Accessing ultrashort reaction times in particle formation with SAXS experiments: ZnS precipitation on the microsecond time scale

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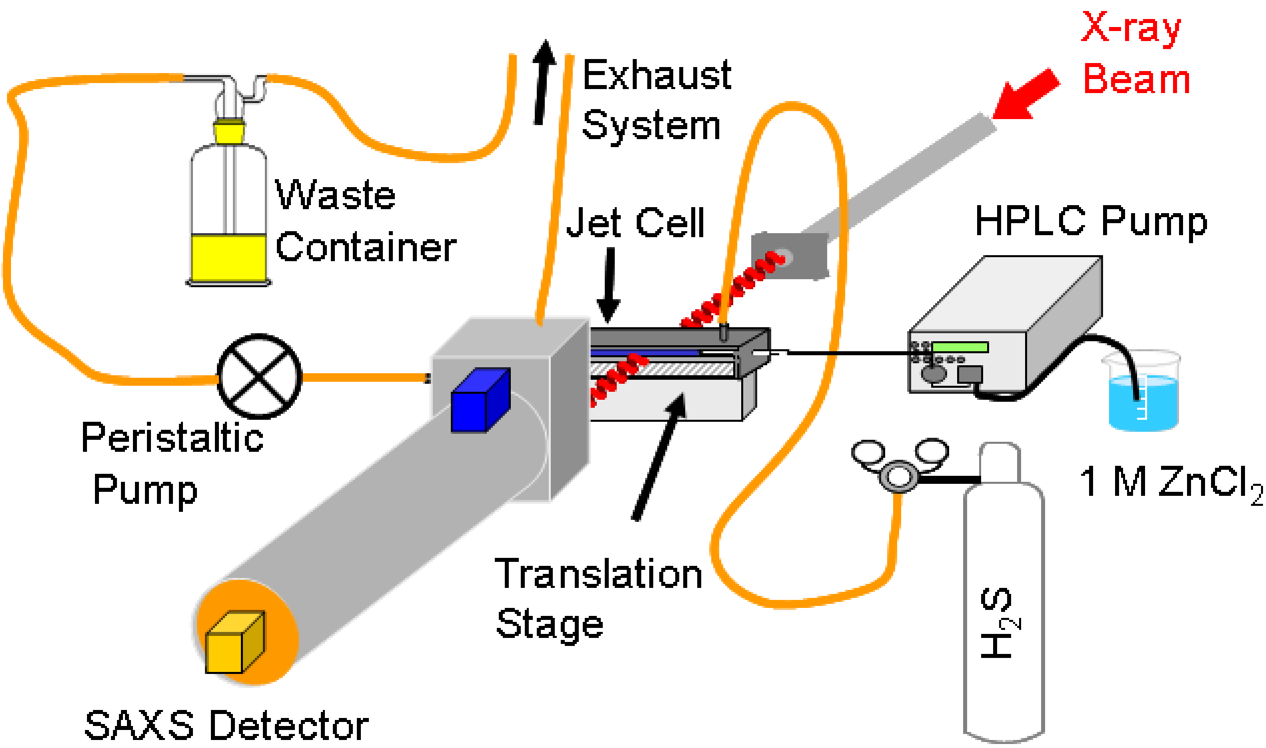
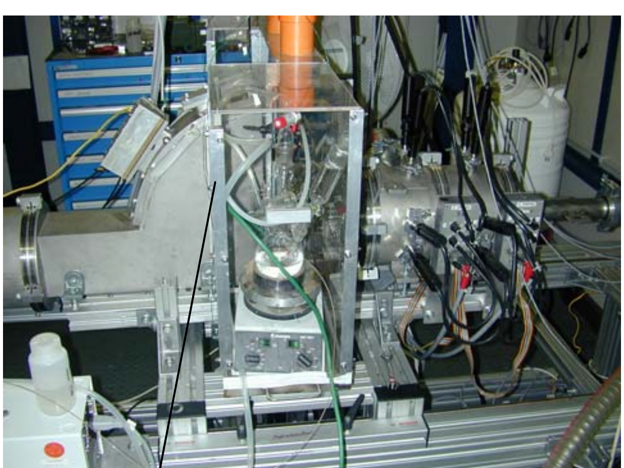
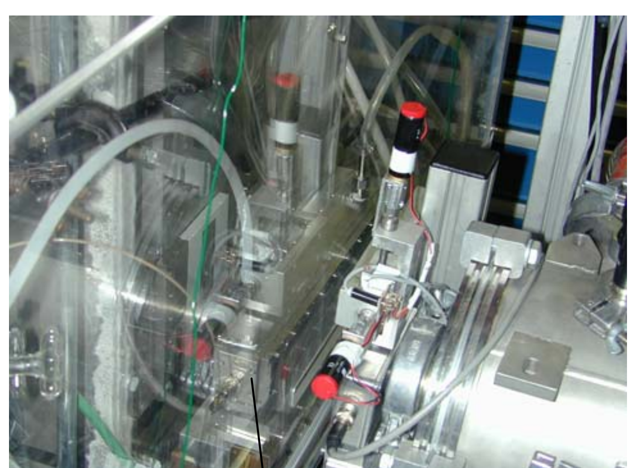
Experimental Setup



