Supplementary Information File for:

Nucleation in Sessile Saline Microdroplets: Induction Time Measurement via Deliquescence-Recrystallization Cycling

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SI1
Details of Chemical Products

Product	Vendor	Properties
Sodium chloride, NaCl	R.P Normapur ®	Purity = 99.5% Refractive index = 1.5442
Polymethylmethacrylate, PMMA	ALLRESIST GmbH	Molecular weight= 950,000 g/mol Refractive index = 1.395
Polydimethylsiloxane, PDMS oil	Alfa Aesar	Molecular weight = 1250 g/mol Viscosity = 10 cSt Refractive index = 1.3990
Ultrapure water	via Milli-Q Purifier	resistivity = 18.2 MΩ·cm TOC value < 5 ppb

SI2

Details of Instrumentation

To avoid microdroplet spreading and coalescence, we coated the glass cover slip with a hydrophobic PMMA resin. For this, glass coverslips (18-mm diameter, cleaned via plasma treatment) were spincoated at 4000 rpm for 1 min (SPIN 150, SPS) with PMMA which were then annealed for 10 min at 170°C. The coverslips were then covered with a 0.8 mm thick layer of PDMS oil. The saline microdroplets were generated on the cover slip by a micropipette with an internal diameter of 0.5 um (Femtotip Eppendorf). The micropipette is mechanically controlled by a home-made motorized micromanipulator consisting of 3 miniature translation stages (piezo electric, MS30 Mechonics) which allows displacement of the micropipette holder in three dimensions by steps of 16 nm. A series of 16-bit images were obtained using an optical microscope (Zeiss Axio Observer D1 equipped with an ANDOR neo sCMOS camera). Images were processed using FIJI software (Image J, NIH, USA) which calculates σ for each region containing microdroplets.

