



Optimizing wetting and jetting

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IMI Tech Talks at InPrint
Munich, November 2019

Founded in 1796, KRÜSS is the global market leader in the field of surface tension and interfacial tension instruments

The development of CA instruments started in the early 1990's

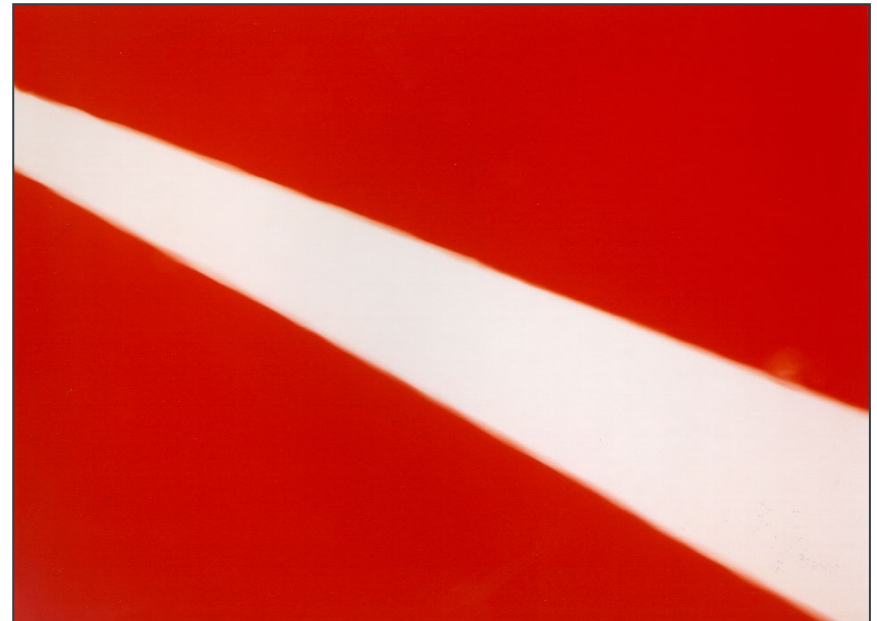
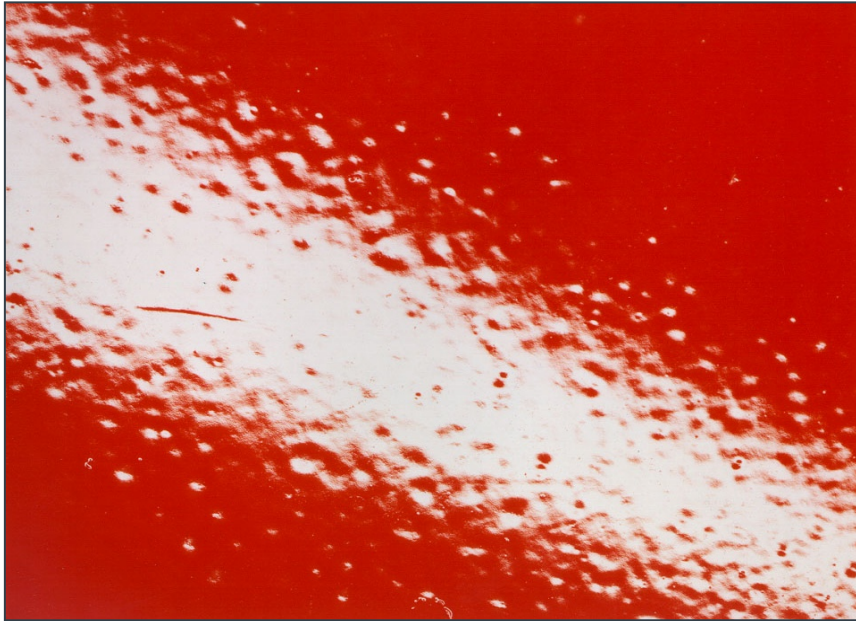
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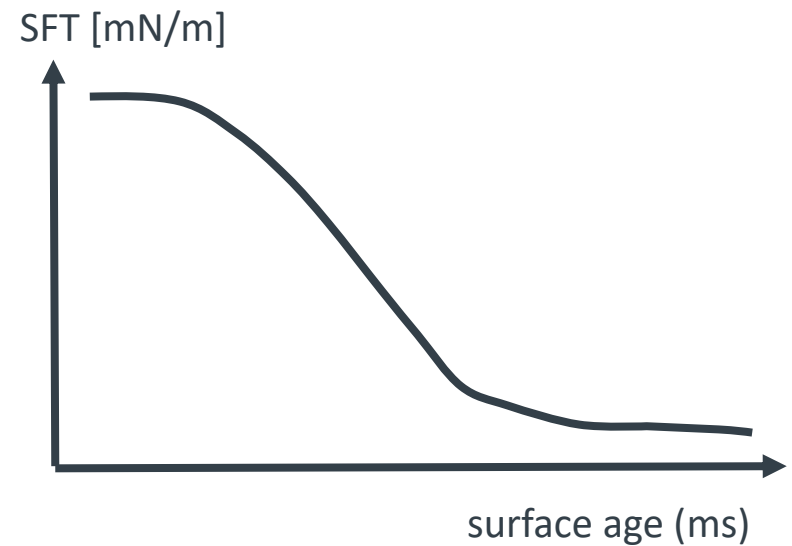
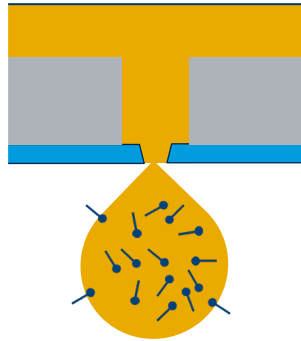
Motivation

Surface tension in the field of inkjet

Surface and interfacial tension directly influence the quality of coatings



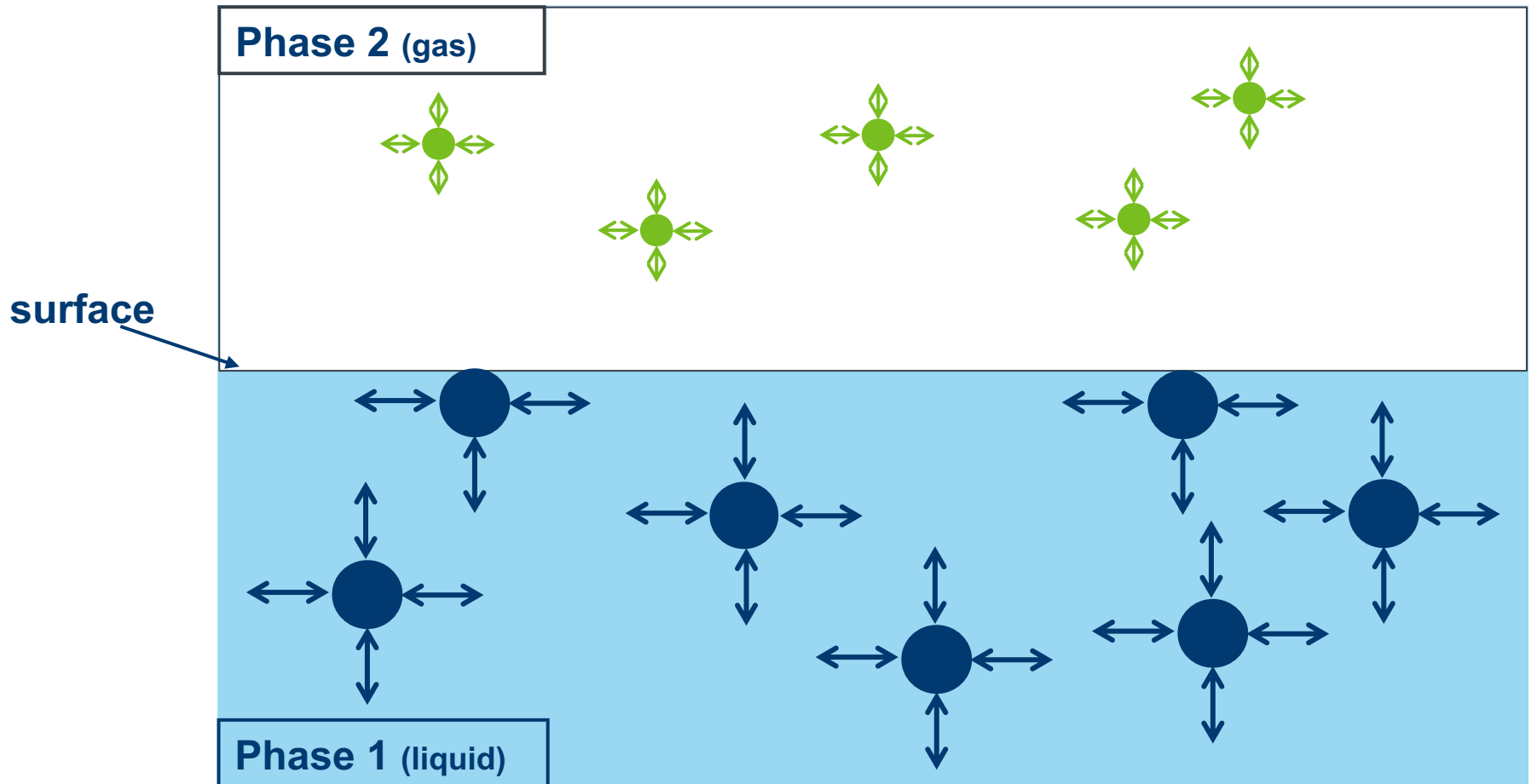
The surface tension of the drop impinging onto the substrate depends on surfactant (concentration) and the flight time



