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Unveiling structure

APPLICATION NOTE

Release of coating material during dispersion of a commercially available TiO_2

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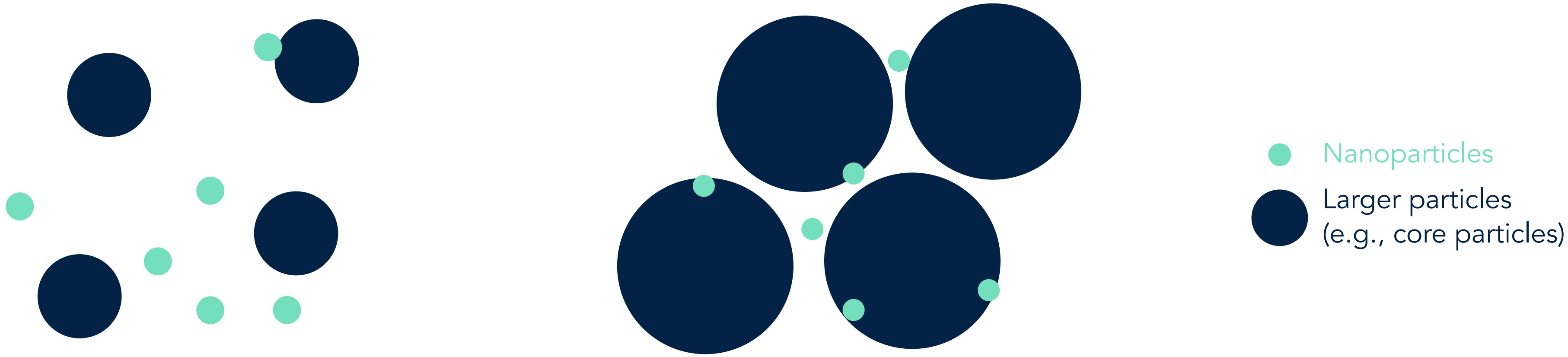
Definition of nanomaterial according to the European Commission

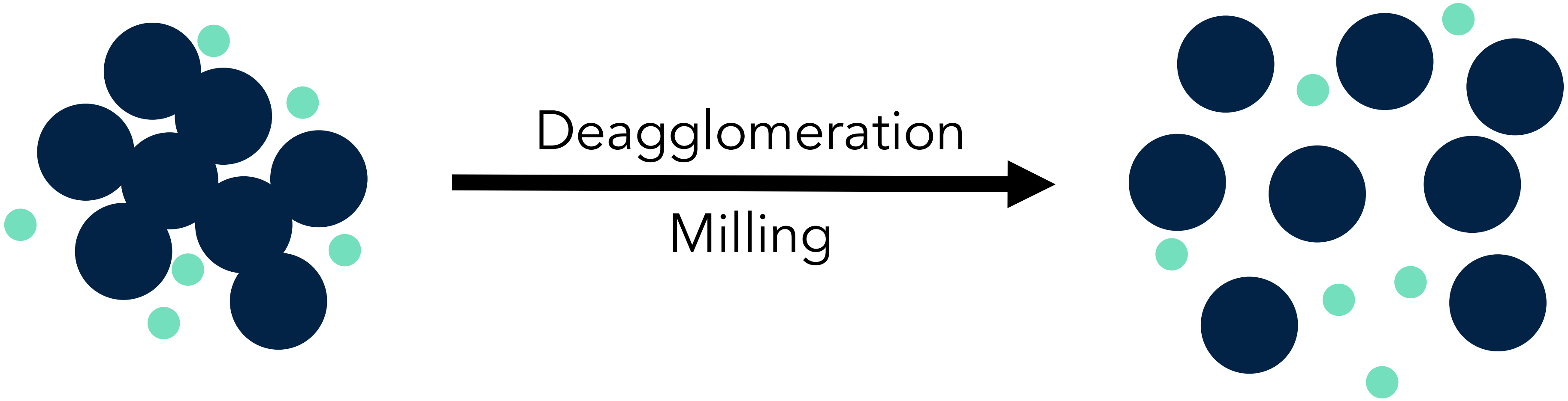
„ … 50 % or more of the particles in the number size distribution […] in the size range 1 nm -100 nm." https://euon.echa.europa.eu/definition-of-nanomaterial



Sample A **Sample B**

The nanoparticle number fraction in both cases is 60%, but the total amount of nanoparticles in a sample (or per gram sample) are very different due to the different sizes of the particles with diameter > 100 nm. From a practical perspective Sample B is of lesser concern than Sample A.

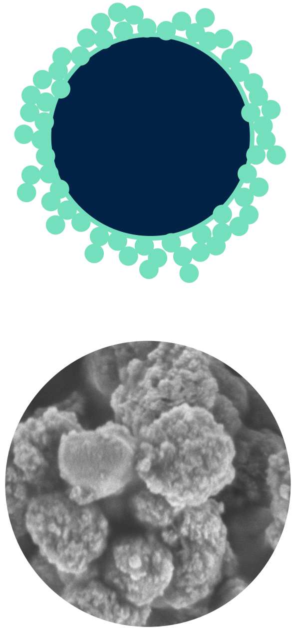
Reducing the nanoparticle concentration by milling ?

