Supplementary material

Towards a framework for evaluating and reporting Hansen solubility parameters: Applications to particle dispersions

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Materials & Methods

Synthesis of SiN_x

A tubular hot-wall reactor was used to synthesize SiN_x nanoparticles.[1] The reactor consists of a ceramic reaction tube, a furnace, a gas feeding system, a filter, and an exhaust gas burning system. The precursor gases were fed through a gas nozzle that is supported by a co-axial sheath gas flow that reduces the chemical vapor deposition (CVD) growth on the inner walls of the reaction tube and the recirculation of the precursor gases. The gas mixture was then pyrolysed in the 80 cm long hot zone of the reaction tube. This hot zone was created by a resistively heated furnace. The reaction tube had an inner diameter of 60 mm and a length of 2 m. After pyrolysis, the nanoparticle-laden waste gas was filtered through a porous membrane. The waste gas was burned, and the nanoparticles were harvested from the filter, either in ambient or inert atmosphere. After collection of the nanoparticles, a sieving step was added to exclude unwanted CVD-particles and aggregates bigger than 63 µm (mesh size).
Two precursor gases were used, ammonia (N50, Air Liquide) and 10 % monosilane in argon (UHP Silane, Argon N50, Air Liquide). The sheath gas was nitrogen. Process parameters used for the synthesis of SiN_x nanoparticles of this work were: 20 slm of nitrogen sheath gas and 2.6 slm of precursor gas mixture, resulting in a total gas flow of 22.6 slm. The molar precursor ratio for the gas mixture $r = \frac{\dot{v}(NH_3)}{\dot{v}(SiH_4)}$ was 3. The synthesis temperature was 900 °C and the pressure inside the reactor was kept constant at 1 bar.

Probe liquids

All probe liquids (PLs) used in this study including their abbreviations are listed in Table S1. As described in the previous work of Süss et al.[2] and Stauch et al.,[3] liquids were selected in such way that their HSP coordinates span a wide range of the 3D Hansen space.

Table S1: List of PLs used to study the dispersion behavior of SiN_x nanoparticles along with their HSP values.

Liquids	Abbreviation	$\delta D/MPa^{0.5}$	$\delta P/MPa^{0.5}$	$\delta H/MPa^{0.5}$
Acetone	Ace	15.5	10.4	7
Diacetone alcohol	DAA	15.8	8.2	10.8
Ethanol	EtOH	15.8	8.8	19.4
Ethyl acetate	EA	15.8	5.3	7.2
Hexane	Hex	14.9	0	0
2-Propanol	IPA	15.8	6.1	16.4
Methanol	MeOH	14.7	12.3	22.3
N-Methyl-2-pyrrolidone	NMP	18	12.3	7.2
Propylene carbonate	PC	20	18	4.1
Tetrahydrofuran	THF	16.8	5.7	8
Toluene	Tol	18	1.4	2
Water	-	15.5	16	42.2

Dispersion procedure

SiN_x dispersions (0.0083 wt.%) were prepared by dispersing the powder in a defined set of PLs (listed in Table S1). The suspensions were introduced into an ultrasonic bath (Elmasonic S30, 37kH, 80 W, Elma Schmidbauer GmbH) for 30 minutes at room temperature, for adequate mixing. The water inside the bath was replaced every 10 minutes to avoid overheating.

Scanning electron microscopy imaging

Scanning electron microscopy (SEM) was performed using a JEOL JSM-7500F microscope. The acceleration voltage was set to 5 kV. Samples of SiN_x dispersed in acetone, diacetone alcohol, ethanol, N-Methyl-2-pyrrodinone, toluene and water were prepared according to the dispersion procedure described above. Then, 1 µl of dispersion was dropped on a cleaned silicon wafer. Samples were dried overnight under ambient conditions.

Analytical centrifugation analysis

Analytical centrifugation (AC) measurements were performed with a LUMiSizer® 651 (LUM GmbH, Berlin, Germany). For a typical AC run, a blue-light wavelength of 410 nm was used. Polycarbonate and polyamide cells (LUM GmbH, Berlin, Germany) with an optical path length of 2 mm were used depending on their compatibility with liquids. The sample cells were filled with 300 µl of the sample. The temperature was set to 7 °C for all measurements. This is in accordance with the recommendation made by Uttinger et al.[4] to avoid convective instabilities due to thermal gradients. Sample cells filled with the SiN_x dispersions were inserted into the rotor immediately after the ultrasonication step. Centrifugation was performed with no delay at 1500 rpm corresponding to a relative centrifugal acceleration (RCA) of 327 at the cell bottom for 50 minutes.