Basics about Interfacial Tension

Surface tension is a result of intermolecular interactions within the liquid phase

Interactions with the gas phase can be neglected



In thermodynamics, interfacial tension correlates changes in interfacial area with changes in the free energy of a system

$$dG_0 = \sigma \cdot dA$$

$$[\sigma] = \left[\frac{\text{work}}{\text{area}} \right] = \frac{\text{J}}{\text{m}^2} = \left[\frac{\text{force}}{\text{length}} \right] = \frac{\text{N}}{\text{m}}$$

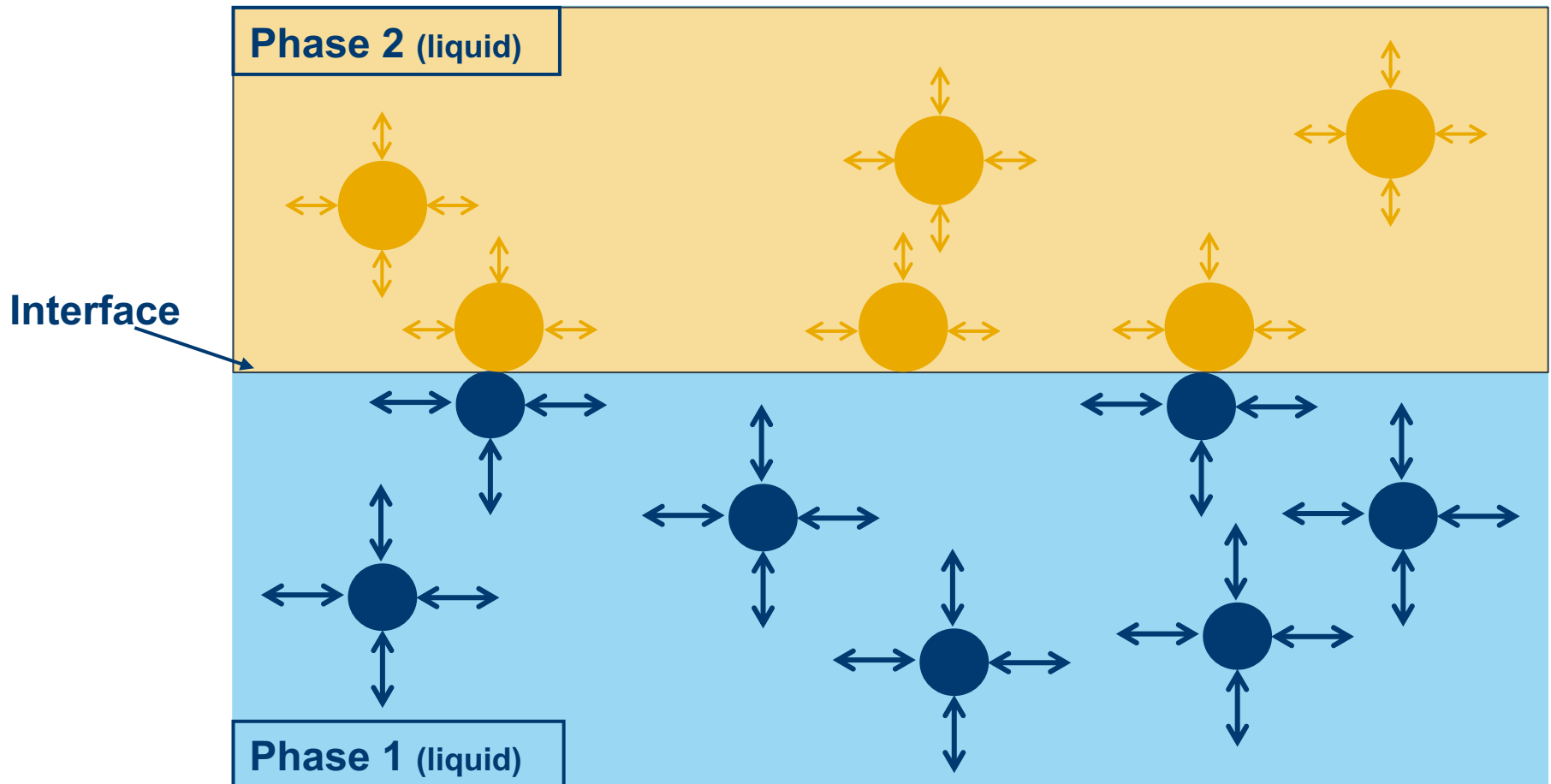
Surface tension is a result of intermolecular interactions within the liquid phase

