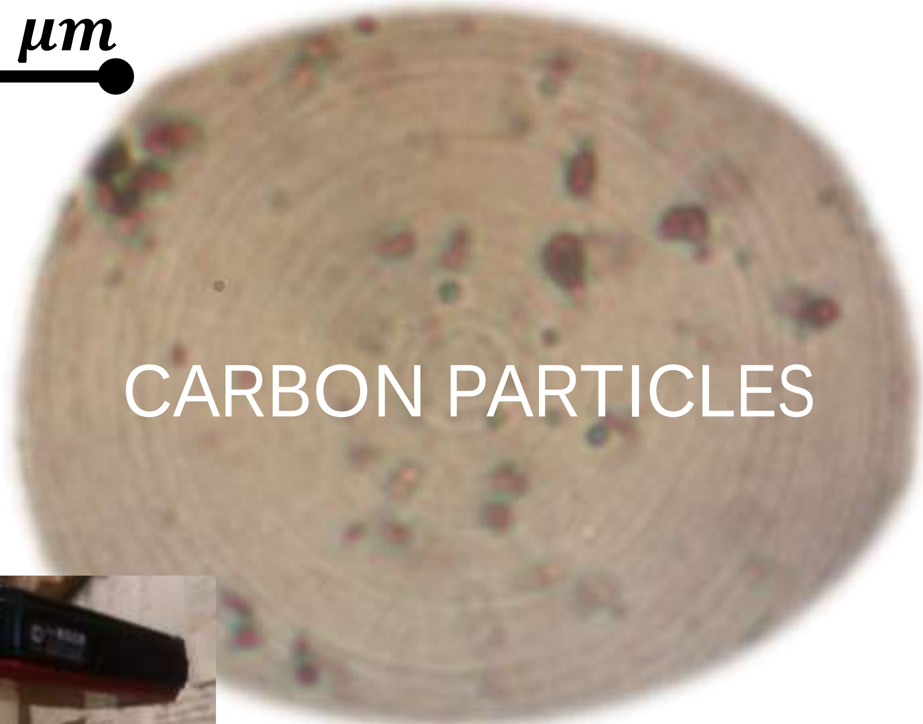
Experiments

Experimental equipment

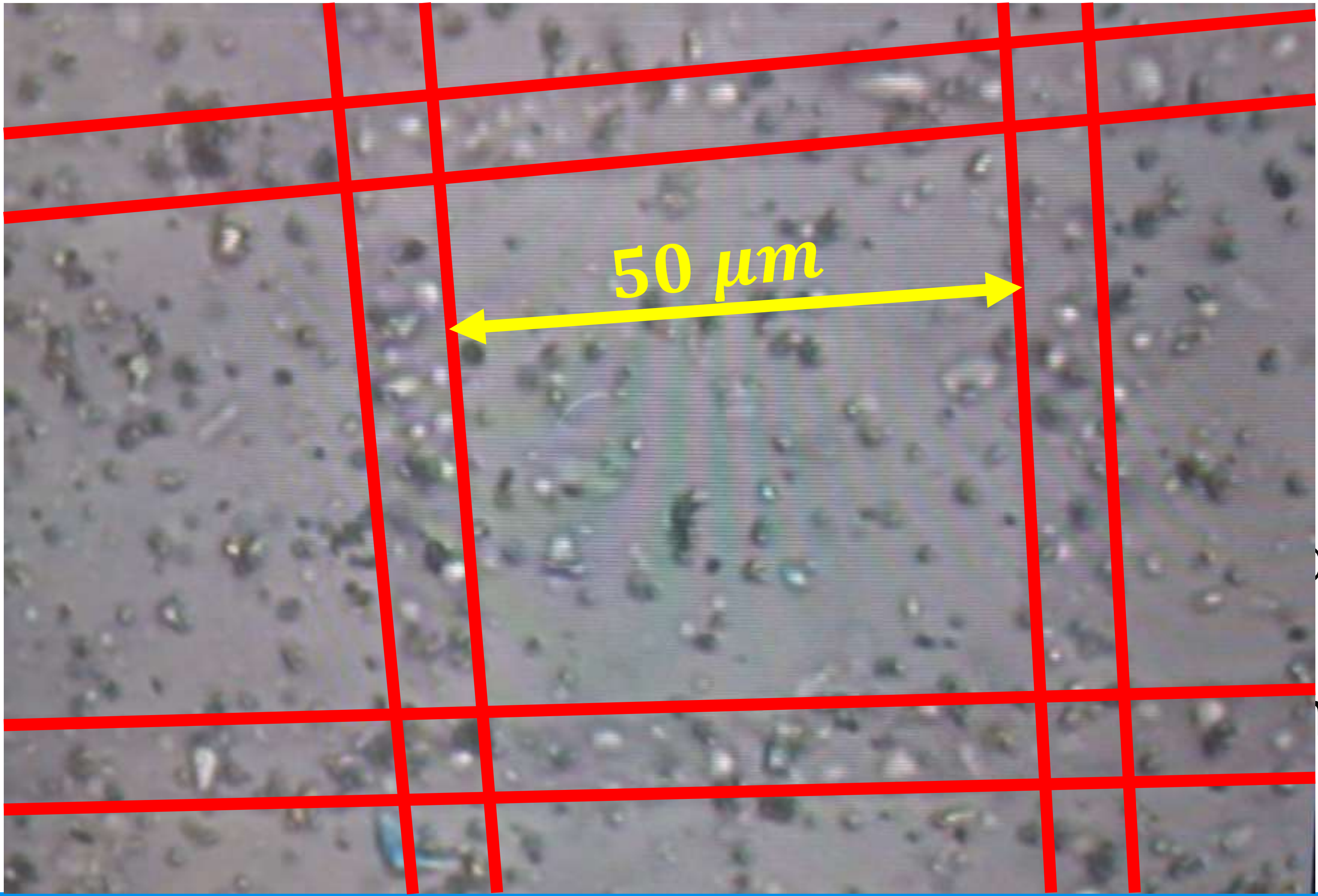
Our tried particles

$100\ \mu m$





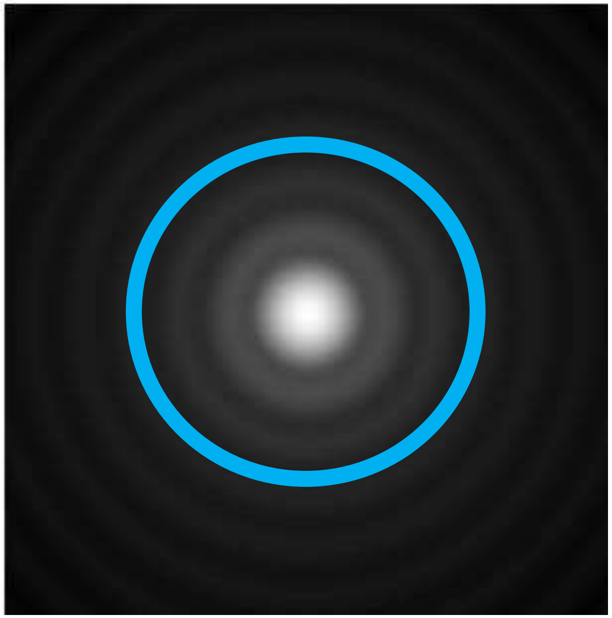
Callibration of the size



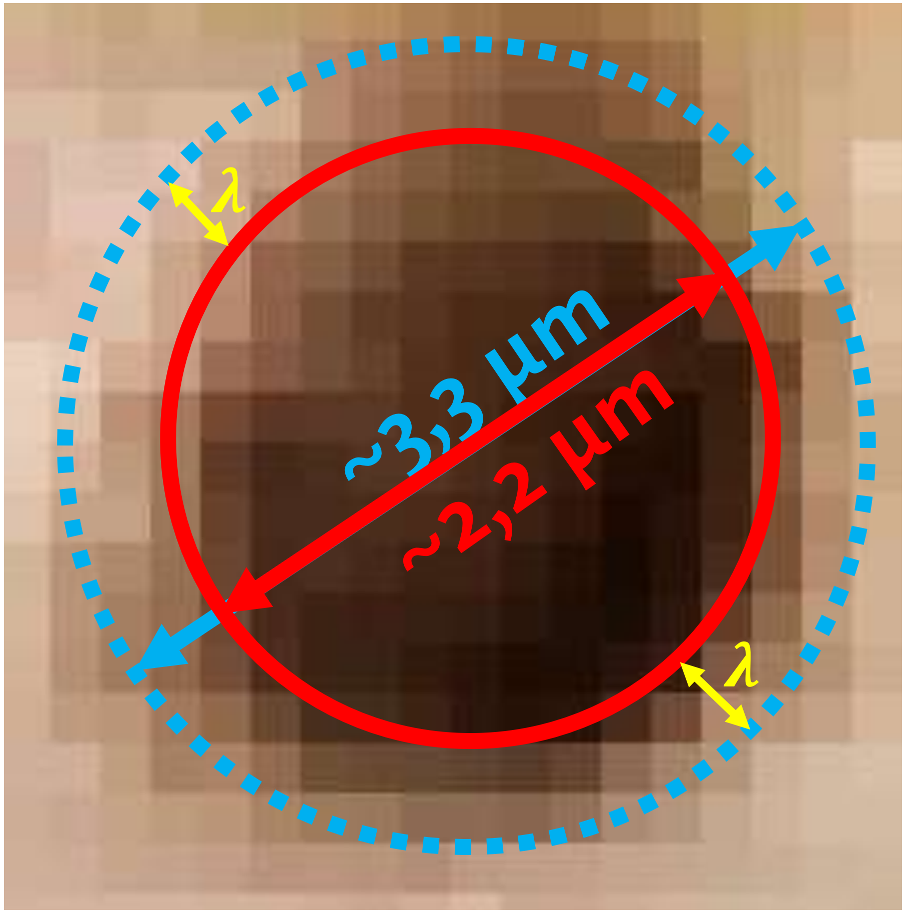
d

n,

Particle size measurement problem? Diffraction of light



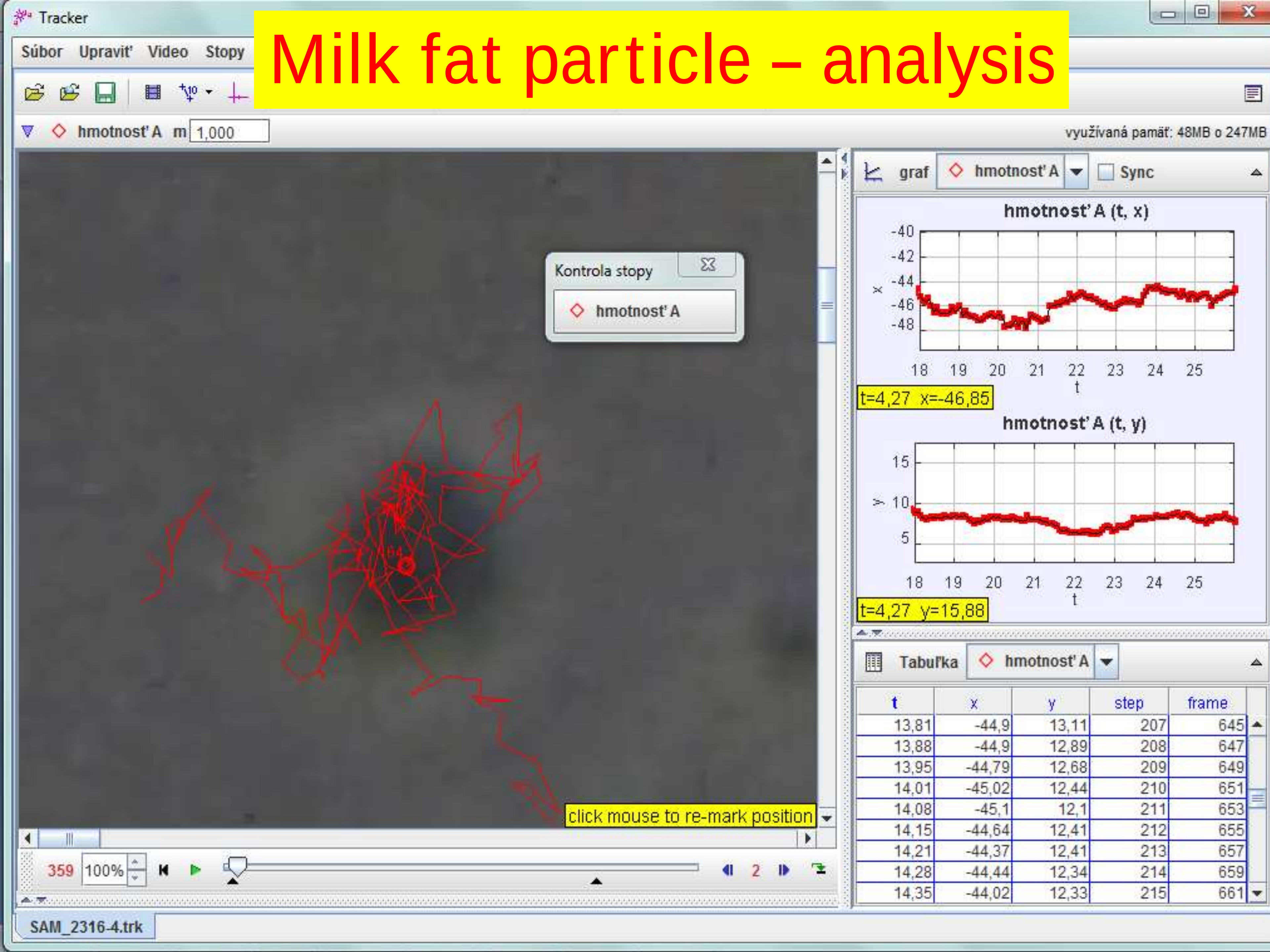