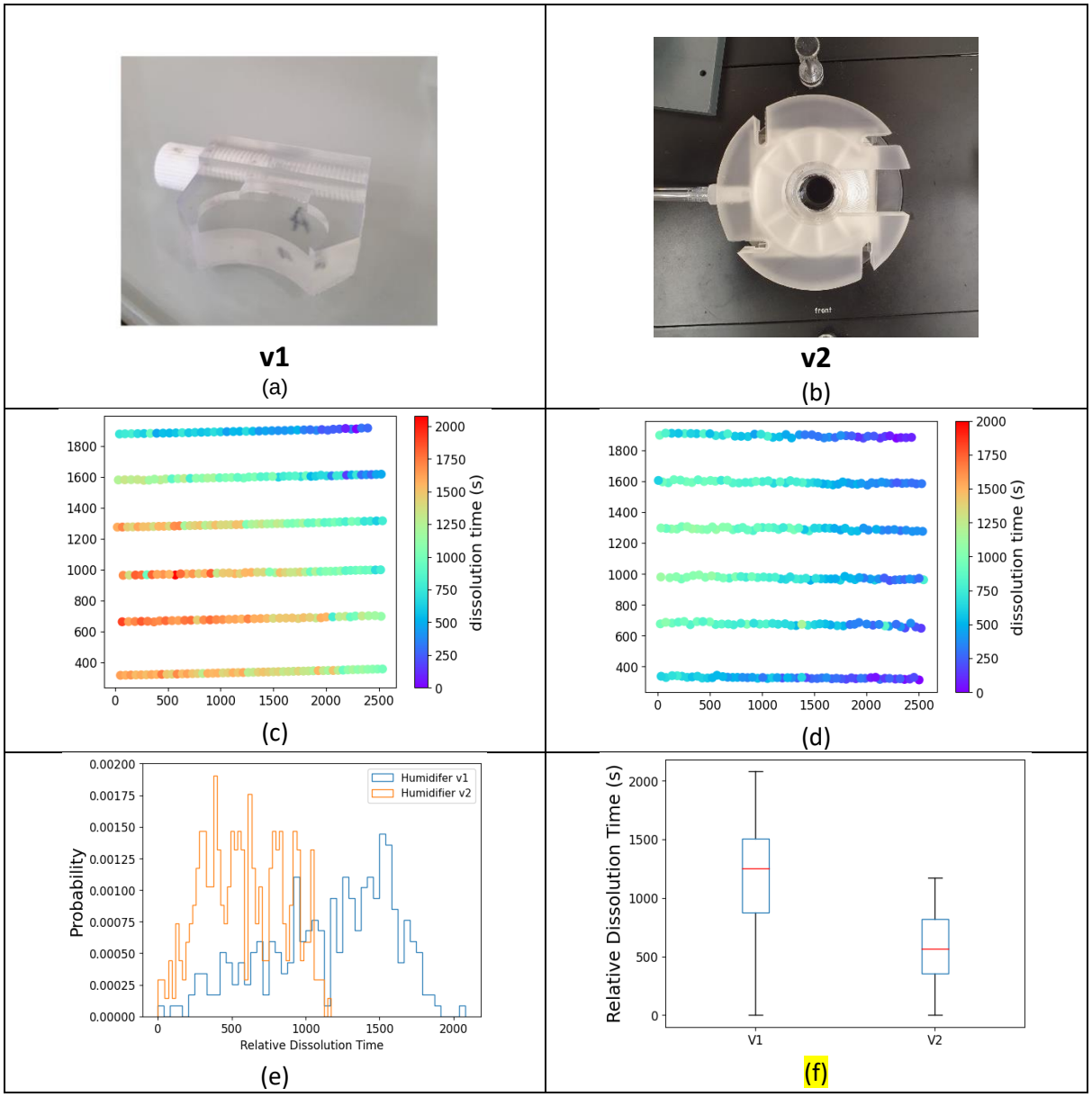
SI3

Humidification control and dispatching module

The humidification chamber (airflow module dispatcher) was custom fabricated via SLA 3D-printing (Formlabs, clear resin).

Improving Spatial Homogeneity

To choose airflow module dispatchers, we compared measured distributions of tDISS in both models (v1 and v2).



	V1	V2
mean	1162	584.0
standard deviation	426	275
skewness	-0.516	0.0448
kurtosis	-0.599	-0.976

We have significantly improved the spatial homogeneity by making the humidifier system more symmetric. This is illustrated in the map of dissolution times (c,d), histogram and the box plot (e,f), and the values of mean, standard deviation, skewness and kurtosis (Note that the minimum dissolution time is set to zero).

With this v2 design, to assess asses the speed at which the humidity can be changed, we measured the %RH in the microdroplet generation chamber with “dry” air (directly obtained from compressed air pipelines) and our humid air.