Liquids tend to minimize their surface area

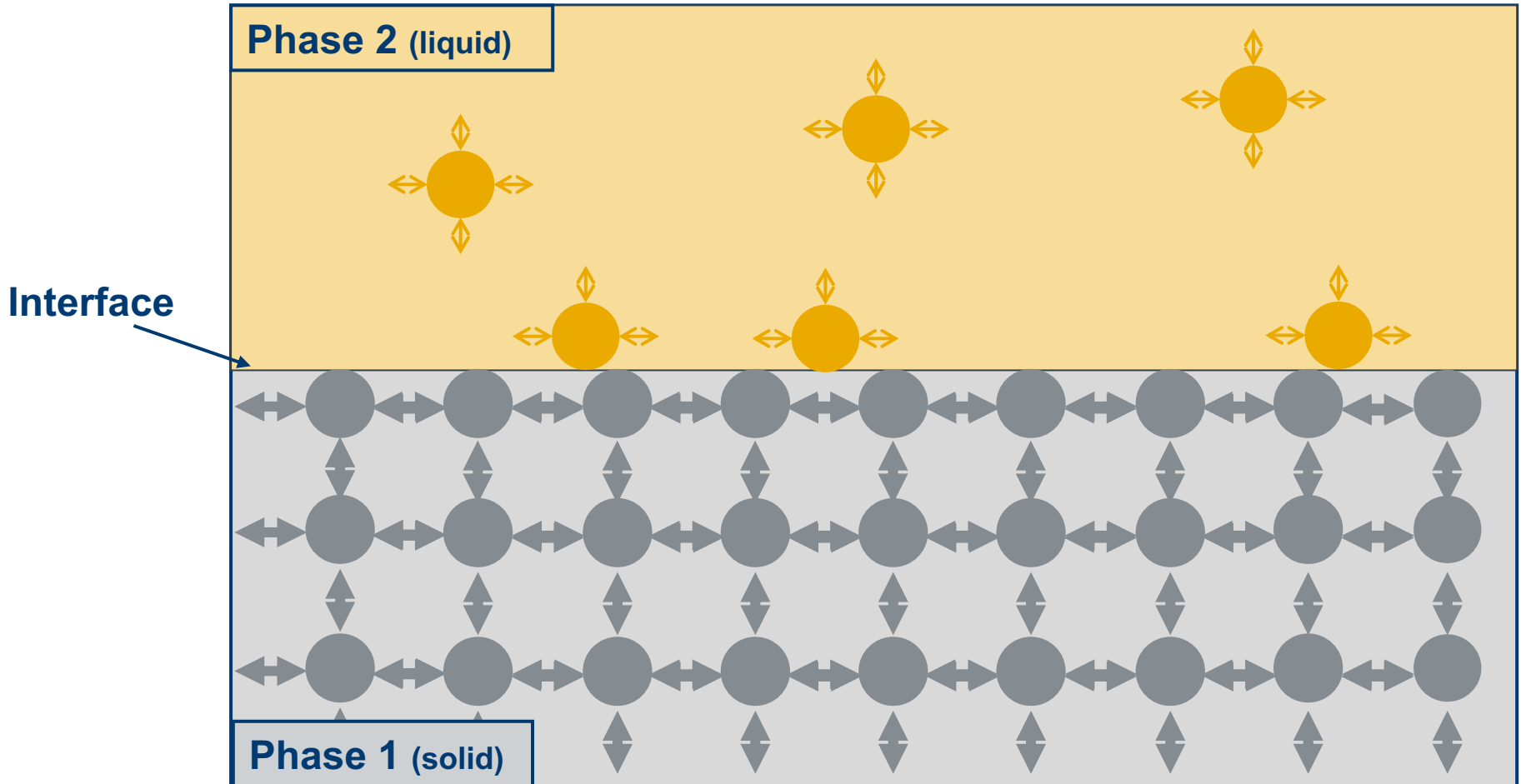


Interfacial tension is a result of intermolecular interactions within and between two adjacent liquid phases

Here molecular interactions across the interface cannot be neglected

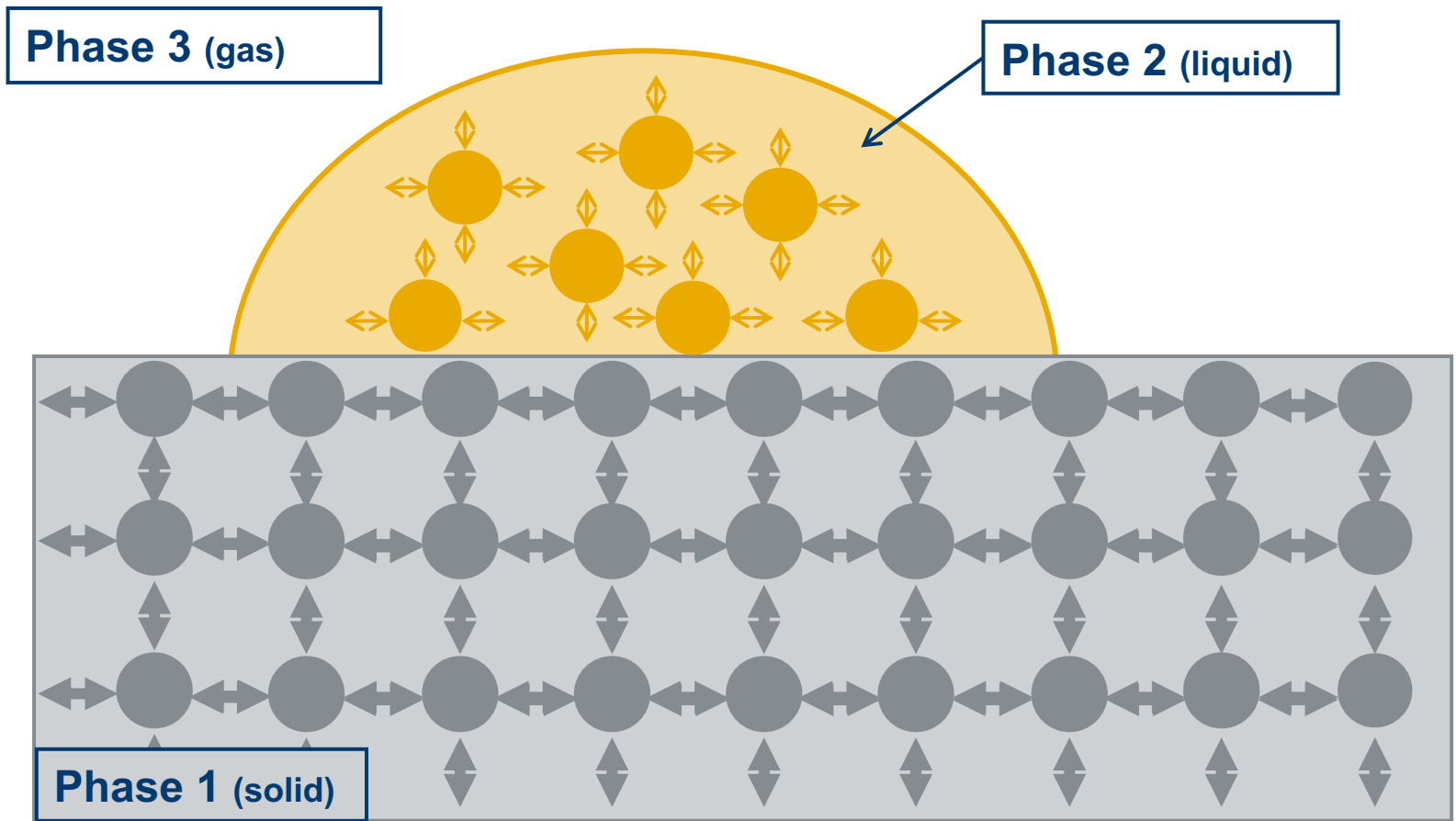


Solid samples cannot adjust their surface area...



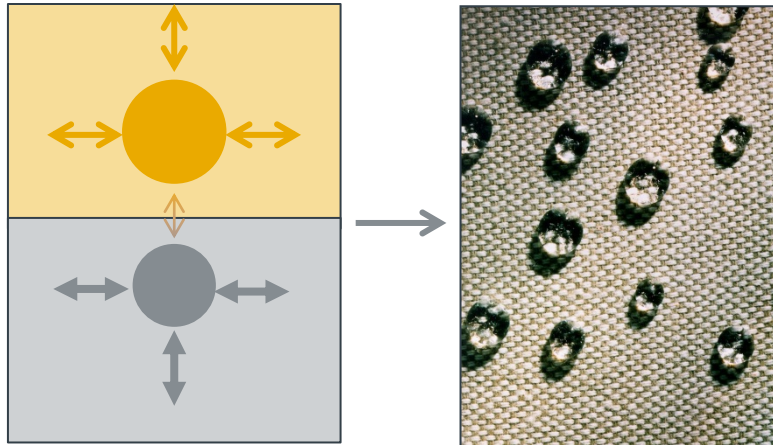
...but they influence the liquid drop shape across the interface

