TiO_2 nanoparticle dispersions studied by sedimentation analysis: Hansen Parameters vs. DLVO interpretations

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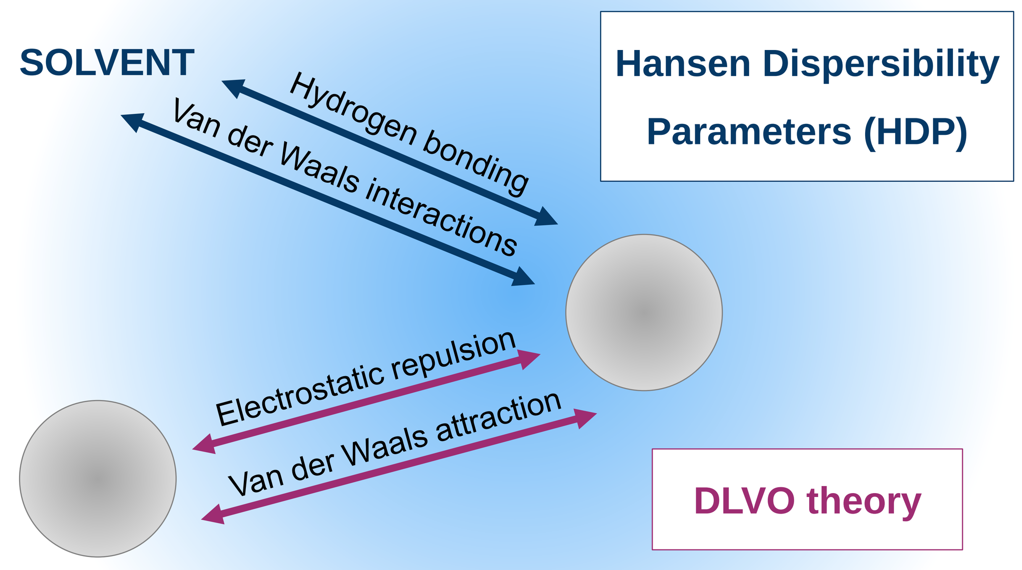
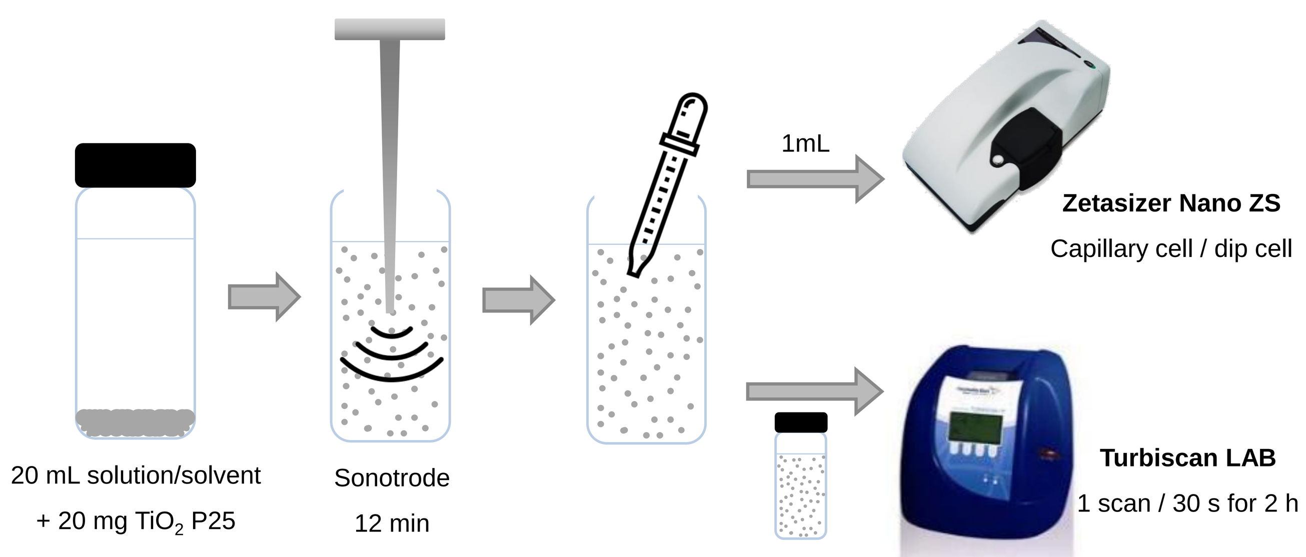
Introduction