S score and stability trajectory

9-point moving averaged raw data for the transmission profiles was accessed from the AC software (SepView®). The raw data was manually copied into spreadsheet software and saved as comma-separated or "xlsx" file formats. Scientific libraries in Python language were used for calculating S scores and plotting stability trajectories. Numerical processing was performed with NumPy[5] and Pandas[6] and plotting was done using Matplotlib.[7]

The transmission profile (T_i) was normalized by subtracting the corresponding mean of the profile $\bar{T}_i$ across radial position and dividing by the standard deviation σ_{T_i} of the profile resulting in a normalized profile (Z_i). This step is also known as z-normalization and is repeated for each profile captured.

$$Z_i = \frac{T_i - \bar{T}_i}{\sigma_{T_i}} \quad (1)$$

Further, the median of each normalized profile is calculated.

$$\tilde{Z}_i = median(Z_i) \quad (2)$$

The median absolute deviation (MAD) is then calculated for each transmission profile, resulting in an S score $\tilde{S}_i$ for each time point.

$$\tilde{S}_i = median(|Z_i - \tilde{Z}_i|) \quad (3)$$

Stability trajectories were obtained by plotting the calculated S scores versus time.

Calculation of Hansen parameters

HSP values were calculated using HSPiP (Hansen Solubility Parameters in Practice, 5th edition, version 5.3.06) software.