A solid surface is characterized by its Surface Free Energy

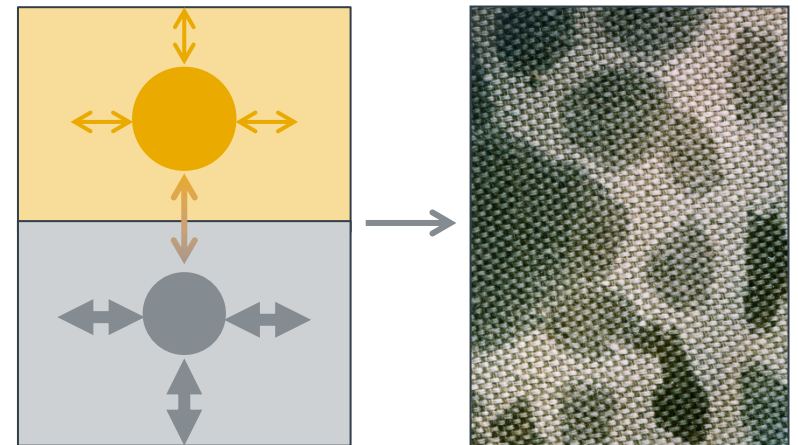


...but they influence the liquid drop shape across the interface

Interfacial interactions can differ from being very weak to being very strong

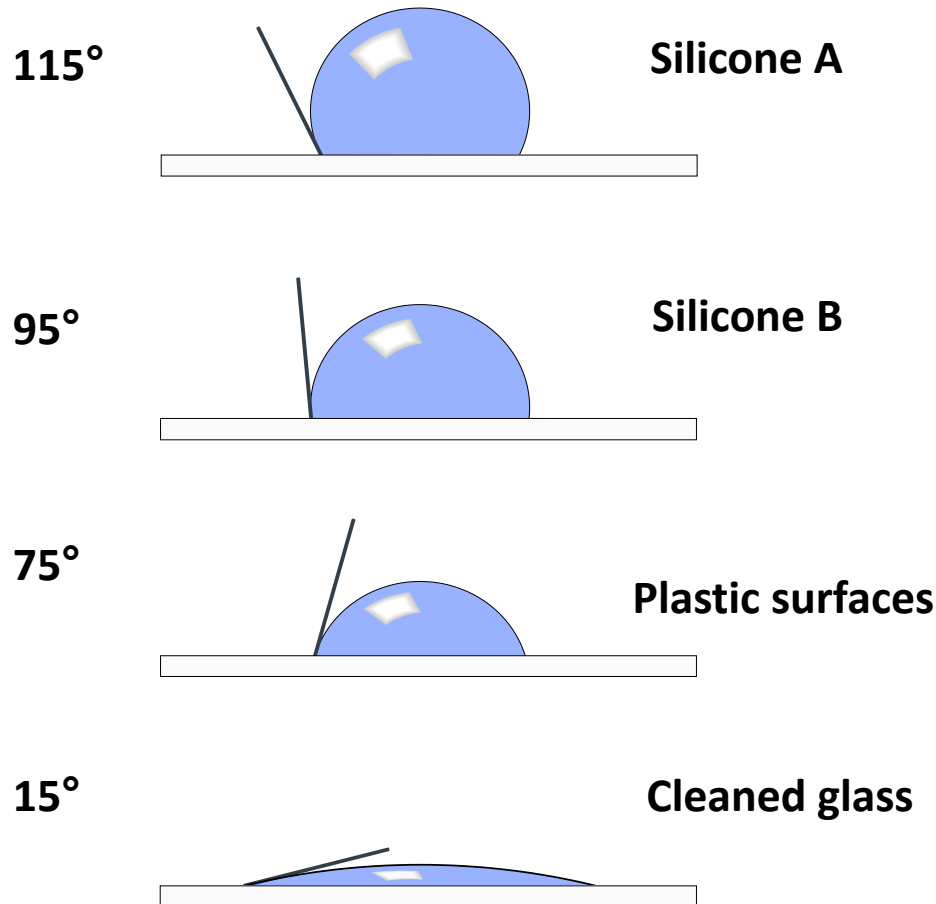


Water-plastic, e. g. polypropylene (PP)-fabric
 $\sigma = 50 \text{ mN/m} \Rightarrow$ does not wet



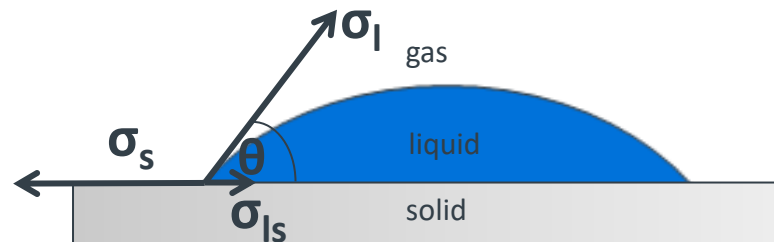
Benzine-natural fibers, e. g. cleaning solvent on cotton
 $\sigma < 1 \text{ mN/m} \Rightarrow$ complete wetting

The contact angle of water is a measure for the surface free energy of solids



Young's Equation relates the contact angle with the interfacial tension

$$\cos \theta = \frac{\sigma_s - \sigma_{ls}}{\sigma_l} \iff \sigma_s = \sigma_{ls} + \sigma_l \cos \theta$$



- σ_l = surface tension liquid
- σ_s = surface free energy of solids
- σ_{ls} = interfacial tension between solid and liquid
- θ = contact angle

For liquids the values of surface tension are in the range between 18 and 73 mN/m

Liquid	Surface Tension	Dispersive Part	Polar part
N,N-Dimethyl-Formamide	37,1	29,0	8,1
n-Decane	23,9	23,9	0,0
n-Heptane	20,4	20,4	0,0
n-Hexane	18,4	18,4	0,0
n-Octane	21,8	21,8	0,0
n-Tetradecane	25,6	25,6	0,0
nitro-Ethane (Schultz)	31,9	27,5	4,4
nitro-Methane (Schultz)	36,8	29,8	7,0
Phthalicsäure-diethylester 22°	37,0	30,0	7,0
sym-tetrabrom-Ethane (Ström)	49,7	49,7	0,0
sym-tetrachlor-Ethane (Ström)	36,3	36,3	0,0
Toluene (Schultz)	28,4	26,1	2,3
Tricresyl-phosphate (Fowkes)	40,9	39,2	1,7
Water (Rabel) @ 22°	72,3	18,7	53,6
Water (Ström) @ 20°	72,8	21,8	51,0
a-brom-Nephtalin (Busscher)	44,4	44,4	0,0
Diiodo-Methane (Ström)	50,8	50,8	0,0

Solids exhibit often a surface free energy in the same range

Solid	σ [mN/m]
Polyamide (Nylon)	41,4
PE	30,3 – 35,1
PET	40,9 – 42,4
PMMA	44,9 – 45,8
PP	29,7
PTFE	18,0 – 21,0
PDMS	22,2
Glass	40 – 112

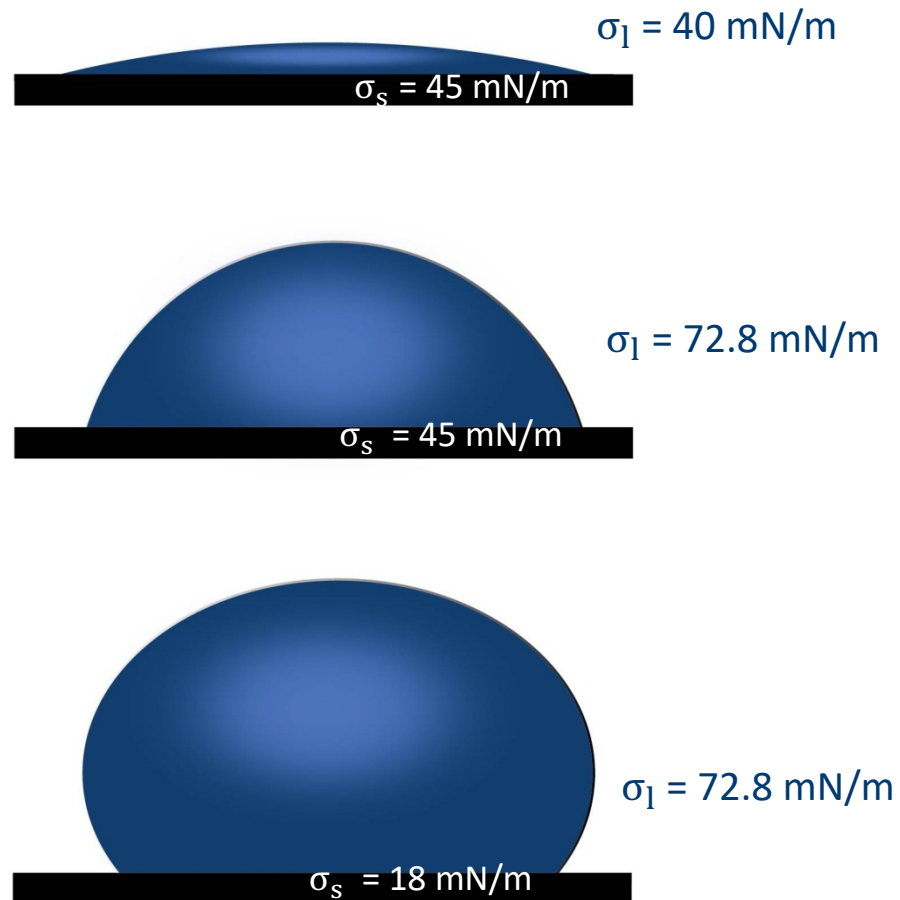
Clean metal surfaces can exhibit very high surface free energy values

A freshly tempered metal surface is completely wetted by any liquid

Solid	σ [mN/m]
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PET	40,9 – 42,4
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PP	29,7
PTFE	18,0 – 21,0
PDMS	22,2
Glass	40 – 112
Copper (111) (calculated)	2000
Tungsten (110) (calculated)	4000