Photos of Experimental Setup

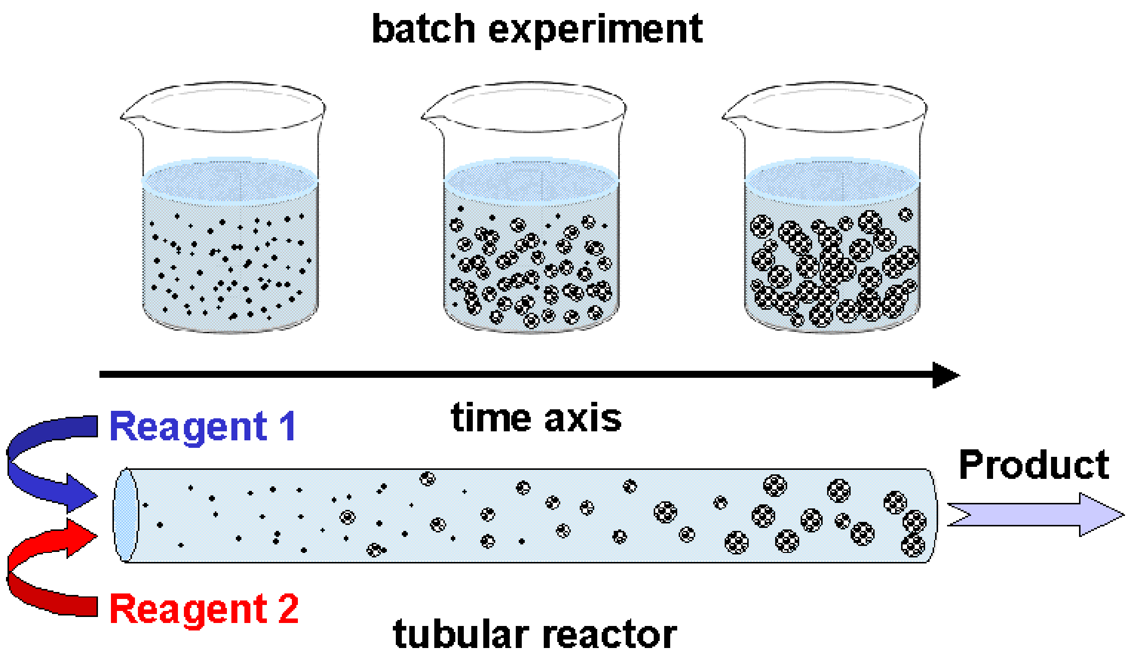


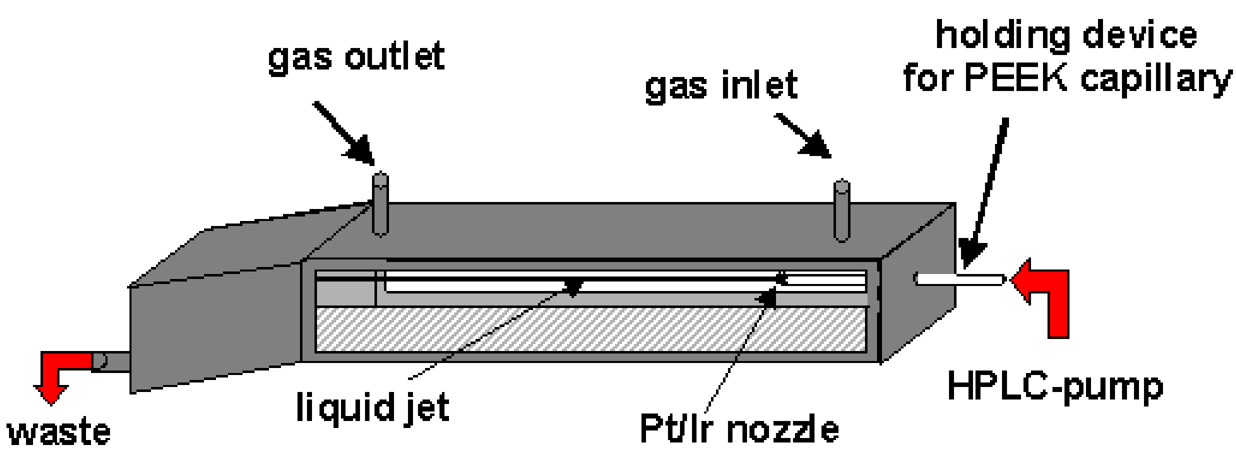


gas-tight housing
containing the experimental setup

liquid jet cell in housing

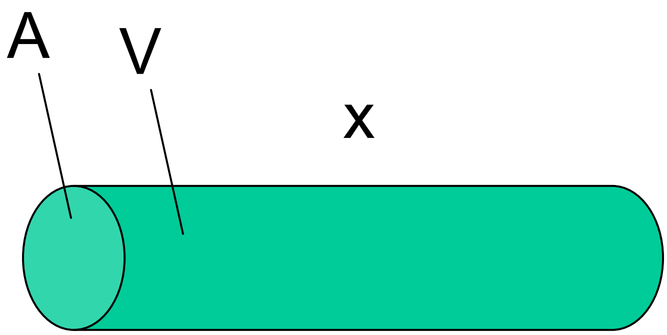
Tubular Reactor Concept





Laminar or turbulent flow?

d = 2r
50µm



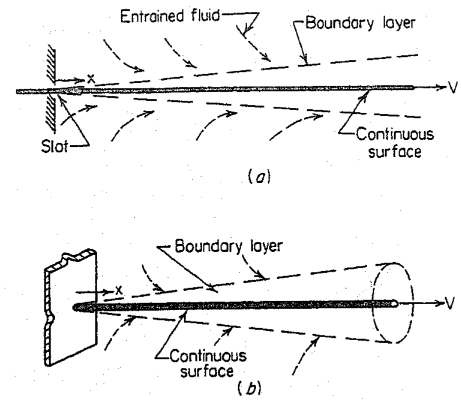


FIG. 5-73. Continuous surfaces. (*a*) Continuous flat surface. (*b*) Continuous cylindrical surface. [*Sakiadis, Am. Inst. Chem. Engrs., J.*, **7**, 221, 467 (1961).]

Taken from: R.H. Perry, C.H. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill Inc., New York, 1973, p. 5-55 – 5-58.