Supplementary Results

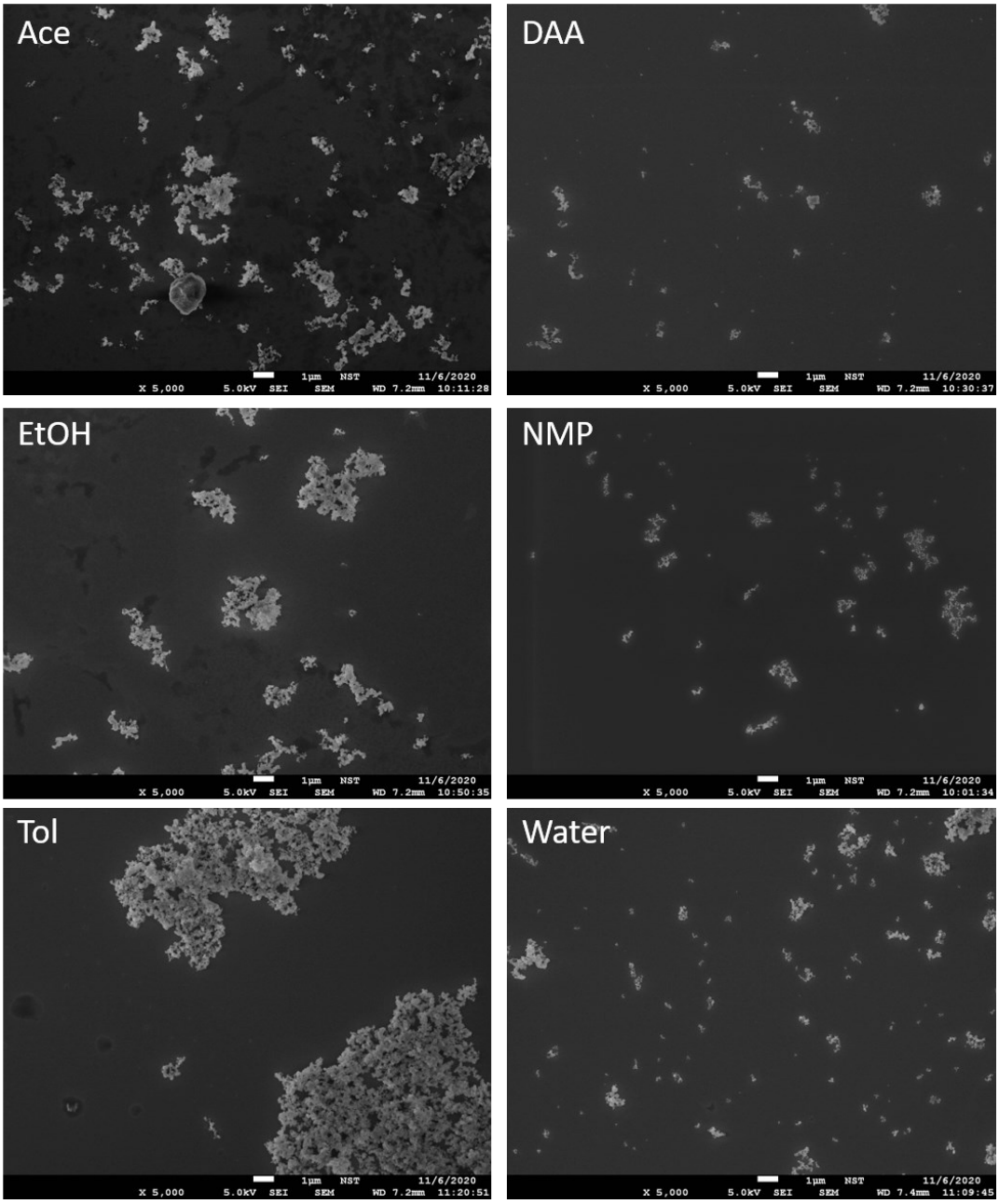

Figure S1: SEM micrographs of SiN_x dispersions (0.0083 wt. %) in acetone (Ace, upper left), diacetone alcohol (DAA; upper right), ethanol (EtOH, middle left), N-methyl-2-pyrrodinone (NMP, middle right), toluene (Tol, bottom left), and water (bottom left) at a magnification of 5 kx.

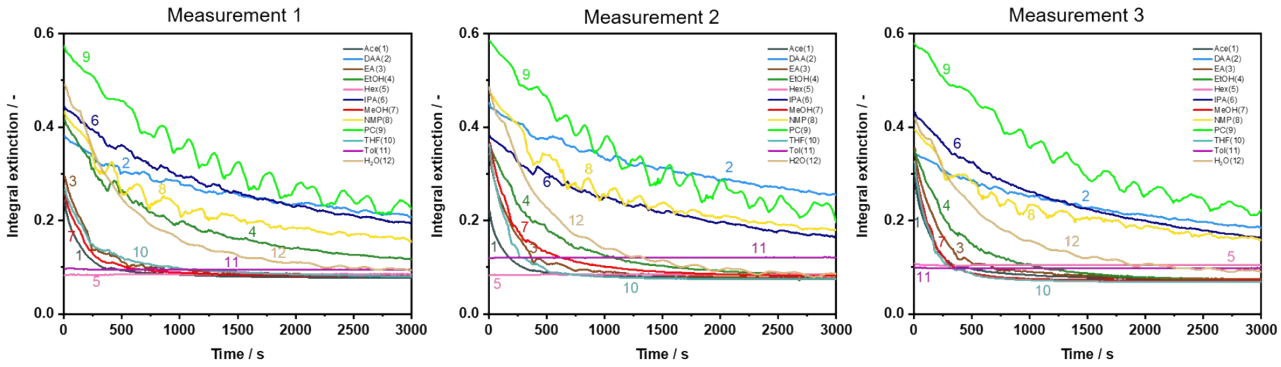

Figure S2: Integral extinction (IE) over time for the region of interest (ROI) of 10 mm under the sample filling level for SiN_x particles dispersed in all twelve PLs. The plot shows IE curves for three independent AC measurements recorded over 50 minutes.

Supplementary Figure S2 depicts the change in integral extinction (IE) with time for SiN_x particles dispersed in all twelve PLs used for this study.

A threshold IE value is required to evaluate the sedimentation times for different PLs, which can be used to evaluate the relative sedimentation times (RST). RST values are then used to order and rank the PLs as good or poor. The two major issues here are intersecting IE curves, and a wavy IE curve (for instance as seen for solvent PC). With the former, the selection of a threshold IE value becomes arbitrary, and with the latter, the IE curve intersects with the threshold IE at multiple time points. Both these aspects leave the user in perplexity, which eventually leads to multiple ranking possibilities based on the RST. Changes in RST order can directly affect the assignment of good or poor liquid for evaluation of HSP.