Wetting is influenced by liquid's surface tension and solid's surface free energy

Relationship between surface tension and surface free energy



Both the surface free energy of solids and the surface tension of liquids are more than just *one* value

Its distribution into *polar* and *disperse* parts can be important

Interfacial Tension

$$\sigma = \sigma_D + \sigma_P$$

σ_D = disperse part of the interfacial tension

- ◆ Van der Waals-interaction (Keesom, Debye, London)

σ_P = polar part of the interfacial tension

- ◆ Lewis acid-base interaction
- ◆ Hydrogen bonding (as special case of Lewis interaction)

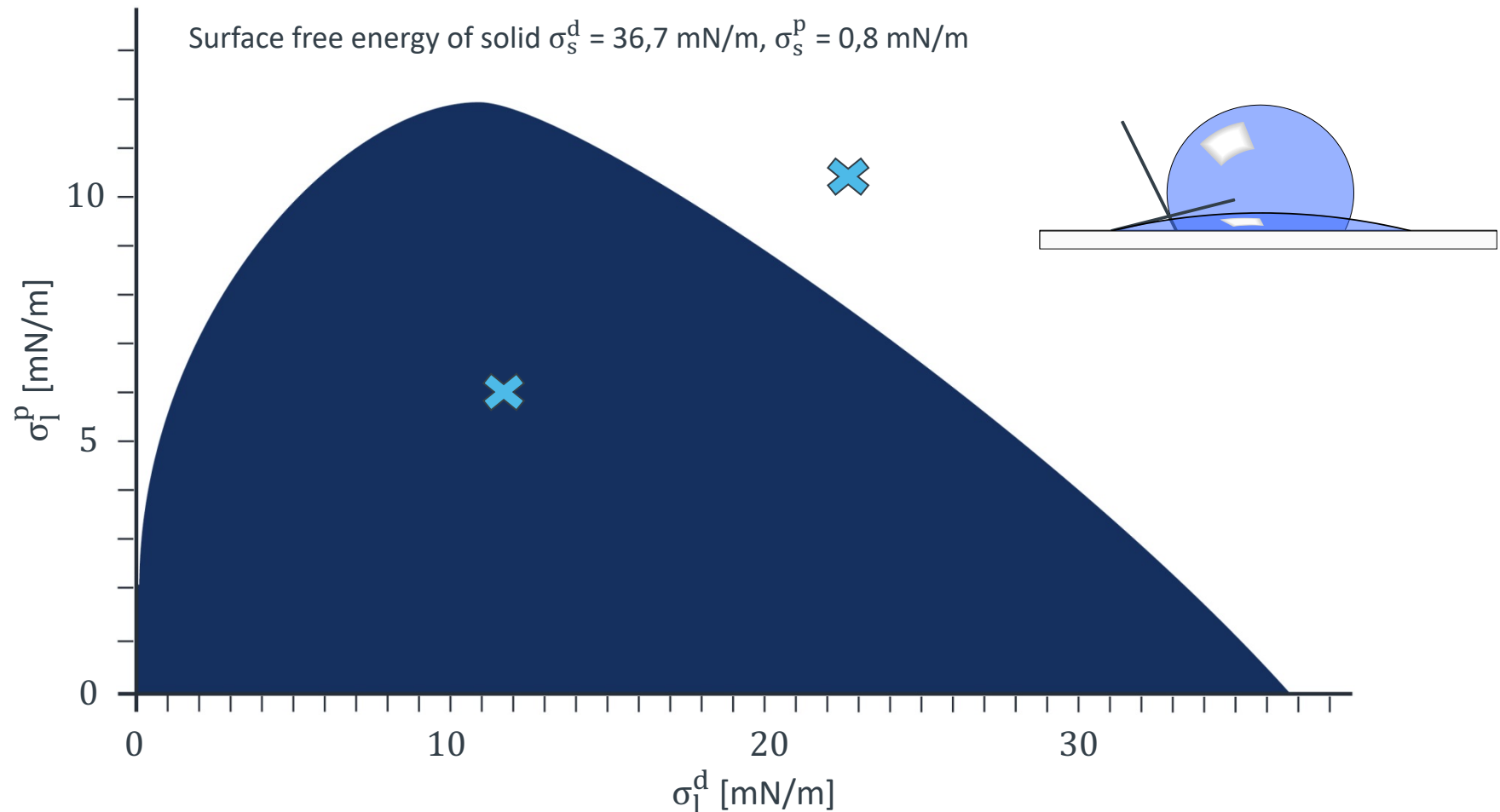
Rule of thumb: *Polar* interacts solely with *polar* and *disperse* solely with *disperse*

For liquids the values of surface tension are in the range between 18 and 73 mN/m

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The wetting envelope shows which liquids would completely wet a particular solid

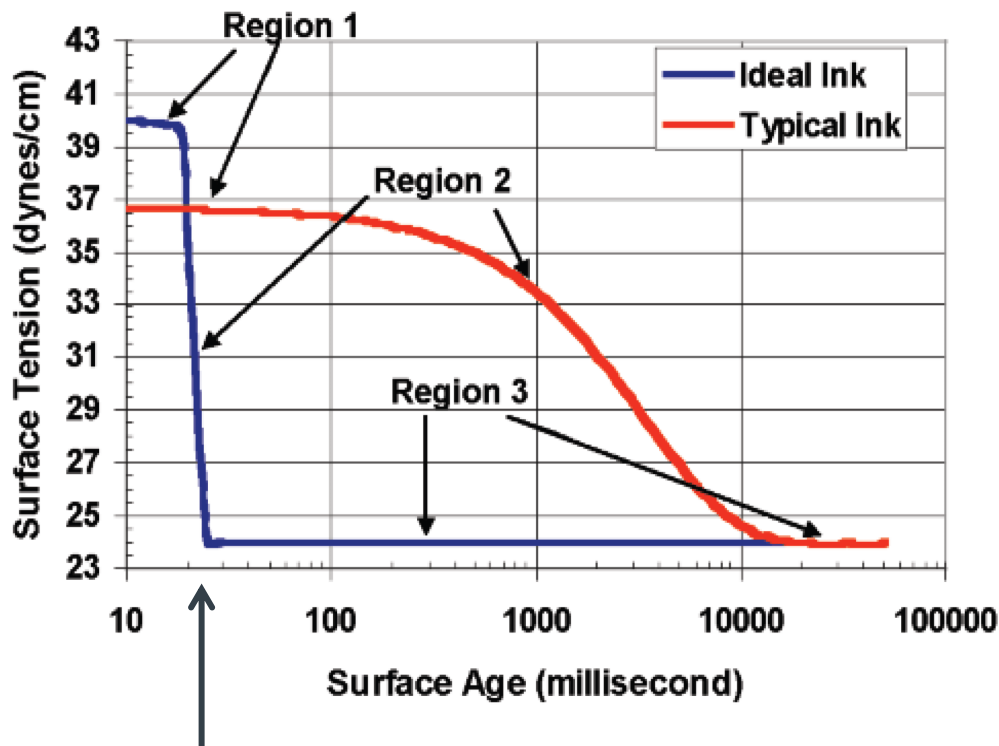
Wetting Envelope



What does this mean for my Inkjet process?