TiO_2 nanoparticles (NPs) are among the most widely used NPs due to interesting optical and catalytic properties. Rationalizing and **predicting the stability** of TiO_2 NP dispersions facilitates the conception of formulated products. **Hansen Dispersibility Parameters**[1] (HDP), considering hydrogen bonding, polar and dispersive interactions between particles and a dispersing media, have been shown to be an effective approach[1,2]. Although **electrostatic interactions** (DLVO) can be of great amplitude between inorganic NPs, their contribution has not been studied in HDP approach[3–5]. **Zeta potential** is used to discriminate **DLVO** and **HDP** contributions to TiO_2 P25 NPs dispersions stability, detected by **multiple light scattering sedimentation (Turbiscan)** [6–8]. The method is first validated in aqueous media then applied to dispersions in 20 organic solvents.



Method



Zeta potential ζ is related to the strength of electrostatic repulsion between NPs. Turbiscan analysis gives the ***TSI*** (turbiscan stability index) and **SMLS** (Static Multiple Light Scattering) **diameters** that can be correlated to **stability**. *T* is transmitted and *BS* is backscattered light.

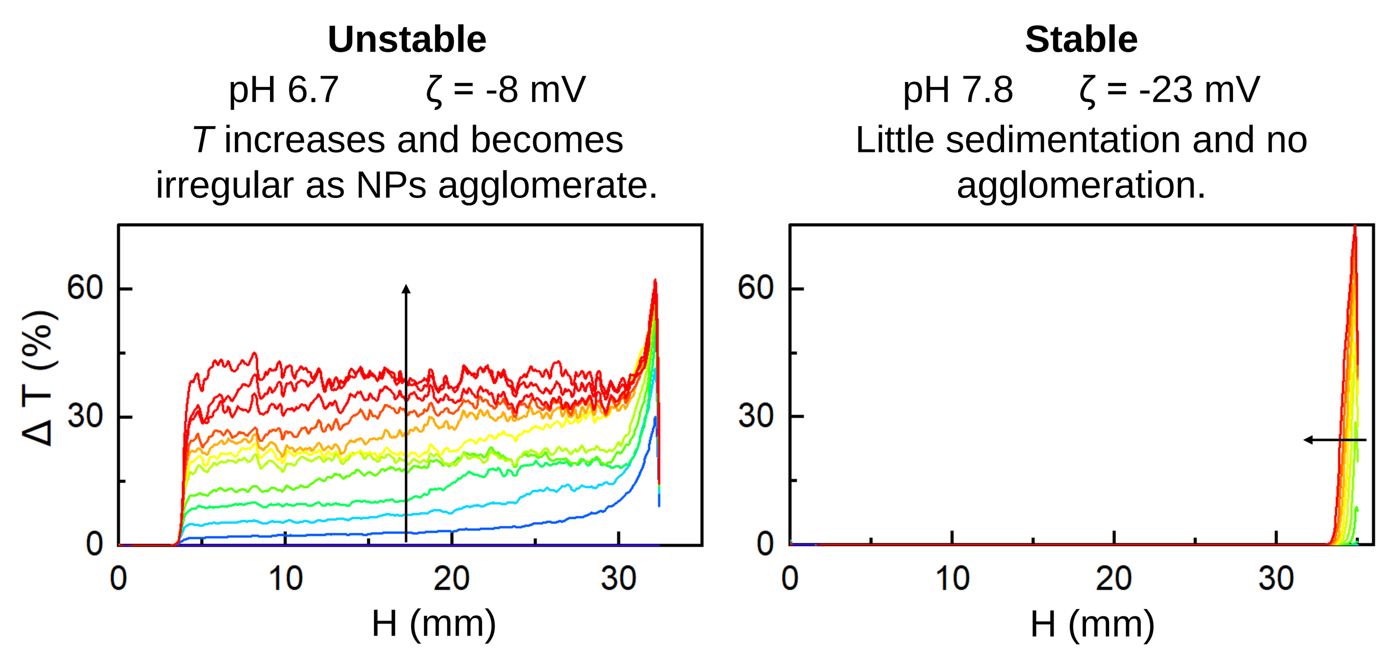
$$TSI(t) = \frac{1}{N_h} \sum_{t_i=1}^{t_{max}} \sum_{z_i=z_{min}}^{z_{max}} |BS,T(t_i,z_i) - BS,T(t_{i-1},z_i)|$$