Moving on to deciding good or poor PLs, we now discuss to what extent it impacts the evaluated HSP values. Following the method described by Süss et al. [2], solvents are incrementally considered as good and the results obtained are summarized in supplementary Table S2. A minimum HSP interaction distance is plotted with the number of liquids ranked as good in Figure S3. We see that the minimum is reached when all eleven liquids are considered as good. As a result, there is ambiguity, this time in the final HSP value to choose trust and report. Furthermore, what is not considered is the number of wrong in and wrong out PLs, i.e., outliers.

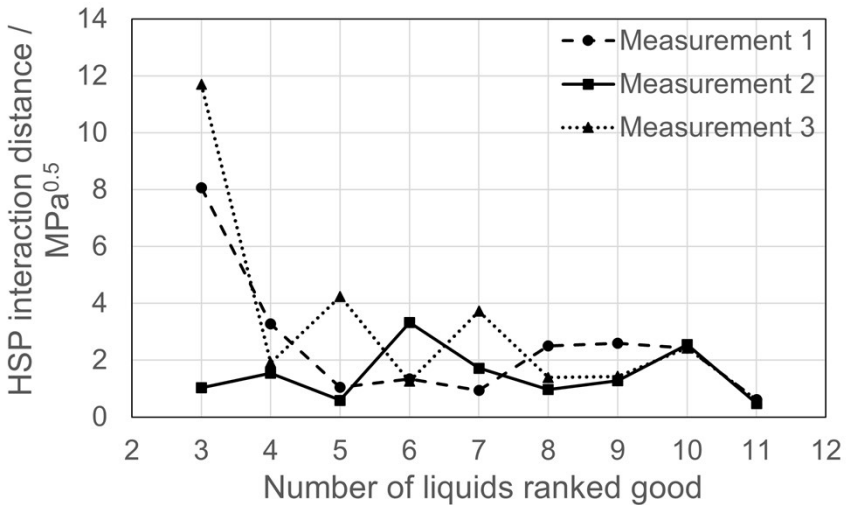

Figure S3: HSP interaction distance vs number of PLs ranked good for all three AC measurements.

Table S2: HSP interaction evaluation at IE = 0.25 for measurement 1 (top), measurement 2 (middle) and measurement 3 (bottom).

Number of liquids ranked good	$\delta D/MPa^{0.5}$	$\delta P/MPa^{0.5}$	$\delta H/MPa^{0.5}$	R	HSP interaction distance	Poor liquids inside sphere	Good liquids outside sphere
2	19.0	15.6	6.8	3.9		1	2
3	16.9	9.5	15.8	3.9	8.1	0	2
4	16.3	9.4	14.3	3.9	3.3	0	3
5	17.2	11.0	10.8	3.9	1.0	0	5
6	17.0	10.2	9.8	3.9	1.3	0	6
7	16.5	9.1	13.2	3.9	0.9	0	6
8	16.2	9.5	14.3	3.9	2.5	0	6
9	16.4	8.7	13.2	3.9	2.6	0	8
10	16.5	9.0	10.8	3.9	2.4	0	9
11	16.4	9.0	10.2	3.9	0.6	0	9

Number of liquids ranked good	$\delta D/MPa^{0.5}$	$\delta P/MPa^{0.5}$	$\delta H/MPa^{0.5}$	R	HSP interaction distance	Poor liquids inside sphere	Good liquids outside sphere
2	16.7	11.4	10.0	3.9		1	2
3	17.1	11.3	9.3	3.9	1.0	1	2
4	17.3	10.5	10.4	3.9	1.5	0	4
5	17.2	11.0	10.7	3.9	0.6	0	5
6	16.4	10.4	13.6	3.9	3.3	0	5
7	16.3	9.8	15.2	3.9	1.7	0	6
8	16.2	9.5	14.3	3.9	1.0	0	7
9	16.5	8.8	13.4	3.9	1.3	0	8
10	16.5	9.0	10.8	3.9	2.5	0	9
11	16.4	8.9	10.4	3.9	0.5	0	10