The ink's dynamic SFT is used to balance between proper drop formation at the nozzle and proper wetting

Comparing the dynamic SFT profile of an „ideal“ and a typical ink



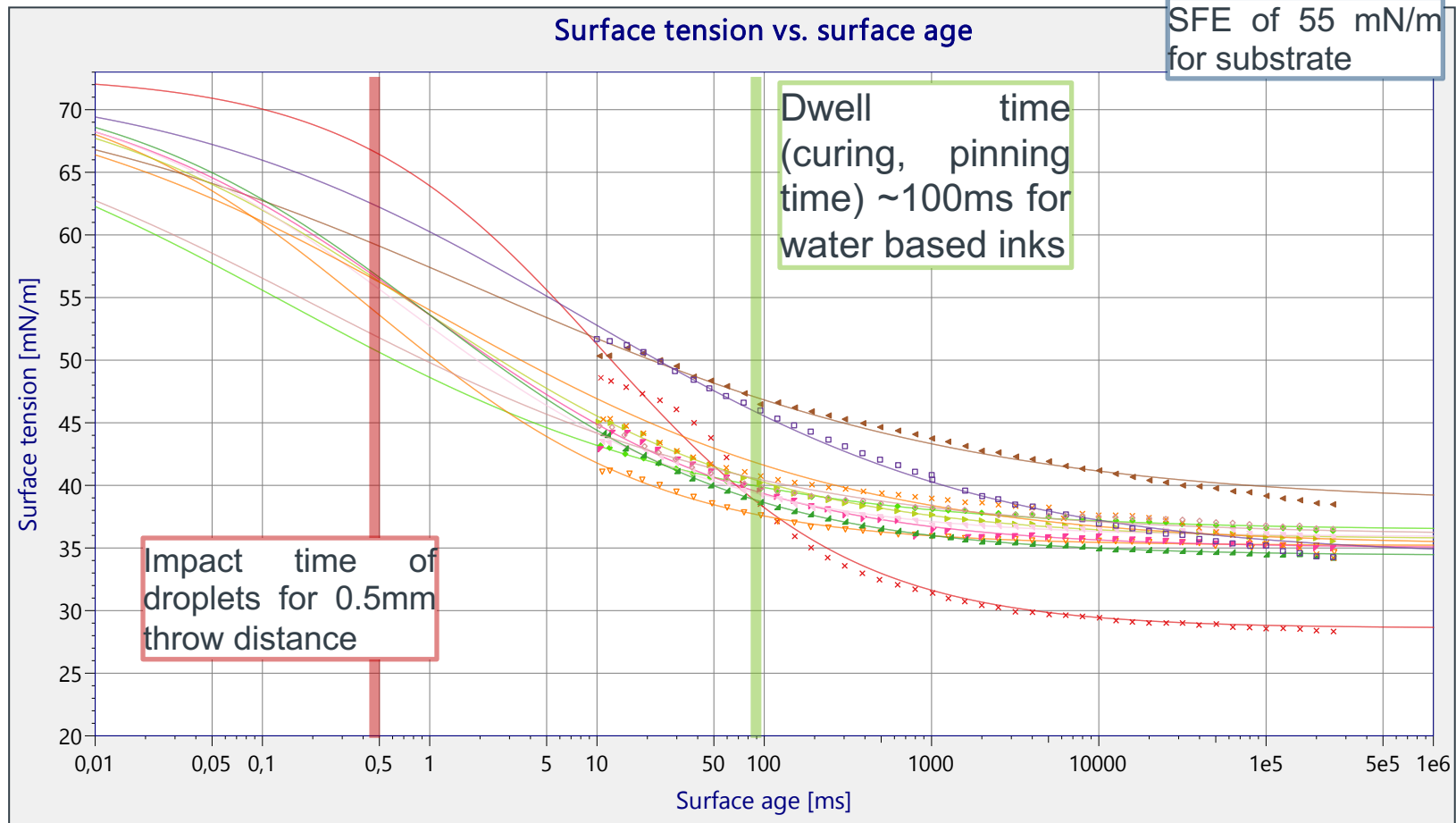
Region 1: SFT should be high enough to ensure meniscus recovery inside the nozzle
⇒ drop formation

Region 2/3: SFT should decrease quickly towards static SFT
⇒ wetting of substrate under controlled conditions

Usually the droplet hits the substrate within 20ms after start of drop formation

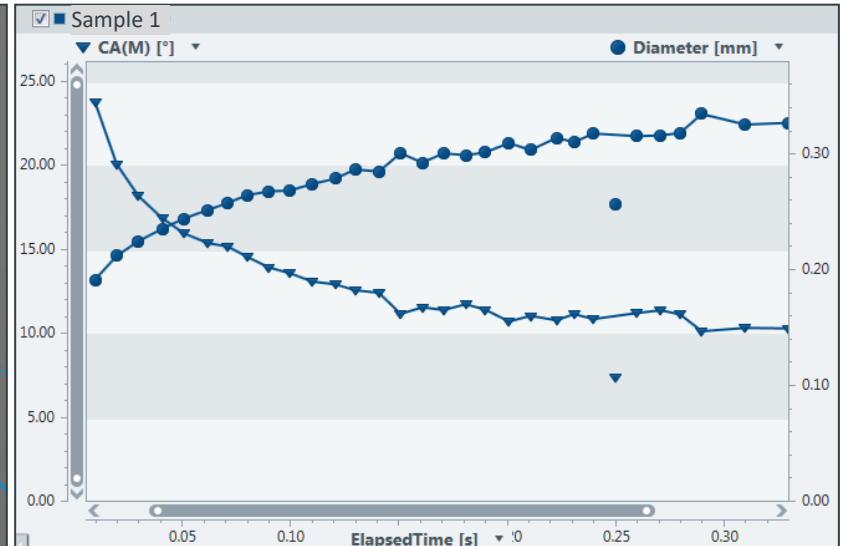
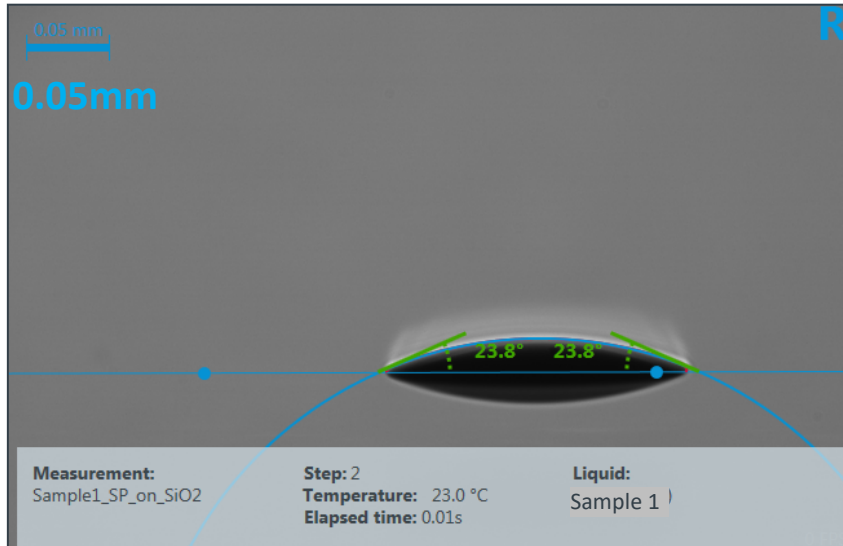
Looking at dynamic SFT to determine the behaviour of ink drops at different points during Inkjet printing

BP100 measurements (including Hua-Rosen fit)



The immediate spreading of the droplets after impingement on any substrate is monitored

Changing of CA and droplet diameter over 300ms for Sample 1



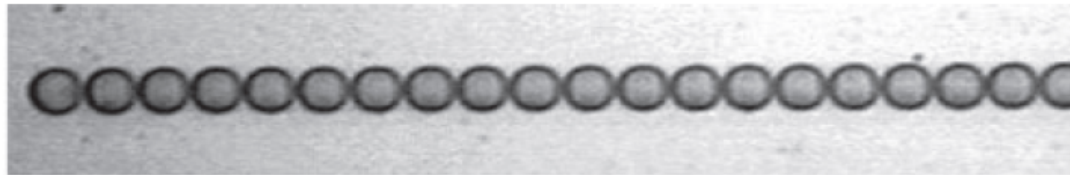
Results

	CA(M) [°]	CA(L) [°]	CA(R) [°]	Volume [µL]	Temperatur...	Time
Sample 1 (Air) [35] Page 1 / 1						
1	16.89	16.89	16.89	0.00	23.0	12:09:46
2	23.79	23.79	23.79	0.00	23.0	12:09:46
3	20.10	20.10	20.10	0.00	23.0	12:09:46
4	18.21	18.21	18.21	0.00	23.0	12:09:46
5	16.89	16.89	16.89	0.00	23.0	12:09:46
6	15.99	15.99	15.99	0.00	23.0	12:09:46
7	15.40	15.40	15.40	0.00	23.0	12:09:46
8	15.21	15.21	15.21	0.00	23.0	12:09:46
9	14.61	14.61	14.61	0.00	23.0	12:09:46