Measuring **ζ in solvents** is more challenging: a glass dip cell is used. DLVO stabilized dispersions were excluded from **HDP** calculation. The ***RTSI*** (Relative *TSI*) and $\mathbf{d_{SMLS}}$ were used to compare solvents.

$$RTSI(t) = TSI(t) \times \frac{\eta}{(\rho_{particle} - \rho_{solvent})}$$

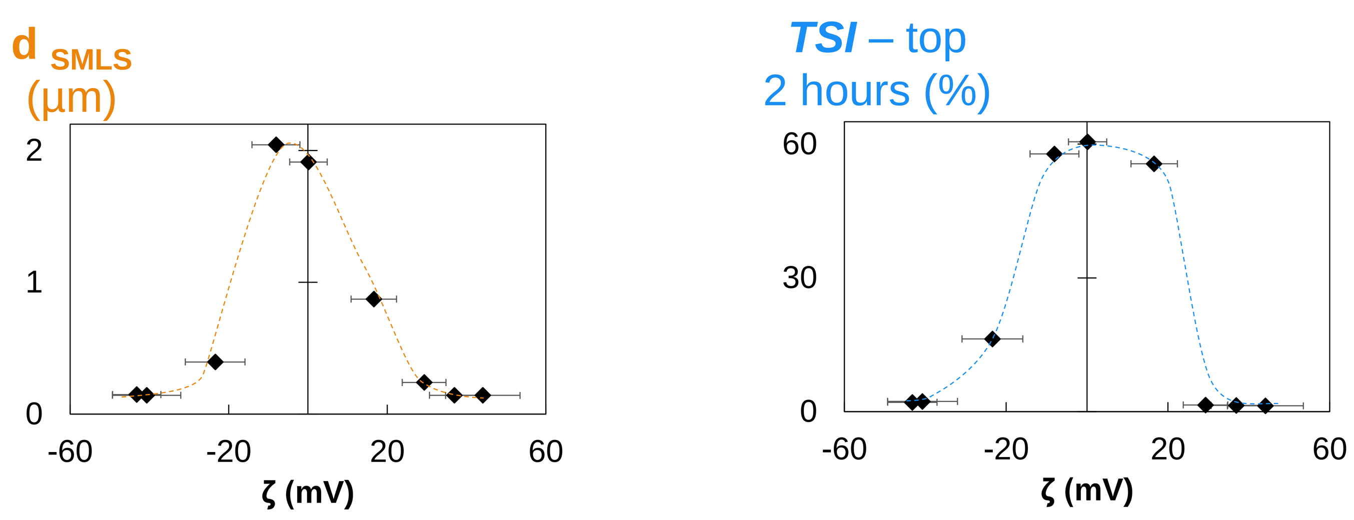
Aqueous dispersions

pH-dependant stability was observed in 1 g/L TiO_2 dispersions. HCl, NaOH and NaCl are used to adjust pH and keep ionic strength at 10^{-3} M. Stabilisation due to electrostatic repulsion is visible on Turbiscan profiles.



