Nanoparticles and Taylor Dispersion as a Linear Time-Invariant System

Philipp Lemal,[a] Alke Petri-Fink,[a,b] and Sandor Balog[a]*

[a]Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

[b]Chemistry Department, University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland

ABSTRACT: The physical principles underpinning Taylor dispersion offer a high dynamic range to characterize the hydrodynamic radius of particles. While Taylor dispersion grants the ability to measure radius within nearly five orders of magnitude, the detection of particles is never instantaneous. It requires a finite sample volume, a finite detector area, and a finite detection time for measuring absorbance. First we show that these practical requirements bias the analysis when the self-diffusion coefficient of particles is high, which is typically the case of small nanoparticles. Second we show that the accuracy of the technique may be recovered by treating Taylor dispersion as a linear time-invariant system, which we prove by analyzing the Taylor dispersion spectra of two iron-oxide nanoparticles measured under identical experimental conditions. The consequence is that such treatment may be necessary whenever Taylor dispersion analysis is not optimized for a given size but dedicated to characterize broad groups of particles of varying size and material.

Corresponding Author

sandor.balog@unifr.ch

Supporting Information

Contents

1. Model fit

For each particle system we had six taylorgrams resulting from three independent runs and two detection points (windows). To fit our model against the experimental data, we used unconstrained nonlinear model fit. Each taylorgram was fitted with a bimodal linear combination of Equation 3:

(SI-1) $$A(t) = a + b \cdot [\, y \cdot A_x(t_0, \kappa 1/p, \Delta t, \delta t, t) + (1 - y) \cdot \; A_x(t_0, \kappa 2/p, \Delta t, \delta t, t)]$$

where one mode interpreted the citric acid and the other the SPIONs. The parameters included

- a baseline : $a\ (au)$
- an amplitude: b
- a residence time: $t_0\ (s)$
- a time parameter addressing the injected volume: $\Delta t\ (s)$
- a time parameter addressing the detected volume: $\delta t\ (s)$
- two 'variance' parameters for each mode: $\kappa = p\, r\ (s)$ where $p = \pi\, \eta\, Y^2 / 2\, k_B T$ and the corresponding temporal variance is $\sigma^2 = \kappa\, t_0/2$
- a factor bounded between 0 and 1 weighting the linear combination of the two modes: y

The Gaussian fit also consisted of a linear combination of two modes

(SI-2) $$A(t) = a + b \cdot [y \cdot g(t_0, \sigma 1) + (1 - y) \cdot g(t_0, \sigma 2)]$$

where the parameters included

- a baseline: $a\ (au)$
- an amplitude: b
- a residence time: $t_0\ (s)$
- two widths, one for each mode: $\sigma\ (s)$
- a factor bounded between 0 and 1 weighting the linear combination of the two modes: y

For single window analysis the hydrodynamic radius was determined directly from the variance and residence time

(SI-3) $$r = \frac{4\, k_B\, T}{\pi\, \eta\, Y^2} \frac{\sigma^2}{t_0},$$

and to combine the analysis of the results obtained from two windows, a linear function with two parameters—intercept and slope— was fitted against the paired data points of variances versus residence times:

(SI-4) $$y(t) = y_0 + \left(\frac{\pi\, \eta\, Y^2}{4\, k_B\, T}\right) \cdot r \cdot t$$

2. Fit parameters

The list below displays the fit parameters of the small SPIONs for each run (3) and window (2) for Equation 3 and the Gaussian model, respectively.

Run: 1
Window: 1

Equation 3
Baseline: 0. au
Amplitude: 0.991
t_0: 944.861 s
Δt: 23.447 s
δt: 43.244 s
κ1: 2.93 s
κ2: 0.158 s
y: 0.501

Gaussian
Baseline: 0. au
Amplitude: 1.007
t_0: 956.615 s
σ1: 46.607 s
σ2: 19.403 s
y: 0.373

Run: 2
Window: 1

Equation 3
Baseline: 0. au
Amplitude: 0.993
t_0: 945.119 s
Δt: 22.443 s
δt: 43.181 s
κ1: 2.996 s
κ2: 0.169 s
y: 0.499

Gaussian
Baseline: 0. au
Amplitude: 1.009
t_0: 956.37 s
σ1: 46.929 s
σ2: 19.378 s
y: 0.374

Run: 3
Window: 1

Equation 3
Baseline: 0. au
Amplitude: 0.991
t_0: 946.015 s
Δt: 22.937 s
δt: 43.072 s
κ1: 2.996 s
κ2: 0.164 s
y: 0.503

Gaussian
Baseline: 0. au
Amplitude: 1.006
t_0: 957.513 s
σ1: 46.689 s
σ2: 19.319 s
y: 0.38

Run: 1
Window: 2

Equation 3
Baseline: 0. au
Amplitude: 0.992
t_0: 625.869 s
Δt: 20.132 s
δt: 39.502 s
κ1: 3.009 s
κ2: 0.186 s
y: 0.492

Gaussian
Baseline: 0. au
Amplitude: 1.022
t_0: 635.965 s
σ1: 42.634 s
σ2: 17.838 s
y: 0.318

Run: 2
Window: 2

Equation 3
Baseline: 0. au
Amplitude: 0.988
t_0: 625.356 s
Δt: 20.289 s
δt: 39.527 s
κ1: 3.006 s
κ2: 0.184 s
y: 0.49

Gaussian
Baseline: 0. au
Amplitude: 1.019
t_0: 635.532 s
σ1: 42.845 s
σ2: 17.85 s
y: 0.316

Run: 3
Window: 2

Equation 3
Baseline: 0. au
Amplitude: 0.982
t_0: 627.16 s
Δt: 18.481 s
δt: 39.384 s
κ1: 3.073 s
κ2: 0.208 s
y: 0.486

Gaussian
Baseline: 0. au
Amplitude: 1.012
t_0: 636.431 s
σ1: 42.944 s
σ2: 17.797 s
y: 0.318

- *Equation 3, Single windows*
  Hydrodynamic radius: (6.3, 6.3, 6.4, 6.1, 6.3, 6.3) nm

- *Gaussian, Single windows*
  Hydrodynamic radius: (12.1, 12.0, 12.1, 9.6, 9.5, 9.5) nm

- *Equation 3, Two windows combined*
  Hydrodynamic radius: mean, 99%confidence interval (6.0, 5.5, 6.4) nm, intercept $y_0 = 50.8\ s^2$

- *Gaussian, Two windows combined*
  Hydrodynamic radius: mean, 99%confidence interval (4.6, 3.9, 5.3) nm, intercept $y_0 = 1134.3\ s^2$