Number of liquids ranked good	$\delta D/MPa^{0.5}$	$\delta P/MPa^{0.5}$	$\delta H/MPa^{0.5}$	R	HSP interaction distance	Poor liquids inside sphere	Good liquids outside sphere
2	19.0	15.6	6.8	3.9		1	2
3	16.9	9.5	15.8	3.9	11.7	1	3
4	16.3	9.4	14.3	3.9	1.9	0	3
5	17.2	11.0	10.8	3.9	4.2	0	5
6	17.0	10.2	9.8	3.9	1.3	0	4
7	16.5	9.1	13.2	3.9	3.7	0	6
8	16.2	9.5	14.3	3.9	1.4	0	7
9	16.4	8.7	13.2	3.9	1.4	0	8
10	16.5	9.0	10.8	3.9	2.4	0	9
11	16.4	9.0	10.2	3.9	0.6	0	9

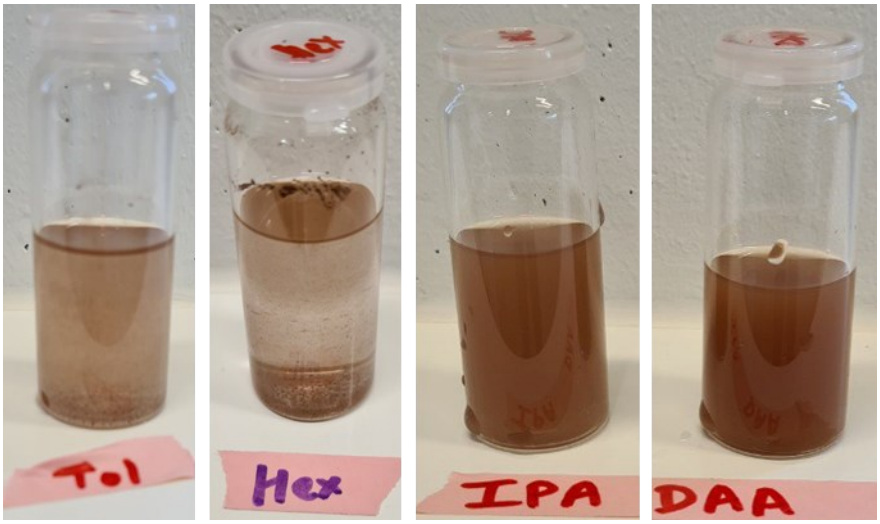

Figure S4: Photographs of vials filled with freshly prepared SiN_x dispersions in Toluene (Tol), Hexane (Hex), 2-propanol (IPA) and Diacetone alcohol (DAA). The vials became transparent immediately after preparation in case of Tol and Hex indicating poor dispersibility of SiN_x particles in these PLs.

Table S3: Possible scoring permutations for HSP evaluation.

N liquids	No information Q_0	Known good liquids Q_m			Known poor liquids Q_l			Known good and poor liquids Q_{lm}		
		M = 1	M = 2	M = 3	L = 1	L = 2	L = 3	M = 1, L = 1	M = 2, L = 1	M = 2, L = 2
3	3	2	1	0	1	0		1	1	
4	10	6	3	1	4	1	0	3	2	1
5	25	14	7	3	11	4	1	7	4	2
6	56	30	15	7	26	11	4	15	8	4
7	119	62	31	15	57	26	11	31	16	8
8	246	126	63	31	120	57	26	63	32	16
9	501	254	127	63	247	120	57	127	64	32
10	1012	510	255	127	502	247	120	255	128	64
11	2035	1022	511	255	1013	502	247	511	256	128
12	4082	2046	1023	511	2036	1013	502	1023	512	256
13	8177	4094	2047	1023	4083	2036	1013	2047	1024	512
14	16368	8190	4095	2047	8178	4083	2036	4095	2048	1024
15	32751	16382	8191	4095	16369	8178	4083	8191	4096	2048
16	65518	32766	16383	8191	32752	16369	8178	16383	8192	4096
17	131053	65534	32767	16383	65519	32752	16369	32767	16384	8192
18	262124	131070	65535	32767	131054	65519	32752	65535	32768	16384
19	524267	262142	131071	65535	262125	131054	65519	131071	65536	32768
20	1048554	524286	262143	131071	524268	262125	131054	262143	131072	65536