T variations over 2 hours: low and high ζ dispersions

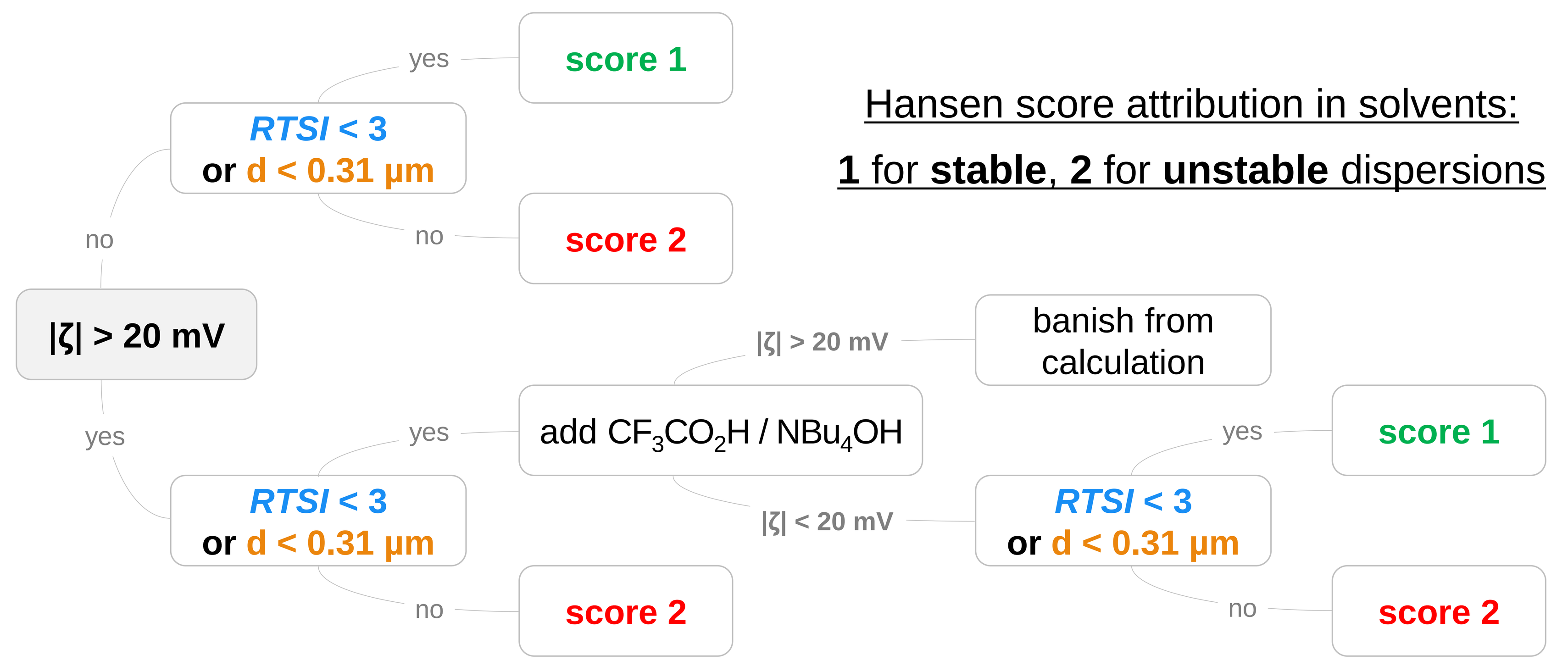
Turbiscan monitoring over **2 hours** discriminates stable and unstable dispersions. Both ***TSI*** and $\mathbf{d_{SMLS}}$ correlate with ζ, in accordance with DLVO theory: they can be used as **quantitative descriptors** of dispersions **stability**.