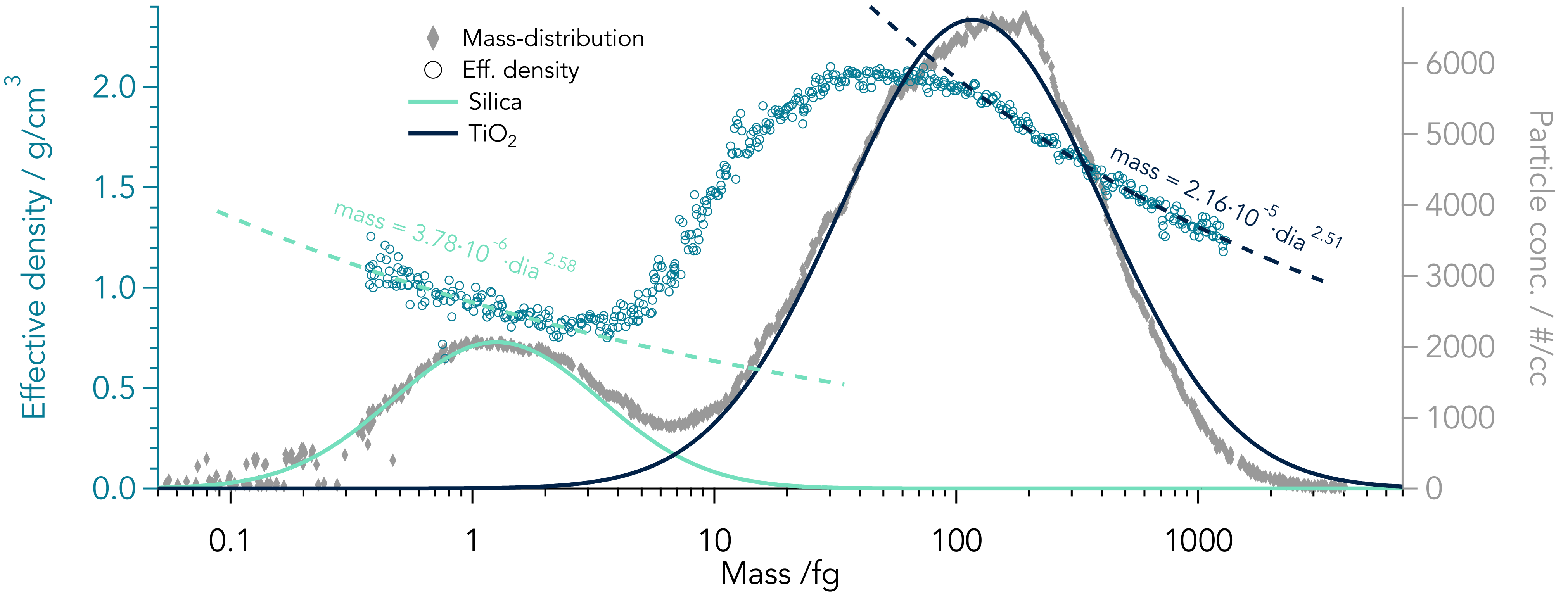


The milling or dispersion of a single large particle produces numerous smaller particles. This can lead to an apparent increase in the average particle size, since sizing methods normalize the result by the signal intensity. Here, the fraction of unbound nanoparticles is „diluted" due to an increase in overall particle number.

The absolute number of nanoparticles in one gram of material is a suitable alternative to such a number-percentage.

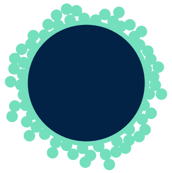
White pigment for dispersion paints

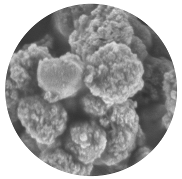




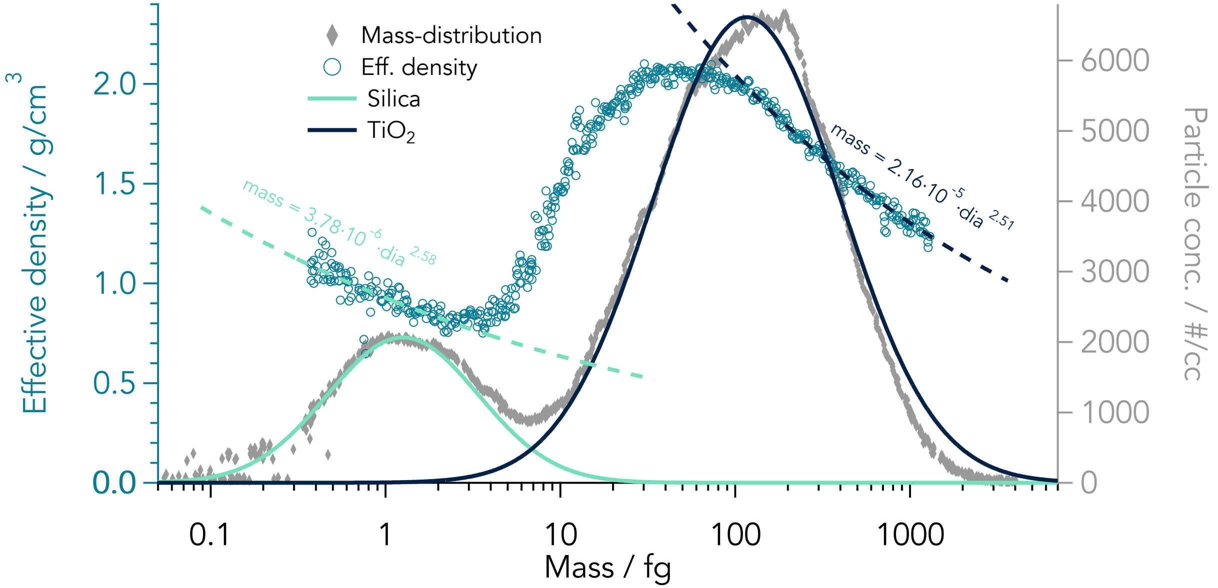
Core-shell structure: Rutile with layers of dense (hard) and precipitated (soft) silica