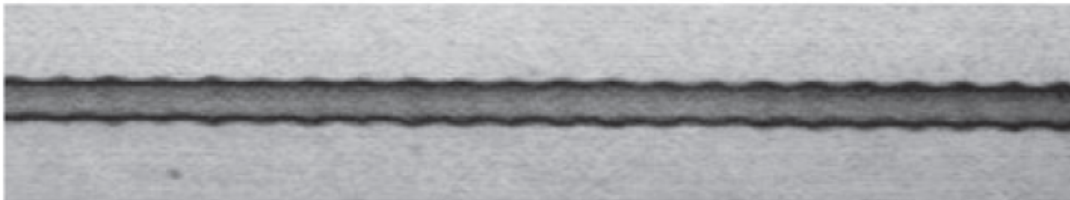
The contact angle defines the printhead travers velocity and dosing frequency (i.e. drop spacing) for stable printing

Picture from Derby, Annu. Rev. Mater. Res. 2010. 40:395–414

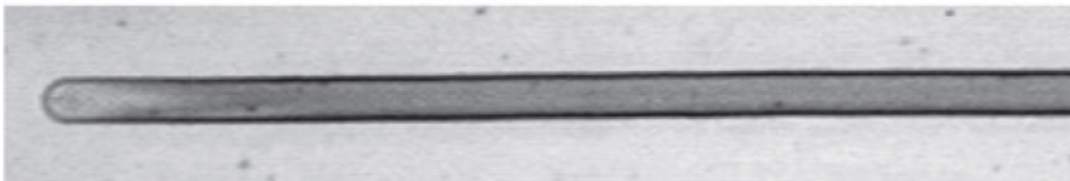
Drops printed with fixed printhead velocity and frequency



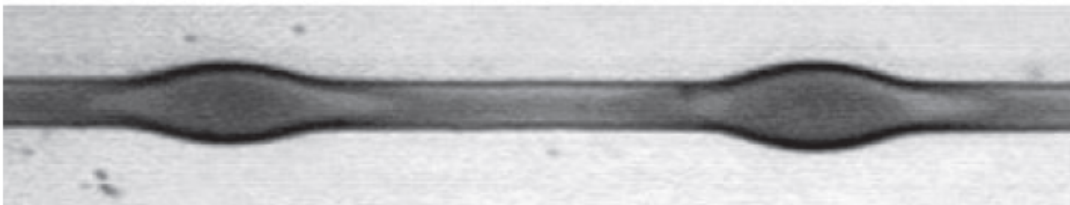
No coalescence, contact angle too high



Initial, incomplete coalescence, receding contact angle too high and/or advancing contact angle still too high



Straight line after coalescence



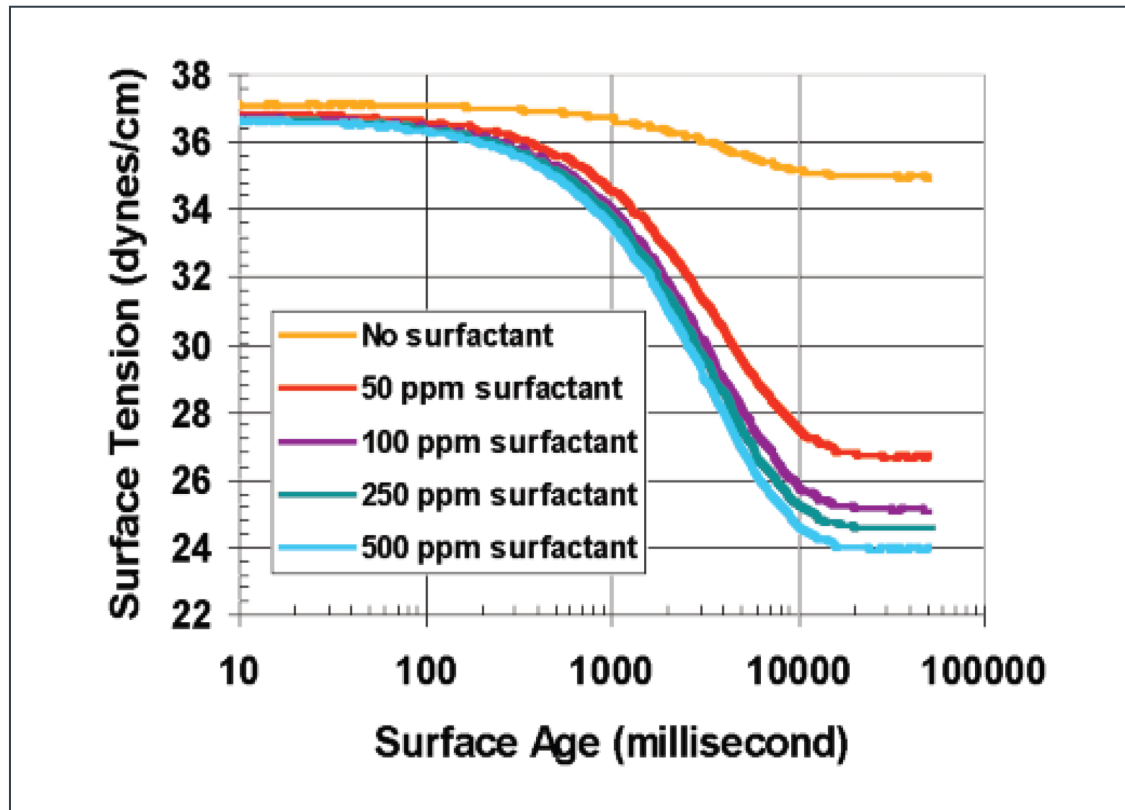
Bulging, contact angle too small

150 μm

Methods to characterize and optimize Inkjet processes

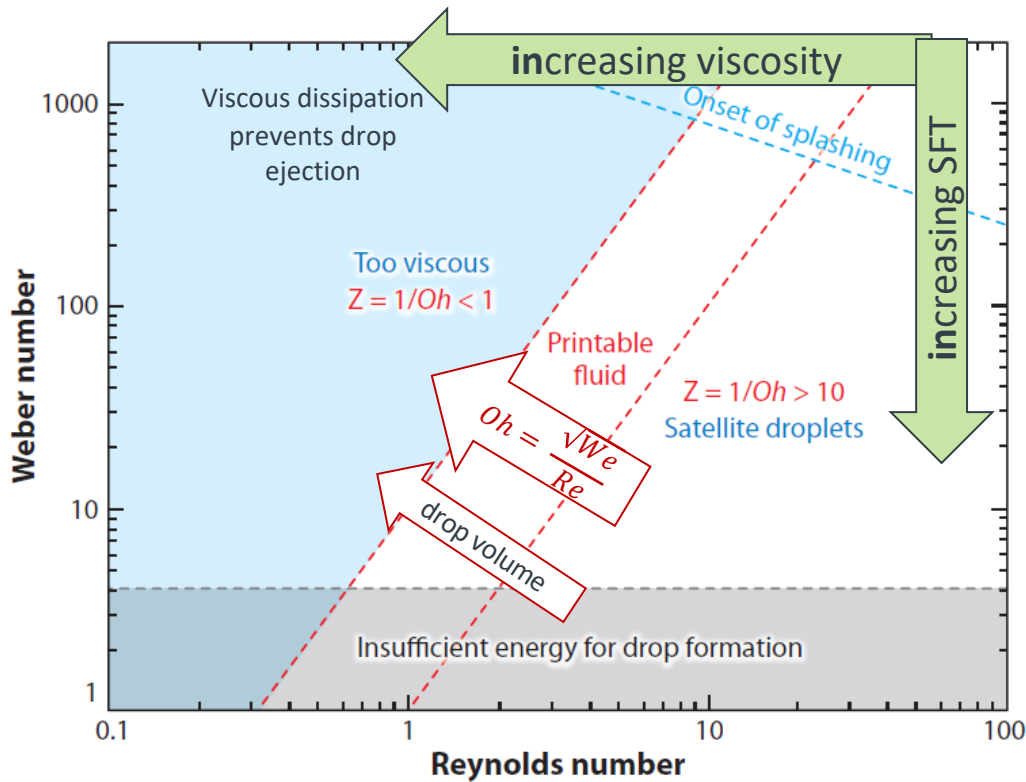
Ink optimization can be done by investigating dynamic surface tension

Impact of surfactant concentration on dynamic behavior of SFT as measured with BP100



With known surface tension and viscosity, the jettability can theoretically be predicted or measured with DSA Inkjet