Airy disc – small point source image



-Apparent size of particle is about 2λ larger than real one

-Substraction of 2λ is unusable for small particles **(less than 1µm)**

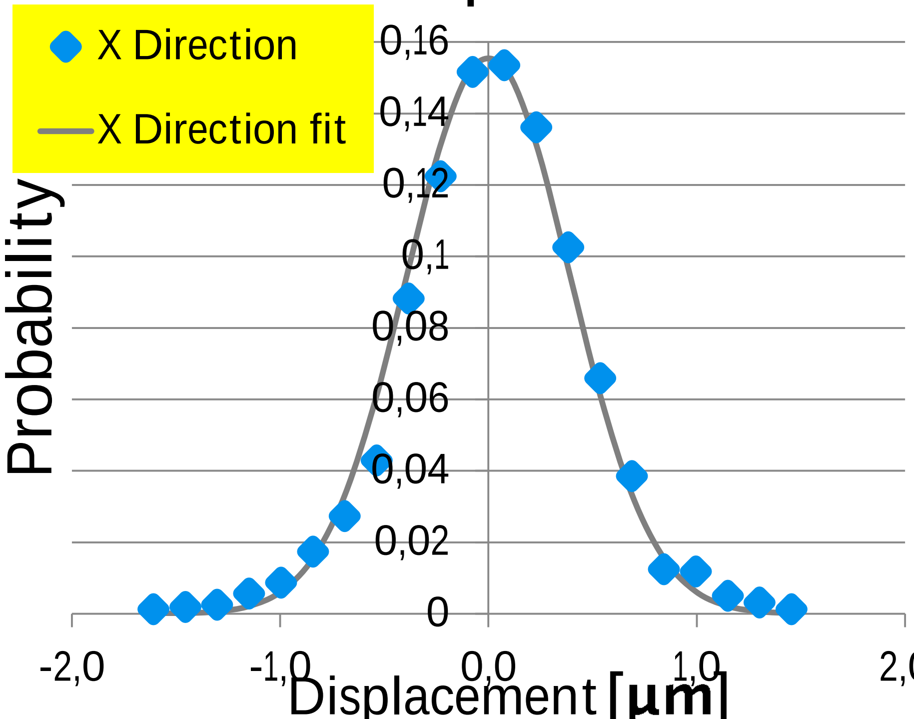
Milk fat particle – analysis

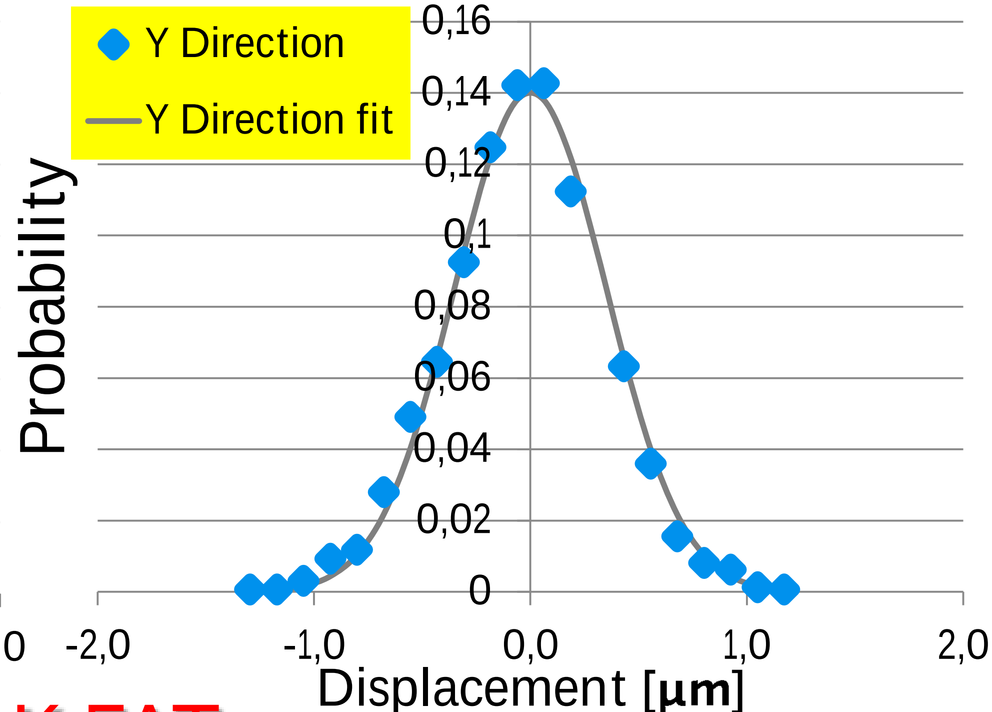


Experiment 1: Radii determination

Probability distribution function – effective radii determination