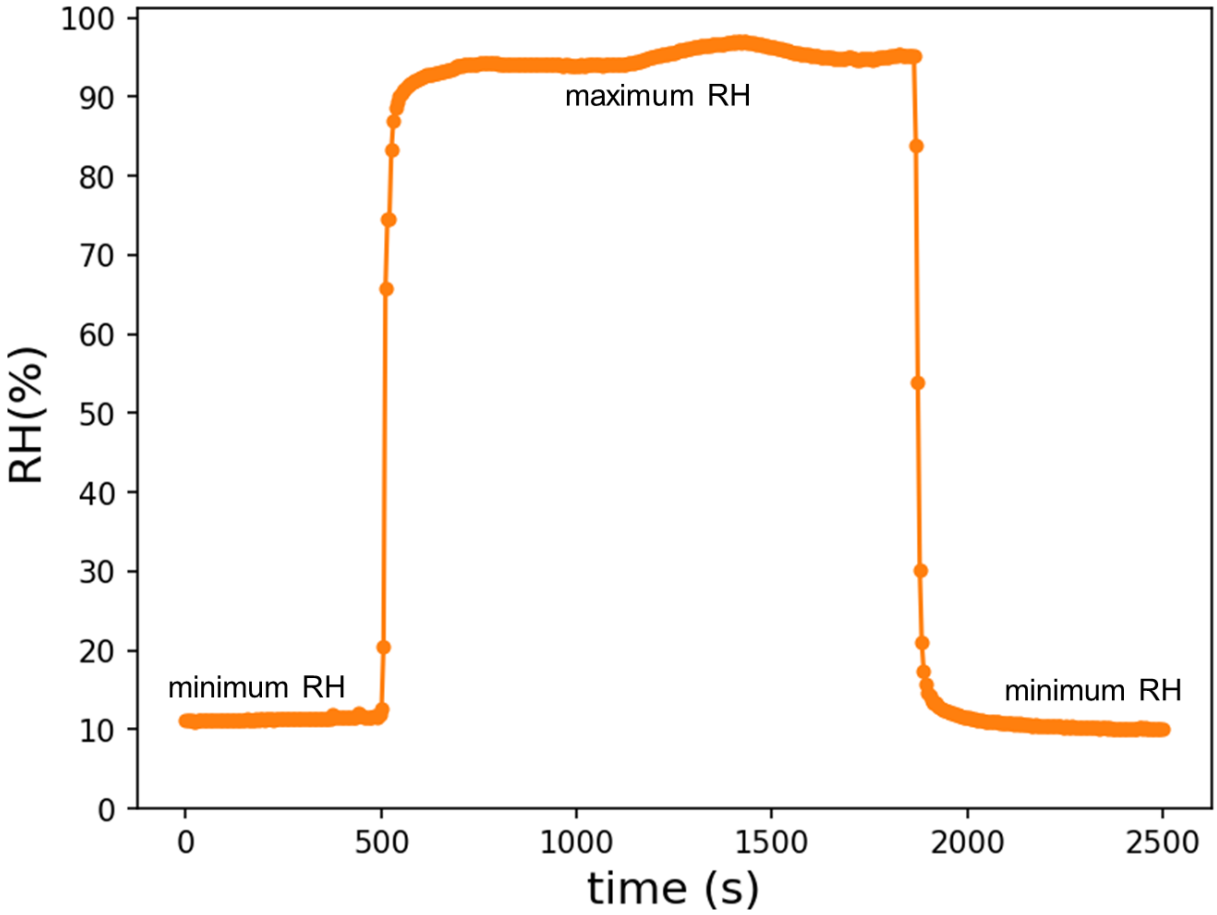
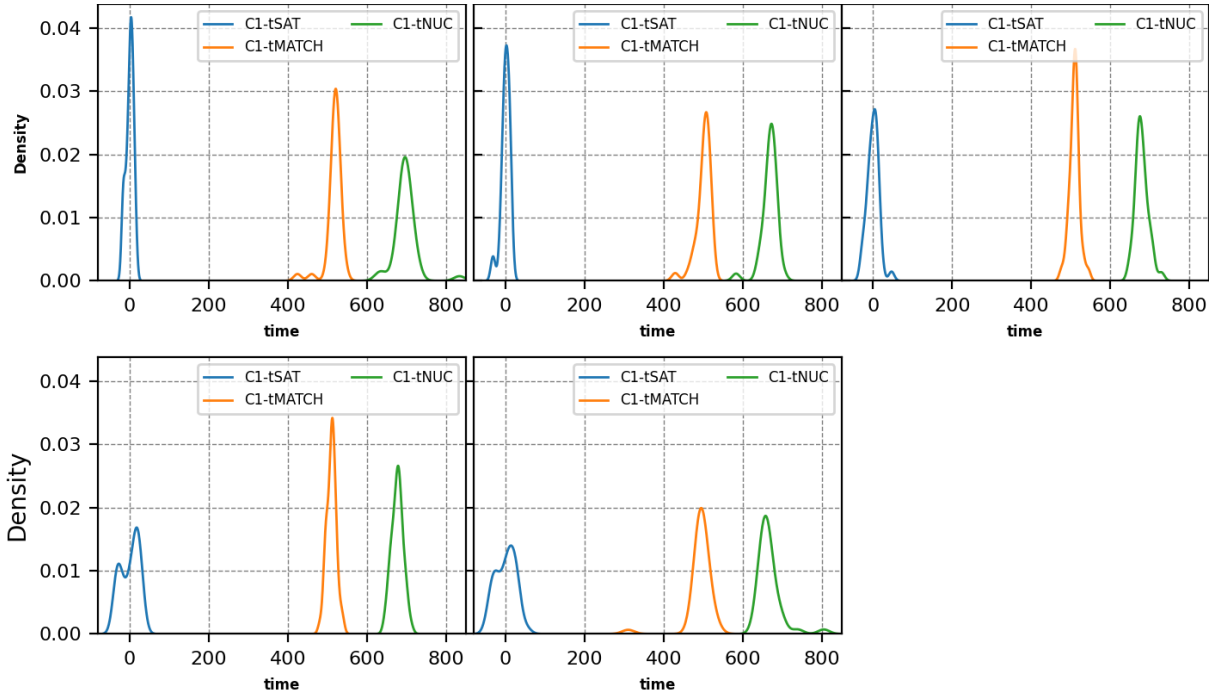