White pigment for dispersion paints: Low intensity deagglomeration





m_{50}	d_{50}	Particles per gram	Mass fraction		«Fractal»-index
			measured	spec-sheet	
Precipitated aggregated silica					
1.7fg	139nm	$9.9 \cdot 10^{11}$ /g	0.2%	<18%	2.58
Spherical rutile core + silica coating					
117 fg	482 nm	$40 \cdot 10^{11}$ /g	99.8%	>82%	2.51

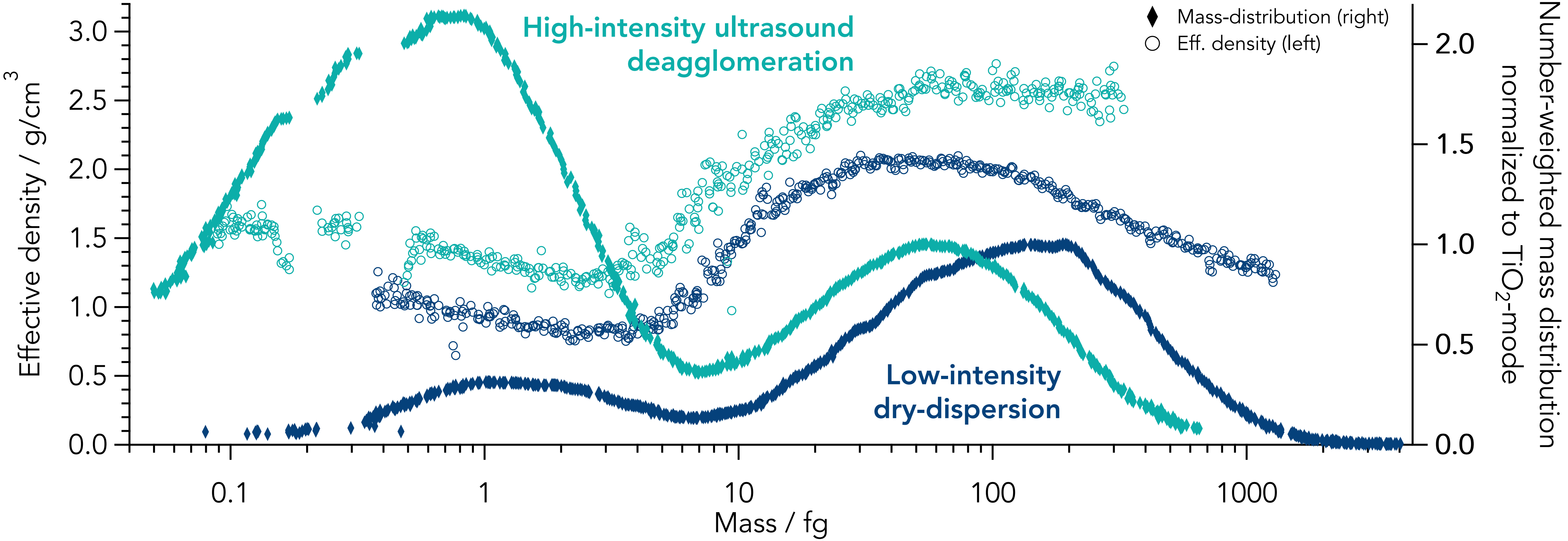


1. A fraction of the silica coating is sheared off during the deagglomeration in a venturi-nozzle.
2. The effective particle densities are below the material densities (silica: 2.2 g/cm^3; rutile: 4.2 g/cm^3) and decline with increasing particle size, which is characteristic for aggregated and agglomerated particles.
3. Number-weighted distributions of the particle mass allow to calculate the **total number of particles per gram.**

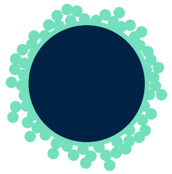
Low vs high deagglomeration intensity

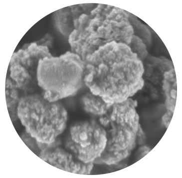
Increasing amount of sheared off coating material