X/Y displacement during constant time ~ 66ms





$D_x = 0,49\ \mu m^2/s$

$R_x \approx 0,98 \mu m$

MILK FAT PARTICLES

$D_y = 0,61\ \mu m^2/s$

$R_y \approx 0,80 \mu m$

Nearly spherical particle » $R_x \approx R_y$

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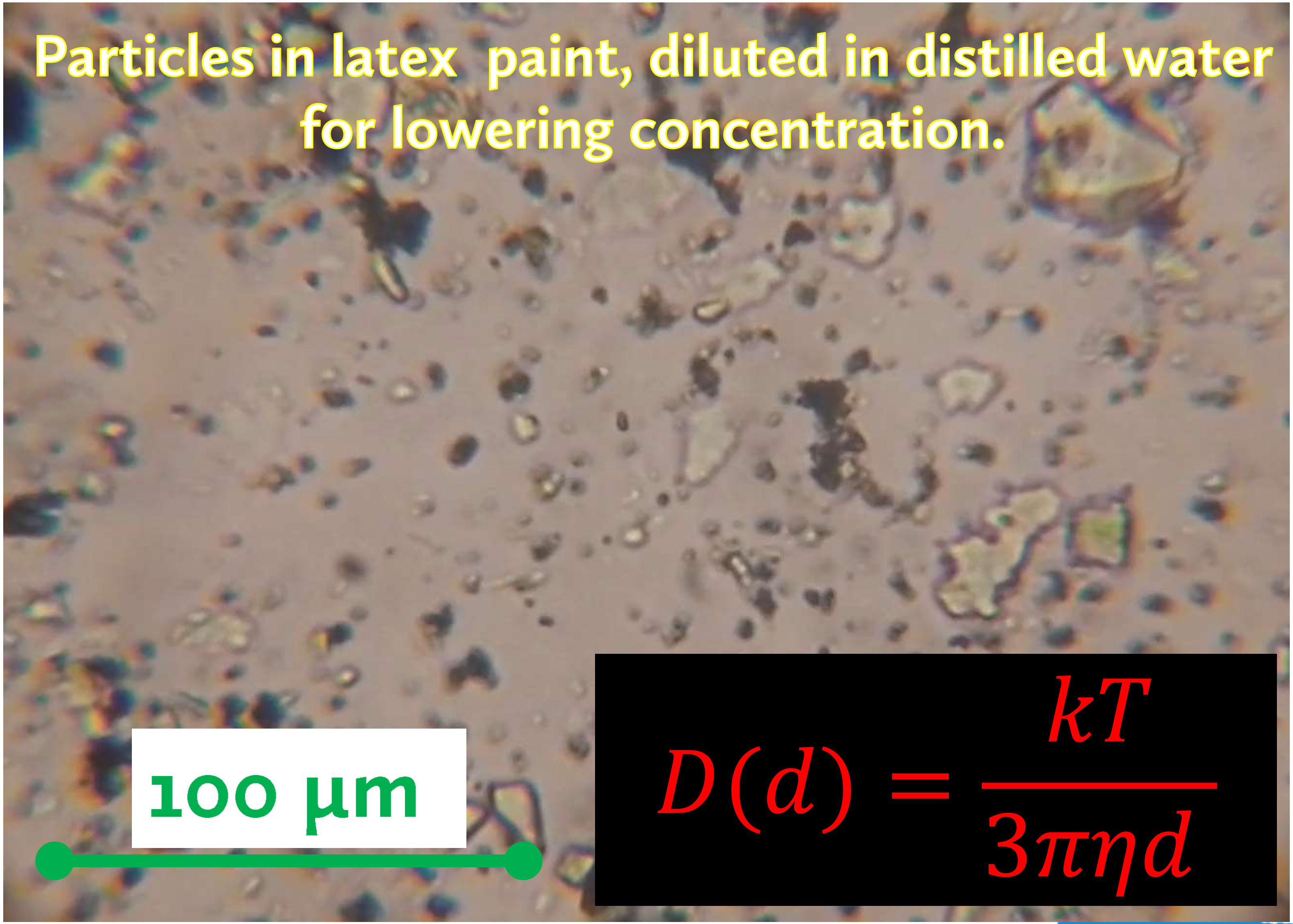
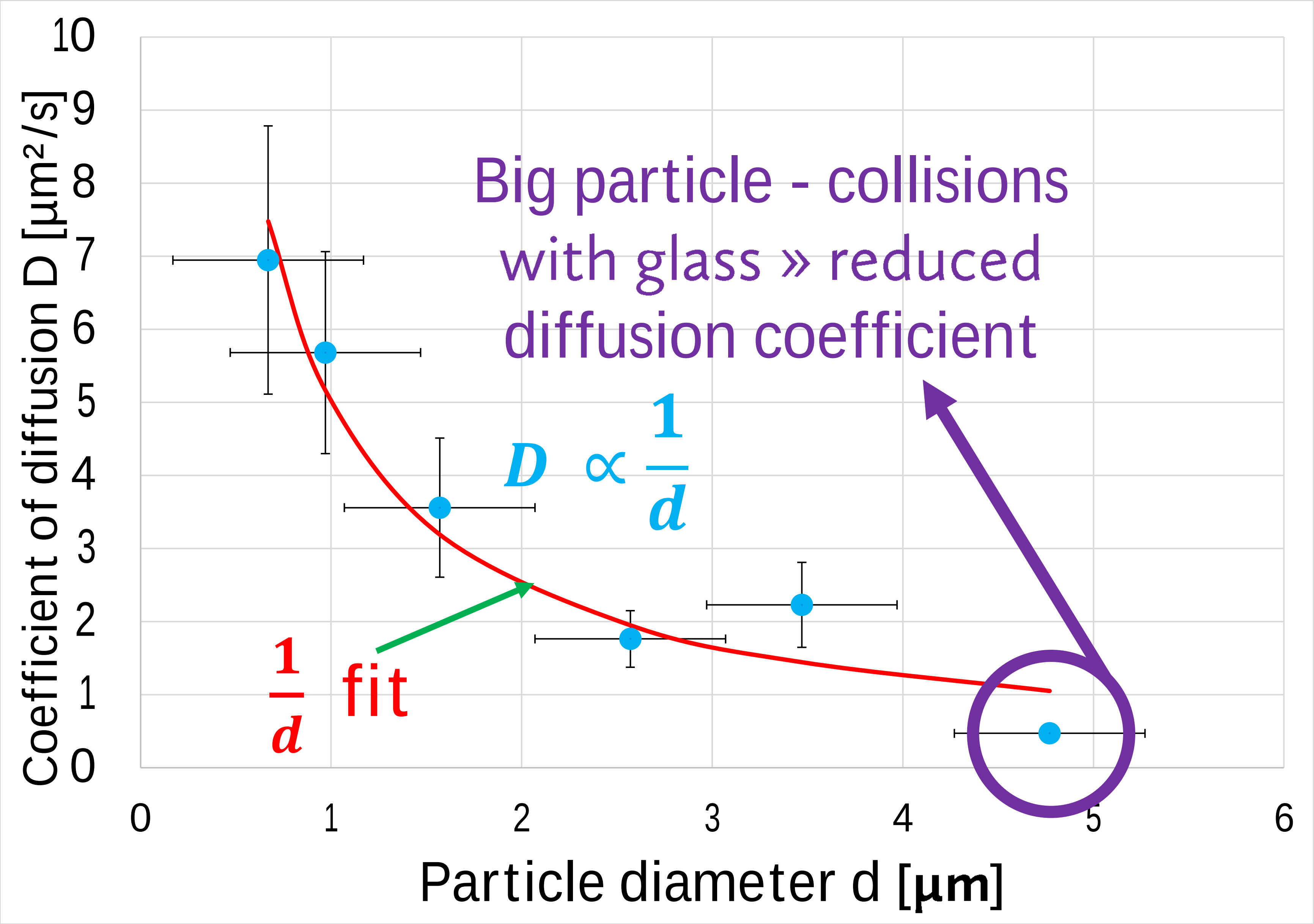
Experiment 2: Particle Size