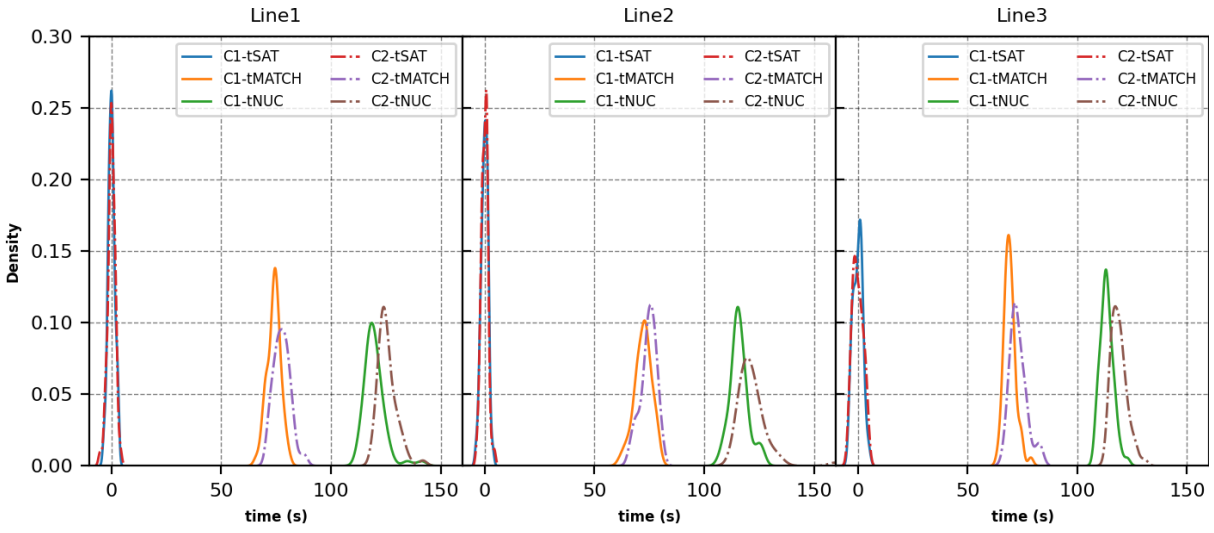
Figure S1 Relative humidity vs time in the humidifier when RH is shifted from minimum to maximum value and vice versa. This suggests that our humidity control system can almost instantaneously change the RH of our microdroplet generation chamber (negligible lag period). We also show we can maintain a reasonably stable RH as needed.

SI4
Distribution of sigma-curves characteristic points versus time

Distribution of sigma-curves characteristic points versus time for BDs lines.



