

Supplementary material

for

The Self-Assembly of Silica Nanoparticles at Water-Hydrocarbon Interfaces: Insights from *In-Operando* Small-Angle X-Ray Scattering Measurements and Molecular Dynamics Simulations

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The scattering of the suspended particles

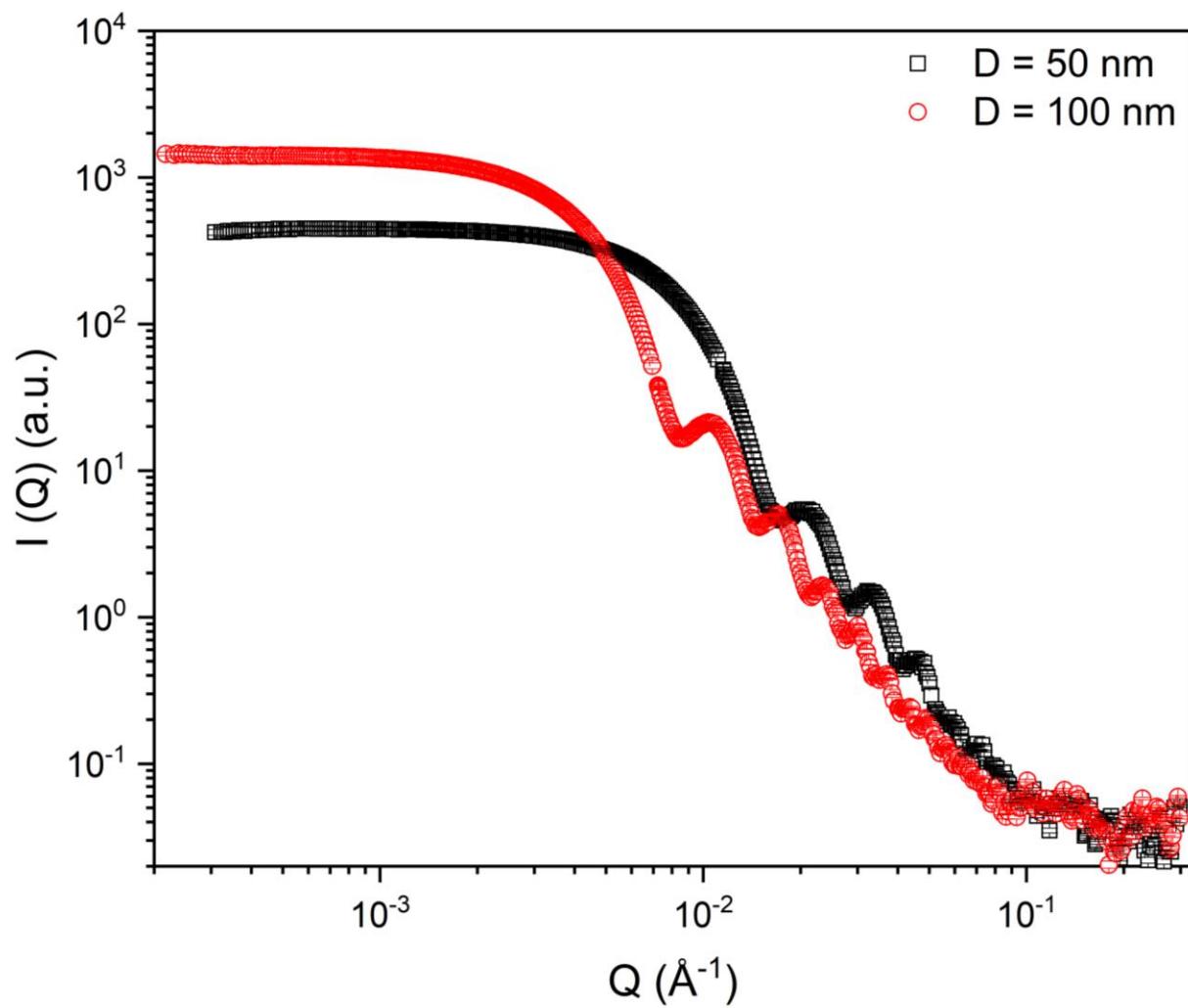


Figure S1. Scattering curves of silica nanoparticles with diameters of 50 nm and 100 nm suspended in MilliQ water.