Observation - explanation



$$D(d) = \frac{kT}{3\pi\eta d}$$

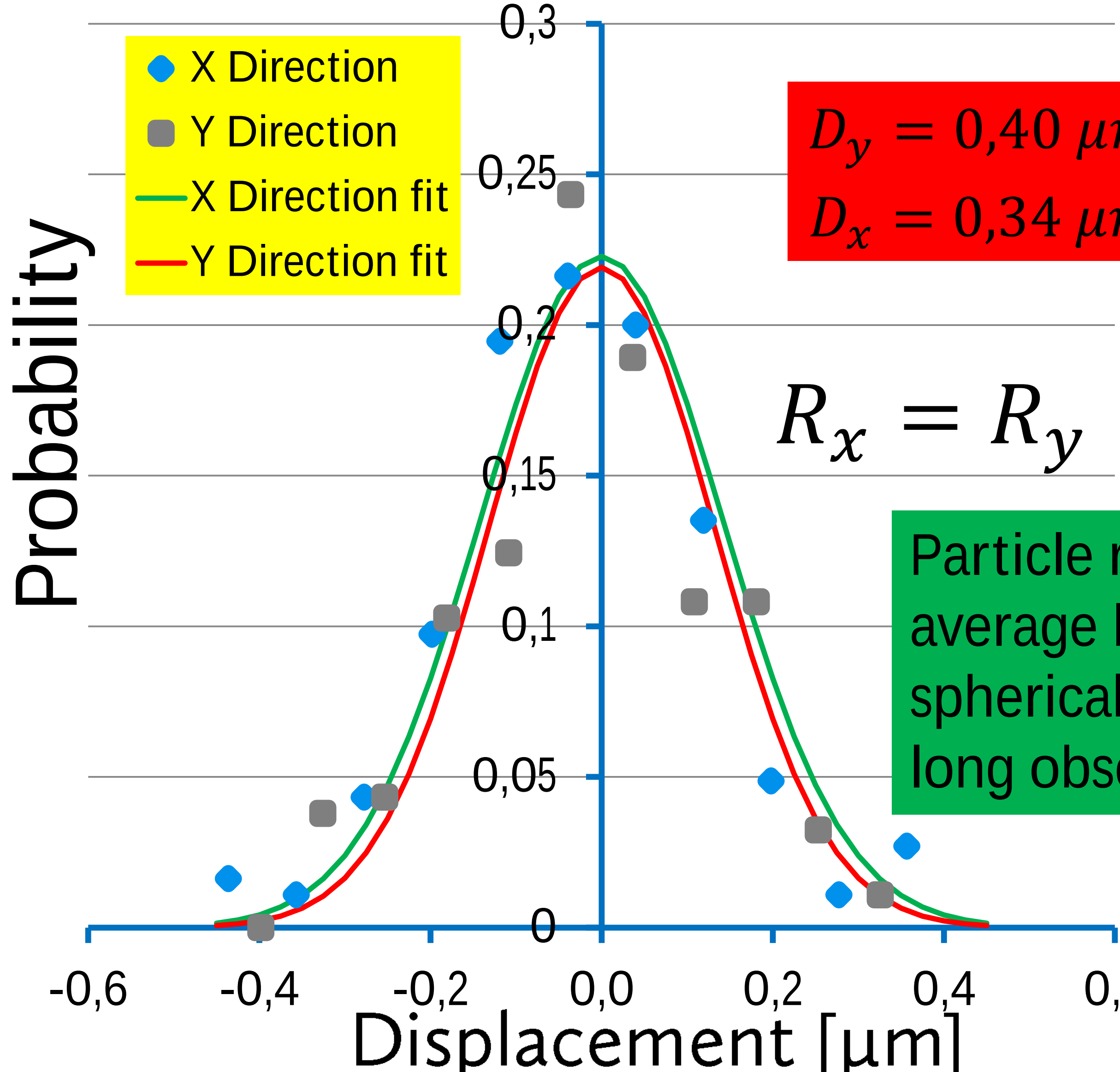
Particle size



Experiment 3: Particle Shape

Influence on the diffusion

X-Y position analysis



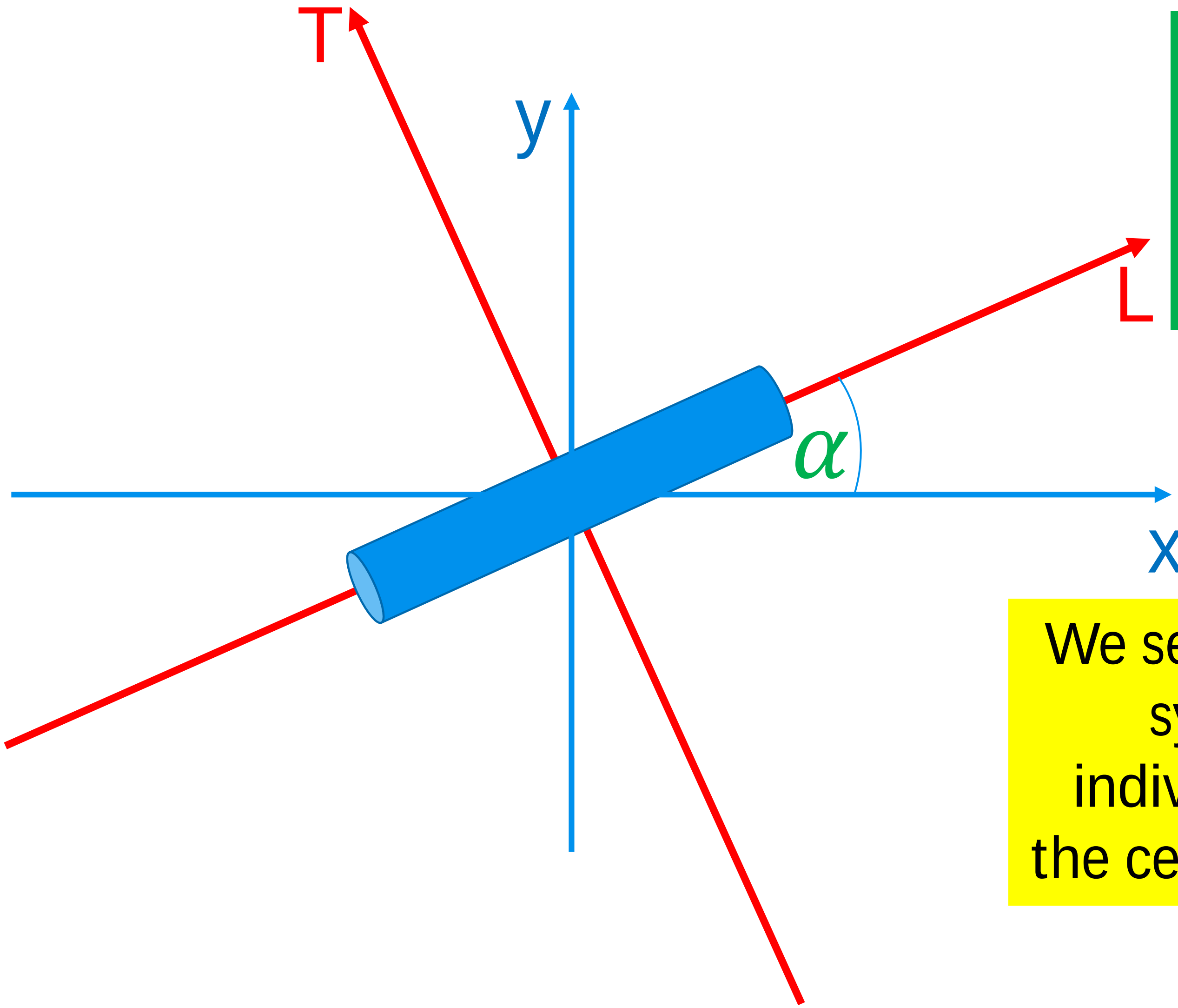
$D_y = 0{,}40\ \mu m^2/s$

$D_x = 0{,}34\ \mu m^2/s$

$$R_x = R_y = 1{,}02\ \mu m$$