Fully deagglomerated TiO_2-particles, higher and constant eff. density

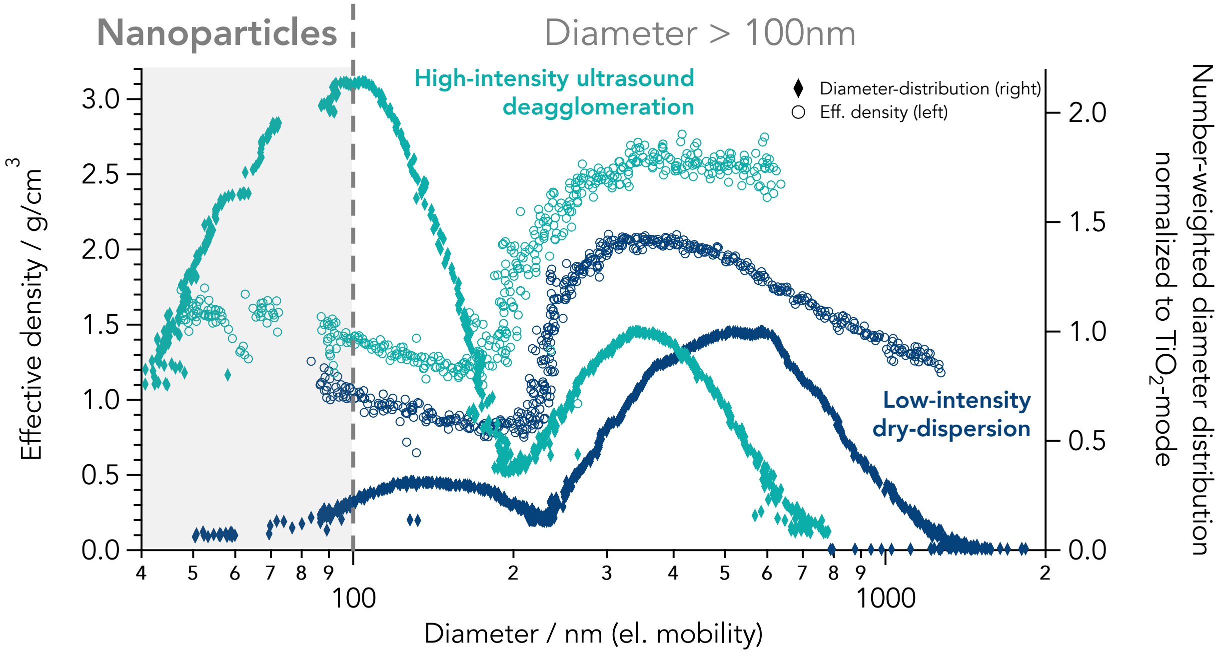


Release of nanoparticles during deagglomeration



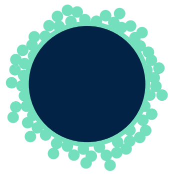


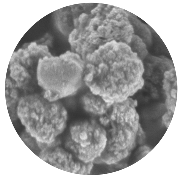
Total particle number	Nanoparticle content		Mass fraction of isolated silica
	percentage	absolute	
dry-dispersion in venturi nozzle; 4bar air pressure			
$50 \cdot 10^{11}$ /g	**4%**	**$2 \cdot 10^{11}$ /g**	0.2%
ultrasound deagglomeration in water; energy input 200J/ml			
$380 \cdot 10^{11}$ /g	**47%**	**$180 \cdot 10^{11}$ /g**	4%



1. With increasing deagglomeration intensity 1st more of the silica coating gets sheared off, consequently the total amount of particles increases by factor ≈ 8 and 2nd the TiO_2-particles are fully deagglomerated. The density indicates the isolated core particles are still coated with some of the soft silica.
2. The total amount of nanoparticles increases by factor 90. The deagglomeration also reduces the mass and size of the core particles and thus increases their number. This «dilutes» the nanoparticle concentration.

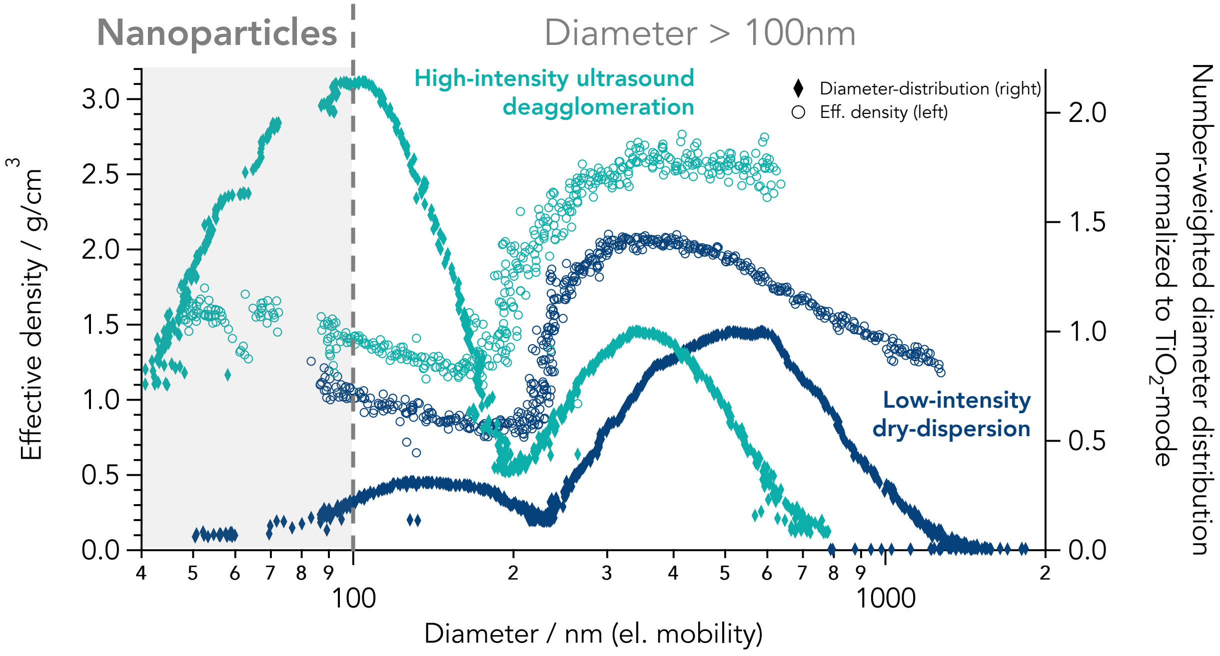
Effect of deagglomeration method





Sheared off silica coating			Rutile core + coating		
m_{50}	d_{50}	fractality	m_{50}	d_{50}	fractality
dry-dispersion in venturi nozzle; 4bar air pressure					
1.3 fg	139 nm	2.58	117 fg	496 nm	**2.51**
ultrasound deagglomeration in water; energy input 200J/ml					
0.47 fg	86 nm	2.79	61 fg	356 nm	**2.99**