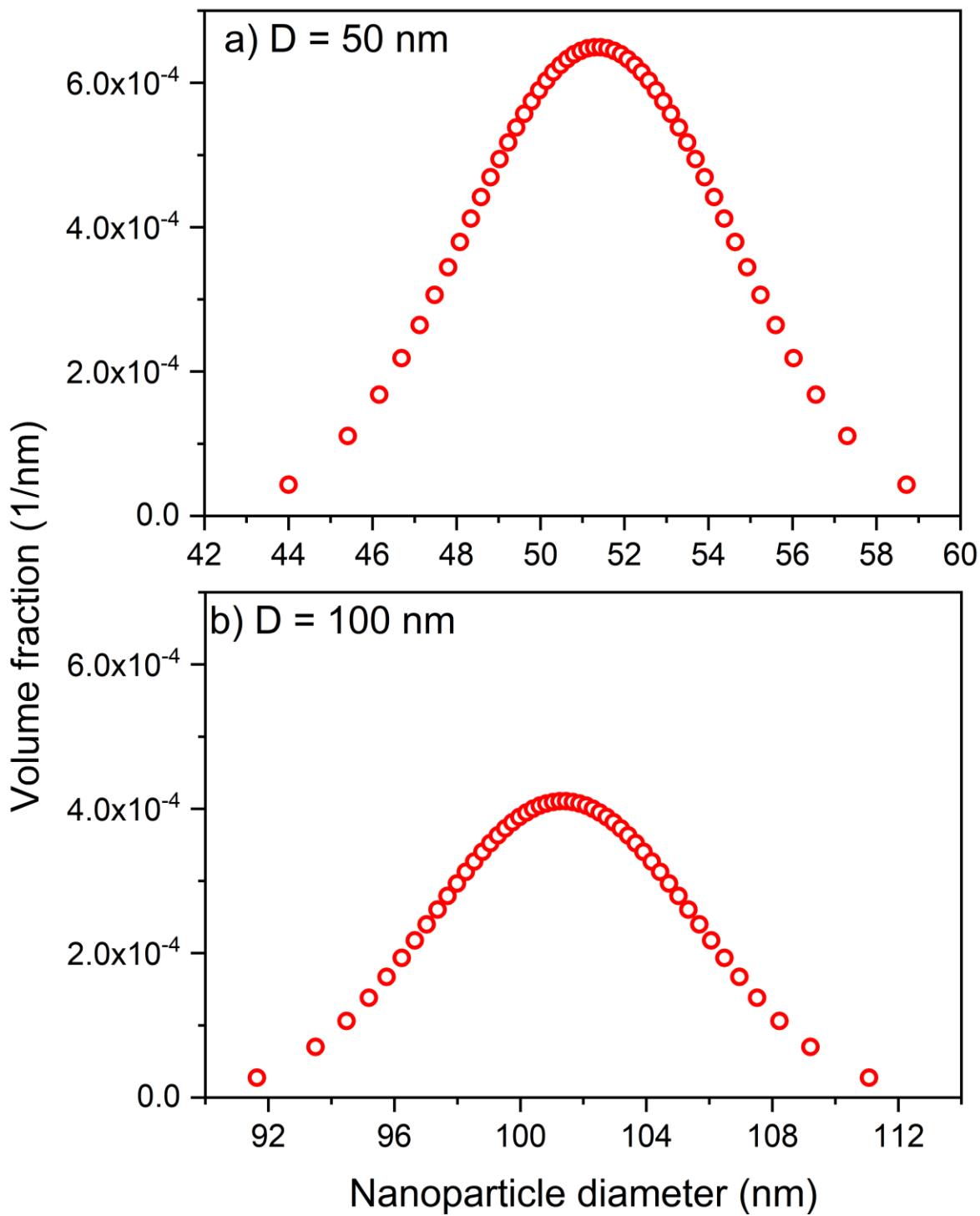


Figure S2. The size distribution of the suspended silica nanoparticles with a diameter of (a) 50 nm and (b) 100 nm governed from the USAXS/SAXS modeling.

Table S1. LJ parameters and the charges for atomic species of silica nanoparticles, toluene, and heptane.