Particle rotates – average behavior as a spherical particle (for long observation time)

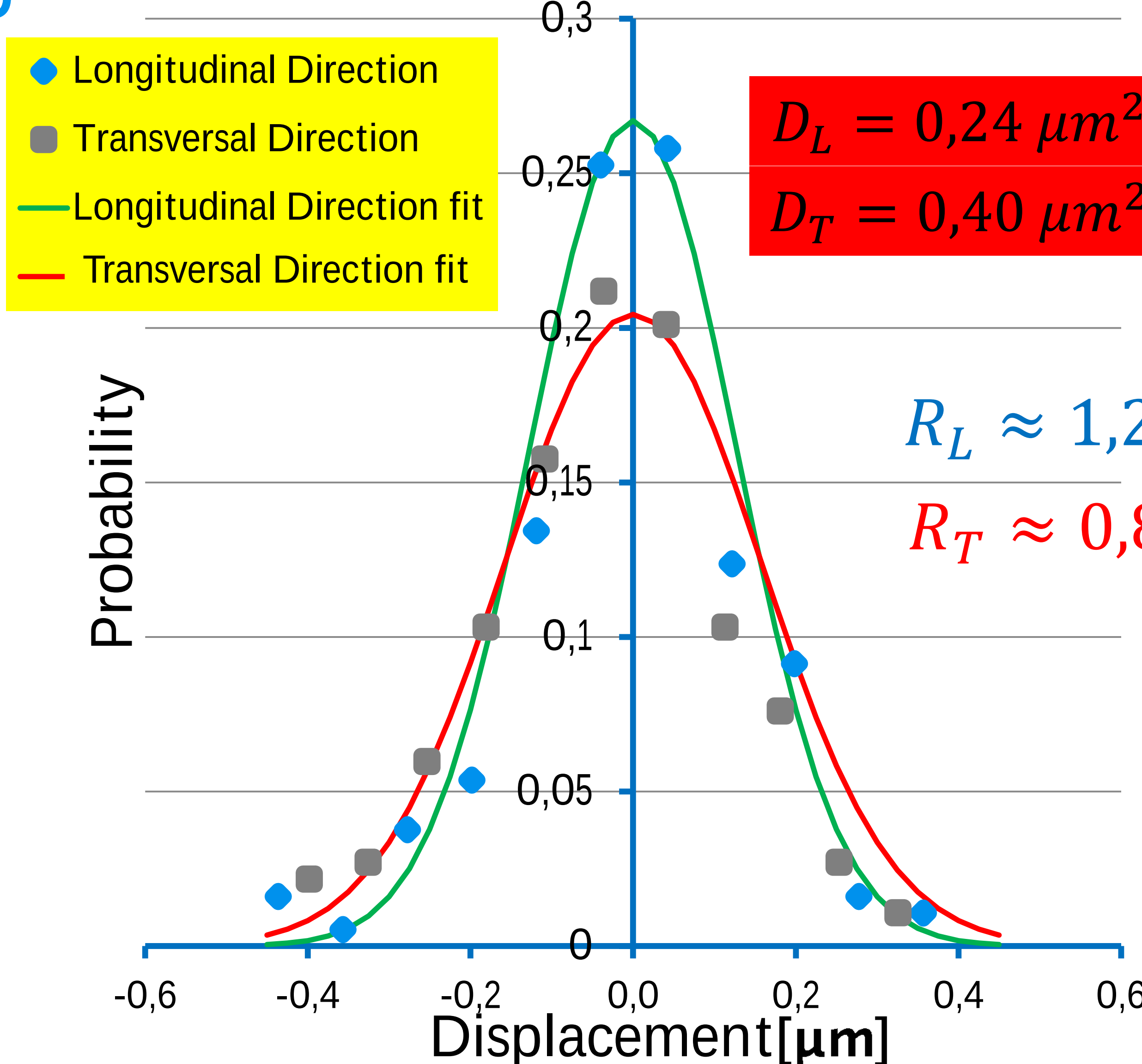
But – change of coordinate system makes difference!



We will analyse the motion of the particle ALONG and PERPENDICULARY to its main axis

We set NEW coordinate system for each individual time step in the center of the particle.