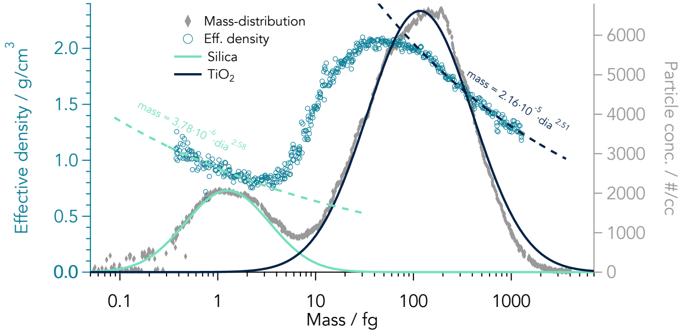
mass = $\text{diameter}^{\text{fractal-index}}$



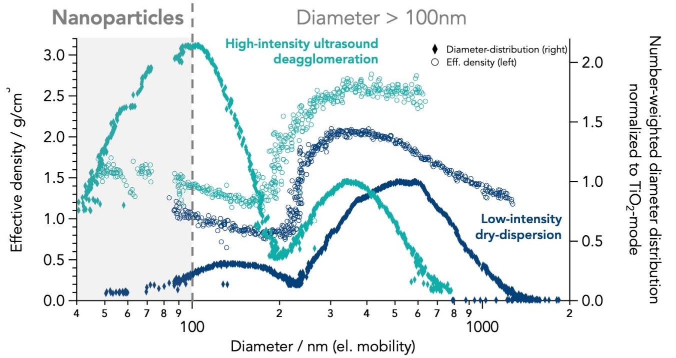
1. There is a clear difference in the structure of the particles, indicated by a change in fractality and density.
2. A fractal index of 2.99 indicates that the rutile particle are **spherical and non-aggregated** after sonication
3. The increase in effective density and fractality for precipitated silica (pure as well as in pigment preparations) has been observed by femtoG recently. For this effect, there is **no explanation** yet.

Summary

1. The particle mass is a fundamental unit that describes the size of a particle.
   → There is one mass, but 10+ equivalent diameters



2. Multicomponent systems can be analyzed in <15 min
   → Breakage and restructuring can be observed.



1. The number-fraction and the absolute number of nanoparticles in a powder carry different information.

Total particle number	Nanoparticle content		Mass fraction of isolated silica
	percentage	absolute	
dry-dispersion in venturi nozzle; 4bar air pressure			
$50 \cdot 10^{11}$ /g	**4%**	**$2 \cdot 10^{11}$ /g**	0.2%
ultrasound deagglomeration in water; energy input 200J/ml			
$380 \cdot 10^{11}$ /g	**47%**	**$180 \cdot 10^{11}$ /g**	4%

Disclaimer

The analysis and results presented in this application paper pertain specifically to the sample evaluated during this study. While the described technology offers a novel approach to determining the coating adherence stability on titanium dioxide core particles and is generally applicable to any coated particles, the specific results may vary depending on the batch of the sample analyzed, as well as the feedstock and processing conditions used. Therefore, the findings and conclusions should not be generalized to all coated particles without further validation on different batches, feedstocks, and processing conditions. The data and conclusions presented herein are provided for informational purposes only and should not be interpreted as guarantees or warranties of performance for other samples or under different conditions. In no event shall femtoG be responsible or liable for any direct, indirect, punitive, incidental, special, or consequential damages whatsoever arising out of or connected with the use of, misuse of, or reliance upon such results or analysis.

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Appendix 1: Experimental setup

What is a particle? Importance of sample preparation!

The preparation of a sample material prior to any particle size analysis defines which structural level will be detected. Often there is no “smallest dispersible unit”. With increasing dispersion intensity (~force) and increasing dispersion duration (~energy) the particles become smaller. This can be used to characterize the mechanical stability of coating and the gradual release of nanoparticle during dispersion.

Different dispersion method are compatible with the femtoG method:

Dry dispersion
Powder → Aerosolization → Deagglomeration in Venturi nozzles

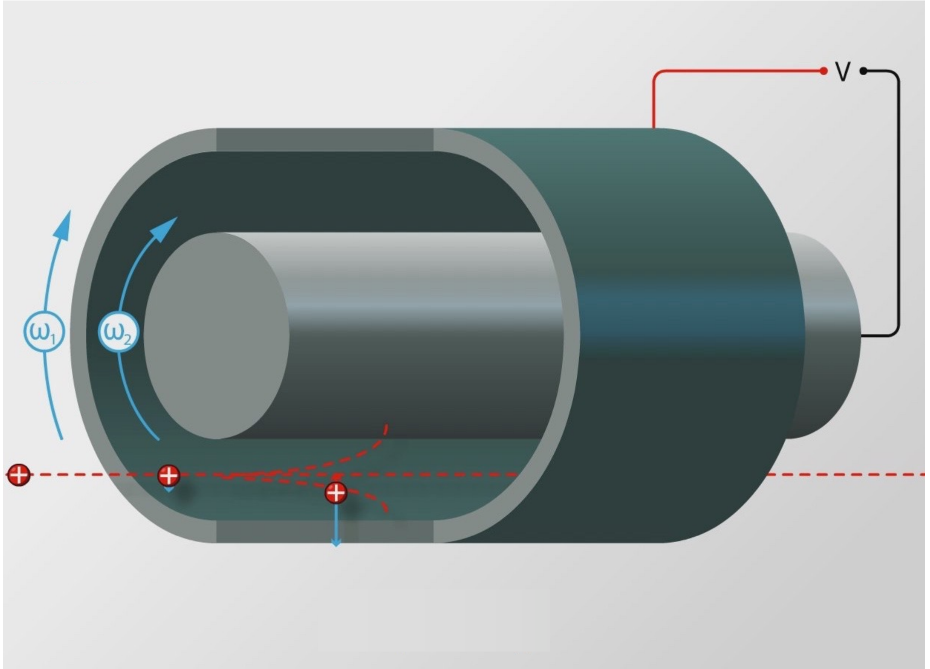
Wet dispersion
Suspension → sonification 10 – 1000 J/ml → Spray dispersion