Atom	σ (nm)	ε (kJ/mol)	q (e)	Ref.
Parameters for Silica				
Si	0.33020	7.7006×10^{-6}	2.1000	[1]
O bridging	0.31664	0.650190	-1.0500	[1]
O nonbridging	0.31664	0.650190	-0.9500	[1]
H	0.00000	0.000000	0.4250	[1]
Parameter for Toluene				
C (Toluene ring)	0.35000	0.292880	-0.1150	[3]
H (Toluene ring)	0.24200	0.125520	0.1150	[3]
C (Toluene tail)	0.35000	0.276144	-0.0650	[3]
H (Toluene tail)	0.25000	0.125520	0.0600	[3]
Parameters for Heptane				
C (Heptane terminal)	0.35000	0.276144	-0.1800	[3]
H (Heptane terminal)	0.25000	0.125520	0.0600	[3]
C (Heptane center)	0.35000	0.276144	-0.1200	[3]
H (Heptane center)	0.25000	0.125520	0.0600	[3]

σ is the finite distance at which the interatomic potential is zero.

ε is the depth of the potential well.

q is the atomic charge.

Fractals dimensions

- From the Intensity vs. q (\AA^{-1}) plots, where $I(q)$ is proportional to $q^{-\tau}$. Where, $\tau = D_m$ (mass fractal) and $\tau = 6 - D_s$ (surface fractal)
- From experimental data, if $\tau < 3$, then it is a mass fractal
 - For $3 < \tau < 4$, then it is a surface fractal
- Fractal dimension can lie within the following ranges
 - $0 < D_m < 3$ (mass fractal)
 - $2 < D_s < 3$ (surface fractal)¹⁻⁵
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Table S2. Calculations of fractal dimensions for distance-dependent measurements

Sample ID		Fractal type	Fractal dimension	Description
Heptane – 50 nm	0.00 mm	Surface fractal	$D_s = 2.3845$	Rough surface fractals
	0.25 mm	Surface fractal	$D_s = 2.3994$	Rough surface fractals
	0.50 mm	None		
	0.75 mm	None		
	1.00 mm	None		
	1.25 mm	None		
	1.50 mm	None		
Heptane – 100 nm	0.00 mm	Surface fractal	$D_s = 2.4883$	Rough surface fractals
	0.25 mm	Surface fractal	$D_s = 2.4517$	Rough surface fractals
	0.50 mm	None		
	0.75 mm	None		
	1.00 mm	None		
	1.25 mm	None		
	1.50 mm	None		
Toluene – 50 nm	0.00 mm	Surface fractal	$D_s = 2.51705$	Rough surface fractals
	0.25 mm	Surface fractal	$D_s = 2.6443$	Rough surface fractals
	0.50 mm	None		
	0.75 mm	None		
	1.00 mm	None		
	1.25 mm	None		
	1.50 mm	None		
Toluene – 100 nm	0.00 mm	Mass fractal	$D_m = 2.1613$	Clustered network
	0.25 mm	Mass fractal	$D_m = 2.23573$	Clustered network
	0.50 mm	Mass fractal	$D_m = 2.17751$	Clustered network
	0.75 mm	Mass fractal	$D_m = 2.15417$	Clustered network
	1.00 mm	Mass fractal	$D_m = 2.25469$	Clustered network
	1.25 mm	None		
	1.50 mm	None		

Table S3. Calculations of fractal dimensions for time-dependent measurements

Sample ID		Fractal type	Fractal dimension	Description
Heptane – 50 nm	00 min	Surface fractal	$D_s = 2.3712$	Rough surface fractals
	03 min	Surface fractal	$D_s = 2.3805$	Rough surface fractals
	08 min	Surface fractal	$D_s = 2.3851$	Rough surface fractals
	11 min	Surface fractal	$D_s = 2.3845$	Rough surface fractals
Heptane – 100 nm	00 min	Surface fractal	$D_s = 2.4965$	Rough surface fractals
	03 min	Surface fractal	$D_s = 2.4799$	Rough surface fractals
	08 min	Surface fractal	$D_s = 2.4844$	Rough surface fractals
	11 min	Surface fractal	$D_s = 2.4883$	Rough surface fractals
Toluene – 50 nm	00 min	Surface fractal	$D_s = 2.5284$	Rough surface fractals
	03 min	Surface fractal	$D_s = 2.4964$	Rough surface fractals
	08 min	Surface fractal	$D_s = 2.5034$	Rough surface fractals
	11 min	Surface fractal	$D_s = 2.5170$	Rough surface fractals
Toluene – 100 nm	00 min	Mass fractal	$D_m = 2.6297$	Clustered network
	03 min	Mass fractal	$D_m = 2.6655$	Clustered network
	08 min	Mass fractal	$D_m = 2.2381$	Clustered network
	11 min	Mass fractal	$D_m = 2.1613$	Clustered network

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