Longitudinal and Transversal movement



$D_L = 0{,}24\ \mu m^2/s$

$D_T = 0{,}40\ \mu m^2/s$

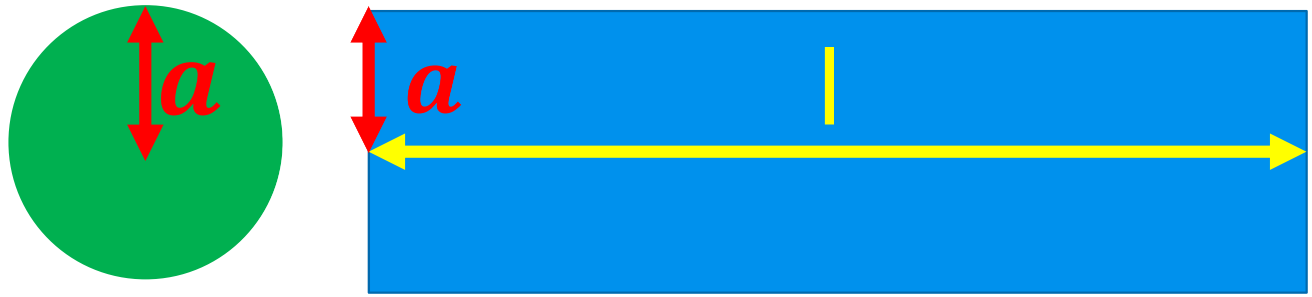
$R_L \approx 1{,}28\ \mu m$

$R_T \approx 0{,}82\ \mu m$

Particle moves more in transversal direction than longitudinal

Explanation

$$a < l$$



$$F_{collisions} \propto a^2 \qquad F_{collisions} \propto al$$

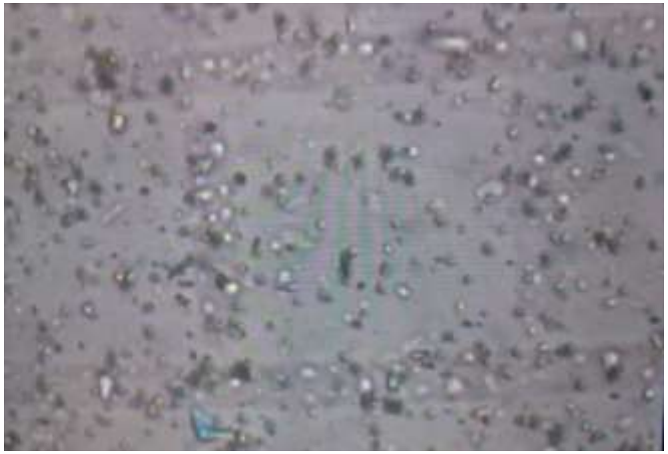
$$F_{viscous} \propto a \qquad F_{viscous} \propto \sqrt[3]{la^2}$$

(Perrin formula)

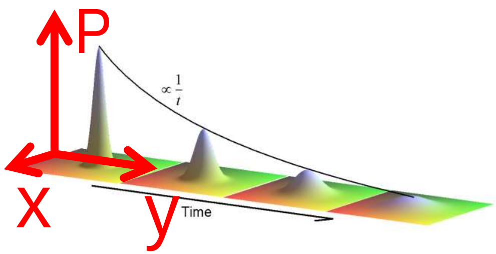
$$\frac{F_{collisions}}{F_{viscous}} \propto a < \frac{F_{collisions}}{F_{viscous}} \propto \sqrt[3]{al^2}$$

Conclusion

- Observation of the Brownian motion (latex paint, milk, carbon particles)

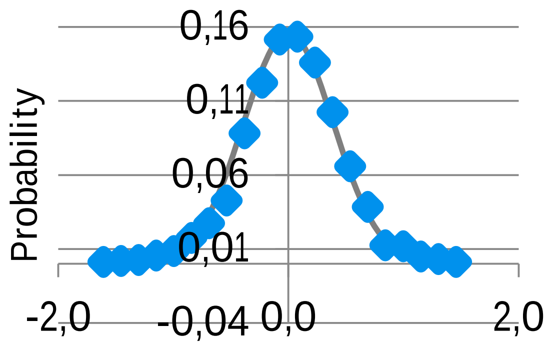


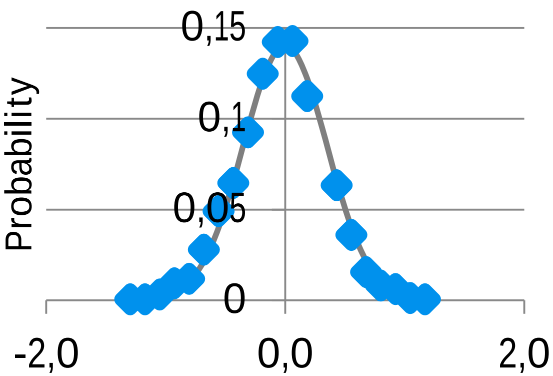
- Theory – Diffusion equation

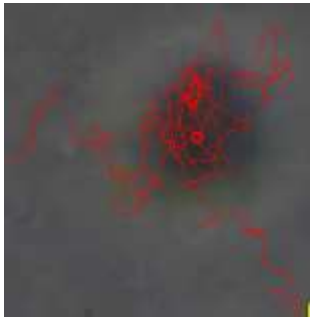


$$D\nabla^2 P = \frac{\partial P}{\partial t}$$

- Analysis of diffusion movement of spherical particle – determination of effective radii R_x and R_y $\quad R_x \approx R_y$