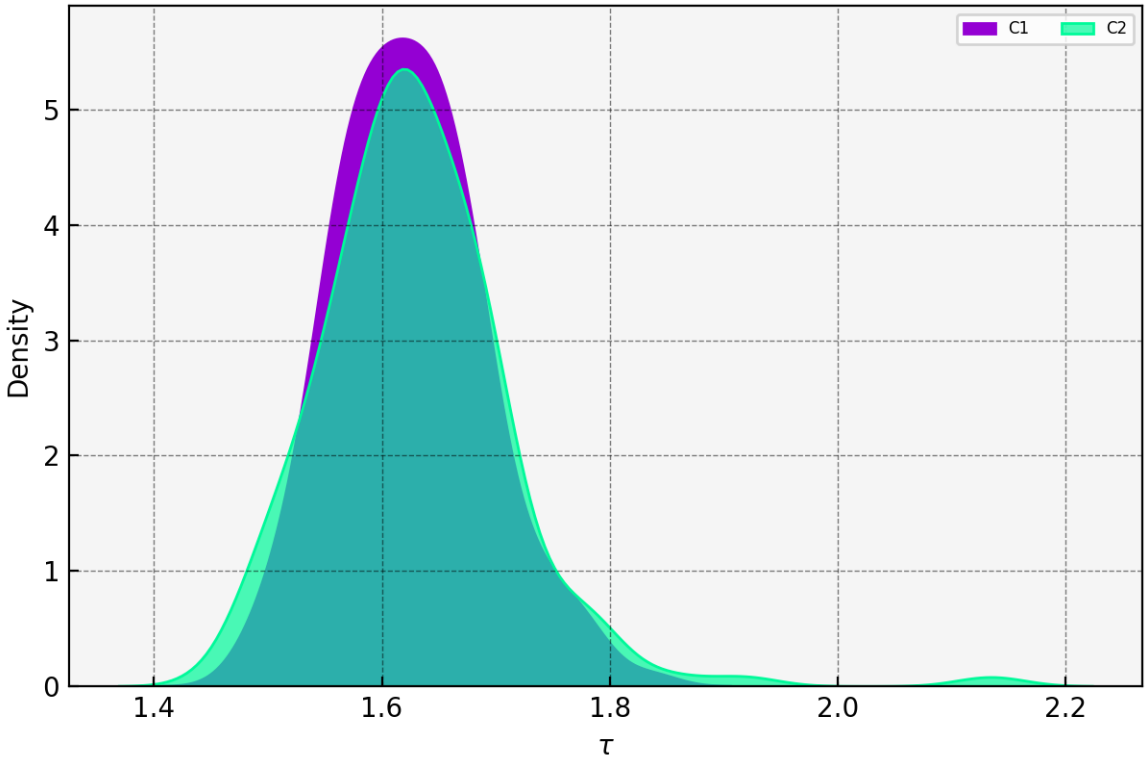
Distribution of sigma-curves characteristic points versus time for SDs lines.



SI5

Cycle-to-cycle nucleation times shift.

Distribution, for SDs datasets, of dimensionless induction times, while cycle-aggregated. There is no evidence of cycle shifting.



SI6

Anderson-Darling k-sample test for different aggregation subsets.

Anderson-Darling k-sample test tests for:
-“null hypothesis **H0**: samples data are drown from the same distribution”
-“alternative hypothesis **H1**: samples data are drawn from different distributions”.
We fix risk to reject H0 despite true at a usual value of p-value=.05.

BD: Big Droplets datasets (line number)
k=5
(1, 2, 3, 4, 5) -> 1.7277 / 0.0606 Ok
The pooling of every BD datasets succeeds.

SD: Small Droplets datasets (SD_cycle_line format, ex: SD23 is line 3 in cycle 2)
K=6
['SD11', 'SD12', 'SD13', 'SD21', 'SD22', 'SD23'] -> 2.5189 / 0.0212 X
The pooling of every datasets fail.
We can then try different combinations of 5 among 6 datasets.
K=5
['SD11', 'SD12', 'SD13', 'SD21', 'SD22'] -> 2.6507 / 0.0191 X
['SD11', 'SD12', 'SD13', 'SD21', 'SD23'] -> 2.9413 / 0.0131 X
['SD11', 'SD12', 'SD13', 'SD22', 'SD23'] -> 3.2549 / 0.0087 X
['SD11', 'SD12', 'SD21', 'SD22', 'SD23'] -> 0.6200 / 0.2275 Ok
['SD11', 'SD13', 'SD21', 'SD22', 'SD23'] -> 1.3282 / 0.0984 Ok
['SD12', 'SD13', 'SD21', 'SD22', 'SD23'] -> 2.7799 / 0.0162 X
There are combinations which succeed test, we choose the highest statistical significance (0.2275).