working fluids: water, ethanol, acetone, hexane, …

Direct sampling from reactor

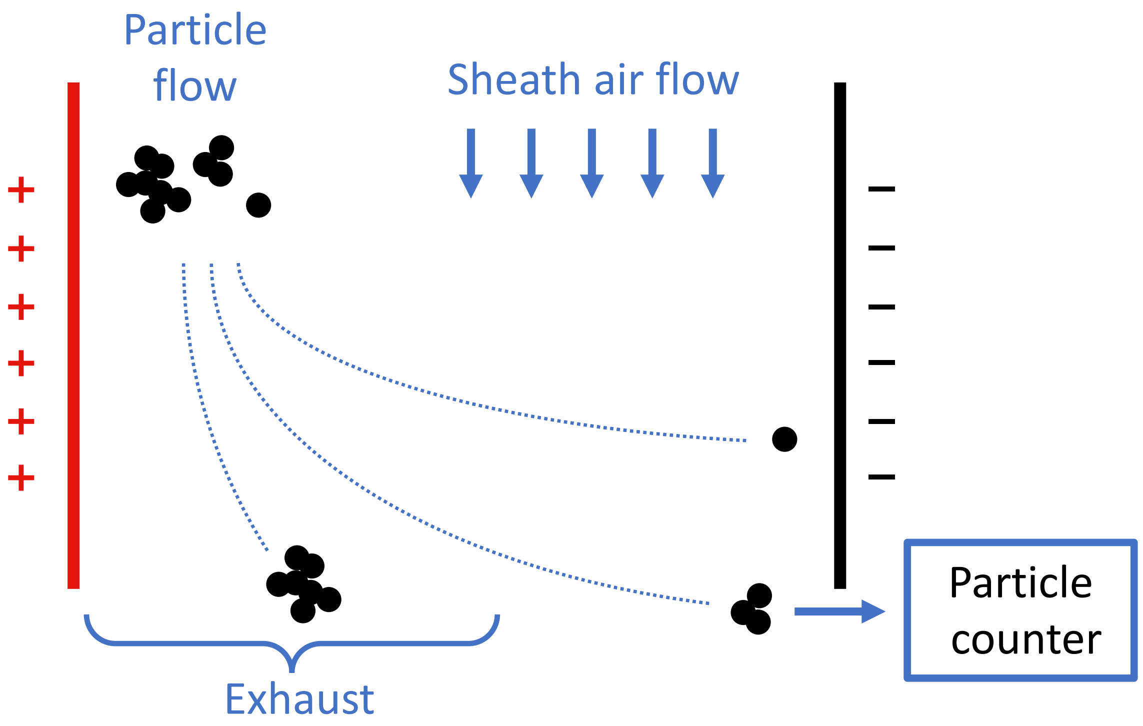
What is the true size of a particle? → Parallel analysis of mass and diameter!