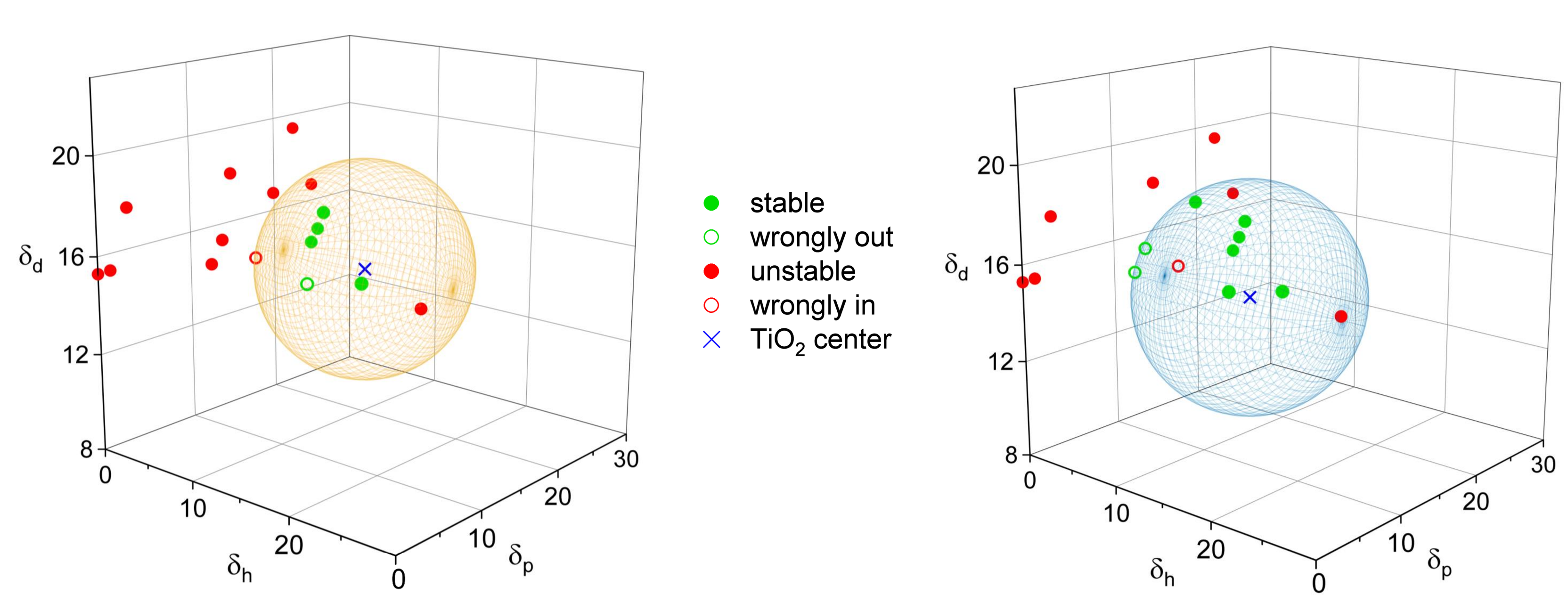
ζ correlation with *TSI* and SMLS diameter in aqueous dispersions

Hansen Dispersibility Parameters determination

Hansen score attribution in solvents:
1 for stable, **2** for unstable dispersions



Hansen scores are given on arbitrary criteria (*RTSI* < 3, d < 0.31 µm) and when electrostatic repulsion is negligible, i.e. |ζ| < 20 mV. Score 2 is also given to unstable dispersions at high |ζ| (no electrostatic contribution).



Fit 0.9
$\delta_d = 15.1$ $\delta_p = 15.5$ $\delta_h = 14.1$

Fit 0.7
$\delta_d = 14.5$ $\delta_p = 12.7$ $\delta_h = 12.7$

References

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Conclusion

- ✓ Turbiscan $\mathbf{d_{SMLS}}$ and ***(R)TSI*** are reliable **stability descriptors** to discriminate samples within **2 hours**
- ✓ **5/20** solvents would have been **misplaced** in the Hansen sphere without **DLVO considerations**
  In 3/20 solvents, **stability cause** is **unidentified** (|ζ| > 20 mV and highly stable): 2-MeTHF, $CHCl_3$ and DMSO
  2/20 solvents were **electrostatically stabilized**: pyridine and EtOH, and destabilized at low |ζ|
- ✓ $\mathbf{d_{SMLS}}$ gives a more **precise HDP sphere** than *RTSI* (Fit = 0.9, smaller radius)
- ✓ Determined **HDP** for **TiO_2 P25** are $\delta_d = 15.1$ $\delta_p = 15.5$ $\delta_h = 14.1$

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