SI7
Modeling of DITs with a Weibull distribution function

$S(x) = exp(-x^k)$

With $x = \frac{\tau - location}{scale}$

DATA	k	Location	Scale	R2	MSE
SD_{SUP}	2.281658	1.475360	0.165096	0.998777	0.000105
BD_{SUP}	1.989330	1.285815	0.056227	0.994003	0.000477

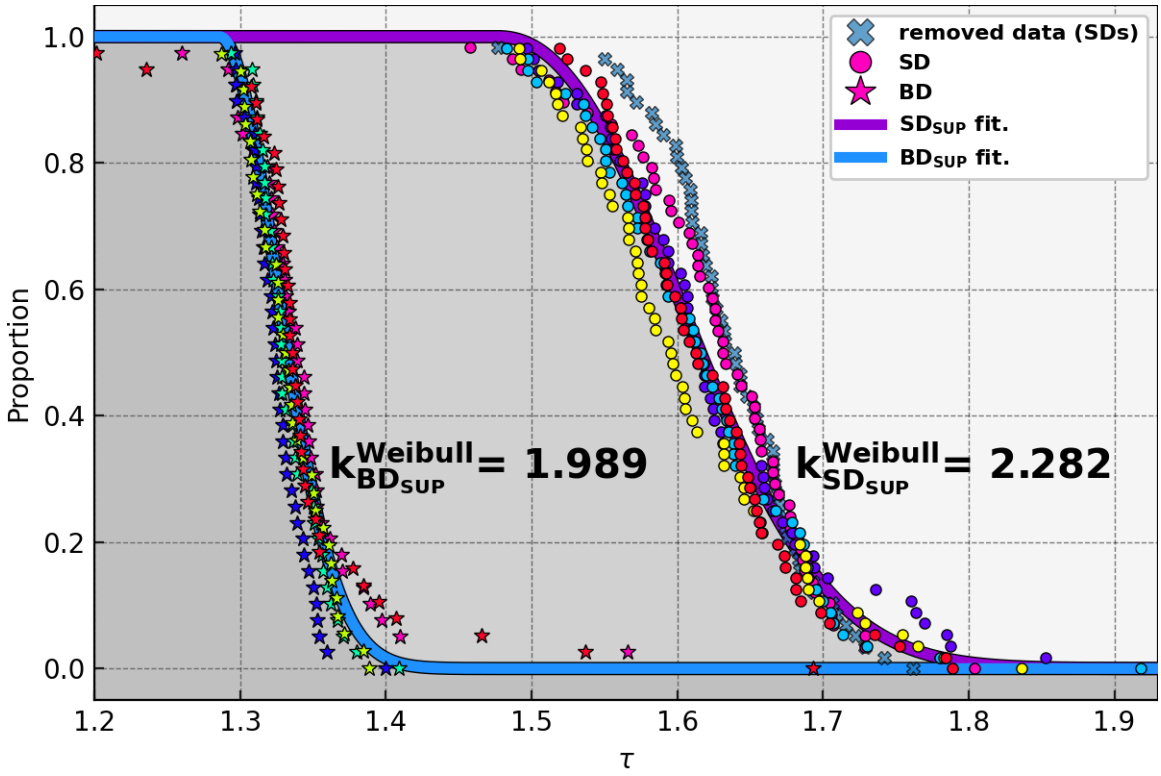


Figure 8. Survival function (sf) plot of Dimensionless Induction Times τ (DITs). Supersaturation **sf** data for SD and BD droplets are superimposed on respective best fits 'SD fit.' And 'BD fit.'. 'removed data (SDs)' is the data of the only line in SD datasets removed by Anderson-Darling k-sample test: line 3 in cycle 1.