Flow = V/time = 5.5 ml min^{-1} => 5.5 10^{-6} $m^3 min^{-1}$
= 9.2 10^{-8} $m^3 s^{-1}$

x = V/A, v = x/time
=> v = V/(A*time) = Flow/A

A= πr^2 = 3.14 * 625 μm^2 = 1.96 10^3 μm^2 = 1.96 10^{-9} m^2
v = Flow/A = 9.2 10^{-8} $m^3 s^{-1}$ / 1.96 10^{-9} m^2 = 47 m s^{-1}

$(N_{Re})_{x,crit} = v\rho x/\mu$ = 200000
(Perry, p. 5-56) for continuous cylindrical surface
=> $x_{crit} = N_{Re}\mu / (v\rho)$

v = velocity [m s^{-1}]
r = radius of cylinder [m]
x = distance to cylinder edge [m]
μ = fluid viscosity [kg $m^{-1}s^{-1}$]
ρ = fluid density [kg m^3]
δ = thickness of boundary layer [m] (laminar flow)

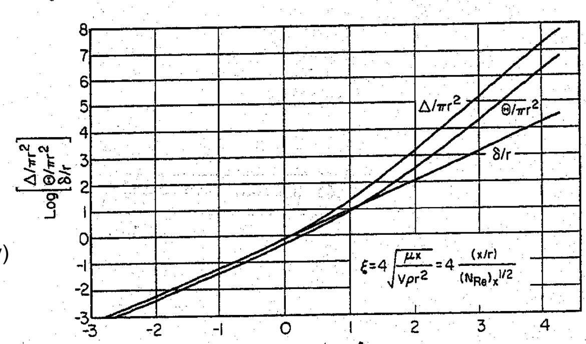
$\rho^{20°C}_{H2S}$ = m/V = 34 g / 24 dm^3 = 34 10^{-3} kg / 24 10^{-3} m^3 = 1.42 kg m^3
dyn. viscosity: η_{H2S} = 11.7 10^{-6} Pa s = 1.17 10^{-5} kg $m^{-1}s^{-1}$ = μ

=> $x_{crit} = N_{Re,crit}\,\mu / (v\rho)$
= 200000 * 1.17 10^{-5} kg $m^{-1}s^{-1}$ / (47 m s^{-1} * 1.42 kg m^3)
= 0.035 m => after 35 mm turbulent gas flow !

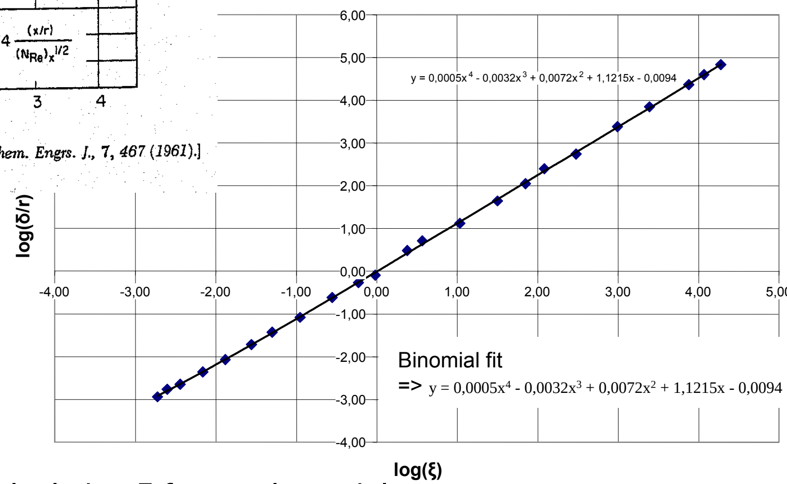
Thickness boundary layer (Perry, Handbook of Chem. Eng.)

Boundary layer thickness δ can be determined from plot (from δ/r at given ξ)

Original (Perry)