Centrifugal Particle Mass Analyzer



Centrifugal force vs electrostatic force

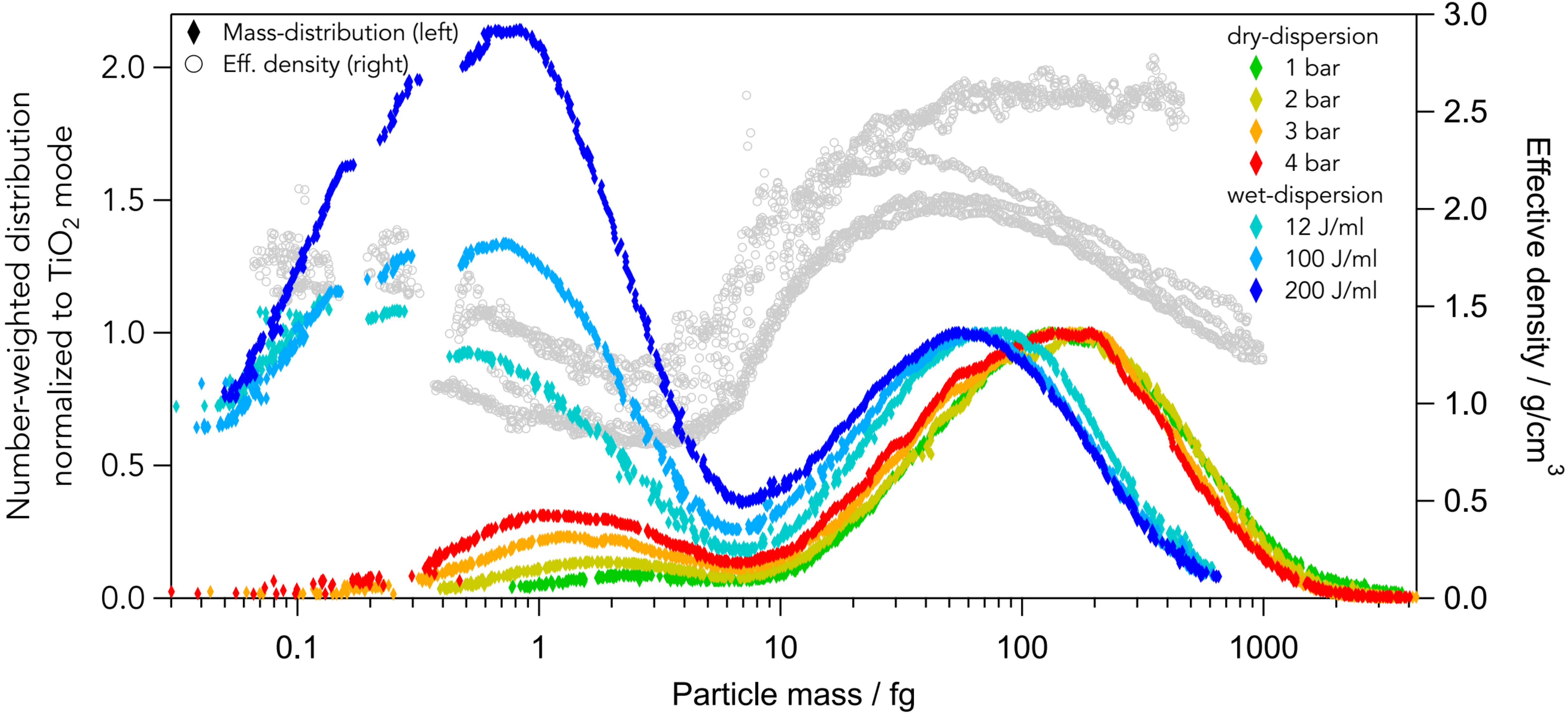
Particle mobility size analyzer



Electrostatic force vs drag force

Appendix 2:
Full data set

Coating stability:
Dry dispersion vs. ultrasound dispersion in water



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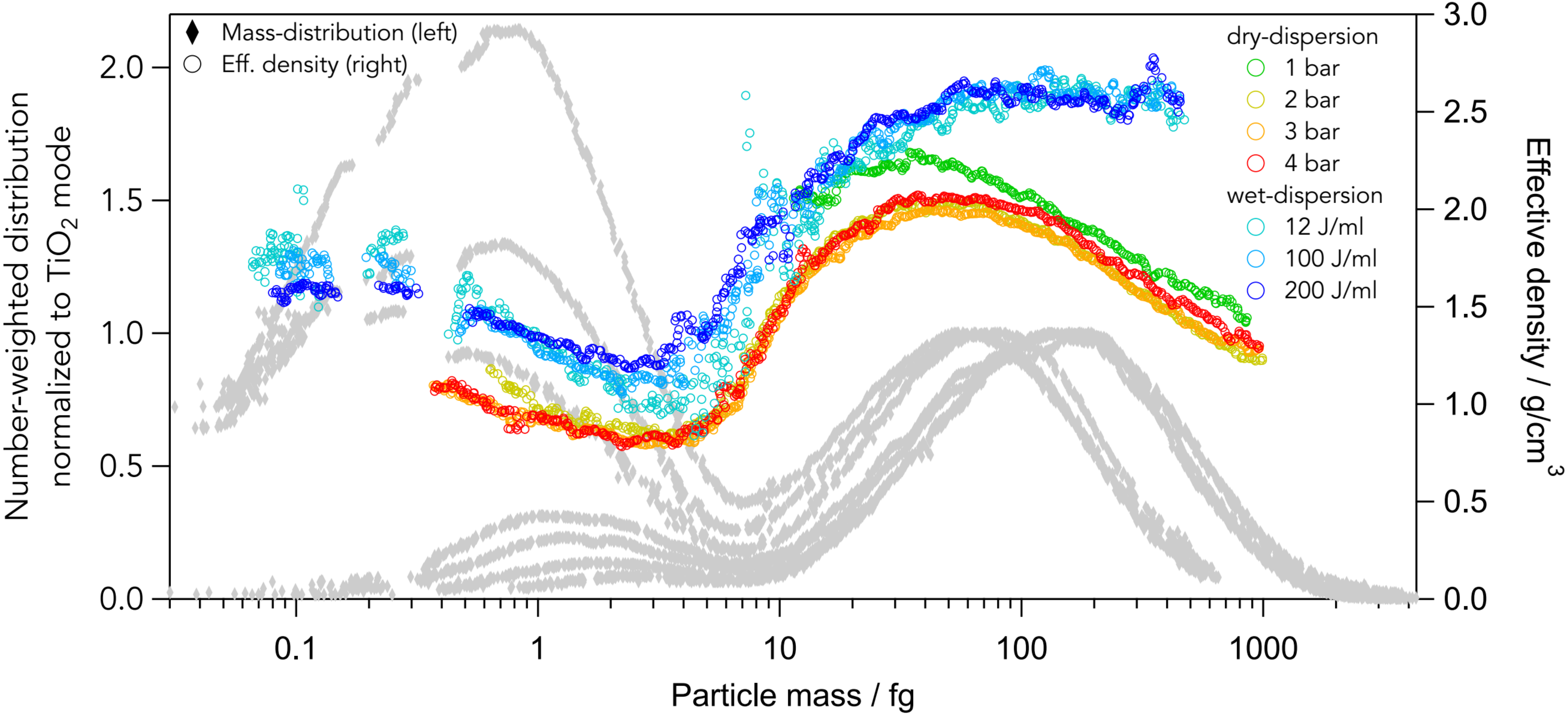