SI8
Supersaturation Calculation from DITs
Determination of Supersaturation Ratio at Refractive Index Matching

The refractive index of NaCl solution at ambient conditions is plotted against supersaturation ratio. The supersaturation ratio that corresponds to the refractive index of PDMS oil is the supersaturation ratio during refractive index matching (S_m). Data were taken from https://www.topac.com/Salinity_brix.html.

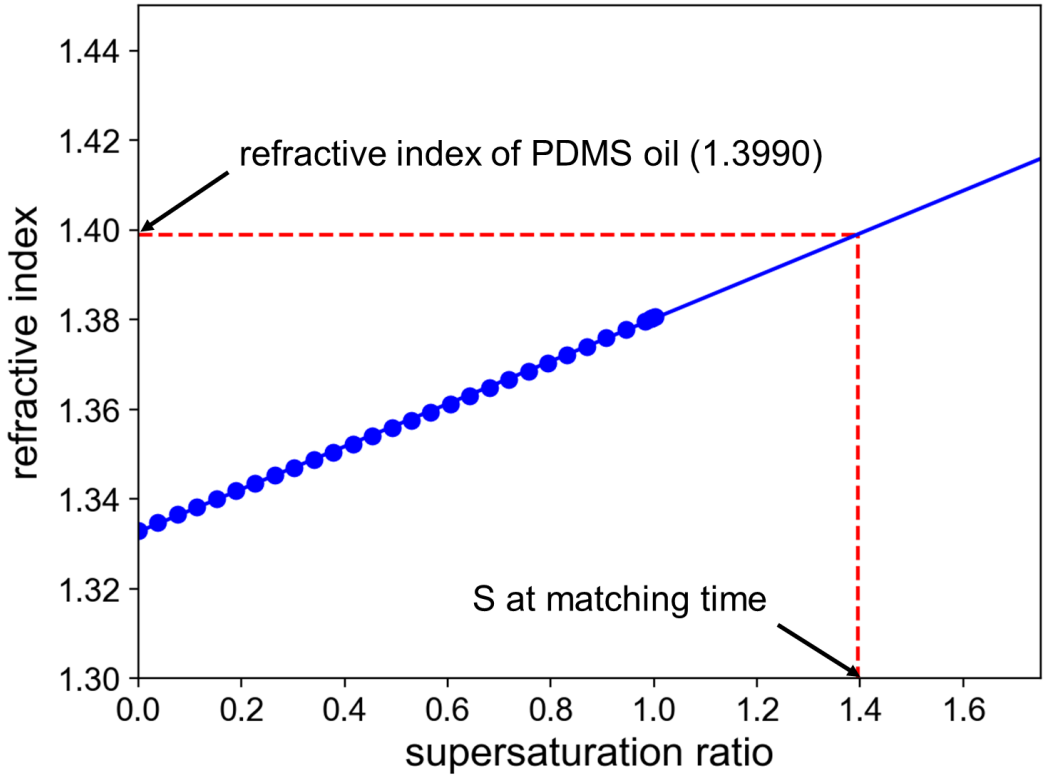


Figure S2 Refractive index as a function of supersaturation ratio. The refractive index of the droplet matches that of the PDMS oil at S = 1.3990.

From the hypothesized linear volume decrease with time (coefficient alpha), we have, for Vsat the droplet volume at saturation:

V(t) = Vsat (1- alpha*(t - tsat)) eq1

With mass conservation on dissolved salt: S(t)V(t)= cste
Equation 1 can be expressed in terms of supersaturation (with Ssat=1)
1/S(t) = 1 - alpha*(t - tsat) eq2

If we express volume decrease between tsat and tmatch, we can extract alpha:

Alpha = (1 - 1/Smatch) / (tmatch - tsat)

Knowing alpha, and expressing equation 2 at dimensionless nucleation time tau

Snucleation = (1 - tau*(1-1/Smatch))^-1