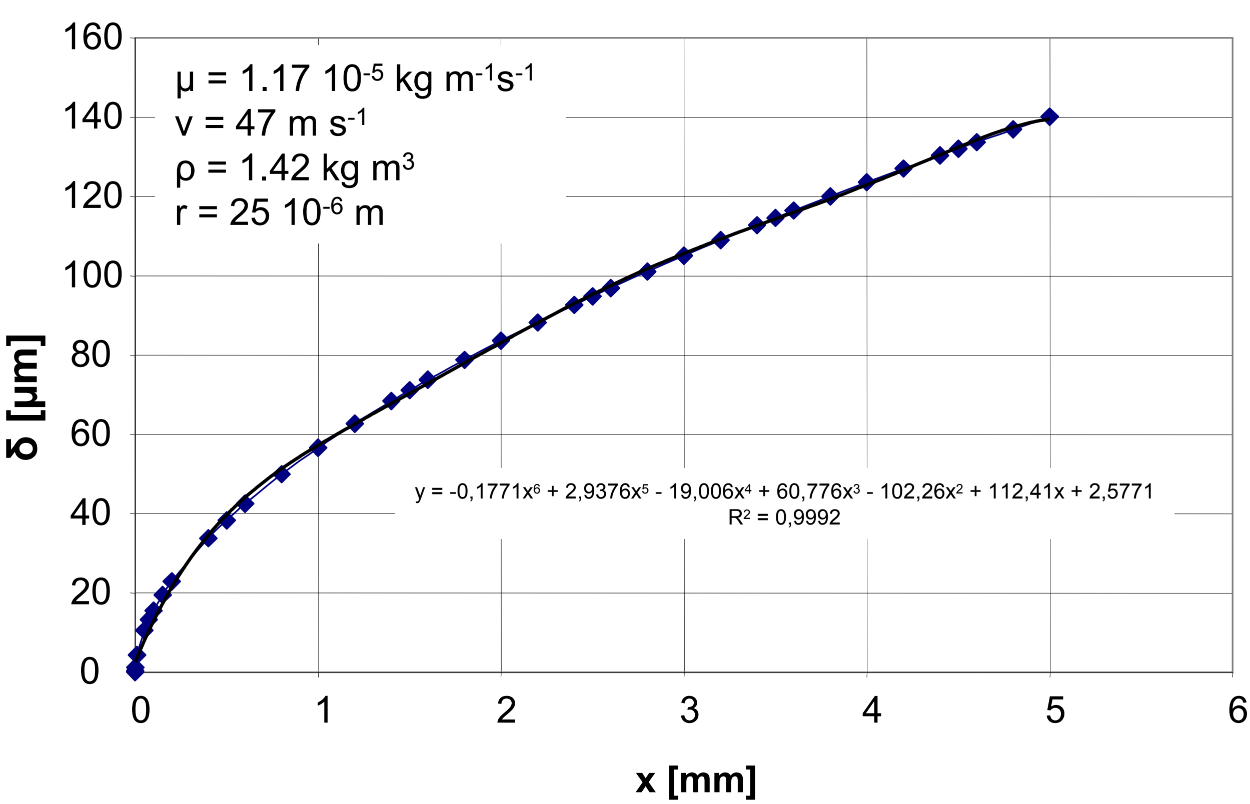


undary-layer parameters for continuous cylindrical surfaces. [Sakiadis, Am. Inst. Chem. Engrs. J., 7, 467 (1961).]



$\xi = 4\ ((\mu x)/(v\rho r^2))^{1/2}$

Using x in $\xi = 4\ ((\mu x)/(v\rho r^2))^{1/2}$ and calculating δ from polynomial
$y = 0{,}0005x^4 - 0{,}0032x^3 + 0{,}0072x^2 + 1{,}1215^x - 0{,}0094$
one can calculate the following plot of δ with respect to x which can be again fitted by a polynomial as shown in the plot