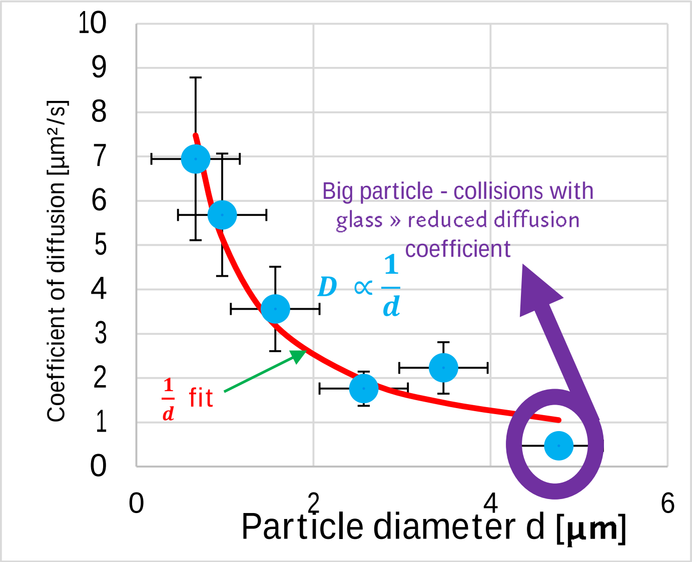


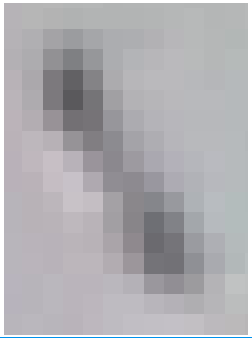




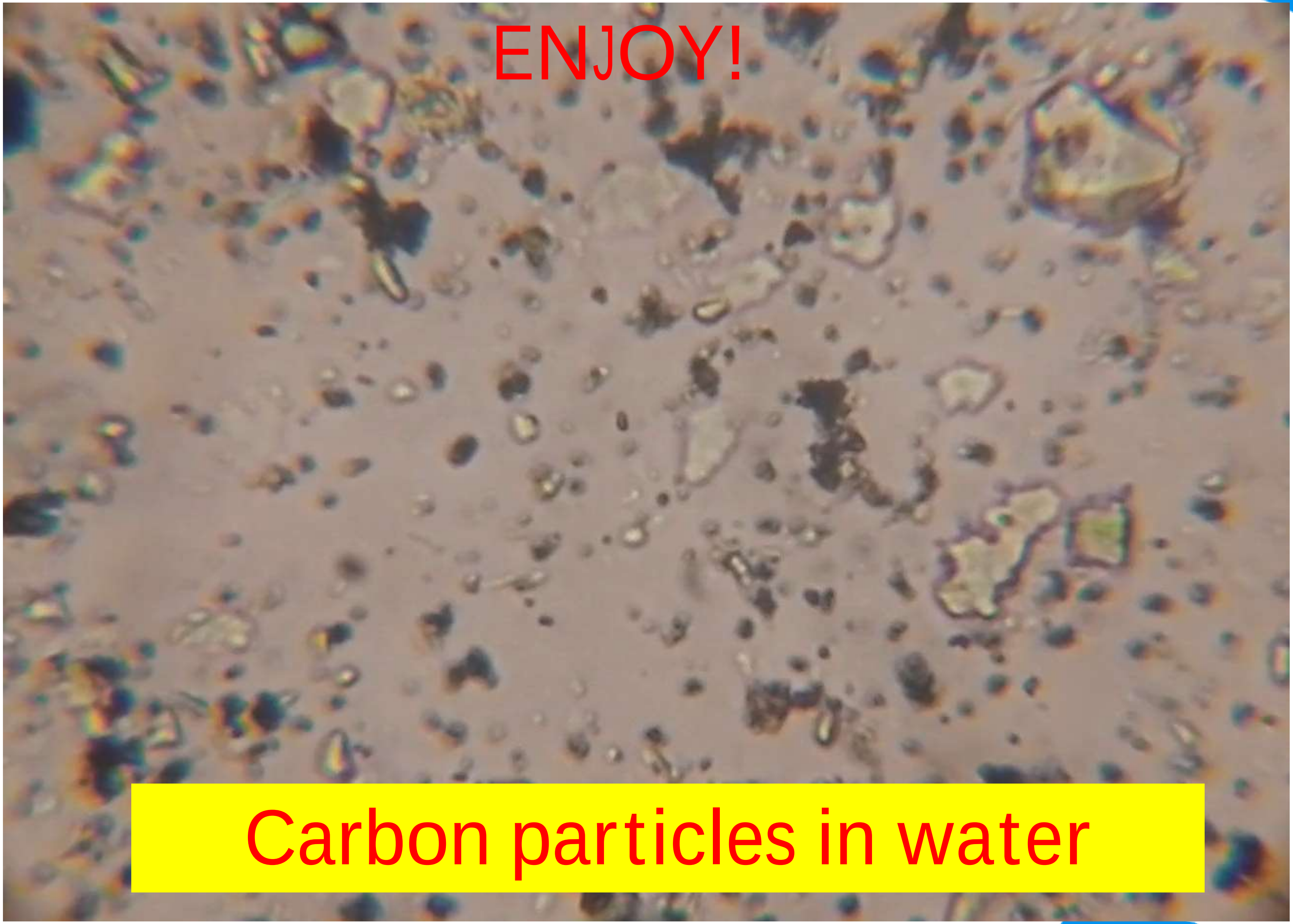
Conclusion

- Measurement of diffusion coefficient in dependence on particle radius – theory $D \propto \frac{1}{d}$ – confirmed
- Analysis of diffusion movement of strongly aspherical particle
  - Behaves like spherical particle in a laboratory frame – $R_x \approx R_y$
  - Asphericity detected from analysis of the longitudinal and transversal movement $R_T > R_L$





Thank you for your attention!


ENJOY!
Carbon particles in water

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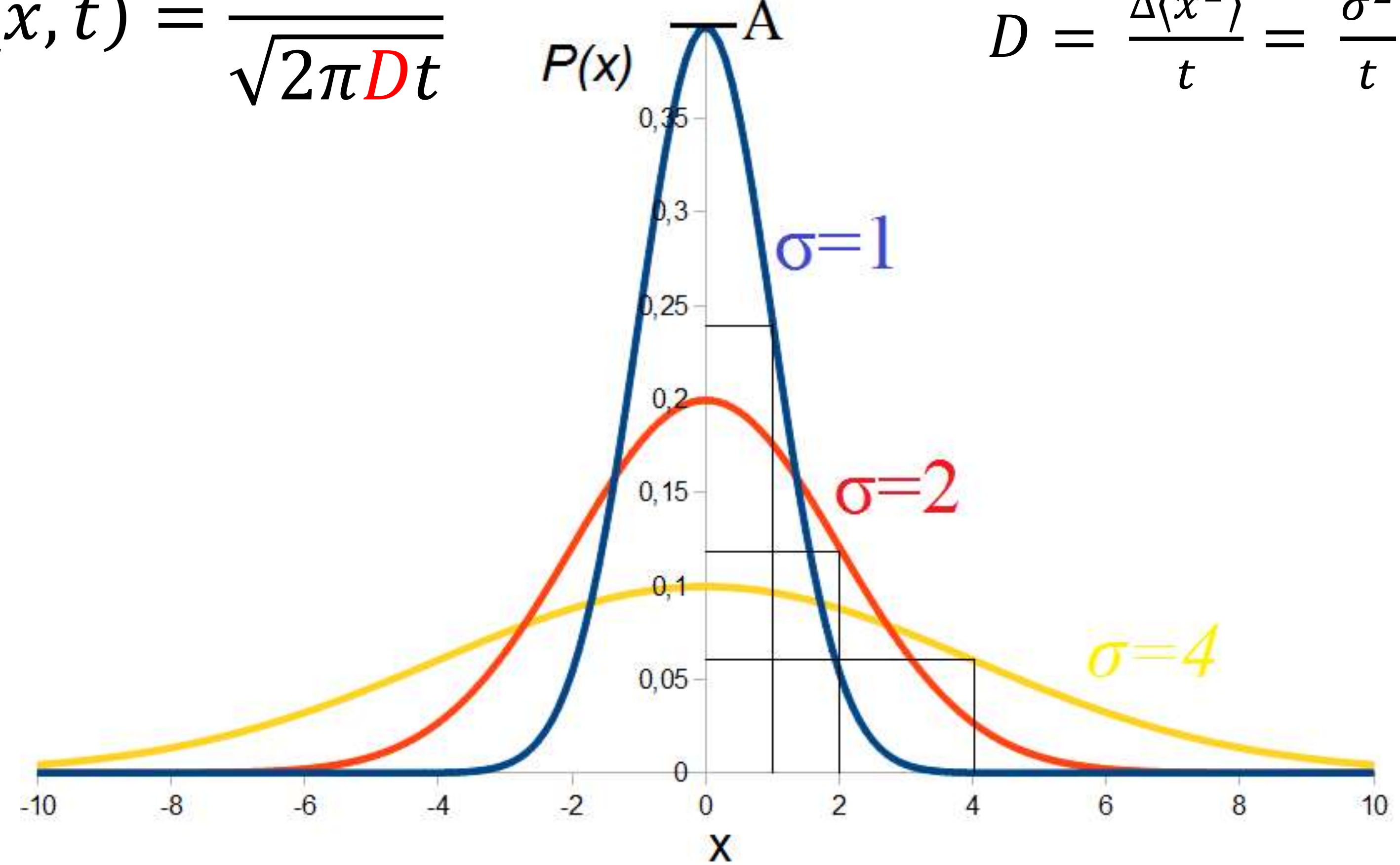
Appendix

Probability distribution function in 1D

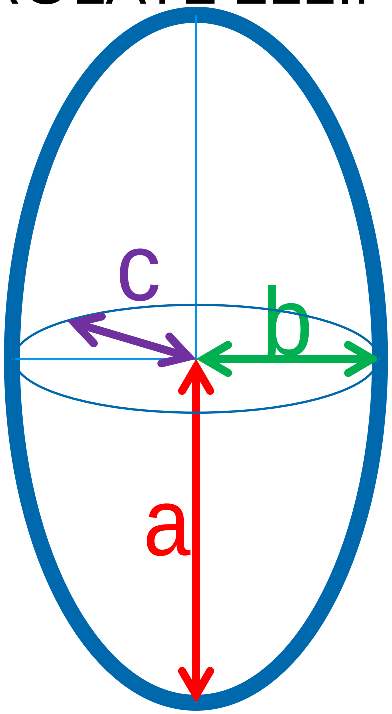
$$P(x,t) = \frac{e^{-\frac{x^2}{2Dt}}}{\sqrt{2\pi Dt}}$$

$$D = \frac{\Delta\langle x^2 \rangle}{t} = \frac{\sigma^2}{t}$$



Perrin formulas – drag coefficients

PROLATE ELLIPSOID



$$\boldsymbol{c = b < a}$$

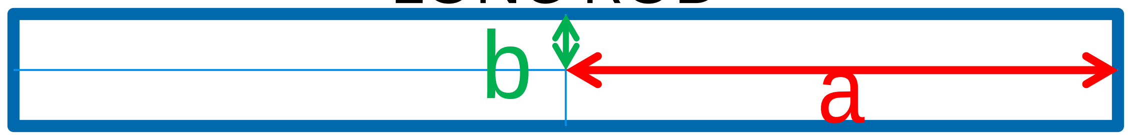
$$f_0 = 6\pi\eta R$$

$$R = (ab^2)^{\frac{1}{3}}$$

$$P = \frac{a}{b}$$

$$\frac{\boldsymbol{f}}{f_0} = \frac{P^{-\frac{1}{3}}(P^2 - 1)^{\frac{1}{2}}}{\ln\left[P + (P^2 - 1)^{\frac{1}{2}}\right]}$$