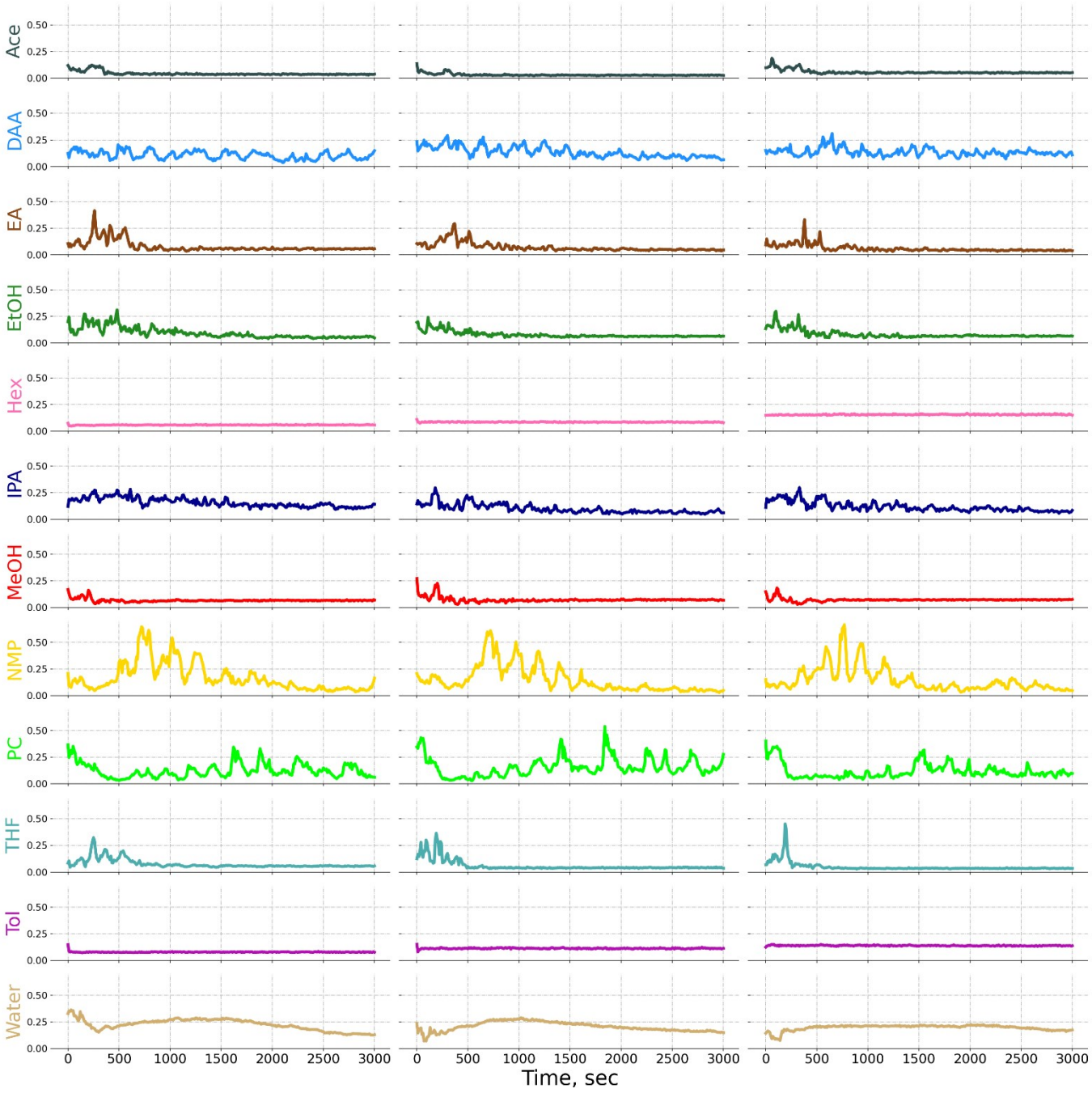

Figure S5: Stability trajectories of SiN_x dispersions in all twelve PLs for three independent AC measurements.

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