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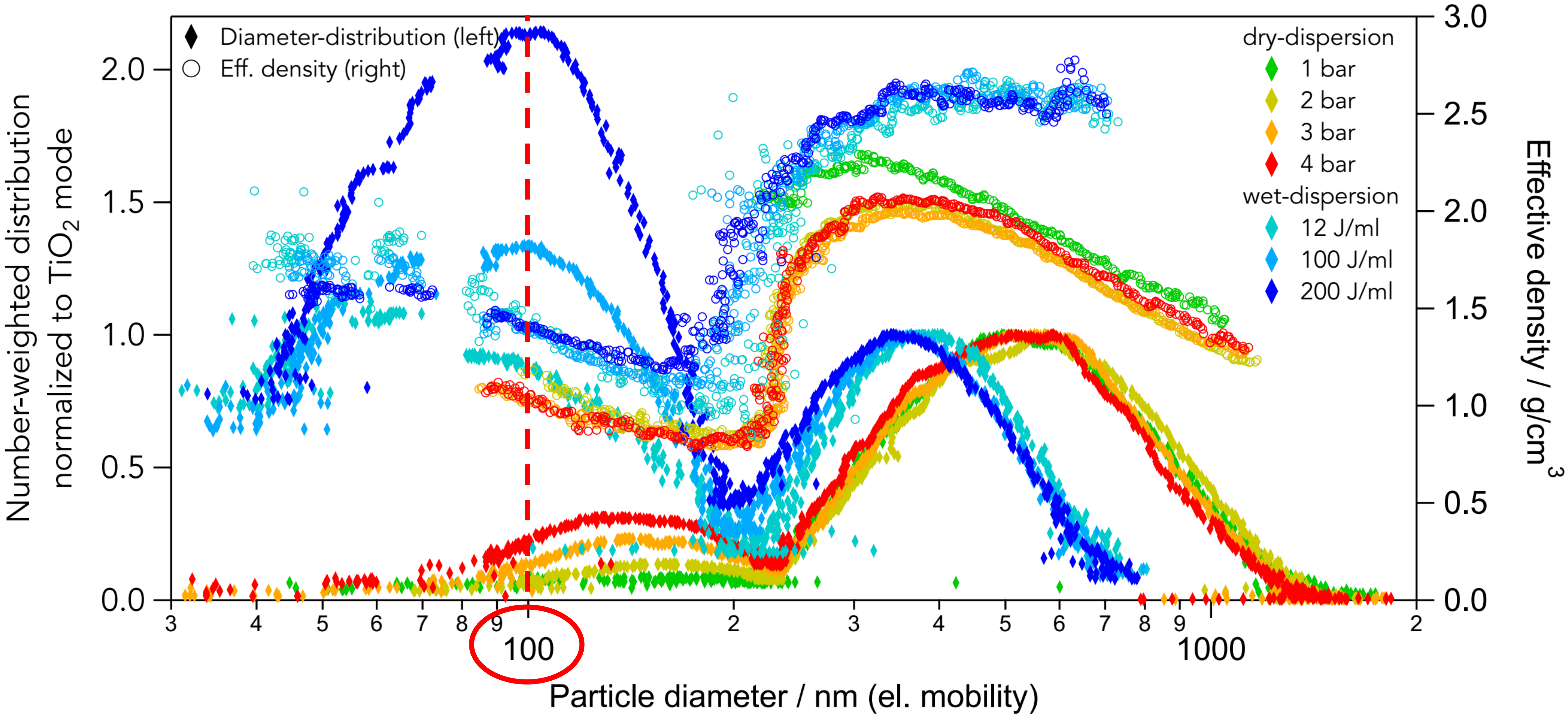

Nanoparticle content vs. deagglomeration

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	Dry-dispersion				Wet-dispersion		
	1 bar	2 bar	3 bar	4 bar	12 J/ml	100 J/ml	200 J/ml
Total							
Total particle number / g^{-1}	3.6E+12	3.6E+12	4.5E+12	5.0E+12	2.3E+13	2.8E+13	3.8E+13
Nanoparticle content by number (sub-100nm el. mobility dia.)	0.2%	1%	3%	4%	49%	45%	47%
Absolute nanoparticle content / g^{-1} (sub-100nm el. mobility dia.)	**5.7E+09**	**3.9E+10**	**1.2E+11**	**2.0E+11**	**1.1E+13**	**1.3E+13**	**1.8E+13**
Silica							
Mode mass / fg	2.2	1.7	1.4	1.3	0.22	0.38	0.47
Mode diameter / nm	175	156	146	139	60	79	86
Total particle number / g^{-1}	1.6E+11	3.2E+11	6.9E+11	1.0E+12	1.5E+13	1.9E+13	2.9E+13
Number fraction	5%	9%	15%	20%	65%	68%	75%
Mass fraction	0%	0%	0%	0%	2%	3%	4%
TiO2							
Mode mass / fg	141	141	125	117	73	65	61
Mode diameter / nm	522	539	514	496	380	361	356
Total particle number / g^{-1}	3.4E+12	3.3E+12	3.8E+12	4.0E+12	8.0E+12	9.0E+12	9.4E+12
Number fraction	95%	91%	85%	80%	35%	32%	25%
Mass fraction	100%	100%	100%	100%	98%	97%	96%