Phase plot taken from: Derby, Annu. Rev. Mater. Res. 2010. 40:395–414



$$We = \frac{\rho v^2 d}{\sigma}$$

$$Re = \frac{\rho v d}{\eta}$$

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\eta}{\sqrt{\sigma \rho d}}$$

All details can be found in the corresponding application report No. 289

Application Report

Application report: AR289
Industry section: Inkjet printing
Author: Stefan Benn, Dr. Thomas Willers
Date: 04/2019



Method:



Drop Shape Analyzer – DSA Inkjet

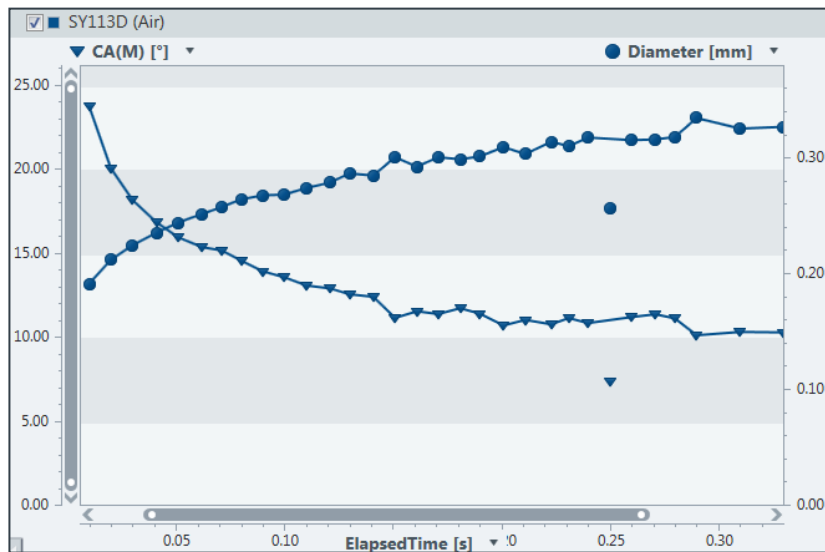
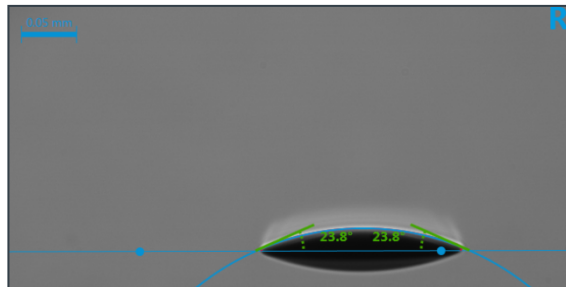
Keywords: inkjet printing, drop watching, surface tension, viscosity, drop volume, drop velocity, satellite drops

How waveform, surface tension, and viscosity affect the jetting behavior in inkjet printing

An illustration of basic relationships with the Drop Shape Analyzer – DSA Inkjet

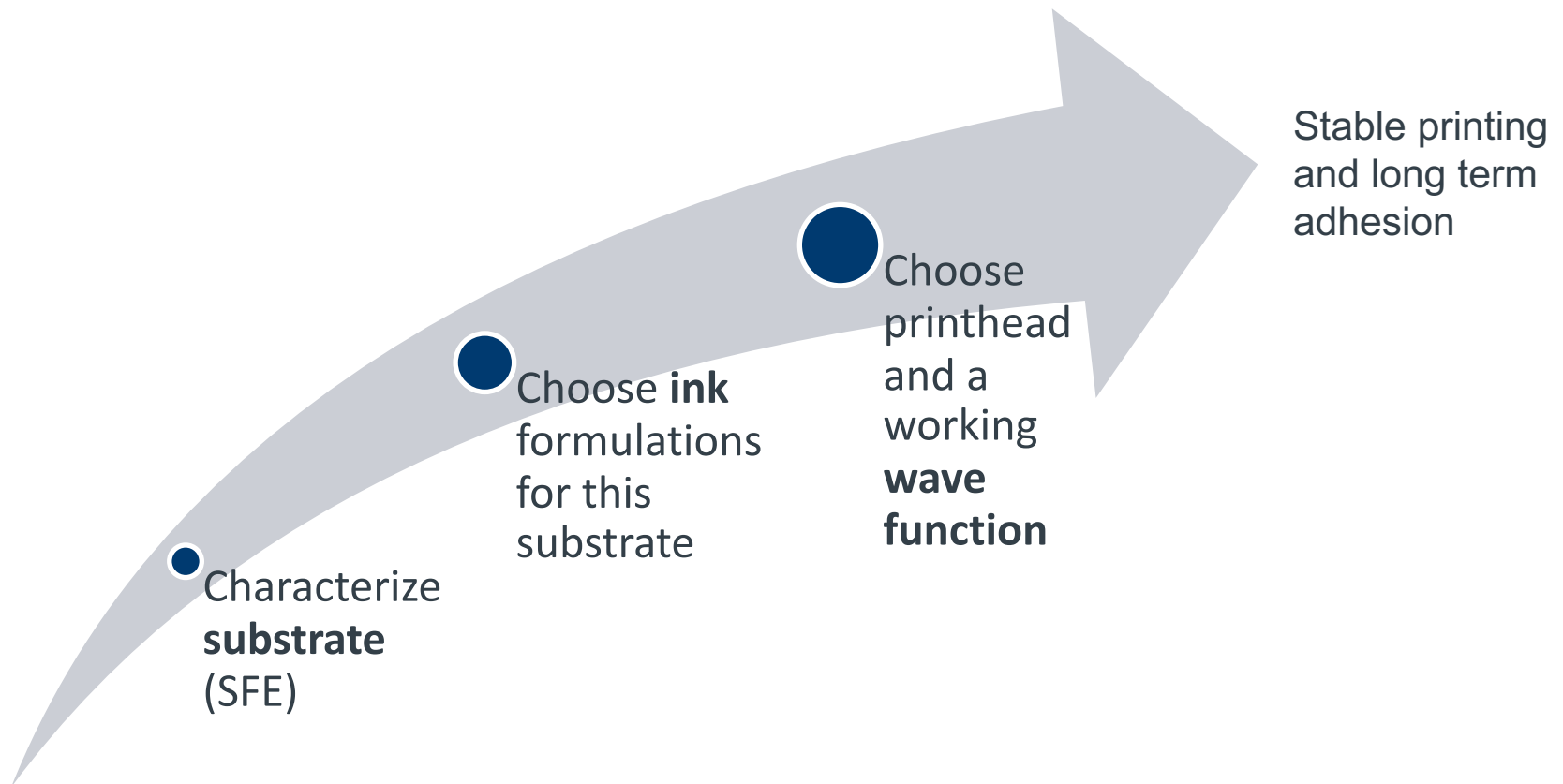
The contact angle upon impinging and during wetting can be observed with our Drop Shape Analyzer

Changing of contact angle and droplet diameter over 300ms for a typical inkjet ink



Take home message and further information

Take home message: Printing goes from nozzle to substrate, but its optimization from substrate to nozzle and waveform



Do you want to know more? Visit our booth 647 in hall A6!

See our instrumentation for Ink and Surface Characterisation as well as the new DSA Inkjet dropwatcher in action!

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Did you liked this way of lecture and insights? Learn more during the next IMI Inkjet Winter Workshop!

Learn about Inkjet Ink Characterisation and many other aspects of inkjet technology with industry experts

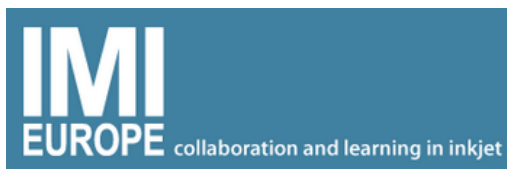


INKJET INK CHARACTERISATION

VISCOSITY, DISPERSIONS, JETTING & SURFACES

Wed 29 - Thu 30 January, 2020

This course covers rheology and surface tension measurements, particle and dispersion assessment, as well as drop visualisation and print quality analysis. Course leaders include KRÜSS, ImageXpert and Malvern Panalytical.



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Learn about Surface Tension, Wetting, Jetting, Particle Size, Bulk and Interfacial Rheology, Dispersion Stability, and Polymer Characterization with industry experts





Advancing your Surface Science

Do you have questions?

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