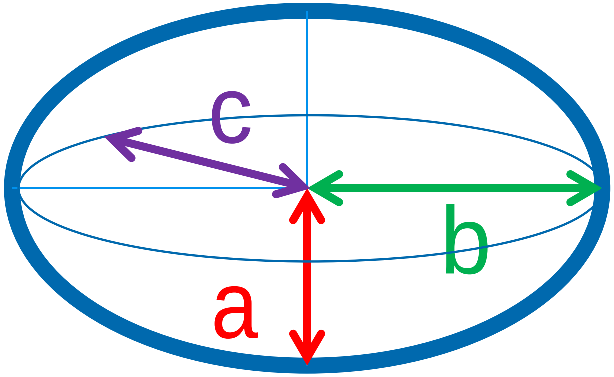
LONG ROD



$$R = \left(\frac{3}{2}b^2 a\right)^{\frac{1}{3}}$$

$$\frac{\boldsymbol{f}}{f_0} = \frac{\frac{2^{\frac{1}{3}}}{3} P^{\frac{2}{3}}}{\ln[2P] - \frac{3}{10}}$$

OBLATE ELLIPSOID



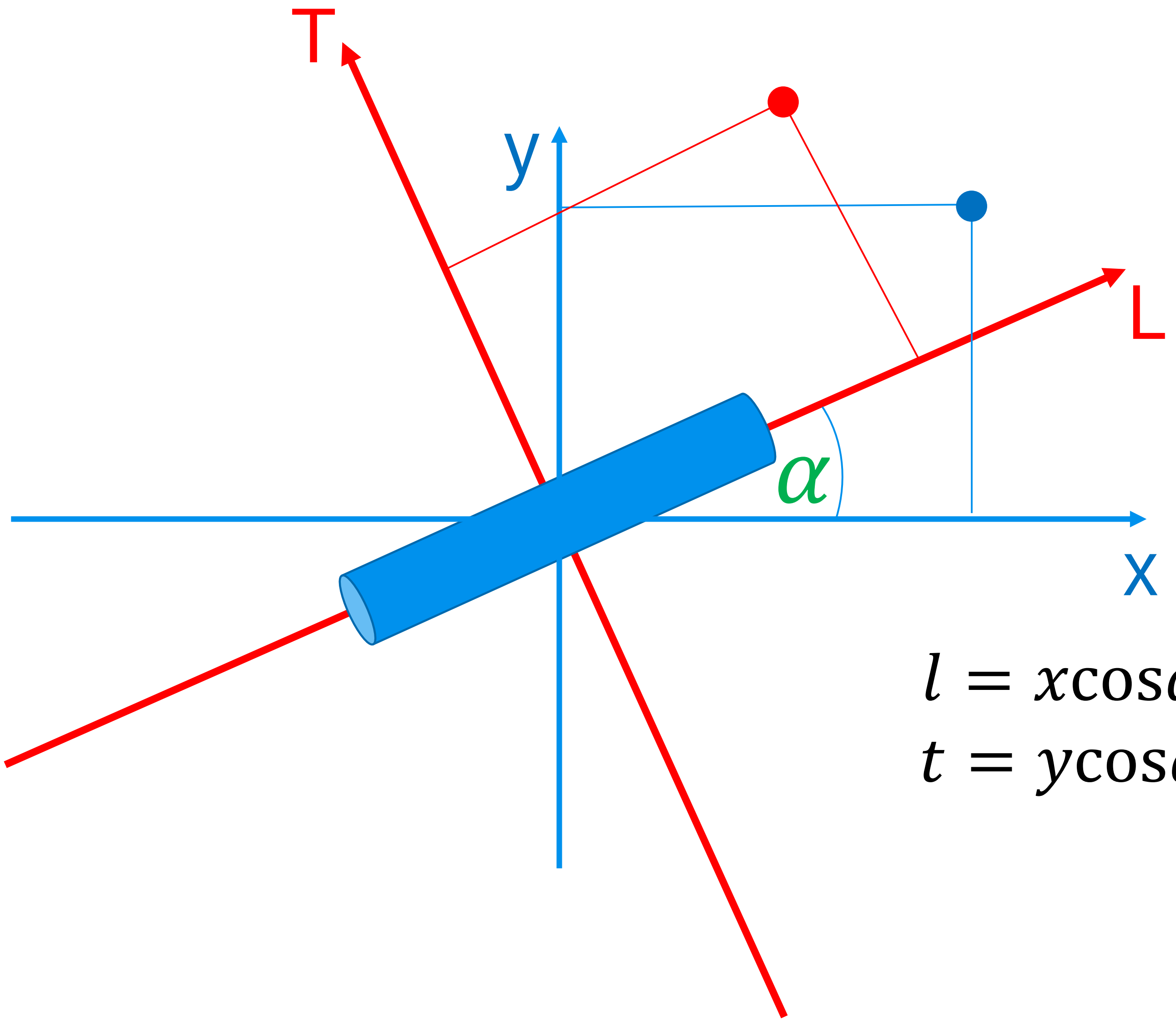
$$\boldsymbol{c = b > a}$$

$$\frac{f}{f_0} = \frac{(P^2 - 1)^{\frac{1}{2}}}{P^{\frac{2}{3}}\tan^{-1}\left[(P^2 - 1)^{\frac{1}{2}}\right]} \qquad P = \frac{a}{b}$$

$$R = (a^2 b)^{\frac{1}{3}}$$

$f_{PROLATE} = \left\{\frac{P^{-\frac{1}{3}}(P^2 - 1)^{\frac{1}{2}}}{\ln\left[P + (P^2 - 1)^{\frac{1}{2}}\right]}\right\} 6\pi\eta[Pb^3]^{\frac{1}{3}}$
$f_{OBLATE} = \left\{\frac{(P^2 - 1)^{\frac{1}{2}}}{P^{\frac{2}{3}}\tan^{-1}\left[(P^2 - 1)^{\frac{1}{2}}\right]}\right\} 6\pi\eta[P^2 b^3]^{\frac{1}{3}}$
$f_{LONG\ ROD} = \left\{\frac{(P^2 - 1)^{\frac{1}{2}}}{P^{\frac{2}{3}}\tan^{-1}\left[(P^2 - 1)^{\frac{1}{2}}\right]}\right\} 6\pi\eta[Pb^3]^{\frac{1}{3}}$

Changing coordinate system! - equations



$$l = x\cos\alpha + y\sin\alpha$$
$$t = y\cos\alpha - x\sin\alpha$$

Mass of the particle

- Type equation here.

$$\frac{1}{2}kT = \frac{1}{2}mv^2$$

$$ma = -fv + X$$

$$\frac{d^2x}{dt^2} = -3\pi\eta d\frac{dx}{dt} + X$$

$$\frac{\overline{dx^2}}{dt} = kT\frac{1}{3}\pi\eta r + Ce^{\frac{-6\pi\eta r}{m}t}$$

t-time between collisions - ~10(-8)s