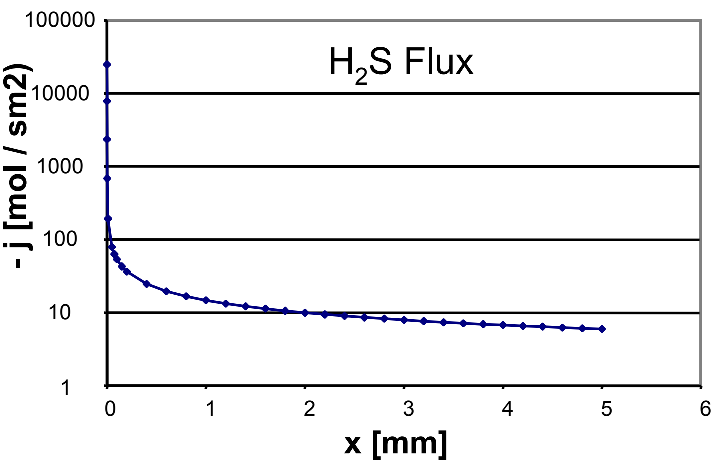


Thus (for v = 47 m/s and 50µm nozzle), δ can be calculated by the polynomial
$\delta = -0{,}1771x^6 + 2{,}9376x^5 - 19{,}006x^4 + 60{,}776x^3 - 102{,}26x^2 + 112{,}41x + 2{,}5771$

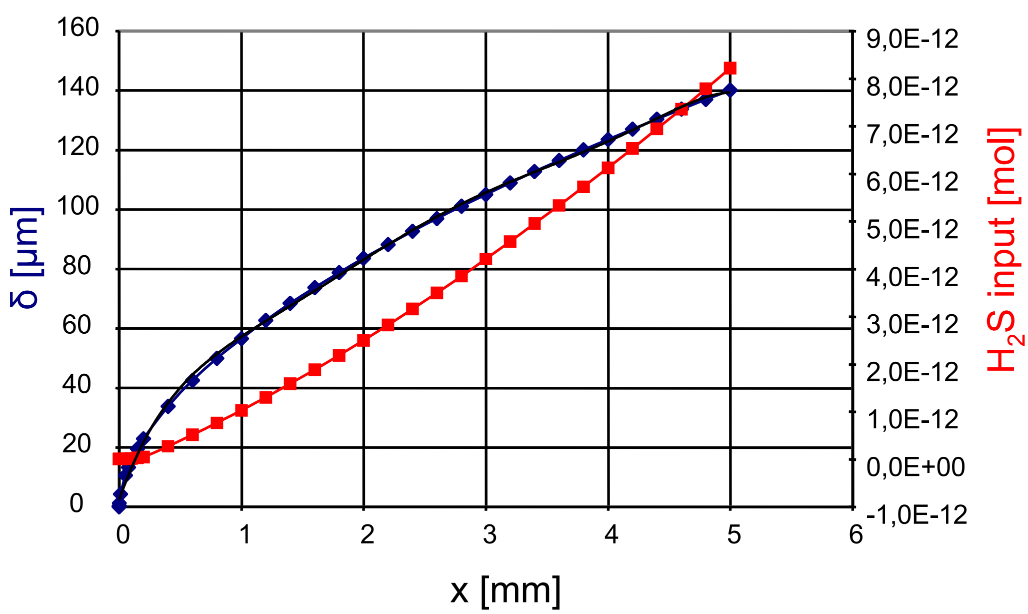
How much H_2S through boundary layer?

Flux through boundary layer:
$j = -D\ (dc/dz) = -D\ (dc/\delta)$
D = self diffusion coefficient = 0.2 cm^2s^{-1} = 2.0 10-5 m^2s^{-1}
(gases in air typically 0.1-0.25 cm^2s^{-1})
$c_0(H_2S)$ = 41.7 mol m^{-3} (=> 1000*(1/24dm^3); 24 dm^3 := 1 mol)
dc = c0 - c_{jet} = 41.7 mol m^{-3} (assumption no H_2S in jet, all consumed)

calculation of the flux through boundary layer over the jet results a set of data, which can be used to calculate the input of H_2S into the jet

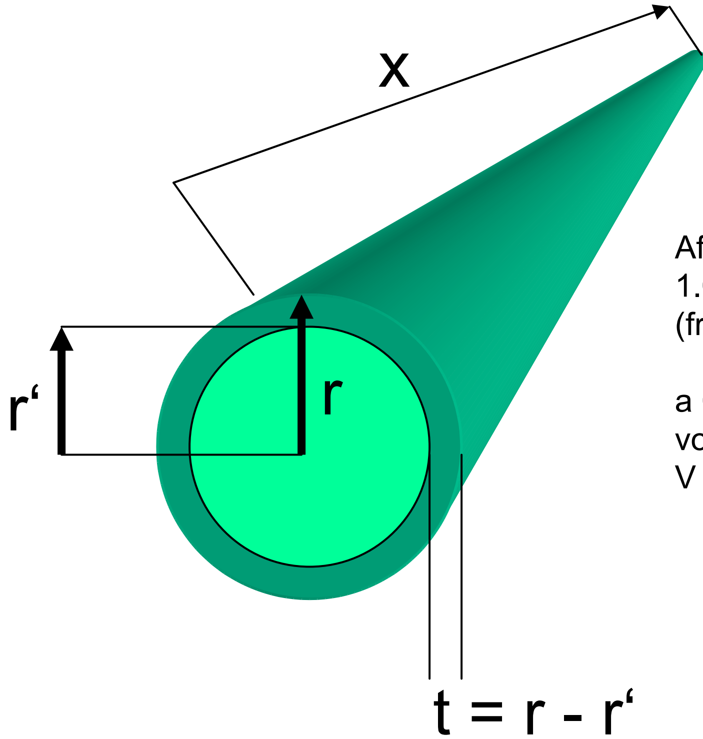


That calculation was done by treating the boundary layer as small sections increasing stepwise in thickness (for each section the thickness of the layer and the respective flux were assumed to be constant). The respective times required to pass those short fractions of the boundary layer surface were calculated from the velocity of the jet.



Reynolds number:
$(N_{Re})_x = v\rho x/\mu$ = 29272 for x = 5 mm => lamilar flow ($(N_{Re})_{x,crit}$=2 10^5)

Is formation of particle possible?



After 1 mm jet length
$1.03\ 10^{-12}$ mol H_2S in jet
(from figure)

a 0.5 µm thick top layer of liquid jet has a volume of
$V = x\pi(r^2 - r'^2) = 7.78\ 10^{-14}\ m^3$

=> $c(H_2S) = 1.03\ 10^{-12}$ mol / $7.78\ 10^{-14}\ m^3$ = 13.24 mol m^{-3} (for 0.5 µm layer!)
= 0.0132 mol dm^{-3}
$c(Zn^{2+})$ = 1 mol dm^{-3} = 1000 mol m^{-3}

diffusion constant of H_2S in water: $D^{H2O}_{(H2S)} = 1.41\ 10^{-9}\ m^2s^{-1}$

Particles: r_g = 12 nm, t_P = 17 µs, $\sigma_P = 4\ 10^3$ kg m^3, $M_{ZnS} = 98.4\ 10^{-3}$ kg mol^{-1}
=> $V_P = 7.24\ 10^{-24}\ m^3$ => $m_P = 2.90\ 10^{-20}$ kg => $n_P = 2.94\ 10^{-19}$ mol (H_2S needed)
$\langle x^2 \rangle = 2Dt$ => $x = (2Dt)^{1/2} = 2.19\ 10^{-7}$ m => diff. sphere $V_{sph} = 4.40\ 10^{-20}\ m^3$
sphere of diameter $4.38\ 10^{-7}$ m (438 nm = 2 x) contains $5.83\ 10^{-19}$ mol H_2S

Particles: r_g = 17 nm, t_P = 21 µs, $\sigma_P = 4\ 10^3$ kg m^{-3}, $M_{ZnS} = 98.4\ 10^{-3}$ kg mol^{-1}
=> $V_P = 2.06\ 10^{-23}\ m^3$ => $m_P = 8.23\ 10^{-20}$ kg => $n_P = 8.36\ 10^{-19}$ mol (H_2S needed)
$\langle x^2 \rangle = 2Dt$ => $x = (2Dt)^{1/2} = 2.434\ 10^{-7}$ m => diff. sphere $V_{sph} = 6.04\ 10^{-20}\ m^3$
sphere of diameter $4.87\ 10^{-7}$ m (487 nm = 2 x) contains $7.99\ 10^{-19}$ mol H_2S

$\Rightarrow$in both cases enough H_2S present to form respective particles by diffusion!